When asked to explain entropy, a teacher of engineering said “Oh, I don’t know what entropy is; nobody knows what it is; you just use it”. Quoted by J.H. Hildebrand.

“Fundamental questions were settled 50 years ago.” From a letter explaining to an author why his submission was rejected.

Moins ils savent, moins ils doutent, mais la doute est porte de la véritée. Parot.

ADIABATIC THERMODYNAMICS OF FLUIDS

A monograph

Last addition March 2018
# TABLE OF CONTENTS

**Forword**  Page 10  
**Abstract**  Page 14

**ACKNOWLIDGEMENTS**  Page-18

## I. INTRODUCTION

I.1. Elements of hydrodynamics  Page 19

I.2. Hamiltonian and Lagrangian formulations of hydrodynamics  Page 23
   *Action principles. Lagrange multipliers. The Lagrangian of Fetter and Walecka. Kinetic energy. Hamiltonian. The velocity potential*

I.3. The temperature  Page 27
   *The ideal gas law.*

I.4. The internal energy and the first law  Page 28

I.5. A Lagrangian for rotational motion?  Page 31
   *The danger of defining a theory by a set of equations*

I.6. On the possibility of a Lagrangian in the case of dissipation  Page 34

I.7. Hydrodynamics of potential flow  Page 34

I.8. An alternative formulation of hydrodynamics  *To be completed, modified?*  Page 36

## II. ACTION PRINCIPLE FOR GLOBAL THERMODYNAMICS

II.1. The internal energy and the free energy  Page 38
   *Functional relations. Legendre transformations. Normalization of the energy*

II.2. The ideal gas  Page 39

II.3. The two time scales of thermodynamics  Page 41
   *Adiabatic process. Dissipative process*

II.4. Action principle for Thermodynamics  Page 43
   *An action functional. Interpretation of the action principle. Free energy and enthalpy.*

II.5. Lowest energy and maximal entropy  Page 46
   *The energy functional. Maximal entropy. Imperfect analogy, entropy vs pressure*

## III. LOCALIZATION

III.1. Hamiltonian density and the adiabatic equations of motion  Page 48
   *Hydrostatic condition. Thermodynamic pressure and the pressure on the walls. ‘Main assumption’. Adiabatic condition. Chemical potential.*

III.2. The kinetic energy  Page 52

III.3. The Lagrangian and adiabatic dynamics  Page 53
   *The on-shell value of Lagrangian is the pressure*

III.4. The second law  Page 55
III.5. Work and pressure  Page 57
  Adiabatic systems. Pressure and Lagrangian density.
III.6. Lesson to be learned from the expansion of the ideal gas  Page 62
  Entropic rubber. Some questions
III.7. Local thermodynamical potentials  Page 63
III.8. Conservation laws and the stress tensor  Page 65
  The equalisation of pressure?
III.9. Minimal energy and maximal entropy.  Page 68
  The classical Lagrangian paradigm. Maximal entropy at a fixed value of the energy density. A new formalization of the two laws of thermodynamics. Taking stock
III.10. The third law and the normalization of entropy  Page 69
III.11. Galilei invariance  Page 70
III.12. Remark concerning the space of variations.  Page-72
  Add statement about Gibbs and Prigogine

IV. APPLICATIONS TO SIMPLE SYSTEMS

IV.1. The propagation of sound in an ideal gas  Page 77
  Radial waves
IV.2. The van der Waals gas  Page 80
IV.3. Saturation  Page 84
  Interpretation of the velocity potential
IV.4. The dew point and the bubble point, Maxwell’s rule  Page 87
  The adiabatic relation. A fundamental question. Calculating the dew point for Argon.
IV.5. The critical point  Page 94
IV.6. Sound propagation in pure phases and at the critical point  Page 95
IV.7. Refinements of the expression for the internal energy  Page 97
  The heat capacity. The speed of sound
IV.8. Generalization; the cubic equation of state  Page 97
IV.9. Stability  Page 98
Tables  Page 199

V. A THEORY OF FLUID MIXTURES

V.1. Variables and potentials  Page 106
  Molar fractions and ‘free energy of mixing’
V.2. Entropy and equations of motion  Page 109
  Adiabatic systems
V.3. Mixture of 2 ideal gases  Page 112
  Dalton’s law.
V.4. The Gibbs-Dalton hypothesis for ideal gases ...  Page 114
V.5. ... and what lies behind it  Page 117
  Condensation
V.6. Gibbs-Dalton hypothesis for some real gases  Page 121
V.7. The simplest mixtures. Boltzmann theory  Page 123
VI. IMMISCIBLE FLUIDS

VI.1. Ideal gases with mutual interaction  Page 133

VI.2. Mixtures of two van der Waals gases  Page 141
The spinodal. Mixtures. Calculation of the line of coexistence.

VI.3. Sample applications - first example  Page 144
Binary van der Waals mixtures. Formulas. Points that are critical to the experimenter.

VI.4. Mixture of two van der Waals fluids. Second example  Page 145
The square root interaction density for mixtures. Nitrogen and Argon.

VI.5. Helium and Xenon  Page 158
The adiabatic condition. Summary. The entropy Coexistence. Van der Waals and Whitney.??

VI.8. The square root interaction density  Page 164
Needs checking? HERE COMES VI.3, VI.4, VI.6, VI.8 to page 180, out of place. ???

VI.4. Overview of the ethane-propane system  Page ???

VII. SPEED OF SOUND IN MIXTURES

VII.1. Propagation of sound in a Gibbs-Dalton mixture  Page 167
Equations of motion for ideal gases. Propagation matrix. Two types of mixtures. Summary. Type 1 mixture, similar gases. Type 2 mixture, disparate gases.

VII.2. A simple model of interactions  Page 177
Variants.

VII.3. Two van der Waals gases. sound speed  Page 180
First experiment on sound speed in He/Xe. To be done.
VIII. SUPERFLUID HELIUM

VIII.1. Experiments and interpretation  Page 178
- E. Thermodynamic pressure and the pressure on the walls. F. Critical behaviour.

VIII.2. First analytic model.  Page 185

VIII.3. Dynamical equations of the model.  Page 191
- Fountain effect revisited. Final remark.

VIII.4. Rotational flow  Page 196

Tables  Page 197
- Project 5. Try to understand flux quantization in the new formulation.

IX. ATMOSPHERES

IX.1. Introducing gravitation  Page 193
- The van der Waals atmosphere

IX.2. Mixed, isentropic  Page 195

IX.3. Nitrogen and Oxygen  Page 195

IX.4. Air and Argon  Page 198
- The significance of a uniform lapse rate
- The singular and the critical points.

IX.5. Air and H2O. Introduction  Page 199
- Standard method.

IX.6. Phase separation in a mixture of Air and Water  Page 202
- Statement. Present goal.

IX.7. Polytropic atmospheres  Page 205
- Emden’s theorem. The effect of entropic forces.

IX.8. The isentropic atmosphere  Page 206
- What physics is involved?

IX.9. Reply to Maxwell  Page 208
- The U

X. ROTATIONAL FLOW

X.1. The scalar velocity potential is essential  Page 210

X.2. The constraint and the Euler-Lagrange equations  Page 211

X.3. Cylindrical Couette flow  Page 212

X.4. The action principle provides a kinetic potential  Page 218
- Viscosity. The energy momentum tensor

X.5. Stability of laminar Couette flow by the action principle  Page 219
- Boundary conditions.
X.6. A proposal

Main result. Surface tension. Entropic forces.

X.7. Conclusions

Future experiments


X.9. Vortices

XI. Astrophysics

XI.1. Introduction

XI.2. A compressible fluid rotating in a gravitational field.

XI.3. Earth and Mard

XI.4. Neptune and Uranus. Venus and Pluto

XI.5. Saturn and Jupiter. the sun. haumea. Galaxies.

XI.6. summary and conclusions

XII. Special and General relativity

XII.1. Special Relativity. The notoph gauge theory

XII.2. Non Relativistic limit and Galilei transformations

Galilei invariance

XII.3. General Relativity


Introduction to General relativity. Part 3.

XII.4. Variational principles in Special and General relativity

XII.5. Gravity waves. Relativistic Hydrodynamics On the way

Odds and ends

XI. Sources for Einstein’s equations

XI.9. Superfluid Helium. Part B.

Galilei invariance

XI.10. Generalized Couette flow, cells

XI.11. Convection and viscosity. Benard’s experiments

XI.12. Adiabatic Analysis

XI.13. Criticism of the classical analysis

XI.14. The role of viscosity

Project 9. Describe Benard cells in terms of elliptic functions.

REFERENCES

INDEX

Figures Incomplete list.
1.1.2. Equation of continuity, page 21, eps file improve, BW
1.3.1. Thermometer, page 26. eps file. Color
1.4.1. Carnot cycle, page 29, eps file. Color
1.7.1. Irrotational flow, page 34, eps file BW
2.3.1. Time scales, page 41, eps file. Color
3.5.1. Vessel with piston and spring, page 56, eps file.Color
3.5.2. A vessel with 2 pistons, page 59, eps file. BW
4.2.1. Van der Waals' pressure., page 80, eps file. Color
4.3.1. Maxwell’s rule, page 82, eps file. Color
4.4.2. The common tangent, page 89, eps file.
4.4.3. Argon 1, page 90, eps file Color
4.4.4. Argon 2, page 90, eps file Color, same page
4.4.5. Argon 3, common tangent, page 91, eps file. Improve BW
4.6.1. He sound, page 92, eps file. BW Add text (ref)
4.6.2. He sound, page 94, eps file. BW Add text (do)
5.2.1. Entropy path, page 108, eps file. BW
5.5.1. Gibbs-Dalton 1, page 115, eps file. Color
5.5.2. Entropy path, condensation, p 117, nothing done
5.6.1. Excess free energy., page 118, eps file. BW
6.6.3. Gibbs-Dalton 3, p 120, eps file. Color. Same page?
5.7.1. Dissociation 1, page 125, eps file. BW
5.7.2. Dissociation 2, page 125, eps file.BW
6.1.2. Free energy, p 134, eps file. BW
6.1.3. Common tangent, p 136 eps file. Color
6.1.4. Range, p 136 eps file. Color. Same page
6.1.5. Symmetry, p 138 eps file. Color
6.1.6. Coexistence, p 138 Color. Same page
6.2.1. Van der Waals pressure, p 139 eps file. Color Incomplete
6.2.2. Methane and propane, p 141 esp file. Color
6.2.3. Methane and propane, p 137. esp file. Color. same page?
6.2.4. Same, p 138. eps file. BW
6.4.1 eth-pro6, p 144. eps file. BW
6.4.2 eth-pro7, p 148 eps file. BW
6.4.3 eth-pro8, p 149 eps file. EPS
6.4.4 eth-pro9, p 152 eps file. Color
6.4.5 p 151 eps file. Color
6.4.6 p 152 eps file. Color
6.4.7 p 152 eps file. Color
6.4.8 p 153, Ni + A, cfg file. Color
6.4.9 p 154 cfg file These two figs have the wrong color for the radial lines. Color
6.4.10 p 154 cfg file. Color
6.4.11 p 155
6.4.12 p 155
6.4.13 p 156
6.4.14 p 156
He-Xe files missing

6.5.1. Sim19a, He-Xe p 154, eps file
6.3.2. Sim19b, p 132, eps file
6.3.3. Sim19c, page 133, missing.
6.3.4. Sim19d, page 133, eps file.
6.3.5. Sim20, page 134, eps file.
6.3.7. Section1, page 135 eps file.
6.3.10. Sim20.2, page 136 eps file. Should be 6.3.9?
6.3.10. Sim20.3. page 136 eps file.
6.3.11. Sim20.4, page 137, eps file.
6.3.15. Oct18.2, page 139, eps file
6.4.1. Nov12.1, p 135, eps file
6.4.2. Loci of chemical potentials, page 156, p 157, eps file
6.4.3. Nov13.2, p 136,
6.4.4. Nov13.3, page 151, eps file
6.4.5. Nov13.6, p 151, eps file
6.4.6. , p 151, eps file
6.4.7. , p 151, eps file
6.4.8. p 152 Ni-A eps file
6.4.9, p 153 eps file
6.4.10, p 153 eps file
6.4.11, p 154
6.4.12, p 154
6.4.13, p 155
6.4.14, p 155
6.5 He-Xe made somewhere
7.1.1.Fig.4.III, p 168 eps file. Color
7.1.2. Fig. 5. III, p 169 eps file. color?
7.2.1. Fig. 6. III, p 171 eps file
7.2.2. Fig. 7. III, p 172 eps file
more to come
8.1.1. Fig. 8.1.1, p 177 eps file
8.1.2. Fig. 8.1.2, p 178 eps file
8.1.3. Fig. 8.1.3, p 179 eps file
8.1.4. Fig. 8.1.4, p 180 eps file
8.1.5. Fig. 8.1.5, p 154 nothing done, Hall
following files missing
8.3.1. Fig. 8.3.1, p 160 eps file
8.3.2. Fig. 8.3.2, p 160 eps file
8.3.3. Best fit p 160 eps file
8.3.4. Cv, p 160 eps file
9. Atmospheres
9.8.1. The U. nothing done
10.3.1. Couette p 211 find it
10.3.2. Couette page 211 eps file
10.5.1. Stage 1, p 220 gfc file
10.5.2. Andereck, p 220 eps file to find
10.5.3. Stage 2 nothing done

The rest obsolete?
11.3.1. Centrifugal page 201
11.5.1. Temp. page 205
11.6.1. Velocity page 208
11.6.2. temp page 209
11.8.1. cell page 219
11.8.2. cell page 220
11.8.3. page 220
11.8.3. triangle page 221 eps file
11.8.4. hex page 222 eps file
27b Symm1. p66, eps file
28. Dulcie1 p68, eps file
28a Dulcie1a p68, eps file
29. Dulcie2, p68, eps file
29a Dulcie2a p69, eps file
30. Dulcie3 p 69, gcf file
30 Dulcie3a p 69, eps file
30a Dulcie4, eps file
31. Maria1 p69, eps file
31a Maria2 p69, eps file, p 70
31b Maria3 p70, gcf file, p 70
Foreword

“Thermodynamics is usually subdivided into a theory dealing with equilibrium and into one concerned with irreversible processes”.

The quotation (Tisza 1961) is testimony to the meaning that was and still is ascribed to the word “thermodynamics”. Why is the enormous literature on adiabatic, non equilibrium thermodynamics sometimes excluded from consideration? Why is the study of dissipative thermodynamics referred to as “non-equilibrium thermodynamics”? Laplace explained the speed of propagation of sound in air by postulating that the process is adiabatic; it is neither equilibrium nor dissipative. What about 200 years of atmospheric science? If it is regarded as an application of mere hydrodynamics then it is high time for an upgrade, for it is not possible to understand atmospheres without the concept of temperature.

This book is my attempt to understand thermodynamics, in the formulation as a Eulerian field theory of temperature, pressure, densities and entropies, and completely integrated with hydrodynamics. Another hope was, and remains, to make classical thermodynamics more easily accessible to physicists with other specialities, people like myself who neglected to study the subject in school. To this end the difficulties are emphasized rather than glossed over.

The title was chosen to suggest that the subject is not the classical theory of equilibrium thermodynamics, but a dynamical theory (also classical) in which the variables are functions of position and time. Naturally, this implies an integration of hydrodynamics into thermodynamics. The attention is not limited to equilibria though of course the determination of equilibria is a major part of the study. Alternative titles such as ‘extended thermodynamics’ were rejected because of close associations with particular trends and dogmata. I feel a close affinity to the school of Prigogine who used the term ‘local thermodynamics’ as opposed to ‘global (classical) thermodynamics’. ‘Non-equilibrium Thermodynamics’ would be inappropriate, for the important distinction is not between equilibrium and non-equilibrium but between adiabatic and non-adiabatic. Statements are heard everywhere to the effect that entropy is not defined for systems out of equilibrium. And yet adiabatic processes, defined as processes in which there is no change of entropy, are commonplace. Laplace, departing from an older theory due to Newton, postulated that the entropy of each particle remains constant during this dynamic, non-equilibrium process. There may be some ambiguity in the concept of “fixed entropy”. In this book it is in full accord with Gibb’s formulation of the minimum energy principle,
but more precise. To focus on unary systems, for simplicity, an adiabatic system is governed by a Lagrangian and the specific entropy density is fixed. Within such a system is Laplace’s theory of sound propagation developed.

A particular fetish of mine has played a major role: a strong preference for Lagrangian variational principles. This has proved to be an essential advantage in dealing with interesting applications, such as the theory of mixtures and the integration with General Relativity. But at the start of this project this was but a distant goal, since a variational formulation of hydrodynamics was then available only for the special case of irrotational flows. Some generality had to be sacrificed, provisionally. Thus at the outset it was clear that turbulence and related phenomena could be described only subsequent to further development. The required generalization of the variational principles to include general flows has been relegated to a second volume. As the work progressed and I had to study many fields that I had previously neglected, I came to realize that the potential benefits of action principles is much greater than I had anticipated. I learned that some, perhaps all those branches of physics that do not yet have an action principle formulation have very low predictive power; they describe but they do not predict. This applies to astrophysics and atmospheric science, to electromagnetism of materials and to hydrodynamics. I hope to convince some readers of this, but the first evidence will not be presented until Chapters V and VI, with the new theory of mixtures.

In its original form, Gibbs’ variational principle is a criterion for recognizing the states of equilibrium from among all the configurations of a composite physical system as being states of lowest ‘energy’. In this book the principle is applied within the context of an action principle, the Euler-Lagrange equations of which are the fundamental relations of thermodynamics. Gibbs’ ‘energy’ is the Hamiltonian of an action principle with a fully developed canonical structure. An adiabatic system is characterised by a Lagrangian and by a fixed entropy. The generalized action principle that is the core of the theory is limited to adiabatic processes; more precisely to processes where the entropy is fixed, see Section II.3 and especially Section II.4.

The approach to equilibrium via dissipation is always difficult and in most of this book we aspire only to understand adiabatic dynamics. Dissipation is usually characterized by a much longer time scale and is preferably studied as a sequence of adiabatic equilibria, with the object of discovering the final, absolute equilibrium and not the processes that lead to it. It is here that entropy becomes an essential part of our understanding and it is here that we shall take a far from confident attitude. We read that “The proper definition of entropy for systems that are out of equilibrium is still an issue of debate”. Actually this is a mis-statement, for the entropy of an adiabatic system, at equilibrium or not, is a very clear concept. What is not well understood is the distribution of entropy between the components of heterogeneous systems, even at equilibrium, and the way that dissipation affects this distribution. It is for this reason that we prefer to reverse the usual presentation of thermodynamics, offered most convincingly by Callen, who approaches a problem by, first, making use of what is understood about the entropy, and only then introduces an adaptation of the principle of minimum energy to the type of process under consideration. The point is that the action principle covers, not only equilibria, but all of adiabatic dynamics as well. We follow the lead of Prigogine (1970) in that we confidently apply
adiabatic thermodynamics to systems that are adiabatic though out of equilibrium, in particular, to stationary or quasi-static phenomena. See the Wikipedia article on Adiabatic Processes, dated 2015. An important caveat is that the problem of defining the entropy for non-adiabatic configurations has a quite different character when approached from the statistical point of view. See for example Lieb and Yngvason (2013).

The entire theory is based on a hydrodynamical action principle that is due to Lagrange (1760), resurrected by Lamb (1932) and brought to my attention by Fetter and Walecka (1980). Their theory is explicitly Galilei invariant and so is all of this book.

A large part of the book is dedicated to the study of mixtures. In spite of the very great emphasis on the work of Gibbs, who addressed himself especially to the study of heterogeneous systems, it breaks with Gibbs and with tradition in several respects. Gibbs and almost all other others describe heterogeneous systems in terms of the total volume and molar fractions; here they will be replaced by densities, the natural thermodynamic variables, for I find that it greatly facilitates both clarity and convenience. The reader will be spared the Gibbs-Duhem relation and Euler’s law, any discussion of intensive and extensive variables and “open” systems. Instead he will enjoy much more dramatic presentation of the properties of mixtures in the two-dimensional density plane.

Localization (the transition from global to local thermodynamics) is far more natural in this formulation where densities replace extensive variables.

Of great consequence is the general attitude that will be taken with regard to binary fluids. It is a very common practice to treat a mixture of fluids as a single fluid with properties that interpolate between the properties of the components. This is sometimes a successful device but in this book I insist on respecting the number of degrees of freedom. If a mixture occasionally behaves like a unary system then the challenge is to understand how this comes about, as a result of interactions. The theory of mixtures in thermodynamics will be approached in a manner, not entirely orthodox, implied by the reliance on action principles.

Another special feature of this book is an unusual emphasis on the role of gravitation in thermodynamics. Gravitation enters as an important tool to help produce a useful separation of phases, as gas and liquid, and immiscible fluids. It enters as an essential complication in the observation of critical phenomena, as Bénard cells, and it is a controversial element in the theory of atmospheres. And yet the fundamental role of gravity in determining the equilibrium state of an isolated atmosphere has never been subjected to experimental investigation, nor to sufficient theoretical study. This book includes a preliminary study of mixed atmospheres and a unification of General Relativity with Thermodynamics, provisionally limited to the case of irrotational flows. An extension to include general flows has been found recently. It is presented in chapter X and it will be developed in a second volume.

As in all textbooks on classical thermodynamics the exposition relies very heavily on the wonderful example of the ideal gas. Most applications are subsequently upgraded to include the van der Waas fluids. The avowed plan is to describe the fundamentals in great generality but, even so, analogous systems such as magnetic phenomena and electrical circuits will not be discussed. The important roles of statistical mechanics and
quantum mechanics will be alluded to when appropriate, but a full development of those subjects is beyond our scope. Among applications that regrettably have not been included is electrolysis. The main application is to the dynamics of fluids, fluid mixtures and phase transitions, in terms of concepts that are close to those of the experimenter.

A major struggle has been to find a variational principle for hydrodynamics that allows for rotational motion, vortices and turbulence. At the time of this writing, September 2017, the problem has found a solution. The non-relativistic version presented in Chapter X. The relativistic version has been published on arXiv.
Abstract

Unlike the traditional approach to thermodynamics, this book begins with a brief exposition of hydrodynamics. At this stage the development is limited to potential flows, because, until recently, that is all that could be done, but also for didactic reasons.

At the core of thermodynamics is the Gibbsean minimum energy principle, generalized to include the hydrodynamical degrees of freedom; that is, localized as a field theory of density, pressure, temperature and entropy. The theory is referred to as local, as opposed to traditional, global thermodynamics. The main foundation is the variational principle of Gibbs, with a modification recommended by Prigogine. (Chapters I-III.)

Section I.1. This work was motivated by the realization that fundamental principles tend to be neglected in some branches of physics. The equation of continuity is the heart and soul of hydrodynamics. It is incorporated into all developments, including Astrophysics.

Section I.2. No less important is the use of variational principles, most of all Lagrange’s action principle. Our work is kicked off to a promising start with the discovery of an action principle for hydrodynamics that is due to Lagrange.

Section I.3. The temperature lifts the relatively simple science of hydrodynamics to the much deeper problem of thermodynamics.


Section II.1. The fundamental relations interpreted as Euler-Lagrange equations.

Section II.2. The ideal gas.

Section II.3. The two time scales of thermodynamics.

Section II.4. The action functionals for thermodynamics.

Section II.5. Maximum entropy; Gibbs’ axioms.

Section III.1. Thermodynamics for moving fluids in Gibbs’ formulation. The Hamiltonian. Derivation of the hydrostatic equation from thermodynamics, important insight.

Section III.2. Synthesis of the action principle for hydrodynamics and Gibbs’ theory.

Section III.3. The first action principle for thermodynamics, embodying the classical theory of equilibrium thermodynamics. Adiabatic Thermodynamics. The Lagrangian used throughout this book.

Section III.4. The second law.

Section III.5. The on shell value of the Lagrangian is equal to the pressure.

Section III.7. The thermodynamical potential densities.

Section III.8. Conservation laws and the stress tensor are meaningful within the context of an action principle only. The energy momentum tensor.

Section III.9. Here the Hamiltonian of adiabatic thermodynamics is identified and this entails a positive step in our effort to understand what entropy is about. After this advance the canonical structure of one-component thermodynamics is non degenerate.

Section II.10. Nernst’s Third law.

Section III.11. Most works on hydrodynamics neglect, abuse or ignore Galilean invariance. The Lagrangian is invariant; the Hamiltonian is not.
First applications. Chapter IV

This first application, to the phase transitions of the van der Waals gas, is a very good example of the application of both variational principles. The entropy change is related to the surface tension, while the principle of maximal entropy leads directly to Maxwell’s rule. The speed of propagation of sound is calculated above and at the critical point.

Section IV.1. The speed of sound; the first example of non-equilibrium, adiabatic thermodynamics, a subject initiated by Laplace.
Section IV.2. The van der Waals gas, determination of the free energy density.
Sections IV.3-4. Saturation. Maxwell’s rule.
Section IV.5. The critical point for the van der Waals gas.
Sections IV.6-7. Sound propagation near the critical point.

Mixtures. Chapters V-VII

Mixtures occupy a major part of this book; the treatment can be said to be radical. The variables are densities, the pressure and the specific entropies. Unlike the popular molar fractions, these are natural thermodynamical variables. There is no Gibbs-Duhem relation and all the principal variables are intensive. The basic object of study is the Lagrangian density, consisting of a kinetic part, the free energy, to which is added an explicit interaction term, and the entropy.

Most radical is the explicit modeling of the assigned entropy of a mixture as a linear function of the densities. There is no need to introduce the concept of entropy of mixing, nor free energy of mixing; with the use of densities as fundamental variables all mixing terms disappear. The central problem is to determine the entropy functional; this was achieved in special cases.

Section V.2. We take a very radical approach that offers a model for the entropies of mixtures in general.
Section V.4-6. The Gibbs-Dalton hypothesis, valid for ideal gases, has been generalized to the case of mixtures defined by their constituents and by their mutual interaction. In the case of chemical interactions the explicit modeling of the entropy appears to be a step towards a more complete theory that actually makes predictions beyond the mass action law. The explicit introduction of Lagrange multipliers associated with the conservation laws helps us discover a new, sensible ansatz for the kinetic energy. For the case of dissociation, Saha’s equation is the first result that drops out. We study the temperature dependence of the molecule/atom transition in hydrogen, a process famously used by Saha in the study of the main sequel of stars in the Russell-Hirzberg diagram. Other chemical processes have not yet been studied in depth.

Section VI.1. Immiscibility is a very rich subject. We explore the effect of a primitive type of interaction, using several different methods: the common tangent, exploiting symmetry and finally direct search, the only method that works in general - and it does work, very well.
Section VI.2-4. Immiscible van der Waals fluids. Efficient calculation of coexistent mixtures.
Sections VI.4-7. Applications to Alkalines, ideal gases, Nitrogen and Oxygen.
Chapter VII is a study of sound propagation in mixtures of ideal gases and van der Waals fluids. The theory of propagation of sound in mixtures takes full account of the several degrees of freedom. With the inclusion of an appropriate interaction it is easy to account for observations, but perhaps there is not enough observations available to determine the interaction. A major project is to determine interactions that account for the speed of sound at all temperatures and densities and, at the same time, for critical behavior and for the limits of miscibility. A fair number of cases are found to satisfy this condition.

Section VII.1. We calculate the propagation matrix and chart the two sounds that must appear when the gases do not interact with each other, against the concentration. It is found that there are two kinds of sound, different in the relative phase of the oscillations of the two components.

Section VII.2. We try two types of interactions and find that the free interaction energy density

\[ f_{\text{int}} = \alpha \sqrt{\rho_1 \rho_2} \]

works very well to bring the theory in good agreement with experiment, for both types of gases. The alternative,

\[ f_{\text{int}} = \alpha \rho_1 \rho_2 \]

is not effective. The mixtures studied are N-Ar and He-Xe.

Chapter VIII. A tentative alternative to the standard theory of superfluid helium is presented. This theory is simpler than Landau’s theory, but no attempt has been made, at this point, to understand the various instabilities, or the quantization of vortices.

Chapter IX. Atmospheres

Atmospheres form a major field of applications, especially mixed atmospheres. At this stage only a part of work in progress is included in the book.

Chapter X

is concerned with the limitation that characterizes our work till now, the limitation to potential flow.

Here we finally take up the challenge of rotational flows and vorticity, at first in the very particular context of Couette flows. A Lagrangian-Hamiltonian theory is presented for non potential flows that is in substantial agreement with the Navier Stokes equation in the case of non viscous flow and in the case of stationary flows of viscous fluids.

In the following sections we study the interesting question of the correct number of independent dynamical degrees of freedom, in binary systems and in various kinds of mixtures.

November 2017.

ACKNOWLEDGEMENTS

I thank all the people who have helped me with criticism, most especially Professor Hidenori Sonoda in Kobe University, Tore Haug-Warberg of NTU in Trondheim and the members of the Bogoliubov Institute in Dubna. I am grateful to The Yukava Institute in Kyoto, The Physics Division of NTNU in Trondheim and above all the Bogoliubov Institute for Theoretical Physics in Dubna for hospitality.
I. INTRODUCTION

Thermodynamics as we see it is an extension of hydrodynamics by temperature. It is difficult to believe that the work of Archimedes could have happened without an extensive prehistory of practical and theoretical work, but all we have is the archeological evidence of highly developed ‘pneumatic societies’ (Heyerdahl 1987). Historical hydro-thermodynamics began with experiments by R. Boyle during the 17th century and took off at the start of the 19th century with the work of Carnot, Mariotte, Gay-Lussac, Joule and many others, interpreted by Laplace, Fourier, Poisson, Thomson, Clausius and others. The first steps are concerned with the dynamics of fluids, principally gases, and consist of the identification of the main observables, density and pressure, and relations between them. Thermodynamics proper starts with the definition of temperature and begins its modern development, after a very hard struggle (Truesdell 1980, Müller 2007), with the introduction of the concept of entropy.

The story of the early stage of this developing science is ably presented in numerous textbooks. The following summary is therefore somewhat abbreviated, up to the point where we try to lay the foundations of adiabatic thermodynamics on the platform laid down by Gibbs, in Chapter II.

I.1. Elements of hydrodynamics

The nature of a liquid. Density

For an initial introduction to this subject the book by Ramsey (1936) is recommended. It begins with a very lucid explanation of what it is that characterizes a fluid. For a complete treatment of classical hydrodynamics the book by H. Lamb (1916) is famous, but difficult. For another extended text on hydrodynamics, see Sedov (1971). A fluid may be either a gas or a liquid. There is no precise distinction between the two, but the gas is the better intuitive model and the easier to understand. Consider a closed, rigid vessel filled with a gas, in the absence of discernible, macroscopic motion and in the approximation in which gravitation and other external influences are neglected. The most elementary concepts attached to this system are the volume $V$ of the vessel (fully occupied by the gas) and the total mass $M$. The average mass density is $M/V$ and we suppose that we can define a local mass density $\rho(x)$ at each point $x$ in the gas. In the first experiments we may assume that this density is uniform and constant in time, in which case $\rho(x, t) = M/V$, but in principle it is a density field defined in the interior of the vessel, varying from point to point, and with time. Hydrodynamics is a theory of fields on space-time.

Throughout this chapter we are concerned with simple systems, to the exclusion of mixtures, where additional dynamical variables are needed.

All quantities will be given with reference to the cgs system of units: centimeters, grams and seconds. The statement ‘$\rho = 3$’ means that the density is 3 grams per cubic centimeter. Molar densities will be used in Chapter VI and in some later chapters.

There are enough units to cause confusion. For example, the basic unit of energy is either the erg or else the much larger Joule,

$$1 \text{ erg} = 1 \text{ g cm}^2/\text{s}^2, \quad 1 \text{ Joule} = 10^7 \text{ erg}.$$  

The cgs unit of pressure is one Pascal,

$$Pa = 10 \text{ erg/cm}^3$$
or the mega-Pascal, $1\, MPa = 1\, J/cm^3$. The basic unit of energy density is $erg/cm^3$. In a context that often adds energy density to pressure it would be convenient to use either $erg/cm^3$ or $J/cm^3$ for both. But that is not customary. The *Joule* is often used for energy and *Joule/cm$^3$* for energy density but more commonly the *bar*,

\[ 1\, bar = 10^5\, Pa = 10^{-1}\, MPa, \]

is used for pressure; it is essentially the same as one standard atmosphere; precisely $1\, bar = .986\, atm$ or $1\, atm = 101325\, Pa$, by definition. So in that case just divide the numerical value of the pressure (given in bars or atmospheres) by 10 and you have it in $Joule/cm^3$, then add it to other contributions to the energy density given in the same unit.

**Pressure**

Consider a vessel filled with a fluid, and furnished with a piston that can be moved to change the total volume, without changing the mass, thus affecting the density, supposed uniform. Move the piston very slowly, so as not to agitate the fluid; this requires a force $F$, say. See Fig. 1.1.1.

![Fig.1.1.1. Vessel with piston.](image)

The most elementary experiment of hydrodynamics measures the force $F$ that is required to displace the piston. If the surface of the piston is normal to the displacement $dx$ and has area $A$, then the change in volume is

\[ dV = Adx. \]

The work done by the piston is $Fdx$ and the **average pressure** against the piston is defined to be

\[ P = F/A. \]

The pressure is expected to be uniform across the face of the piston. Usually, the pressure against any other portion of the walls of the vessel is not measured. But it can be measured, at the wall and in the interior, and it is a common experience that the pressure on the piston is transmitted through the fluid and that, in the case that there is no motion and no external forces, it is uniform. We postulate the existence of a field $p$ over the extent of the fluid, eventually varying with position and with time, reducing to the value $P$ at the boundary. See Gibbs (1878) page 139 and Section III.5.

The pressure on the walls can be understood in terms of classical particles bouncing off the walls. The notion of a pressure field in the bulk is the first axiom of hydrodynamics; it
can be supported intuitively by placing imaginary walls that divide the fluid into separate compartments. At equilibrium the two sides of such a wall are subject to forces of equal magnitude, in opposite direction. But such walls are not real, so to prevent macroscopic flow it is necessary to suppose that the parts of the fluid exert forces on each other; it is thus not possible to maintain, as in the classical atomic picture of a collisionless gas, that the particles of the fluid do not interact with each other, but only with the walls. This circumstance leads to certain difficulties in connection with the interpretation of ideal gases, to be discussed later. The resolution of the paradox is fundamental for an understanding of thermodynamics.

We have identified two of the three fields needed to describe a simple fluid. The third is a vector field $\vec{v}$, interpreted as being the instantaneous velocity of motion of a small portion of the liquid centered at a point. This fluid velocity is not interpreted in terms of the motion of individual atoms, nor is it associated with Brownian motion; it is entirely macroscopic and defined by the displacement of the fluid.

This completes the enumeration of the dynamical variables of a simple, hydrodynamical system and we are ready to begin the description of the simplest relations and the simplest experiments.

Energy

Theoretical hydrodynamics embodies a hallowed principle, conservation of energy. The energy expended by an external force, by moving the piston in Fig.1.1.1 inwards a distance $dx$ (making $dV < 0$) is

$$Fdx = -p dV.$$ 

This energy must be conserved, somehow, and kept in reserve by the liquid. In fact, substantially the same amount of energy is found to be returned to the piston if it is subsequently withdrawn. This is of course an idealization, but in most cases to be covered in this book it is true to very high accuracy if the motion of the piston is slow enough; the fluid behaves like an elastic body, more precisely as a spring, as is required for the good functioning of pneumatic operating systems.* This concept of mechanical work and energy is hydrodynamical. It is carried over to thermodynamics but in the wider context it is not conserved. The law of conservation of energy in thermodynamics depends on the introduction of the concepts of temperature and heat.

Equation of continuity

Experience shows that total mass is preserved. This law is expressed locally by the equation of continuity,

$$\dot{\rho} + \text{div}(\rho \vec{v}) = 0.$$  \hspace{1cm} (1.1.1)

To get a more concrete visualization of what this means, consider a portion $\Sigma$ of the available volume, and integrate

$$\int_{\Sigma} d^3x \left( \dot{\rho} + \text{div}(\rho \vec{v}) \right) = 0.$$ 

* But see Section III.4.
By Gauss’ theorem the second term can be converted into an integral over the boundary $\partial \Sigma$ of the volume $\Sigma$, so that the last equation is the same as

$$\frac{d}{dt} \int_{\Sigma} d^3 x \rho = \int_{\Sigma} d^3 x \dot{\rho} = - \int_{\partial \Sigma} \rho \vec{v} \cdot d\vec{\sigma}; \quad (1.1.2)$$

that is, the increase of mass in $\Sigma$ is accounted for by the flow of mass inwards through the boundary. The verification of the equation of continuity justifies the interpretation of $\rho \vec{v}$ as a mass current.

In a ‘Newtonian fluid’ each element of the fluid is assumed to accelerate in accordance with Newton’s law, in the absence of other forces, in response to the pressure gradient,

$$\rho \frac{D\vec{v}}{Dt} = -\vec{\nabla} p. \quad (1.1.3)$$

This is the simplest case of an equation attributed to Bernoulli (1738) but already known to Newton. The total variation with time that appears here is partly due to the passage of time and in part caused by the motion of the fluid element through the displacement $d\vec{x} = dt \vec{v}$, which induces the change $\delta \psi = d\vec{x} \cdot \vec{\nabla} \psi$ in the value of any function $\psi$. Thus

$$D\vec{v} = dt \vec{v} + dt (\vec{v} \cdot \vec{\nabla}) \vec{v}.$$

Most fluids considered in this book are assumed to be Newtonian.

The next sections continue the formal development and leads us to the core of our subject. More intuitive aspects of hydrodynamics are presented in Sections 7 and 8 of this chapter.
I.2. Hamiltonian and Lagrangian formulations of hydrodynamics

The Hamiltonian formulation of classical mechanics was invented after the equations of motion had been established and it may therefore be said that it is a mere reformulation. The same objection may be raised with respect to the Hamiltonian formulation of hydrodynamics. But experience has shown and continues to show the value of the Hamiltonian and Lagrangian formulations in most fields of physics. Helmholtz and Maxwell are two of the many physicists who sought action principle formulations for every branch of physics. * One conclusion of our work is that hydrodynamics and thermodynamics are not exceptional and that a Lagrangian formulation is very valuable.

A remark by Poincaré expresses very precisely what I feel when confronted with a theory that is presented as a list of equations: *

“We cannot content ourselves with formulas simply juxtaposed which agree only by a happy chance; it is necessary that these formulas come as it were to interpenetrate one another. The mind will not be satisfied until it believes itself to grasp the reason of this agreement, to the point of having the illusion that it could have foreseen this.”

The only context in which a collection of equations take on aspects of an organized entity with a soul is one that is governed by a principle of least action.

I find nothing more discouraging than a paper that begins by declaring that “the following $n$ equations will be used in our calculation.”

But the most pervasive argument in favor of action principles is their immense predictive power.

Action principles. Lagrange multipliers

An action principle is a physical law or statement to the effect that something, ‘the action’, tends to assume a minimal or maximal value. For a simple example let $\rho$ be the density of a fluid and let $W[\rho]$ be a functional that may be interpreted as an energy density, varying with position through its dependence on $\rho$,

$$W[\rho](x) := W(\rho(x)).$$

The total energy is

$$E = \int d^3 x W[\rho].$$

The problem is to determine the density that minimizes the total energy; this leads to the requirement that

$$\delta E = \int d^3 x \delta W = \int d^3 x \delta \rho \frac{dW}{d\rho} = 0. \quad (1.2.1)$$

This, as it stands, is not yet meaningful unless we specify the class of allowed variations of the density. We cannot allow all variations; to have any hope that there is a minimum

* For references to papers of this period see the review by Bordoni (2014).
* See works on ‘extended thermodynamicics’, e.g. Müller (1980).
energy we have to be dealing with a fixed quantity (mass) of fluid,

\[ M = \int d^3x \rho. \]

This implies that the variation of the density is restricted by the condition

\[ \delta M = \delta \int d^3x \rho = \int d^3x \delta \rho = 0. \]

In the absence of any restrictions on \( \delta \rho \), Eq.(1.2.1) implies that \( dW/d\rho = 0 \), a statement that is too strong; when the variation is restricted in this way it implies less, only that \( dW/d\rho \) is constant,

\[ \frac{dW}{d\rho} = c, \quad \text{say}. \]

Indeed, that is sufficient, since in that case

\[ \int d^3x \delta \rho \frac{dW}{d\rho} = c \int d^3x \delta \rho = 0. \]

An efficient way to deal with this kind of situation is to modify the action by including a Lagrange multiplier. Let \( \lambda \) be a real number and consider the modified action

\[ E_\lambda = \int d^3x \left( W(\rho) + \lambda \rho \right). \]

Now

\[ \delta E_\lambda = \int d^3x \delta(W + \lambda \rho) = \int d^3x \delta \rho \left( \frac{dW}{d\rho} + \lambda \right) = 0. \]

Here, if we impose no restrictions on the variation, we get

\[ \frac{\partial W}{\partial \rho} + \lambda = 0. \]

Since the value of \( \lambda \) is not fixed, this says that \( W \) is a constant, which is the correct answer. This method is just a trick to allow us to forget the troublesome restriction to be imposed on the variation of the density, but it turns out to bring additional advantages.

**The Lagrangian of Fetter and Walecka**

A variational formulation of simple hydrodynamics may be found in a book by Fetter and Walecka (1980). The action, actually discovered already by Lagrange (1760), is *

\[ A = \int dt \int d^3x \mathcal{L}, \quad \mathcal{L} = \rho(\dot{\Phi} - \lambda - \vec{v}^2/2) - W(\rho), \quad \vec{v} := -\vec{\nabla}\Phi. \quad (1.2.2) \]

* \( \mathcal{L} \) is the Lagrangian density, ‘the Lagrangian’ is the space integral \( \int \delta^3x \mathcal{L} \) and “\( A \)” is ‘the action’. 

22
The kinetic energy density $\rho \vec{v}^2/2$ has been included, as well as a Lagrange multiplier $\lambda$ and a term $\rho \dot{\Phi}$. This last term will be present in all our work; it has a number of different personalities and interpretations.

In the first place, if the velocity vanishes, and $\dot{\Phi}$ is just a constant, then it serves as the required Lagrange multiplier associated with the mass. Hence it can absorb the Lagrange multiplier and no explicit $\lambda$-term will be needed to allow for the fixing of the mass. But later this term will be related to the escape velocity and the energy of evaporation and more generally to the latent heat, and it will help us formulate the principle of maximal entropy. Most important, with the introduction of a time derivative, it turns the Hamiltonian density $\rho \lambda + \rho \vec{v}^2/2 + W$ into a Lagrangian density.

Following Fetter and Walecka we suppose that
\[ \vec{v} = -\nabla \Phi. \]

In this case, when the velocity can be expressed as the gradient of a scalar field, the velocity is said to be irrotational and the flow $\rho \vec{v}$ is said to be of potential type. That is a strong restriction on the velocity field, but we shall see that this provisional loss of generality still allows a large field of applications. The restriction to potential flows will be lifted in Chapter X. The appearance of the kinetic energy in the Lagrangian and in the Hamiltonian seems completely natural, but the fact that this leads to the correct equations of motion is worthy of notice. It will be shown that the appearance of the Lagrange multiplier as an adjunct to the velocity potential $\Phi$ is appropriate.

Now we have two scalar fields to vary. The variation of $\Phi$ and $\vec{v}$ gives
\[ \delta A = \int dt \int d^3x (\rho \delta \dot{\Phi} - \vec{v} \cdot \delta \vec{v}) = 0. \]

A point that deserves to be strongly emphasized is that the variations of $\dot{\Phi}$ and $\vec{v}$ are not independent, and that both are determined by the variation $\delta \Phi$ of the dynamical field variable $\Phi$. Consequently, to deduce the differential form of the last equation it must be rewritten as
\[ \delta A = -\int dt \int d^3x \delta \Phi \left( \dot{\rho} + \vec{\nabla} \cdot (\rho \vec{v}) \right) = 0 \]

(We have made an integration by parts. ‘Boundary terms’ are irrelevant in this context, but see Section 3.8.) Since $\delta \Phi$ is arbitrary, the continuity equation follows,
\[ \dot{\rho} + \vec{\nabla} \cdot (\rho \vec{v}) = 0. \]  

Independent variation of the density gives
\[ \dot{\Phi} - \vec{v}^2/2 = \frac{dW}{d\rho}. \]

The Lagrange multiplier disappears when we take the gradient,
\[ \rho \dot{\vec{v}} + \vec{\nabla} \vec{v}^2/2 = -\vec{\nabla} p, \quad p := \rho \frac{\partial W}{\partial \rho} - W. \]
The fact that the combination $D\vec{v}/Dt$ appears here, as it should, is due to the identity

$$\vec{\nabla} \vec{v}^2/2 = (\vec{v} \cdot \vec{\nabla}) \vec{v},$$

which is true by virtue of $\vec{v} = -\vec{\nabla} \Phi$. For a general vector field we have instead the identity

$$\vec{v} \wedge (\vec{\nabla} \wedge \vec{v}) = \vec{\nabla} (\vec{v}^2/2 - (\vec{v} \cdot \vec{\nabla}) \vec{v}).$$

The Hamiltonian is

$$H[\rho, \vec{v}] = \int d^3x \left( \rho \vec{v}^2/2 + W(\rho) \right)$$

and the Poisson bracket

$$\{A, B\} = -\int d^3x \left( \frac{\partial A}{\partial v_i} \frac{\partial B}{\partial x_i} - \frac{\partial A}{\partial \rho} \right).$$

Here $A, B$ are functionals of $\vec{v}$ and $\Phi$, with $\vec{v}$ defined as $-\vec{\nabla} \Phi$. The two fundamental equations (1.2.3) and (1.2.4) are the Hamiltonian equations of motion,

$$\dot{\rho} = \{\rho, H\}, \quad \dot{\vec{v}} = \{\vec{v}, H\}. \quad (1.2.5)$$

We shall return to these formulas below.

The restriction to gradient flows will be lifted in Chapter 10.

Thermodynamics is usually understood as a study of equilibria. Here we have taken hydrodynamics as our starting point, as an introduction to what we call adiabatic thermodynamics, thus making it clear that we are aiming for a more encompassing theory. The next step is to introduce the temperature.

The velocity potential

The variable $\Phi$ will come to play a very important role in the theory. Apart from the fact that its gradient is the velocity of flow, it plays a role even in the case that there is no flow. If there is no flow and no external forces, then the two Euler-Lagrange equations combine to give $\dot{\Phi} = R T (n + 1)$. When the entropy is fixed there is a relationship between $T$ and $\rho$ that allows to express the value of $T$ in terms of the density. If the volume is fixed this relates $\dot{\Phi}$ to the total mass, as expected because of the role of this variable as a Lagrange multiplier for the constraint on the mass. When it is not of interest to know the total mass we can treat the value of $\dot{\Phi}$ for the system at rest as an adjustable constant.

A generalization of this action principle will be introduced in Chapter X. The Euler-Lagrange equations associated with the Fetter-Walecka Lagrangian are standard and widely used in wider contexts.
I.3. The temperature

For a full appreciation of this topic there can be no more enjoyable introduction than that of Saha and Srivastava (1935).

The observation that a body, solid or fluid, can be hot or cold is familiar, as is the observation that, in a contact between two bodies, the difference tends to dissipate. It is observed that “heat” passes from the hot to the cold, never in the opposite sense. And if no change occurs, then both bodies must have the same temperature. This is the basis for the invention of thermometers; see the book just mentioned.

It is assumed that the temperature can be measured at each point of a fluid, at all times, so that there is a (scalar) field $T$, in principle time dependent, to be accounted for, in addition to density, pressure and the flow vector. That is the mark of thermodynamics, as compared to mere hydrodynamics.

![Fig.1.3.1. Thermometer.](image)

One of the earliest laws that was derived from experiment was the **Gas Law**, according to which, at equilibrium (no motion and all fields constant in time),

$$p = R\rho T. \quad \text{The ideal gas law.} \quad (1.3.1)$$

where $R$ is a constant and $\rho$ is the molar density. * The Joule is an energy unit equal to $10^7$ erg. Since our densities shall be given in grams (not mols) per cm$^3$ we shall have

$$p = \frac{R}{m}\rho T,$$

where $m$ is the molecular weight. Sometimes $R_i$ will stand for $R/m_i$ where $m_i$ is the molecular weight of the $i$'th component of a mixture. A gas for which this law is valid is

* If the densities are measured in mols per cm$^3$ then it is a universal constant,

$$R = .8314 \times 10^8 \text{(cm/sec)}^2/K = 8.314 \text{Joule}.$$
often called an ideal gas. When this relation holds, when this or some other relation is used to express $T$ in terms of $\rho$, then the temperature ceases to be an independent variable and the theory reduces in most respects to hydrodynamics. But temperature is vital to any understanding of thermodynamics. By admitting the temperature as one of the dynamical variables we are adding another dimension to the dynamics. The Euler-Lagrange equation that comes from variation of the temperature gives us the “adiabatic condition” that gives meaning to the terms adiabatic derivative and adiabatic thermodynamics. Bringing this equation to the front of the investigation is an important aspect of this treatise.

Example. Ordinary air at normal conditions (293 degrees Kelvin) has molecular weight 29 and a density of \(0.012g/cm^3\), thus, with the density \(\rho = 0.0012g/cm^3\),

\[
p = \frac{0.8314}{29} \times 10^8 \times 0.012 \times 293 = 1.008 \times 10^6\text{ergs},
\]

with the density \(\rho = 1.2/29(\text{mol/Lit})\). Alternatively,

\[
p = 0.08314 \times 10^5 \times \frac{1.2}{29} \times 293 = 1.008\text{ bars}.
\]

I.4. The internal energy and the first law

Heat and Internal Energy

The first treatise on thermodynamics was probably the work of Boyle, dating from 1660. But further development had to wait until Thomas Savery invented the steam engine and Sadi Carnot took up the study of its efficiency.

It was pointed out that some fluids behave, when worked by a piston, as elastic springs. When work is done on the fluid, by compressing it, it appears to gain energy and to be able to return it later, for when the piston is withdrawn slowly, it is pushed out by the pressure of the fluid, the fluid produces mechanical energy. * When the principle of energy conservation was recognized it became necessary to suppose that the fluid is capable of storing energy in some form, ready to release it when offered the opportunity. This led to the idea that there must be a function $U$, depending on the volume and on a second variable, the “heat content” $Q$, such that, for variations of the equilibrium configurations,

\[
dU = dQ - pdV.
\] \hspace{1cm} (1.4.1)

This conclusion is contradicted by observation. The equation defines $dQ$ but there is no variable or function $Q$; $dQ$ is not a perfect differential. The idea of “heat content” belongs to the older, material interpretation of heat; it does not exist in modern thermodynamics.

The idea of an energy functional expressed in terms of relevant dynamical variables is valid, but the “heat content” is not one of those dynamical variables.

* This is an oversimplification; much more will be said about this comparison later on.
The figure that more than anyone else dominates the earliest part of the history of thermodynamics is Sadi Carnot. When it was found that heat can be converted to mechanical energy, by the steam engine, he set out to determine the most efficient “heat engine” (Carnot 1824). In a cyclical engine you must supply heat at high pressure, then remove it at low pressure. The long and painful process that led from this observation to the second law of thermodynamics is recounted in most books on thermodynamics, most entertainingly by Truesdell (1980).

Entropy. Carnot cycle

In a nutshell, the conclusion is that there is no function \( U(V, Q) \) that satisfies Eq.(1.4.1); that equation needs an integration factor: there is a variable \( S \), related to \( dQ \) by \( dQ = TdS \) and a function \( U(V, S) \) such that

\[
dU(V, S) = TdS - pdV. \tag{1.4.2}
\]

The variable \( S \) is called the entropy and the energy \( U \) is called the internal energy. The factors \( T \) and \( p \) are the partial derivatives of this function,

\[
\left. \frac{\partial U}{\partial V} \right|_S = -p, \quad \left. \frac{\partial U}{\partial S} \right|_V = T. \tag{1.4.3 - 4}
\]

Another way to state this result is that the differential \( dU + pdV \) is not exact. It needs a multiplier. After a time it was realized (Clausius 1887) that the multiplier is \( 1/T \): \( (dU + pdV)/T = dS \).

The experimental evidence for this statement is very direct.

Consider an ideal engine that can exchange heat with a reservoir and that can do mechanical work by pushing on a piston. Suppose its operation is cyclic and that it starts with volume \( V_1 \), pressure \( p_1 \) and temperature \( T_1 \). See Fig. 1.4.1. The changes are supposedly slow; the kinetic energy will be neglected; all configurations considered are states of equilibrium. The cycle begins by adding an amount \( dQ_1 \) of heat at constant temperature \( T_1 \) moving the system from point \( A \) to point \( B \). To prevent the temperature from rising the volume is allowed to increase as the pressure decreases. Next the temperature is reduced by reducing the pressure, ending at point \( C \). No heat is added or withdrawn during this stage; the temperature is reduced to \( T_2 \), say. Next an amount \( dQ_2 \) of heat is withdrawn at constant temperature, which implies a reduction of the volume and an increase in pressure. We are at point \( D \). Finally, by a process that does not involve a transfer of heat, the system is returned to the initial state by compression. The fact that this final state is the same as the initial one implies that the two changes in entropy must cancel *, thus

\[
dS_1 - dS_2 = \frac{dQ_1}{T_1} - \frac{dQ_2}{T_2} = 0.
\]

* We can express this fact in another way. Because \( S \) is a state variable, while \( Q \) is not, the integrated change \( \int dS \) of \( S \) around a closed loop is zero while that of \( Q \) is not.
Since \( T_1 > T_2 \), it follows that \( dQ_1 > dQ_2 \), more heat is added to the system than is withdrawn. Energy conservation implies that the difference has been converted to mechanical energy. This description of the \textbf{Carnot cycle} is taken from Holman (1974).

This very abbreviated account of one of the most dramatic developments in the history of science does not do it justice. But since I have nothing original to add to that story I prefer to refer the reader to one of the excellent textbooks. See e.g. Callen (1960).

It is easy to understand the need to introduce an additional variable. We must recognize that, even in the simplest case, it is not enough to discover one equilibrium state for each elementary system. A system at equilibrium is capable of changing, for example, by varying the temperature. Heating will lead to another, distinct set of configurations and consequently there must be (at least) a one-parameter family of equilibria. They are distinguished by the value of the state variable \( S \), the entropy. Heat engines, being cyclical, can convert heat to mechanical energy because \( dQ \) is not a total differential.

Entropy is the most difficult subject in thermodynamics. The concept makes good sense for equilibrium configurations and, as we shall show, it easily extends to adiabatic changes and adiabatic configurations.* But a definition of entropy that applies to irreversible processes is still being debated. ** In this book it will not be neglected, far from it. But we shall omit some material about entropy that may be found in standard textbooks and concentrate instead on our narrow topic: thermodynamics as a Eulerian field theory, and on the role that is played by entropy in that context.

* An adiabatic configuration is a solution of the Euler - Lagrange equations associated to a Lagrangian.
** See for example the discussion after a conference contribution by J.Meixner. (Meixner 1970), as well as references to Prigogine given below.
The First Law and Free Energy

The first law of thermodynamics is the statement that the function $U(V, S)$ exists. It involves the very difficult concept that is entropy.

The birth pangs of the first law of thermodynamics have been discussed in many places, including Truesdell (1980). I shall add some comments that may be new.

The difficulties that were finally resolved by the invention of entropy arise in the discussion of the piston experiment because an element is missing. We know that the system has additional variables, and yet we failed to specify which variables are being kept fixed as we changed the volume. Instead it was assumed, tacitly, that the system is thermally isolated, that no heat enters or leaves the system. This is hazardous, for the concept of thermal isolation is as complicated as the concept of ‘heat flow’. To introduce the first law of thermodynamics it would perhaps be better to discuss another experiment.

Here is a proposal for another way to develop the foundations of thermodynamics. It avoids talking about heat as if it were a substance and it avoids the very difficult concept of an isolated system.

Consider an experiment in which a gas, at rest, is contained in a rigid vessel and the volume is changed with the help of a piston. But we shall not assume that the system is “isolated”. Instead, assume that the system is described by precisely 2 variables. There may be other ways to choose them, but

\begin{quote}
assume that volume and temperature form a complete set of independent variables that suffices to fix the state of the system.
\end{quote}

This is another way to approach the first law of thermodynamics. It implies that there is something that deserves to be called ‘energy’, that can be expressed as a function of $V$ and $T$. Call this energy $F$, and assume that it has a differential

$$dF = -PdV - SdT.$$

This is the same as stating that

$$-P = \frac{\partial F}{\partial V}, \quad -S = \frac{\partial F}{\partial T}.$$

At this stage “$-S$” is simply a partial derivative of $F$; nothing else is known about it. In our experiment the volume is changed just as before; the difference is that we fix the other variable: $T$. We put our vessel in thermal contact with a large heat bath with temperature $T$ to ensure that $T$ cannot change. By defining the experiment properly we avoid all the problems.

In this first experiment only $V$ is changed, $T$ is kept fixed, and the measured pressure is given as the coefficient $-P$ in

$$dF = -PdV, \quad -P := \left. \frac{\partial F}{\partial V} \right|_T.$$

This is a different experiment; there is no guarantee that the new energy $F$ is the same as $U$. And it is not.
The last formula has a simple and direct intuitive content. It defines the pressure as the response of the system to a change in its volume, at constant temperature, given in the units of energy per degree.

Turning from this particular experiment, to one in which both the volume and the temperature are changed, we express the variation of $F$ as

$$dF = -PdV - SdT.$$ 

Here, naturally, appears a second coefficient,

$$-S := \frac{\partial F}{\partial T} \bigg|_V.$$ 

(1.4.5)

Just as $P$ is a measure of the response of the system to a change in $V$ ($T$ fixed), $S$ is a measure of the response of the system to a change in $T$ ($V$ fixed). The first coefficient is easily measured; gradually methods will emerge that allow us to determine the other coefficient as well.

The function $F$ is called the **free energy**; it is related to $U$ by a Legendre transformation,

$$U(V, S) = \left( F(V, T) + ST \right) \bigg|_{S := -\partial F/\partial T}.$$ 

The coefficient $S$ is the **entropy**.

The point of this digression is that, by simply focussing on another experiment, we have introduced the entropy $S$, now clearly a state variable, without tripping over an imperfect differential. It is defined by Eq. (1.4.5).

The first law of thermodynamics is the statement that the function $F$ exists; it is of course equivalent to the existence of the function $U$.

The basic postulate that defines this development is the statement that the state of a system is completely defined by $T$ and $V$. If these variables are fixed, and the expression for the free energy $F(T, V)$ is known, then $S$ and $P$ can be determined, but in general, when the expression for $F$ has not been specified, then $P$ and $S$ are independent variables. It is natural to define an ‘isolated system’ as one that is characterized by fixed values of $S$ and $P$.

**I.5. A Lagrangian for rotational motion?**

One reason for wanting to let go of the restriction to irrotational motion is the hope of eventually developing a theory of turbulence. This would be beyond the scope of this volume. Nevertheless, it is important to know that an irrotational velocity field is not an absolute requirement for setting up a Lagrangian formulation of adiabatic hydrodynamics.

Granted that the equations, the equation of continuity and Bernoulli’s equation, make sense without the restriction to the special case in which the velocity field is a gradient, consider nevertheless the special case of an irrotational vector field, and the Lagrangian

$$\mathcal{L}[\Phi, \rho] = \int d^3x \left( \rho (\dot{\Phi} - \bar{v}^2/2) - W(\rho) \right).$$
Assume that the density is defined over the complement $M$ of a discrete set of lines in $\mathbb{R}^3$, that the field $\Phi$ is a section of a line bundle over $M$ and that $\vec{v} = -\nabla \Phi$ is well defined as a tangent vector field on $M$. For example, let $M$ be the complement of the $z$ axis, and let $\Phi(x, y, z) = \arctan(y/x)$. The flow is horizontal and circular,

$$\vec{v} = \left(\frac{-y}{r^2}, \frac{x}{r^2}, 0\right), \quad r = \sqrt{x^2 + y^2},$$

and the curl is concentrated on the $z$ axis. Variation of $\Phi$ and $\rho$ then gives the correct Hamiltonian equations of motion. The 'vorticity',

$$\int_{\text{loop}} \rho \vec{v} \cdot d\vec{x}$$

is a constant of the motion; that is, the structure class of the section $\Phi$ is a constant of the motion. It follows that the singular line moves with the fluid.

Already, in a remark at the end of Section I.2 it was pointed out that the requirement that $\vec{v}$ be a gradient can be relaxed. But there is one procedure that cannot be recommended. The two Euler Lagrange equations of the Fetter-Lagrange action are the equation of continuity (1.2.1) and the Bernoulli equation (1.1.3). A “theory” could be proclaimed, based on these two equations, without the restriction to potential flow. To fully appreciate the futility of constructing new theories based merely on a set of equations it is sufficient to examine the consequences in this simplest possible case. Suppose that the fluid moves in the manner of a solid body, with the vector field

$$\vec{v} = (-y, x, 0), \quad v^2/2 = r^2/2.$$  

The force field, the centrifugal force is, according to Eq.(1.2.2)

$$-\vec{\nabla}r^2/2 = -\vec{r},$$

directed towards the center, against all experience. Clearly, it is dangerous to transplant equations from their natural habitat to a wider context. * We shall see that this warning should be heeded, not only with respect to equations, but in the applications of concepts as well.

Something of the first importance has been learned here. With the study of action principles, with their high efficiency and strong aesthetical appeal, we become acquainted with certain concepts that become part of our intuition, and with certain types of equations. In the case at hand that includes the concept of kinetic energy and the idea that the negative gradient of this ‘kinetic potential’, $K$, say, constitutes a force. We are tempted to apply this idea to a wider field, looking at an equation of the type $\vec{F} = -\vec{\nabla}K$ as having general validity and using it when there is no action principle. We have seen that this easily leads to serious error. See also Section III.9, and the paper “A Classic mistake...”, Fronsdal 2018.

**LET US NOT USE A TERM LIKE ‘ENERGY’ UNLESS WE ARE WORKING WITHIN AN ACTION PRINCIPLE**

* The same equation does give the correct sign when the velocity is irrotational, as when $\vec{v} = r^{-2}(y, x, 0), \vec{v}^2/2 = r^{-2}/2$, with $-\vec{\nabla}r^{-2}/2 = r^{-3}\vec{r}$ pointing outwards.
I.6. On the possibility of a Lagrangian in the case of dissipation

The importance of a Lagrangian formulation can be judged from the amount of effort that has been expended over the years to achieve an action principle for dissipative phenomena. That this is not an absurdity can be seen from the elementary example of a particle moving in one dimension in a force field derived from a potential and a frictional force of the type $-\mu \dot{x}$. The Lagrangian is

$$\mathcal{L} = \int dx \, e^{-\mu \dot{q}/2} (\dot{q}^2 / 2 - V(x))$$

and the equation of motion

$$\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{q}} - \frac{\partial \mathcal{L}}{\partial q} = e^{-\mu t} \left( \ddot{q} + \mu \dot{q} + \frac{\partial V}{\partial q} \right) = 0$$

Helmholz was the first to attempt a Lagrangian formulation of dissipative thermodynamics. His work was reviewed by Poincaré * who found that it was of inadequate generality. But the subject was still alive in 1970 (Prigogine 1970). See also Prigogine (1965) and Kaufman (1984).

I.7. Hydrodynamics of potential flow

Hydrodynamics can be divided into three parts or stages. The first stage deals with fluids at rest; about this pure hydrodynamics does not have much to say; it is the classical domain of thermodynamics. The second part is concerned exclusively with potential flow, a surprisingly rich subject. One reason for this is that the vortices of superfluid Helium seem to be of this type, except for a tiny neighborhood of the center, a vortex string. This is a subject that will come up in Chapter X.

Here we shall discuss another application.

It turns out that a sustained flow, a stationary but not static system, can exist only if the Cartesian components of the flow velocity vector field are harmonic,

$$\Delta v_i(x, y, z) = 0.$$  

(The justification for this statement will come much later, in connection with the Navier-Stokes equation.) This is a case that can be dealt with very efficiently in 2 dimensions, when for reasons of symmetry the velocity is independent of the third dimension or when the system is a horizontal film with negligible extension in the vertical direction. In 2 dimensions, a harmonic function is the real or the imaginary part of a complex analytic function. We can take the velocity potential to be the imaginary part any complex analytic function of $z = x + iy$, such as

$$\ln z = \ln r + i\theta,$$

where $r, \theta$ are polar variables. Then

$$\vec{v} = -\nabla \ln(\theta) = \frac{1}{r^2} (-y, x)$$

* I have not found the references. But see Kaufman (1984) and references given there.
describes a unique circular flow with angular speed $1/r^2$. This represents a whorl, such as is seen in the wake of ships.

In order to keep the discussion as simple as possible let us suppose that the fluid is incompressible. What is meant or implied by this is that, though the pressure is determined by the need to prevent motion in the radial direction, the effect that the pressure has on the density is negligible. No theory of the origin of the pressure is needed; the pressure is just assumed to be what it takes for the fluid to execute the motion considered. In the case of the circular flow the pressure must be radial, originating from a circular boundary wall.

But perhaps there is no need for the vessel to be circular. To illustrate, take

$$\Phi = \Re(\ln z + z^4).$$

This does not have circular symmetry, its symmetry consists of rotations by 1, 2, 3 or 4 right angles, as is reflected in the flow diagram (red lines) shown in Fig.1.7.1. Counting outwards from the smallest circle six orbits are flows determined by fixing

$$\Phi = \ln r + x^4 - 6x^2y^2 - 6x^2y^2 + y^4 = -5, -3, -2, -1.3, -0.9, -0.75,$$

respectively. The outermost (purple line) flow line is the locus of

$$\Phi = \Re(\ln z + z^4 + 0.24z^8) = -0.597;$$

it is indistinguishable from a square. A perfect fit would perhaps be obtained with an elliptic function. Possibly, an elliptic function can represent a doubly periodic stack of compact flows of this type?
I.8. An alternative, ‘Lagrangian’ formulation of hydrodynamics

Up to now we have been explaining what is called the Eulerian version of hydrodynamics, restricted for the most part to the special case of potential flows, \( \vec{v} = -\nabla \Phi \). It is a “field theory” in which the dynamical variables are the scalar field \( \rho \) and the vector field \( \vec{v} \). There was no need to mention particles.

Another formulation of hydrodynamics is more directly related the particle concept; it is known as the ‘Lagrangian’ formulation and it is sometimes claimed that it is equivalent to the Eulerian version. But in the context of action principles the two versions are anything but equivalent.

Like the theory of potential flows, the ‘Lagrangian’ theory represents the velocity field as a derivative, this time a time derivative,

\[ \vec{v} = \dot{x}. \]

We can think of the vector field \( \vec{x} \) as a kind of potential, but that is not the standard interpretation. Instead, one evokes the motion of a particle that finds itself at the position \( \vec{x}(0) = \vec{a} \), say (a point in space) at time \( t = 0 \) and moves along a curve

\[ C(a) : t \mapsto \vec{x}(t). \]

This interpretation only affects the way that one thinks about the problem; it is permissible to take the other point of view, according to which \( \vec{x} \) is a dynamical field variable. Taking that interpretation we change the notation from \( \vec{x} \) to \( \vec{X} \).

The representation of the velocity field as a time derivative has the same effect as the restriction to potential flow: it makes it possible to develop an action principle. The simplest Lagrangian density is

\[ L = \rho \dot{X}^2 / 2 - W[\rho]. \]  

(1.9.1)

Variation of the density gives

\[ \dot{X}^2 / 2 - \frac{dW}{d\rho} = \text{constant} \]

and variation of \( \dot{X} \),

\[ \frac{d}{dt}(\rho \dot{X}) = 0. \]

This theory differs from the Eulerian theory in several respects and it has its own limitations. First, it does not include an equation of continuity; instead it incorporates a concept of integrability. With a fixed initial value \( \vec{X}(0) = \vec{a} \) one can calculate a path, \( \vec{X}(t) \). Under stationary conditions one may expect that the particles move on closed orbits and such orbits give occasion to integrate, as in the formula for the ‘loop vorticity’

\[ \int_C \vec{\nabla} \wedge \vec{v} \cdot d\vec{x}. \]

The integral makes sense for any closed curve \( C \), but here one selects a curve that happens to be a particle orbit.
“Een experimentator die niet an de tweede hoofdwet gelooft zal men medelijdend aankijken...” G.E. Uhlenbeck, ”Van der Waals revisited”, talk presented on the occasion of the creation of the Van der Waals chair at the University of Amsterdam in 1964.

II. ACTION PRINCIPLE FOR GLOBAL THERMODYNAMICS

By a global thermodynamic system, we mean one that is described by a finite number (usually 4) of variables, such as the equilibrium configurations of a fluid contained in a rigid vessel.

The role of an action functional as a depository of all information about a system is ubiquitous in theoretical physics, including Eulerian thermodynamics. In statistical physics the partition function plays a similar role. It has been maintained that a full expression for the internal energy as a function of the natural variables $V$ and $S$ provides a complete definition of a global thermodynamic system (Massieu 1869).

The internal energy does not reign without competition; a number of Legendre transformations lead to other possibilities that, according to Gibbs (1876), and Callen (1965), contain precisely the same information.

II.1. The internal energy and the free energy

**Fundamental relations. Legendre transformations**

Because of the very abstruse nature of the entropy we shall begin the discussion of the potentials with the free energy $F$, a function that, like the internal energy $U$, contains all intrinsic information about the system. The natural variables of $F$ are $V$ and $T$, much easier to grasp than $V$ and $S$. The relation between $F$ and $U$ is a Legendre transformation *

$$U(S,V) = \left(F(V,T) + ST\right)\big|_{S+\partial F/\partial T=0}.$$  \hspace{1cm} (2.1.1)

The inverse transformation is

$$F(V,T) = \left(U(S,V) - ST\right)\big|_{T=\partial U/\partial S}.$$  \hspace{1cm}

From the expression for the differential $dU$, Eq.(1.4.2),

$$T = \frac{\partial U}{\partial S} \bigg|_{V}, \quad p = -\frac{\partial U}{\partial V} \bigg|_{S},$$  \hspace{1cm} (2.1.2a)

we obtain

$$p = -\frac{\partial F}{\partial V} \bigg|_{T}, \quad S = -\frac{\partial F}{\partial T} \bigg|_{V}.$$  \hspace{1cm} (2.1.2b)

The advantage of basing the first law on $F$ was pointed out in the last part of Section I.4.

* As indicated, the variable $V$ can be eliminated by using the relation $S = -\partial F/\partial T$. It is thus assumed that this equation implies a unique value for $T$, when $V$ and $S$ are given. It is useful to keep this in mind; see Section IV.3.
The free energy was introduced by Helmholtz. The two other potentials that make up the complete collection, first discussed comprehensively by Massieu (1869) and by Gibbs (1876), are the Gibbs function $G(P, T)$ and the enthalpy $H(P, S)$. Two potentials with one common natural variable are related by a Legendre transformation.

The relation (2.1.1) is our first example of a ‘Legendre transformation’. Its significance lies in the fact that it correctly identifies the natural variables of the new function:

$$dU(S, V) = \frac{\partial U}{\partial S} dS + \frac{\partial U}{\partial V} dV = dF + SdT + TdS.$$

The two $dS$ terms cancel, showing that

$$dF = \frac{\partial U}{\partial V} dV - SdT = \left. \frac{\partial F}{\partial V} \right|_T dV + \left. \frac{\partial F}{\partial T} \right|_V dT.$$

That is, provided the function $U$ is well defined, the variation of $F$ (Section I.4) can be expressed in terms of the variables $V, T$ without having to solve equations that may turn out to be multivalued and hence ambiguous.

**Normalization of the energy**

Energy, strictly speaking, is not a well defined physical quantity. We can add a constant term to our formula for the energy and the physics remains unaffected, only changes are important. But in thermodynamics there is an additional ambiguity; if we add a term $cT$ ($c$ constant) to the free energy it will apparently have no effect on $U$, nor on $P$. The only effect is to renormalize the specific entropy; that is, shift this variable by the constant $c$. Until $S$ has been normalized; that is, until the zero point has been fixed, such a shift has no physical meaning. It is a basic tenet of thermodynamics that all physical information about the nature of a substance is contained in the expression given for either $U$ or $F$; therefore the said term cannot contain any physical information. This is a type of “gauge invariance” that can be used to standardize our formulas. See Section III.10.

**II.2. The ideal gas**

The ideal gas is the favorite paradigm of all textbooks on thermodynamics. It is a gas that satisfies two conditions: (1) the pressure is obtained from the formula $p = \mathcal{R} \rho T$ and (2) the internal energy is $U = cT$, with $c$ constant. These properties are satisfied when the free energy is given by the following expression

$$F(V, T) = -\mathcal{R} T \ln (VT^n), \quad \mathcal{R} = \frac{1}{m} \cdot 8314 \times 10^8,$$

where $m$ is the molecular weight of the gas. The exponent $n$ is related to the “adiabatic index” $\gamma$ of the gas by

$$\gamma = 1 + \frac{1}{n}.$$

* See Section IV.3.
According to the statistical interpretation $2n$ is the number of degrees of freedom of the molecules that make up the gas; in our present framework it is just a number: $n = 3/2$ for a monatomic gas, $n = 5/2$ for a diatomic gas. *

In some texts the ideal gas is defined by the gas law alone, while the formula for the internal energy is derived. But this “derivation” appeals to concepts that are outside our context. ** To remain within our subject we shall define the ideal gas in terms of the formula for the free energy, from which both the gas law (the thermal equation of state) and the formula for the internal energy (the caloric equation of state) are derived, as we shall see.

Additional properties are sometimes imputed to the ideal gas, properties that are not implied by the definition that we have given. We intend to stick to our definition: An ideal gas is one that has a free energy density of the form (2.2.1); that is all.

One should have thought that this simple formula (2.2.1) for the free energy of an ideal gas would be presented early and prominently in any text dealing with ideal gases, along with the statement that many properties of ideal gases follow from it. Instead, the ideal gas is often defined by its properties, while the miraculously all-incompassing formula for $F$ is not mentioned.

From Eqs.(2.1.1-2), and the above expression for $F$, there follows respectively that

\[ p = \frac{RT}{V} \tag{2.2.2} \]

and

\[ S/R = \ln(VT^n) + n. \tag{2.2.3} \]

The first is what is called the ideal gas law. The expression for the entropy implies that the polytropic relation, $VT^n = \text{constant}$, is valid for any fixed value of the entropy and this is confirmed experimentally for some gases. When this expression is substituted into the definition $U := F + ST$ one gets the statement that $U = nRT$. *** This result is often accompanied by the confusing comment that, for an ideal gas, the internal energy is independent of the volume. It must be remembered that the natural variables for $U$ are $V$ and $S$ and not $V$ and $T$. **** In terms of $V$ and $S$ the internal energy of an ideal gas is

\[ U(V, S) = nRV^{-1/n} \exp\left(\frac{S}{nR} - 1\right) \tag{2.2.4} \]

and not independent of the volume.

* Only translational and rotational degrees of freedom are counted in this connection. Vibrational and other degrees of freedom and other types of excited states are less relevant. See Landau and Lifschitz (1959).

** An attempt at a derivation within the context fails to convince. Reif (1965).

*** More simply but less clear,

\[ U = (1 - T/\partial T)(F + ST) = (1 - T/\partial T)F = nRT \]

**** See for example Rowlinson (1959) page 13 for a collection of statements that are difficult to interpret.
In this book we shall follow the practice of defining a fluid by its free energy and derive all required properties from that. An ideal gas is a gas that has the free energy given by Eq.(2.2.1).

Some real gases behave in a way that is similar to the ideal gas, especially at high temperature and low density. At lower temperature and higher density the modified ideal gas known as the van der Waals gas is a better approximation to real gases; it is sometimes used for liquids as well. The problem of finding the free energy and an equation of state for liquids is often avoided by using rough approximations (White (1999), p. 21-22.).

II.3. The two time scales of thermodynamics

The traditional point of view (and ours) envisages two quite different types of processes, with two different time scales. For the first type of process the time scale is relatively short and certain phenomena, as radiation and dissipation are often neglected. The propagation of sound in an ideal gas is an example of this type of adiabatic process. It is characterized by the fact that the entropy remains constant, thus in the case of an ideal gas, $VT^n$ is constant in time. When treating such phenomena one usually assumes that there is no interaction with the environment or, rather, that any such interaction is weak enough to be neglected. Processes of the second kind are usually characterized by much longer time scales; they can be ignored over short time intervals, but over longer time periods their effects are often cumulative. For simplicity, by choice, we limit our consideration of dissipative processes to the case when the system can be considered to be in equilibrium with respect to the faster adiabatic processes; the system passes through a sequence of equilibrium states. A process that is considered to be slow in this sense does not necessarily involve interactions with the environment. Consider a fluid in some kind of regular motion, as in flowing through a circular tube. If the energy and the entropy are both preserved then the adiabatic equations of motion apply (see below). But experience shows that the motion will eventually slow down and finally cease altogether. What happens is that the kinetic energy gradually converts to heat by a process that we shall refer to as internal dissipation. This too is a comparatively slow process, neglected in the context of processes of the first type. See Prigogine (1970), where the existence of two time scales is related to the short reaction time and the much longer relaxation time in collision theory. For a rare example of a text that discusses the same point see Palatnik and Landau (1961), p 17. Most textbooks take much less care to explain the meaning of the ubiquitous 'variations' and this is one of the reasons why the study of thermodynamics can be painful.

Perhaps it is better to explain this dichotomy in another way. The better to navigate in a difficult terrain, we choose to address situations in which one of two simplifying factors are operating.

**Adiabatic process**

An adiabatic process is one in which the effects of dissipation are unimportant; this may happen because dissipation produces negligible changes over the period of time covered by the experiment. Ideally, such processes are characterized by conservation laws. An important example is the propagation of sound at high frequencies; the rapid oscillations of pressure are but little affected by dissipation. In this case the same can be said about conduction; the half period during which the temperature is higher at point $a$ than at
point $b$ are much too short for a significant amount of heat to flow from point $a$ to point $b$ by conduction. Then the temperature gradient changes sign and what little heat transfer took place is erased.

**Dissipative process**

A **dissipative process** is one in which dissipation (or conduction or other slow processes) is the only change that is taking place. In practice one prepares a state that is as near to equilibrium as one can; ideally this means that the configuration is at equilibrium with respect to all adiabatic changes. Then dissipation can be viewed as progressing sedately through a sequence of adiabatic equilibria. A slow process is not necessarily dissipative; when a piston is removed slowly no flow of consequence results and the system effectively moves along a continuous family of adiabatic equilibria indexed by the pressure.

The figure is an attempt to create an intuitive image of this situation. Let 3-dimensional Euklidean space stand for all possible virtual states or configurations of the system. The actual physical configurations form a subset that is represented as the union of blue parabolas. States on any parabola form an adiabatic system; a system with fixed entropy. For each value of the entropy there is a unique equilibrium state, a state of lowest energy; this state is the lowest point on the corresponding parabola. When we venture to describe non adiabatic processes we limit our attention, by prudence, to these equilibrium configurations, to changes that progress along the red line.

![Fig 2.3.1. In this sketch of a 3-dimensional ‘space of configurations’ is associated with a fixed expression for the Lagrangian. Each parabola represents states with fixed Lagrangian, entropy and pressure. The red line represents the set of equilibrium states.](image)

It may be remarked that the preceding lacks clarity and precision. We shall return to the matter in a context where the definitions can be made more precise (Section III.3). Without further work we have to be content with this: that there are two kinds of processes that are sufficiently simple to be dealt with and that are usually dealt with independently.

“A process which is slow enough to be considered as passing through a continuous series of equilibrium states is called a quasi-stationary process” (Palatnik and Landau 1961). What we call a (slow) dissipative process is quasi-stationary but not adiabatic.
II.4. Towards an action principle for Thermodynamics

The thermodynamics of a simple system is defined by two Fundamental Relations, namely

$$S = -\frac{\partial F}{\partial T}\bigg|_V, \quad P = -\frac{\partial F}{\partial V}\bigg|_T. \quad (2.4.1-2)$$

For any chosen set of values of the pair \((S,P)\) they constrain the possible equilibrium values of the pair \((V,T)\). Taken together, the set of allowed values of \((S,P)\) defines a 2-dimensional surface in the total 4-dimensional Euclidean space with coordinates \(V,T,S,P\).

According to Maxwell, one of the most important ideas in Gibbs’ thermodynamics is to call attention to these two spaces: the total, 4-dimensional space and the two-dimensional surface of physical states defined by the Fundamental Relations.

Gibbs’ axiom of minimal energy (or the equivalent axiom of maximal entropy) aims to identify the actual equilibrium states on the two-dimensional surface; his variations are confined to this surface.

The famous Action Principles of Physics are supplemented by a principle of lowest energy for the identification of equilibrium configurations, in the manifold of solutions of the Euler-Lagrange equations. To turn Gibbs’ thermodynamics into a principle of least action we must find an action \(A(V,T,P,S)\) with Euler-Lagrange equations that coincide with the Fundamental Relations.

As the title of Gibbs’ paper, “On the equilibrium of heterogeneous substances”, makes clear, it is not about simple systems. After stating the axioms he seems to take the application to simple systems for granted and, without further clarification, he applies them in a context that is a collection of simple systems, each with its own independent variables \((V,T,P,S)\), \((V',T',P',S')\), \((V'',T'',P'',S'')\), ... This leaves a large gap for the reader to fill and the result has been that the potential impact of the paper has not been realized. The most important void to fill is the associated Action Principle.

**An Action Functional**

The following action will serve us well,

$$A(V,T,P,S) = F(V,T) + ST + VP. \quad (2.4.3)$$

This expression applies to a fixed amount of material; that is, to a system with prescribed mass, or to a fixed number of particles, but variable volume and pressure. The walls of the vessel are not fixed, but the mass of the physical system contained in it is. What variations are we to carry out? If we vary \(T\) and \(V\) with \(S\) and \(P\) held fixed we obtain the two equations (2.4.1-2) that are basic for any fluid with a chosen expression for the free energy:

$$\frac{\partial A}{\partial T}\bigg|_{V,P,S} = \frac{\partial F}{\partial T}\bigg|_V + S = 0, \quad (2.4.4)$$

and

$$\frac{\partial A}{\partial V}\bigg|_{T,P,S} = -\nabla p \frac{\partial F}{\partial V}\bigg|_T + P = 0. \quad (2.4.5)$$

This action principle showed up in an attempt to introduce the temperature into the theory of Fetter and Walecka (Fronsdal 2014) and a connection to the work of Gibbs was easily
recognized. It bears a clear imprint of Gibbs’ ideas, but it is not his principle of minimum energy. Instead it is a restatement of the laws of thermodynamics. Gibbs’ axioms refer to an energy functional: we propose to identify this energy functional with the Hamiltonian of the action principle. After appropriate generalisations it will lead us to Gibb’s principle of minimum energy as well as his principle of maximal entropy, for it is a setting in which the two principles are equivalent.

At this point we shall try to arrive at an understanding of the action principle in its present form, without taking into account its potential connection to the energy principle.

**Interpretation of the action principle**

Variation of \( S \) would lead to \( T = 0 \) and variation of \( P \) to \( V = 0 \); clearly therefore, the principle makes sense only if \( S \) and \( P \) are treated as fixed parameters while only \( V \) and \( T \) are varied. Under these conditions the action principle neatly summarizes the laws that govern the properties of the fluid. This provides fundamental insight into the role of the entropy.

The variational equations are not primarily to be regarded as formulas that allow to calculate entropy or pressure, but as constraints on the variables \( V \) and \( T \) for assigned values of \( P \) and \( S \).

Exactly the same point of view can be discerned in Gibbs’ work on the principle of minimum energy. We must specify the value of entropy and pressure before we can evaluate the energy functional. Both \( S \) and \( P \) are parameters that can in principle be chosen freely and that must be fixed to give a meaning to the variational equations. The central, difficult problem is not to discover the formula that allows the entropy to be calculated when the pressure and the density are known, but to assign values to the entropy so as to obtain the correct constraint on those variables. So far, \( S \) and \( P \) play similar roles.

The states contemplated at this point are uniform, equilibrium distributions; there is expected to be exactly one such for each pair of values of the two parameters \( S \) and \( P \). The interpretation of \( P \) is the pressure on the walls, assumed the same everywhere. The second equation constrains the variables \( V \) and \( T \) so as to maintain this pressure. The first equation shows that, for each value of \( P \) there is not one unique equilibrium state, but a one parameter family of such states, labelled by the value assigned to the parameter \( S \).

This insight, that the variables \( P \) and \( S \) are fixed parameters of the variational principle, is very important. It is easily forgotten or obfuscated by subsequent interpretations of the entropy.

As important is the fact that the action principle, by itself, gives no information whatever about the value of the entropy, or the value of the pressure. Nor is there any *a priori* guarantee that the variational equations have solutions for all values of these parameters.

Gibbs postulates that, at equilibrium, among states with fixed entropy and pressure, the energy must be at a minimum. That is; it is at a (local) minimum with respect to certain virtual changes. The proper interpretation of this statement is a difficult question. It is the central issue in equilibrium thermodynamics and it occupies an important place in adiabatic thermodynamics as well.
Gibbs’ geometrical formulation of thermodynamics was enthusiastically promoted by Maxwell; see Rukeyser (1942). Its major role is to introduce the raw and mutually independent variables. The energy functional is, to use a term from quantum mechanics and quantum field theory, “off shell” and subject to no constraints. The laws of adiabatic thermodynamics are the equations of motion of the variational principle and it is of no interest to use these laws to transform or evaluate the energy functional. To approach a specific thermodynamical problem we must determine the off-shell energy functional, choose the expression for the free energy and the values of entropy and pressure; here physical insight is most important. From then on the only equations that can and should be invoked are the equations of motion. There is no danger that a crucial relation has been overlooked and there is less need for ingenuity or additional intuitive insight. * What has just been said applies to adiabatic processes with fixed entropy and pressure. For non adiabatic processes the situation is much more difficult.

**Important.** A Legendre transformation relates the free energy to the internal energy,

\[
U(S, V) = \left( F(T, V) + ST \right)_{S=-\partial F/\partial T|V}.
\]

but note that this defines the internal energy on shell.** Similarly, since \( A \) is stationary with respect to variations of \( V \) and \( T \), the values of \( A \) at stationary points,

\[
A(V, T, P, S)_{on\ shell},
\]

define a function of \( P \) and \( S \), the enthalpy. But that is not to say that our energy functional can be identified with the enthalpy. The variational principle is concerned with virtual variations, emphatically not restricted to the physical states of solutions. The thermodynamic potentials, with the exception of the free energy, are defined on shell via Legendre transformations.

**Free energy and enthalpy**

The function \( F \) plays a central and distinguished role in this formulation of adiabatic thermodynamics. Other formulations are possible, that give this prominent place to one of the other potentials. In the limited context that is being envisaged at this stage all four choices give rise to exactly the same variational equations, modulo Legendre transformations, and all four versions are absolutely equivalent, according to Gibbs (1875) and to Callen (1960). With localization, the functions \( F(T, V) \) and \( U(S, V) \) become densities \( f(T, \rho) \) and \( u(s, \rho) \); both have the density \( \rho \) as one of their two natural variables and that is clearly advantageous since the density is a major variable of hydrodynamics. Rowlinson (1959) page 79 works with \( F \) and gives some hints as to why this choice is preferred. In Landau and Lifshitz “energy” usually means free energy; the practice of referring to

---

* This is an overstatement but it shall stand, for it is a succinct summary of the attitude that is adopted in this book. But see Section III.5.

** See above.
“energy” without precision is widespread. Callen and others emphasize the equivalence of formulations based on either of the four potentials, but his context is global thermodynamics. The integration with hydrodynamics that follows in the next chapter favours the present formulation, based on $F$.

Experiments are usually performed with either the volume or the pressure kept constant. The first situation is realized when the fluid is confined within rigid walls; the other when the volume is determined by the atmospheric pressure. In that case the Gibbs function takes center stage. We shall discuss both possibilities later.

In global thermodynamics the entropy is a parameter, in the local theory to be examined next it is a field. This is one of the reasons why localization is not a straightforward matter.

II.5. Lowest energy and maximal entropy

Gibbs axioms of minimal energy and maximal entropy are stated in the opening of his monumental paper:

The criterion of equilibrium for a material system which is isolated from all external influences may be expressed in either of the following entirely equivalent forms

I. For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations of the state of the system which do not alter its entropy, the variation of its entropy shall either vanish or be negative. If $\epsilon$ denote the energy, and $\eta$ the entropy of the system, and we use a subscript letter after a variation to indicate a quantity of which the value is not to be varied, the condition of equilibrium may be written

$$ (\delta \eta)_{\epsilon} \leq 0. \quad (1) $$

II. For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations of the state of the system which do not alter its energy, the variation of its energy shall either vanish or be positive. This condition may be written

$$ (\delta \epsilon)_{\eta} \geq 0. \quad (2) $$

The nature of the proof is of interest:

That these two theorems are equivalent will appear from the consideration that it is always possible to increase both the energy and the entropy of the system, or to decrease both together, viz., by imparting heat ...

This is very abstract, but the last sentence gives a hint of a quantity of the nature of “energy plus entropy” that is invariant with respect to the joint variation of energy and entropy. We shall see that this quantity is the action.

How shall we interpret Gibbs’ “energy”? In modern thermodynamics of isolated systems the functional that is minimal at equilibrium is usually the free energy $F$ or the Gibbs energy $G$. * Thus, at equilibrium $F$ can only increase. When we take this to be valid it

* It is sometimes assumed that experiments are carried out over a long time, long enough that the system can be seen as being in thermal equilibrium with the environment. On this basis a case has been made for assuming that it is the enthalpy that is minimized. For simplicity we shall restrict ourselves to deal with isolated systems and assign the role of energy to $F$. 

43
follows that the \( A - ST \) can only increase and a variation for which the action is stationary can only decrease the entropy, or at least it can only decrease the value of \( ST \).

Much has yet to be done to complete the formulation of the action principle. The problem of achieving a thorough understanding of the principle of minimum energy will be taken up again in Section 3.9.
III. LOCALIZATION

The term thermodynamics is often limited to refer to the study of systems in equilibrium. The present goal is to unite thermodynamics with hydrodynamics in a framework that we shall refer to as local thermodynamics. The result is a vastly enlarged dynamical framework that is no longer limited to the study of equilibria. The most usual approach starts with the ‘main assumption’ (Callen 1960),

Relations between the thermodynamical variables,

at each point in the fluid, are the same as at equilibrium of the corresponding uniform system.

In Gibbs’ paper (1875-8) this assumption is used throughout, though it is not clearly stated as an axiom. For example: the entropy and any other thermodynamical variable may vary from point to point, but the fundamental relations do not contain any reference to position. At equilibrium Eq.s (2.1.1-2) hold and for them to make sense locally it is enough to interpret V as the inverse density; in what follows V is replaced by 1/ρ. The main assumptions is also known as the ‘assumption of local equilibrium’. The question of the range of its validity is discussed, briefly, by Fitts (1962) who refers to work by Prigogine (1949). *

We have shown that, in the case of a simple system, with a specific choice of the action functional, the variational principle is equivalent to the fundamental relations of thermodynamics. Here, as we apply the ideas to heterogeneous systems we shall continue to base the theory on an explicitly defined action functional.

III.1. Hamiltonian density and the equations of adiabatic processes

The total energy is obtained by integrating an energy density over the extent of the fluid, and the same must be true of the free energy and the other potentials. The densities related to F, S and U will be denoted f, s and u. In the absence of external forces,

\[ A[\rho, T, S, P] = \int_{\Sigma} d^3x \, h + PV, \quad h = f(\rho, T) + sT. \]

For the time being we shall suppose that the system is confined within rigid walls; then the term PV can be ignored, its role being taken over by the boundary conditions.

In the case that the fields are uniform over the volume,

\[ f(\rho, T) = \rho F(V, T), \quad V = 1/\rho. \]

Here f(ρ, T) is the all important free energy density. The density ρ and the temperature T are scalar field variables. The pressure P is the pressure on the boundary, assumed

* In this paper a fundamental expression for the entropy is shown to be valid in certain situations away from equilibrium.
uniform for the time being; the $PV$ term will be discussed in Section III.5. The extensive nature of the entropy * tells us to interpret $\int d^3x s$ as the total entropy of the system.

With regard to the entropy density $s$ it is to be hoped that the specific entropy $S = s/\rho$ is independent of $\rho$ (and of $T$). For we shall see that when that is true the term $sT$ makes no contribution to the pressure and in this case only does the expression that we shall obtain for the thermodynamic pressure accord with the ‘main assumption’. The correct approach to entropy is a major preoccupation of this book; it will be undertaken in specific circumstances, beginning with the simplest. At this point we shall assume only that $s$ can be expressed as a function of $\rho$ and $S$, with $\rho, T$ and $S$ as basic variables, but we shall be led to conclude that a situation in which the specific entropy is not uniform will be encountered only in special circumstances, as when a chemical interaction is taking place (combustion).

Hence $S$, and not $s$, is a field variable independent of the density. The role that is played by entropy in the variational principle is the same as in the case of the global variational principle, but instead of being a pre-assigned number that is held fixed under the variations of $T$ and $\rho$ it is a pre-assigned function of $\rho$. This circumstance can give rise to any number of misunderstandings; it must be understood that $s$ is a definite function of the density and that, for each choice of this function the adiabatic condition (see below) gives a well defined constraint on the pair $T, \rho$. We insist on this point because it will help us confront difficult issues later on.

Variation with respect to $T$ gives the ‘adiabatic condition’

$$\frac{\partial f}{\partial T}\bigg|_{\rho} + s = 0,$$

(3.1.1)

in agreement with the main assumption. Variation with respect to the density, with fixed boundary conditions, and fixed mass, leads to

$$\vec{\nabla} (\mu + T \frac{\partial s}{\partial \rho}) = 0,$$

(3.1.2)

where $\mu$ is known as the chemical potential and is defined by either of two equivalent ways,

$$\mu := \frac{\partial f}{\partial \rho}\bigg|_{T},$$

(3.1.3)

or

$$\mu := \frac{\partial u}{\partial \rho}\bigg|_{s} = 0.$$

(3.1.4)

Here $u$ is the internal energy density; it will be introduced in Section III.7. The first definition is more straightforward; in the second form appears the adiabatic derivative, where $T$ is to be eliminated in favor of $\rho$ and $S$ using (3.1.1).

* “The total entropy is, of course, equal to the sum of the entropies of all subsystems of the isolated composite.” Quoted from Modell and Reid (1974). Let us try to avoid such vague generalizations. See Section III.4.
The hydrostatic condition

A simple equation that is convenient and popular relates Eq. (3.1.2) to the gradient of the thermodynamic pressure, defined by

$$ p = \rho \frac{\partial f}{\partial \rho} - f. $$

Eq. (3.1.2) is, under certain assumptions, the same as

$$ \vec{\nabla} p = 0. $$

We shall use it often, but we need to know its limitations and implications.

From the definition of the thermodynamic pressure we get

$$ \vec{\nabla} p = \vec{\nabla} (\rho \mu - f) = \rho \vec{\nabla} \mu + \mu \vec{\nabla} \rho - \left( \frac{\partial f}{\partial \rho} \vec{\nabla} \rho + \frac{\partial f}{\partial T} \vec{\nabla} T \right) = \rho \vec{\nabla} \mu + s \vec{\nabla} T. $$

Now (3.1.2) becomes

$$ \rho (\vec{\nabla} \mu + T \frac{\partial s}{\partial \rho}) = \vec{\nabla} p + (\rho \frac{\partial s}{\partial \rho} - s) + \rho T \vec{\nabla} \frac{\partial s}{\partial \rho} = 0, $$

which is the general form of the electrostatic condition in the present context, in the absence of external forces and so far without taking into account any effect of flow or kinetic energy.

1. It is seen that, unless $s$ is a linear function of the density, $s = \rho S$, there is a force proportional to the gradient of the temperature and that
2. unless $\partial s / \partial \rho$ is uniform, the gradient of the specific entropy $S$ gives rise to an entropic force that must be included in the balance of forces.

We conclude that, to agree with the universally accepted thesis that the pressure, at equilibrium and in the absence of external forces, is uniform, we need to postulate

1. That the entropy density $s$ is a linear function of the mass density and
2. that the specific entropy density $S$ is uniform.

Nevertheless, neither statement will be given the stature of an axiom, for special conditions may exist where the linearity of the entropy will be violated. There are circumstances where the specific entropy fails to be uniform; as in the case of atmospheric combustion. But both statement will be assumed to hold, as working assumptions, so long as they are not contradicted by experiment.

The justification for referring to the expression (3.1.5) as the thermodynamic pressure will come in Section III.5. The familiar and expected result, the hydrostatic condition (in the absence of external forces), in the naive form $\text{grad} p = 0$, is verified when (a) $s = \rho S$, with $S$ independent of $\rho$ (and of $T$) and (b) $S$ is uniform. This result is not in disagreement with hydrodynamics, but an extension of it. Conventionally, hydrodynamics is developed

47
under the implicit assumption that the entropy density \( s = \rho S \), with \( S \) uniform; that is, the assumption that there are no entropic forces. It is not an axiom, but an observation based on experiments. We remain open to the possibility that we may encounter situations in which the specific entropy is not uniform and that entropic forces become a reality.

The term with \( \text{grad} S \) is an entropic force, present whenever the specific entropy is not uniform. The simple way to look at it is this: if the specific entropy is not uniform then a force is present that tries to make it uniform; just as is the case with the pressure. * It is a surprise to find that the unquestioned use of the relation \( \text{grad} p = 0 \), in the absence of external forces, implies these strong assumptions about the entropy. In the context of atmospheres or stellar structure the relation is replaced by \( \nabla p + \nabla \phi = 0 \), where \( \phi \) is the gravitational potential. This relation is widely used in astrophysics; the fact that it has implications for the entropy was usually not pointed out, but recent publications show an increased awareness of this important point. It means that gravity does not ordinarily give rise to entropic forces.

Once this restriction on the entropy density is accepted a remarkable integration of thermodynamics with hydrodynamics ensues. The Gibbsean variation of the energy with respect to the density gives the hydrostatic condition of hydrodynamics; in the absence of other forces it is the statement that the pressure is uniform. This key feature of hydrodynamics has now merged with one of the two central relations of thermodynamics. Variation with respect to the temperature gives the second principal relation of thermodynamics; it is the adiabatic relation that lies behind the polytropic condition of hydrodynamics.

It is also a striking fact that, if \( S \) is uniform, and only in that case, then the total entropy \( \int d^3x s = \int d^3x \rho S \) is a constant of the motion, as a direct consequence of the conservation of the total mass (the equation of continuity). In the interpretation of the fluid as a collection of particles this assumption means that entropy is assigned to each particle, unrelated to the variation of density and temperature from one point to another, but subject to change through the addition of heat to the system. An additional argument in favor of a uniform specific entropy density, will be discussed in Section III.9.

**Thermodynamic pressure and the pressure on the walls**

So far the pressure term \( VP \) or \( \int d^3P \) has not entered the discussion. Since we assumed that the system is confined to rigid walls the volume is fixed and the pressure term is replaced by boundary conditions. To understand the pressure, as it appears in the form of the thermodynamic pressure defined Eq.(3.1.5), it is necessary to allow for variations of the volume. We have considered local variations of the density. A complimentary, uniform variation of the density, accompanied by a variation of the volume, gives the additional result that \( p = P \) on the boundary; the thermodynamic pressure is equal to the pressure on the walls. (See Section III.5.) It is this circumstance that justifies referring to \( p \) as ‘the pressure”; it is an extrapolation of the pressure at the wall to the interior. But if we choose to fix the spatial extension of the system, then the term \( VP \) in the energy functional becomes redundant. A detailed discussion of the pressure is in subsection III.5 below.

---

* Special situations may call for an additional contribution to the entropy density, independent of the mass density, thus \( s = \rho S + s_{ex} \), the second term is treated as an external field. An idea adapted from Landau and Lifshitz; not needed until Chapter IX.
III.2. The kinetic energy

Here we attempt to complete the synthesis of hydrodynamics and thermodynamics. The hydrodynamical picture of a fluid, as a collection of particles, described by density and flow velocity, suggests that the total energy must include the kinetic energy *

\[ A[\rho, T, S, P, \vec{v}] = \int_{\Sigma} \delta^3 x \, h + VP, \quad h = \rho \lambda + \rho \vec{v}^2/2 + f(\rho, T) + sT, \quad s = \rho S. \]  

(3.2.1)

This is the Fetter-Walecka Hamiltonian of hydrodynamics, with the potential \( W \) now replaced by \( f + sT \). It is an action principle for thermodynamics, limited to the case of irrotational velocity fields. Let us examine the variational equations.

**Note.** We insist, throughout the following discussion, and in most of this volume, that we are treating the case of potential flows exclusively. This limitation will be lifted in Chapter X.

Variation with respect to \( T \), treating \( T, S \) and \( \rho \) as independent variables off shell, leads as before to

\[ \frac{\partial f}{\partial T} \bigg|_{\rho} + s = 0, \]  

(3.1.1)

in accord with the main assumption. If we know the expression for \( f \) and the value of \( s \) we can solve this equation for \( T \), eliminate \( T \) from the Hamiltonian, and revert to hydrodynamics. All that remains of the thermodynamic description is a ‘hydrodynamical equation of state’, a relation between density and pressure. The most commonly used is the polytropic relation \( p/\rho^\gamma = a = \text{constant} \). One interpretation of this formula is that the fluid is an ideal gas and that the entropy is uniform, but information has been lost as a result of eliminating the temperature (a partial on-shell projection) and other interpretations are possible. The expression obtained for the Hamiltonian density will depend on the parameter \( a \) and hence on the entropy.

The other hydrodynamical equations are the Hamiltonian equations of motion namely

\[ \dot{\rho} = \{\rho, H\} = \partial_i \frac{\partial H}{\partial v_i} = -\vec{\nabla} \cdot (\rho \vec{v}) \]  

(3.2.3)

and

\[ \dot{\vec{v}} = \{\vec{v}, H\} = -\vec{\nabla} \frac{\partial H}{\partial \rho} = -\vec{\nabla} (\vec{v}^2/2 + \frac{\partial f}{\partial \rho} + ST). \]  

(3.2.4)

The second equation reduces, in the case of equilibrium (\( \vec{v} = 0 \)) to Gibbs’ variational equation. With a little work (Section III.1) it turns into the Bernoulli equation,

\[ \rho \frac{D\vec{v}}{Dt} = -\vec{\nabla} p, \quad p = \rho \frac{\partial f}{\partial \rho} - f; \]  

(3.2.5)

* Gibbs’ *vis viva*. The kinetic energy will always appear as an adjunct to the free energy, but it shall be added explicitly. Later, when we generalize the theory to include rotational velocity the structure of the kinetic term will change; see Chapter X.
the dynamic generalization of the hydrostatic condition. This result depends on the assumption that $s$ is linear in the density, $s = \rho S$ with $S$ uniform, see preceding section.

The Poisson bracket implied by Eq.s (3.2.3-4), is defined for functions $\rho, \Phi$ of the density and the velocity potential,

$$\{f, g\} = \int d^3x \left( \frac{\partial f}{\partial \rho} \frac{\partial g}{\partial \Phi} - f, g \right).$$

Now that the context explicitly includes motion, the meaning of the term $VP$ in (3.2.1) is unclear. This has been discussed earlier in Section III.2 and it will be taken up again in Section III.5.

We have just examined the simplest example of a hydro-thermodynamic system that combines the Gibbs variational principle with hydrodynamics. In the absence of external forces it follows directly, from the Euler-Lagrange equations, that at equilibrium the pressure is uniform. If we admit from the start that the specific entropy is uniform as well, then it follows that all the fields, including the temperature, are uniform at equilibrium. There is no need for another postulate to reach this conclusion. In the presence of an external force the temperature may not be uniform. See chapter IX.

In the thermodynamics of equilibria great importance is attached to the deep, statistical interpretation developed especially by Boltzmann. This valuable insight has not lead to an accepted definition (interpretation) of entropy for systems that are out of equilibrium. But in the theory of adiabatic fluids an interpretation of this sort, though desirable, is not needed. We define an adiabatic system as one governed by a Lagrangian, anticipating that viable Lagrangians will be found that describe real, physical systems.

### III.3. Lagrangian and adiabatic dynamics

The notion of minimal energy applies to equilibria; to deal with systems that are out of equilibrium the classical procedure is Hamilton’s Principle. The idea originated with Maupertui, who was the first to apply a variational principle to a dynamical system away from equilibrium, perhaps the most important suggestion ever made within theoretical physics. Here we apply the idea to hydro-thermodynamics. In our context it is a simple generalization of the variational principle of hydrodynamics.

The Lagrangian formulation requires the introduction of the velocity potential $\Phi$,

$$A = \int d^3x \left( \mathcal{L} - P \right), \quad \mathcal{L} = \rho(\dot{\Phi} - \overline{v}^2/2 + \lambda) - f(\rho, T) - sT,$$

as in hydrodynamics, Section I.2. The equations of motion derived from this action include the equations of Hamiltonian dynamics derived above. It is perhaps necessary to repeat that the variational principle defined by (3.3.1) is not a principle of minimum energy, for it describes a complete Lagrangian system that affects much more than the states of equilibrium; that is, the configurations in which all the fields are time independent.

The constant $\lambda$ is a Lagrange multiplier, needed to fix the total mass $\int d^3x \rho$. It can be absorbed into $\dot{\Phi}$ and it will not appear in later expressions for the Lagrangian. It shall
be seen that this association between the Lagrange multiplier and the velocity potential is natural; Section IV.3.

We are now in a position to give a precise meaning to the term “adiabatic”. By adiabatic dynamics we mean dynamics that is defined by a Lagrangian, with a definite choice of entropy and external pressure (or spatial extension). Adiabatic dynamics is expected to be a good approximation for dealing with phenomena that are characterized by a short time scale and by conservation laws. It is contrasted with dissipative processes, normally evolving slowly, during which the system takes on a sequence of adiabatic equilibria with different values of the entropy (Section II.3). Note that the entropy profile, not just the total entropy, is an adiabatic invariant.

Some processes that include changes in the pressure on the walls are usually termed adiabatic. In our terminology they are neither adiabatic nor dissipative; they require a special treatment.

**Remark.** The on shell value of the Lagrangian density is

\[
\mathcal{L}|_{\text{on-shell}} = (1 - \rho \frac{\partial}{\partial \rho}) \left( \rho(\dot{\Phi} - \vec{v}^2/2 - \lambda) - f(\rho, T) - sT \right)|_{\text{on-shell}} = p, \tag{3.3.2}
\]

since the derivative term vanishes on shell. * Consequently, if the entropy density is linear in \( \rho \), then the on shell value of the Lagrangian density is equal to \( p \), the thermodynamic pressure. A proposal to identify the Lagrangian density with the pressure, in the context of General Relativity, was put forward by Taub (1954). It seems as if the identification of pressure with Lagrangian density is very natural, for reasons that we do not yet fully understand (see Section III.8.); this would add support for our contention that the entropy is usually linear in the density.

Similarly

\[
\mathcal{L}|_{\text{on shell}} = (1 - T \frac{\partial}{\partial T}) \left( \rho(\dot{\Phi} - \lambda - \vec{v}^2/2) - f(\rho, T) - sT \right)|_{\text{on-shell}} = -u + \rho(\dot{\Phi} - \vec{v}^2/2 - \lambda). \tag{3.3.3}
\]

In particular, in the case that the velocity field is zero, the value of \((u + p)/\rho\) is a constant. \((u + p)\) is the enthalpy density.) If the interaction with the gravitational field is added we get instead

\[
gz + \frac{u + p}{\rho} = \text{constant}
\]

Combining equations (3.3.2 and 3.3.3),

\[
\rho(\dot{\Phi} - \lambda - \vec{v}^2/2 - gz) = -p - u, \tag{3.3.4}
\]

and for an ideal gas

\[
\dot{\Phi} - \lambda - \vec{v}^2/2 - gz = (n + 1)RT. \tag{3.3.5}
\]

* The argument depends on the fact that our Lagrangian includes a Lagrange multiplier; there are no constraints on the variation of the density. Otherwise we could conclude only that the relation holds up to an additive constant.
Alternatively, these useful formulas can be derived by integrating the Bernoulli equation, under the conditions of validity of the latter. Eq. (3.3.4) is universal, so long as the entropy density is linear in the density.

A Lagrange multiplier comes automatically with the velocity potential. It makes it possible to fix the extent of the system. The equations obtained by variation of the density will always contain this constant or, equivalently, take the form of Eq.(3.1.2).

Since the time derivatives appear linearly in the Lagrangian density - the term $\rho \dot{\Phi}$ - the Legendre transformation that defines the Hamiltonian density is slightly unfamiliar:

$$h = \dot{\Phi} \frac{\partial L}{\partial \dot{\Phi}} - L = \rho \dot{\Phi} - L.$$

The variable that is canonically conjugate to $\Phi$ is $\rho$. The inverse transformation is

$$L = \rho \frac{\partial h}{\partial \rho} - h = \rho \dot{\Phi} - h.$$

### III.4. The second law

The second law of thermodynamics represents the highest achievement of the physics of the 19'th century. A simple statement of the law can only serve as an introduction to the subject, for the real meaning is extremely subtle.

**The second law: No change within an isolated system results in a decrease of the entropy.**

It is a property that has a strong appeal in the context of statistical mechanics, but that is beyond the scope of this book.

An example will serve to highlight the difficulties and perhaps clarify the meaning of this statement.

Consider a body that consists of two parts, each an adiabatic system and each at adiabatic equilibrium. In the simplest case it consists of two systems with fixed temperatures $T_1$ and $T_2$. Suppose a small amount of heat is transferred from system 1 to system 2, with no appreciable change in either temperature. The total system is isolated so there is no net transfer of heat to it, but an amount $dQ$ is added to the first system and the same amount taken away from the second system. Such a change could be adiabatic, caused by transfer of liquid from one vessel to another, but we now assume that no transfer of mass takes place. This leaves a transfer by conduction or radiation, but note that no attempt is made to describe the mechanism of transfer. It is assumed that each system makes a transition from one adiabatic equilibrium state to another. Then the following rule holds:

$$dS = dS_1 + dS_2 = \frac{-dQ}{T_1} + \frac{dQ}{T_2}.$$
That is, it is assumed that entropy is an additive property. This is a logical extension of the fact that entropy is an extensive property.

**Additivity assumption.** The entropy of a system that consists of several parts, that do not influence each other in any way, is defined to be the sum of the entropies of the parts.

The second law says that, if the transfer is spontaneous, then $dS \geq 0$; here it implies that $T_1 \geq T_2$. That is, heat flows out of the warmer and into the colder of the two subsystems. It is an example of “internal dissipation” of the total system. Here we must reject an attempt to prove that $T_1 = T_2$ at equilibrium, for that requires an additional assumption. The additional assumption that is needed to reach that conclusion is that, whenever the temperatures are unequal, then heat will necessarily flow.

The internal energy is conceived as a sum of heat energy that increases with the addition of heat and a mechanical energy that decreases when the system performs work. A system is “degraded” when its capacity for doing work is reduced; if this happens when the internal energy is maintained constant then the entropy must increase. A variation of this example is provided by the free expansion of an ideal gas. (See below.) Free contraction, which is not known to occur, would result in a decrease in the entropy. *

We have already, in Section II.5, expressed our doubts about extending the variational principles to include exchange of entropy between parts of the system. Here we are taking up the question once more, in the local context. The original variational principle, and the Lagrangian variational principle, considers variations that hold the entropy distribution fixed. It leads to equations of motion that fix, to a very large extent, the physical configurations. Any suggestion to consider a wider class of variations must verify that it does not lead to internal contradictions. Since the principle of increasing entropy is of the first importance, we propose to allow variations of the entropy (and other variations that may be proposed) but to avoid contradictions we should add a proviso:

An isolated system that exists in a certain configuration will move to one of greater entropy, if one is available.

In the case of an ideal gas that is described in terms of the Euler-Lagrange equations no equilibrium configuration with constant temperature is available when a gravitational field is present.

Classical, statistical mechanics steps out of its domain of competence when it is argued that the temperatures, when equilibrium between the two parts of the system is reached, must be equal. As strongly emphasised by Prigogine we cannot compensate entropy production in one part of the system with entropy reduction in another; entropy is not a conserved quantity. We do not yet have a proof that two bodies in thermal contact must have the same temperature. If you allow variations of the entropy in the formulation of the variational principle you are excluding the case of an ideal gas in the presence of a gravitational field.

* This concept of ‘degradation” was introduced by Lewis and Randall (1938). It is the main idea of their explanation of the second law.
gravitational field. The tendency for entropy to become maximal is limited by the equations of motion. Again, a shift to a state of higher entropy is favoured, provided that one is available.

The fixation on the isothermal equilibrium is strange. General axioms cannot be formulated as conditions that affect only equilibrium states. In statistical mechanics the energy is a property of the system as a whole; it does not address problems in which the temperature is a field that varies from point to point. The existence of systems with variable temperature is acknowledged but removed from consideration as being, by definition, out of equilibrium.

III.5. Work and pressure

We have seen that entropy and pressure play similar roles in the variational principle. But while entropy is a many faceted and subtle concept that we shall continue to study throughout this work, pressure is comparatively easy to understand. Or is it?

In the case of the global system that we started out with, in Section II.4, $P$ was just a number. In the localized system some refinement is needed. In certain situations the pressure on the walls may be the same everywhere, but that is not generally true, even for equilibrium configurations. If the walls are fixed, then the term $P$ in the action is irrelevant, its roles taken over by the boundary conditions, so it remains to consider situations where the volume can change.

The simplest situation is that of a vessel furnished with a piston, moving in a cylinder and having a face that is perpendicular to the direction of motion, as in Fig. 3.5.1. At equilibrium the pressure of the gas against the face of the piston has to be balanced by an externally applied force. When this external force is varied slightly the piston will be set in motion, a motion that can be controlled so as to be slow enough that the flow of the gas is minimal and the kinetic energy is negligible. When the piston is withdrawn the volume increases and, if the entropy does not change, the internal energy of the gas decreases; the gas “does the work” and $\Delta U = -p\Delta V$. Since $U = nRT$, this brings about a calculable change in $T$, and this prediction was confirmed by a crucial set of experiments by Joule and Kelvin (ref.). An essential part of our understanding is that we can interpret the change as a progression through a sequence of adiabatic equilibria, on a time scale that is very slow compared to what is characteristic of adiabatic dynamics. Perhaps the most important lesson is the realization that this is in close analogy with the phenomenon of slow dissipation. It is assumed, and verified, that during the slow motion of the piston, no heat transfer takes place and that, consequently, the total entropy does not change. The context is quasistatic changes of a system with a fixed Lagrangian including fixed boundary conditions, as in Section II.8. In the of case of a homogeneous system with entropy density $s = \rho S$, with uniform mass density $\rho$, it follows that $s$ does not change. But it should be understood that, with a slightly different setup, this simple statement may not always apply. That is, under different conditions both pressure and entropy may undergo changes.
Fig. 3.5.1. Vessel with an addition degree of freedom, including piston with mass $m$ and a spring with spring constant $k$. See Eq. (3.5.1).

Here we are in danger of overlooking some of the most interesting and subtle aspects of gas dynamics. It is indeed true that, under the circumstance just described, when the piston was moved slowly, the entropy did not change. But this is not an inevitable property of every ideal gas; that is, it does not follow from the expression for the free energy density. It is a fact deduced from experiments with certain real gases, approximately ideal, where it has been found that the energy gained from allowing the gas to expand (slowly) is accounted for by the term $-PdV$ in the expression for the change of the internal energy, which implies that the entropy does not change. It tells us something very important about the gases used in the experiment: that the specific entropy density is an adiabatic invariant.

Henceforth we add a working assumption in all our work: that the specific entropy of a homogeneous fluid is an adiabatic invariant. In Gibbs’ work only the total entropy is an adiabatic invariant.

In this book an adiabatic system (with one component) is characterized by a fixed specific entropy density.

This leads to the assertion that the process under discussion is “reversible”. In fact it is found that by pushing the piston back in and reverting to the original volume, the gas seems to revert to the original configuration. But “reversibility” does not always imply that $dS = 0$; it is a term that cannot be rigorously defined and we shall not use it. In short, a process is reversible if it can be reversed; but what means are we allowed to employ?

Consider the opposite extreme, the rapid removal of a wall that results in a finite change of volume. In this case “no work is done by the gas”; by which is meant that no useful work is done to profit the environment, in contrast with the work done on the piston in the case of slow motion. * What happens is that the gas is set in motion. This motion can be

* It is also assumed, tacitly, that no work is done by removing the piston. This is patently false if the piston is withdrawn along its axis, but it may be true if it is replaced by a wall that opens by moving it in its own plane. Alternatively, a weightless piston may be used, released rather than withdrawn. Kelvin and Joule used a stationary, permeable foam.
accounted for, in principle, over the short term, by means of the equation of motion of the adiabatic Lagrangian. Energy conservation means that the value of the total Hamiltonian, that includes the kinetic energy, is unchanged. (This is an idealization; we have to agree to neglect the loss of energy due to friction against the walls.) If the system is isolated there can be no heat exchange with the environment and no change in energy. The flow can change but it cannot cease by virtue of the adiabatic dynamics. Yet one observes that the motion eventually comes to rest, by some mechanism that is not understood within the adiabatic framework. To give it a name we can call it “internal dissipation” or “conversion of the kinetic energy to heat”. Again, this is a development that cannot be predicted on the basis of the definition of the ideal gas; it is an observation to be added to our fund of knowledge of the properties of certain real gases.

During the turbulent phase that sets in when the piston is withdrawn some of the energy is kinetic, contained in the term $\frac{\rho \vec{v}^2}{2}$. But at the end, when the macroscopic motion has ceased, it is observed that the temperature has not changed. Consequently, neither has $U$, since $U = nRT$; the term $-PdV$ in the expression for $dU$ must have been compensated by an increase in the entropy. What (apparently) takes place during dissipation is a change of entropy; the net result being conservation of the value of the internal energy,

$$dU = T\Delta S - p\Delta V dt = 0,$$

or more precisely

$$\int (TdS - pdV) = 0.$$ 

If now we try to recover the original configuration of the expanded gas we can only do so by decreasing the entropy.

It is observed that there takes place a spontaneous conversion of kinetic energy into heat.* To justify the neglect of this process in the context of adiabatic dynamics, we have to assume that its effect is very slow, that dissipation is a slow process.

In the case of an ideal gas the internal energy density is $nRT$ so the temperature does not change in this type of process. Also, in the case of an ideal gas, $p = \frac{RT}{V}$, so that

$$\Delta S = \int \frac{R}{V} dV = R\Delta \ln V.$$ 

In our experience, a fluid given over to itself tries to expand, never will it contract. This exemplifies the most important property of entropy: in a spontaneous process, in which there is no interference from the outside, it can only increase.

**Pressure and Lagrangian density**

Returning to the system illustrated in Fig. 3.5.2, we wish to consider some generalizations. The coordinate $z$ gives the position of the piston. The volume can change only by virtue of the motion of the piston, therefore the term $\int d^3x P$ can be replaced by $APz$.

---

* See Callen (1960), page ???, for a very authoritative discussion of this point.
Now let us review the derivation of the equations of motion, more precisely the variation of the density. So far, except briefly in Section III.3, we have only considered variations that vanish at the boundary. Here we shall repeat the discussion in Section III.3 in more detail. A complimentary variation * of the volume leads to

\[ \delta \int d^3x (L - P) = \delta \int d^3x (p - P) = \int d\sigma p\delta z - AP\delta z = 0, \quad (3.5.1), \]

where the 2-dimensional integral is over the face of the piston and \( A \) is the area of the piston. By replacing \( L \) by \( p \) we have assumed that the entropy density is linear in the density. It follows that \( P \) is equal to the average thermodynamic pressure on the piston. If this were not the case then the identification of \( P \) with the thermodynamic pressure would not be valid. It is also worth while to notice that the identification of the Lagrangian density (on shell) with the pressure on the walls is of great utility and significance.

Quite generally, it follows from the variational principle that the pressure on the wall of a homogeneous system is equal to the value of the Lagrangian density, provided only that the entropy is a linear function of the density.

In this example the expression \( VP \) in the Hamiltonian was replaced by \( AzP \), because \( Az \) is, up to a constant that plays no role, the volume, and \( P \) is the pressure against the face of the piston. The pressure against the wall elsewhere in the vessel is not recorded since the energy does not depend on it, and indeed it is not defined. The expression \( VP \) in the Hamiltonian is a stand-in for a more accurate expression for a part of the energy.

Returning to the system in Fig. 3.5.1, let us load the piston with an inertial mass \( m \) and add the term

\[ m\dot{z}^2/2 - k\dot{z}^2/2 \]

to the Lagrangian. The last term represents the energy of a spring that provides the force that holds the piston against the pressure. Now \( z \) is a dynamic variable and the variation of the total action with respect to \( z \) gives

\[ Ap - kz - m\ddot{z} = 0. \]

The pressure on the piston is no longer an assigned parameter but a variable that is determined by the dynamics. A small initial value of \( Ap - kz \) will start a slow change in the value of \( z \), and this motion is adiabatic. A large value of \( m \) will mimic the slow motion of the piston and a small value of \( m \) will imitate the sudden removal of the piston by an external force.

This motion too is (approximately) adiabatic, but the observed, slow relaxation of the system is not. This approach is appropriate for dealing with balloons and drops held together with surface tension and with self-gravitating heavenly bodies.

By now it must be clear that the term \( VP \) in the Hamiltonian is symbolic. The pressure on the wall may be constant in certain cases of equilibrium, but certainly not so in the general case.

* In Gibbs’ paper, where all results obtained by local variations are supposed to be expressed by the fundamental relations, these global variations are the only one discussed.
Consider the case that there are two pistons, as in Fig. 3.5.2. It may happen that the thermodynamic pressures are different at the two locations. Most notably this will happen if gravitation is taken into account. Then, to ensure the existence of a solution we must replace

$$\int d^3 x P \rightarrow A_1 P_1 z_1 + A_2 P_2 z_2,$$

with a choice of the values $P_1, P_2$ that is not arbitrary. A wrong choice will have the consequence that there will be no equilibrium solutions.

Fig. 3.5.2. A vessel with two pistons.

There are cases when the pressure on the wall is not the same everywhere, even at equilibrium, as in the problem of a vertical column of gas under the influence of gravity. If the walls are rigid the simple solution is to impose boundary conditions. This happens in the last example, in the limit when the mass $m$ of the piston tends to infinity.

The general lesson that should be learned from this example is that boundary conditions have to be compatible with the equations of motion, and that this needs to be verified in each case. A most important case is the one that one encounters when considering a system with non uniform boundary temperature specified, see Section IX.2.

### III.6. Lesson to be learned from the expansion of an ideal gas

The expansions of an ideal gas, the slow expansion and the free expansion, have been covered in the manner of the textbooks, for the most part. But the main lesson that should be learned from these processes deserves more emphasis.

There is an interesting system called entropic rubber. It may be assumed that a rubber band has a free energy and an entropy, the former is a function of the length and the temperature, the latter depends only on the length. * There is a mechanical model of the rubber band that compares it with a conventional spring; stretching the rubber band increases the tension and the free energy, entropy is not involved. Entropic rubber is

* I am not sure how this statement is justified.
another model. We must imagine a system of long polymers of twisting and interlaced molecules, to which a very large set of states are available. Stretching the band results in straightening the strings, and now a reduced number of states is available; in a word, stretching results in a reduction of the entropy. Writing $F = U - TS$, the result of stretching is attributed, in the first model, to a change in the free energy and, in the second model, to an increase of the entropy.

To decide which model is right, or at least closest to reality, there is only one way: experiment. Returning to the expansion of the ideal gas we now realize the following central truth: That slow expansion preserves the entropy, and that free expansion does not, and that these facts are known to be true only because they have been established by experiments for certain gases. ** To say that the gas does no work in the case of free expansion is not an argument that can be advanced as part of the theoretical treatment of the process; it is a statement that summarizes the result of the experiment. Some of the text books make this point quite clear but, in my opinion, with insufficient emphasis. The analogy between entropic rubber and the free expansion of an ideal gas was pointed out by John Baez (2-12).***

**Remark.** Having thus come to know of the existence of entropic forces we are in a better position to appreciate the last term in Eq.(3.1.6). The gradient of the entropy is a force that tends to reduce the entropy gradient, just as a gradient of pressure is a force that tends to reduce the pressure gradient.

**Some questions**

Let us reconsider the phenomenon of free expansion. It is an unequivocal result of the Joule-Kelvin experiment that the net result is an increase of the entropy. But when does this increase occur?

For $t < 0$ the gas is confined in a small volume. The entropy, according to the statistical interpretation, is the logarithm of the number of states with the given energy. (ref.) It can be calculated for the two equilibrium configurations; suppose it is $S_0$ for the gas at rest in the small volume at negative times and $S_2$ for the gas at rest in the larger volume at a much later time. In the meantime two events have taken place.

1. We open the gate; this is a severe interference with the system. The volume is suddenly larger and the entropy should therefore have changed. Remember that the entropy is determined by the number of available states, occupied or not. The difficulty is that, with the gate open, the gas is not at equilibrium and, according to inherited wisdom, the entropy is not defined. Suppose that the entropy at this time, if it can be defined, is $S_1$.

2. What happens after that is that severe convection is taking place. Gradually the fluctuations take on a smaller scale until finally becoming identified only as heat (Callen 1960). Again, since the system was not at equilibrium at the beginning of this process, the initial entropy was not defined, so we cannot ask how much it has changed. Thus, though both $S_0$ and $S_2$ can be determined, $S_1$ can not; perhaps we are free to decide what value to assign to it.

**Historically the most important by Joule and Kelvin.**

*** johncarlosbaez.wordpress.com/2012/02/01/entropic – forces
And what, after all, prevents us from asserting that the expansion is adiabatic? Adiabatic configurations include equilibrium states, but also states with densities that vary from point to point, including the extremely unlikely possibility of a large part of the vessel containing no particles?

Do I dare to suggest that the entire change of entropy happens during the first phase, by the act of removing the gate? It is certain that, by the mere act of defining the hitherto undefined value of the entropy $S_1$ of the system immediately afterwards, the expansion can be brought into the province of adiabatic dynamics. The issue cannot be reduced to a question of reversibility; the process can be reversed or not, depending of what methods are allowed.

Conventional wisdom says that $S_1 = S_0$ so that the entire change from $S_0$ to $S_2$ is attributed to the expansion. But this makes no sense when it comes from a tradition where $S_1$ is not defined! See Section IX.8.

To Joule and Kelvin is attributed measurements that show that the internal energy $U_2$ at the end of the experiment is the same as the internal energy $U_0$ at the beginning. (The Navier Stokes equation suggests a loss of energy due to viscosity, but the meaning of ‘energy’ in that context is unclear.)

The overall transition, from the initial equilibrium in the smaller vessel to final equilibrium in the the larger one, includes a stage where the entropy is not defined. If no dynamical theory accounts for this transition, how are we to normalize the entropies? The experiments tell us that both system, the initial and the final, have the same physical properties, with the same expression for the entropy in terms of density and temperature up to normalization! The answer is that there is are other paths, quasi-static and ‘reversible’, that connects the two configurations: slow expansion and slow expansion in a heat bath.

Finally, what is the distribution of entropy in the system immediately after the gate was opened? With the extra volume available the particles find new states available to them and a purely statistical argument shows that their entropy is greater. Compare Baez op cit.

In the light of these questions it would be useful to know what accuracy has been achieved in the experiments of Joule and Kelvin or by others with more modern equipment.
III.7. Local thermodynamic potentials

Localization, the passage from global thermodynamics to continuum thermodynamics, puts a new face on the theory of thermodynamic potentials. What is discussed here will become important later on, when the set of dynamical variables is expanded to include several densities.

Recall that the global theory deals with the following quartet

\[
\begin{align*}
U(V,S) & \quad ST & F(V,T) \\
VP & \quad VP & \\
H(P,S) & \quad ST & G(P,T)
\end{align*}
\]

of potentials and associated Legendre transformations. The letters ST between the potentials \(U\) and \(F\) reminds us of the substitution \(S \mapsto T\) in the Legendre transformation. The potentials that have appeared so far refer to a fixed quantity of fluid, a fixed total mass as one gram or one mole. To convert them to densities we multiply each by the mass density, \(\rho U = u, \rho F = f\) and so on. In addition, we change variables, setting \(V = 1/\rho\) and \(S = s/\rho\). Then we find that

\[
f(\rho, T) = u(\rho, s) - sT, \quad g(p, T) = h(p, s) - sT, \quad s = -\frac{\partial f}{\partial T}\bigg|_\rho = -\frac{\partial g}{\partial T}\bigg|_p
\]  \hspace{1cm} (3.7.1)

and

\[
g(p, T) = f + p, \quad h(p, s) = u + p, \quad p = \rho \frac{\partial f}{\partial \rho} - f, \quad \dot{p} = u - \rho \frac{\partial u}{\partial \rho}.
\]  \hspace{1cm} (3.7.2)

The first line brings no surprise but the second line informs us that the pressure has joined the family of potentials. Instead of the quartet of global potential energies we now have a quartet of potential densities,

\[
\begin{align*}
\dot{p}(s, \mu) & \quad sT & p(T, \mu) \\
\mu & \quad \mu & \\
u(s, \rho) & \quad sT & f(T, \rho)
\end{align*}
\]

where

\[
\mu := \frac{\partial f}{\partial \rho}\bigg|_T = \frac{\partial u}{\partial \rho}\bigg|_s.
\]  \hspace{1cm} (3.7.3)

For historical reasons, the new variable \(\mu\) is called the chemical potential. It will play an important role in the theory. The natural variables for \(p\) are \(T\) and \(\mu\). The densities related to \(G\) and \(H\) are

\[
h(s, p) = u(s, \rho) + p \quad sT \quad g(p, T) = f(T, \rho) + p.
\]
Among the partial derivatives there is
\[
\frac{\partial p}{\partial T}\bigg|_{\mu} = -s,
\] (3.7.4)
otherwise known as the Clapeyron equation.

In this book we shall rely principally on the density potentials \(u, s\) and \(f\), functions of the density, the entropy density and the temperature. The total number of particles will not be employed as a variable and there will be no distinction between open and closed systems.

In terms of densities the main relations of thermodynamics take the form
\[
\frac{\partial}{\partial T}(f + sT)\bigg|_{\rho, S} = 0, \quad \dot{\Phi} - \vec{v}^2/2 - \frac{\partial}{\partial \rho}(f + sT)\bigg|_{T, S} = \text{constant}, \tag{3.7.5}
\]
or
\[
\frac{\partial f}{\partial T}\bigg|_{\rho} + s = 0, \quad \dot{\Phi} - \vec{v}^2/2 - \mu = \text{constant}, \tag{3.7.6}
\]

III.8. Conservation laws and the stress tensor

What more than any other property characterizes action principles are conservation laws. The most familiar examples are in analytical mechanics and some of them are examples of Noether’s theorem: If the Lagrange function is invariant under a variation \(\delta q_1, ..., \delta q_n\) then the function
\[
\sum_i \delta q_i \frac{dL}{dq_i}
\]
is a constant of the motion. But to prove the most important conservation law, the time independence of the Hamiltonian, one needs a generalization: If the variation of \(L\) is a time derivative, \(\delta L = \dot{K}\), then the function
\[
\sum_i \delta q_i \frac{dL}{dq_i} - K
\]
is a constant of the motion.

This fundamental statement has applications in field theoretic action principles as well.

To apply the technique to the Fetter-Walecka action (1980), let \(\delta q_i = \frac{d}{dt} q_i, i = 1, 2\), and replace \(q_1, q_2\) by \(\Phi, \rho\). With \(\vec{v} = -\vec{\nabla} \Phi\),
\[
\delta A = \int_{t_0}^{t_1} dt \int_{\Sigma} d^3 x \frac{d}{dt} L, \quad L = \rho (\dot{\Phi} - \lambda - \vec{v}^2/2) - W[\rho].
\]
A short calculation, the same that went into the derivation of the Euler- Lagrange equations, with the usual partial integrations, leaves some integrated parts or surface integrals. The following relation is valid on shell,
\[
\int_{t_0}^{t_1} dt \int_{\Sigma} d^3 x \frac{d}{dt} L = \int_{t_0}^{t_1} dt \int_{\Sigma} d^3 x \left( \frac{d}{dt} \rho \dot{\Phi} + \vec{\nabla} \cdot (\rho \vec{v} \Phi) \right).
\]
Integrating from $t$ to $t + dt$,

$$\frac{d}{dt} \int_\Sigma d^3x (\rho \dot{\Phi} - \mathcal{L}) = \int_{\partial \Sigma} (\rho \dot{\Phi}) \vec{v} \cdot d\vec{\sigma} = \int_{\partial \Sigma} (h + p) \vec{v} \cdot d\vec{\sigma}. \quad (3.8.1)$$

This identifies the Hamiltonian density $h = \rho \dot{\Phi} - \mathcal{L}$. The last equality comes from the fact that the value of $\mathcal{L}$, on shell, is the pressure, $\mathcal{L} = p$. Note that what we have called “Hamiltonian density” is the internal energy density, while the scalar factor in the ‘energy flux density’ is actually the enthalpy density, which on reflection is found to be intuitively sensible. Normal boundary conditions make $\vec{v} \cdot d\vec{\sigma} = 0$ and then $d/dt \int d^3x h = 0$.

Next, consider the case that the variation is generated by a spatial derivative, $G = \vec{G} \cdot \vec{\nabla}$ or the infinitesimal rotation $G = \vec{G} \cdot \vec{x} \wedge \vec{\nabla}$ with $\vec{G}$ constant. The effect on the action is

$$\delta A = \int dt \int_\Sigma d^3x G \mathcal{L}.$$

With the help of the equations of motion one obtains

$$\frac{d}{dt} \int_\Sigma d^3x G \mathcal{L} = \int_\Sigma d^3x \left( \frac{d}{dt} \rho G \Phi + \vec{\nabla} \cdot (\rho G \dot{\Phi}) \vec{v} \right)$$

or

$$\frac{d}{dt} \int_\Sigma d^3x (\rho \vec{G} \cdot \vec{v}) + \int_{\partial \Sigma} \left( \rho (\vec{G} \cdot \vec{v}) \vec{v} + \vec{G} p \right) \cdot d\vec{\sigma}. \quad (3.8.2)$$

Note that the term on the left side of the first equation now is a space boundary term, it appears as the last term in Eq.(3.8.2). The interpretation is clear: to conserve the momentum (resp. angular momentum) in the volume it is not enough that the velocity at the boundary be normal to it. In addition, the total force (resp. total torque) on $\partial \Sigma$ must add to zero also. Equivalently,

$$\frac{d}{dt} (\rho \vec{G} \cdot \vec{v}) + \vec{\nabla} \cdot (\rho \vec{v} (\vec{G} \cdot \vec{v})) + \vec{G} \cdot \vec{\nabla} p = 0 \quad (3.8.3)$$

Using the equation of continuity we convert this to

$$\rho \frac{d}{dt} (\vec{G} \cdot \vec{v}) + \rho (\vec{v} \cdot \vec{\nabla}) \vec{G} \cdot \vec{v} + \vec{G} \cdot \vec{\nabla} p = 0.$$

When $G = \vec{\alpha} \cdot \vec{\nabla}$; that is, $\vec{G} = \vec{\alpha}$, constant, this is the Navier-Stokes equation,

$$\rho \frac{d}{dt} \vec{v} + \rho (\vec{v} \cdot \vec{\nabla}) \vec{v} + \nabla p = 0. \quad (3.8.4)$$

The densities of linear and angular momenta are respectively

$$\rho \vec{v} \text{ and } \vec{l} := \rho \vec{x} \wedge \vec{v}$$
and the two ‘conservation’ laws are

\[
\frac{D}{Dt} \rho \vec{v} = -\vec{\nabla} p, \quad \frac{D}{Dt} \rho \vec{l} = -\vec{x} \wedge \vec{\nabla} p.
\]

Neither momentum nor angular momentum is preserved, unless the force, resp the torque is zero. To make this absolutely clear; for any volume \(\Sigma\) the integral of the left side over \(\Sigma\) is zero if and only if the total force or torque on \(\Sigma\) vanishes.

The conclusion is that the use of ‘angular momentum, and more so ‘angular momentum conservation’ in the construction of intuitive arguments about fluids requires careful circumspection.

The local form of the result, Eq.(3.8.3) is an example of a conservation law that involves the stress tensor. As a phenomenological concept it goes back to Cauchy, but its connection to action principles is the work that was done by Emmy Noether when asked by Einstein and Hilbert to clarify the conservation laws of General Relativity. After Noether’s contribution, conservation laws is a subject that is inseparable from action principles. To illustrate, we shall develop an alternative analysis of Fetter-Walecka theory, using concepts and notation from Noether.

Consider first a relativistic, field theory Lagrangian, a function of a scalar field \(\phi\) and its first order derivatives \(\phi^\mu, \mu = 0, 1, 2, 3t\). What follows can easily be generalized to the case that there is any number of fields. The energy-momentum tensor is defined by

\[
T^\nu_\mu = \phi^\nu \frac{\partial L}{\partial \phi_\mu} - \delta^\nu_\mu L.
\]

The simplest example is

\[
L = \frac{1}{2} g^{\mu\lambda} \dot{\phi}_\mu \phi_\lambda,
\]

with the Euler-Lagrange equation \(\Delta \phi = 0\). Then

\[
T^\nu_\mu = g^{\nu\lambda} \phi_\lambda \phi_\mu - \delta^\nu_\mu L.
\]

A completely straight forward calculation gives

\[
\partial_\nu T^\nu_\mu = -\phi_\mu \Box \phi = 0, \quad \text{on shell.}
\]

The operator \(\Box\) is the d’Alembertian. It can easily be verified that this ‘conservation law is valid for any Lagrangian, relativistic or not, that depends exclusively on the fields.

A more relevant example is the Fetter-Walecka theory. The indices run over 0, 1, 2, 3. The energy momentum tensor has components

\[
T^0_0 = \dot{\Phi} \rho v, \quad T^0_i = \Phi_i \rho \\
T^i_0 = -\Phi_i \rho v_j - \delta^i_j L.
\]

(3.8.5)
We can verify the conservation law $\partial_\nu T^\nu_\mu = 0$. It splits into these two cases;

$$\partial_0 T^0_0 + \partial_j T^j_0 = 0$$

is easy to verify, it reduces to

$$\frac{d}{dt} h + \vec{\nabla} \cdot (\rho \Phi \vec{v}) = 0,$$

which is the statement of energy conservation, Eq.(3.8.6). The other one, with $\mu \to i = 1, 2, 3$, becomes

$$\frac{d}{dt}(\rho \Phi_i) - \partial_j(\Phi_i \rho \Phi_j) - \partial_i \mathcal{L} = 0, \quad i = 1, 2, 3,$$

which is the statement of momentum conservation. Making use of the equations of motion we simplify this last equation to recover the Bernoulli equation.

$$\frac{d}{dt} \vec{v} + (\vec{v} \cdot \vec{\nabla}) \vec{v} = -\frac{1}{\rho} \vec{\nabla} \mathcal{L},$$

So we have verified (and re-verified) that the divergence of $T$ is zero, and that the statement expresses the conservation of energy and momentum. We have also learned that the conservation laws of the energy momentum tensor are related to equations of motion of the action principle, but that it contains less information. It has become usual to regard the Navier-Stokes equation as the core of the subject, but it does not give an expression for the energy and it does not relate to the equation of continuity.

In contrast, Fetter-Walecka’s formulation of hydrodynamics is a complete, dynamical field theory, but limited to irrotational velocities.

**The equalization of pressure**

The subject of equalization of pressure was left in an unsatisfactory state in Section II.5; we were unable to show that two systems separated by a movable wall will have the same pressure at equilibrium. This was due to the fact that the volume appears twice in the total energy. Now we are in a better position to reach a reasonable conclusion.

By localization, the variable “volume” has been replaced by two new variables: the density $\rho$ and the total volume $V$. If there are no external forces, then the free energy potential is a function of density, independent of total volume. For a divided system the free energy depends on the two densities only; the volumes $V_1$ and $V_2$ appear only in the term $V_1 P_1 + V_2 P_2$. And now minimizing the energy for fixed total volume evidently leads to $P_1 = P_2$. See Section III.5. When external forces such as gravity are present the pressure is not constant but only continuous.
III.9. Minimal energy and maximal entropy

We are ready to resume the study of the general structure of thermodynamics, including a central and most difficult issue: maximalization of the entropy.

We have an action, a Lagrangian density, a Hamiltonian density defined by the usual Legendre transformation,

\[ h = \dot{\Phi} \frac{\partial}{\partial \dot{\Phi}} \mathcal{L} - \mathcal{L}, \]

and Euler-Lagrange equations that summarize both hydrodynamics and thermodynamics. If we use the adiabatic equation to eliminate the temperature we are left with a non degenerate symplectic structure with one pair of canonical variables; the Hamiltonian is a first integral of the motion and the canonical generator of time translations. What we do not have so far is a Gibbsean principle of minimum energy.

The classical Lagrangian paradigm

So far, the action principle provides all the laws of traditional thermodynamics, including some that go beyond the description of the states of equilibrium. What is missing is part of the interpretation. To complete the picture in this respect we can do no better than to seek inspiration from tradition, for equilibria is the unique concern of a classical and highly successful theory.

We need to understand how it comes about that the Hamiltonian of an action principle tends to have the lowest possible value at equilibrium. The paradigm of an action principle is one that involves dynamical variables \( q_1, ..., q_n \) and

\[ \mathcal{L} = \sum \dot{q}_i^2/2 - V(q_1, ..., q_n) = \sum \dot{q}_i p_i - H(q_1, ..., q_n, p_1, ..., p_n). \quad (3.9.1) \]

This system is non degenerate, each variable has an independent conjugate momentum,

\[ p_i = \frac{\partial \mathcal{L}}{\partial \dot{q}_i}. \]

The equations of motion in Hamiltonian form are

\[ \dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}, \quad i = 1, ..., n. \quad (3.9.2) \]

Here we see what we are looking for: If “equilibrium” is defined as a solution in which nothing varies with the time, \( p_1, ..., p_n, q_1, ..., q_n \) being time independent, then Eq.(3.9.1) tells us that the Hamiltonian must be stationary for that solution. In principle, the equilibrium may be stable or not, for the stationary point may be a maximum or a minimum.

Turning now to our action principle for hydrodynamics, with its one-dimensional canonical structure, we have

\[ \int d^3 x \mathcal{L} = \int d^3 x \rho \dot{\Phi} - H[\rho]. \]
To develop a close analogue with mechanics we should like to define a state of equilibrium as one with $\dot{\Phi} = 0$. We are prevented from doing that because we need to incorporate a Lagrange multiplier into $\dot{\Phi}$, but rather than replacing $\dot{\Phi}$ by $\dot{\Phi} - \lambda$ we can just as well call stationary a configuration with $\dot{\Phi} = \lambda$. The value chosen for $\lambda$ amounts to selecting a system to be studied.

In thermodynamics we must recognize that it does not have a non degenerate canonical structure, for the temperature does not have a conjugate momentum. Variation of the action with respect to $T$ is technically not an equation of motion but a constraint, which is fine for most purposes, but it is, perhaps, the source of the following difficulty.

It has become established that the ‘energy’ functional that takes a minimal value in many applications of thermodynamics to an isolated system (with fixed total volume) is the free energy

$$F = \int d^3x f(\rho, T).$$

The ‘energy’ density is the free energy density $f$. In the next chapter we shall study the application of the theory to the van der Waals gas and this will be confirmed. The Hamiltonian density $h$, on the other hand is defined by

$$L = \rho \dot{\Phi} - h;$$

that is - see Eq.(3.3.1) - $h = f + sT$. The problem is that the ‘energy’ of classical, equilibrium thermodynamics is not the Hamiltonian of the Action Principle. The solution is to interpret the entropy as a time derivative.

This should tell us something about the physical interpretation of entropy. The entropy is a record of past interactions between our system and the environment, an interaction that is no longer active. That is why neither temperature nor entropy appears in the Lagrangian as a time derivative. We shall have to generalize this situation, and we must try to do it without altering the essential properties of the theory.

Consider replacing, in the Lagrangian density, the term $sT$:

$$sT \to T\rho \dot{\sigma} + j(\sigma).$$

We have introduced a new field variable $\sigma$ and a source density $j$. Variation of $T$ gives

$$\frac{\partial f}{\partial T} + \rho \dot{\sigma} = 0.$$

This tells us that $\dot{\sigma}$ is the specific entropy density $S$. Variation of the mass density gives the familiar equation with $S$ replaced by $\dot{\sigma}$. We have a new equation, from variation of $\sigma$,

$$\frac{d}{dt} (\rho T) = \frac{\delta j}{\delta \sigma}.$$

The source $j(\sigma)$ is for us to choose and we shall take advantage of that by demanding that the systems decouple. That is, we interpret the last equation as a condition that
determines the right side, with no implications for the left side. The external part of the enlarged system simply allows the original system to obey its own equations of motion. This is reasonable, for the only thing that we know and want to know about the extension of the system by the new degree of freedom represented by \( \sigma \) is that it should maintain and justify the assumptions that were made about the ‘isolated’ system.

After the replacement (3.9.4) we have two canonical pairs of dynamical variables and a non-degenerate symplectic structure. The Hamiltonian density is

\[
h = \rho \dot{v}^2/2 + f + j(\sigma).\]

The Hamiltonian is extremal for allowed variations of the equilibrium state, variations that do not affect the field \( S = \dot{\sigma} \). Finally, the functional \( \int d^3 x (\rho \dot{v}^2/2 + f) \) is extremal with respect to variations that do not affect the external source \( j(\sigma) \). The term \( j(\sigma) \) is inconsequential and will be dropped from now on.

In the new formulation our Lagrangian and Hamiltonian densities are related by

\[
\mathcal{L} = \rho \dot{\Phi} - \rho T \dot{\sigma} - h, \quad h = \rho \dot{v}^2/2 + f. \tag{3.9.5}
\]

Prompted by the experimental evidence we have moved the term \( sT \) out of the Hamiltonian. The field \( \sigma \) is canonically conjugate to \( \rho T \); the canonical structure is non degenerate.

Finally, just as choosing a state of equilibrium leads to fixing the value of \( \dot{\Phi} \), the fact that the system is isolated implies fixing the value of \( \dot{\sigma} \).

We have developed the interpretation of the entropy in a direction that helps us get a better grasp on its nature. The parameter \( S \) acts like a Lagrangian multiplier, in that the actual value is determined by a one-sided influence of the environment. The system approaches an equilibrium state by giving up energy to the environment while it remains constrained by the principle of least action; this necessarily leads to adopting the highest value of \( S \). The environment has infinite entropy and is not affected in a measurable way; just as the reflection of a small mass from a very large one has no measurable effect on the latter because the momentum change is measurable only through observation of the velocity change \( \Delta v = M^{-1} \Delta p \).

These conclusions are not the result of speculation but are based on the experimental fact that it is the free energy, rather than the internal energy, that is minimal for equilibrium configurations of an isolated system.

III.10. The third law and the normalization of entropy

So far, nothing that has been done defines a zero point of entropy; only differences have a direct physical meaning in terms of heat transfer. But perhaps, to reach absolute zero of temperature we must take all the heat out of it.

The third law is an invention of Nernst, who dedicated a monograph to it. (Nernst 19) It postulates that the entropy is zero at zero absolute temperature, \( T = 0 \). Combined with the second law it has interesting consequences. Consider a system of particles, where each particle has precisely 2 atomic levels, with energy difference \( \epsilon \), say. Each level has a well
defined entropy per particle. A state of equilibrium will have a number of particles in each level. This number can change; typically the population of the higher level will increase as the temperature is raised. It follows that each particle is subject to migrate between the two levels. Then at equilibrium the energy must be stationary with respect to this level switching,

\[ T(S_1 - S_2) + \epsilon = 0 \]

The binding energy \(\epsilon\) is very nearly independent of the temperature; therefore this gives us a very rare example where the assignment of the total entropy of a mixture, between the two components of a mixture, can be predicted.

**III.11. Galilei invariance**

The behavior of a thermodynamical system under Galilei transformations has played an important role in the development of thermodynamics, for there are situations where the question of invariance imposes itself.

The Galilei group is a group of coordinate transformations. We need to understand how this group acts on fields. The geometry of a simple thermodynamic system is 3-dimensional, the fields are defined over \(\mathbb{R}^3\) or a part thereof.

The most important fields are scalar fields and the prototype is the temperature \(T\). Under any transformation of coordinates,

\[ x^i \rightarrow x'^i = x'^i(x), \tag{3.11.1} \]

a scalar field transforms as follows,

\[ T \rightarrow T', \]

the field \(T'\) defined by

\[ T'(x') = T(x). \]

Nothing could be simpler than this fundamental transformation property.

Our theory also employs vector fields, most of them are gradients and transform like gradients. Under the transformation (3.1.1) we have, using the summation convention

\[ \frac{\partial T'}{\partial x'^i} = \frac{\partial x'^j}{\partial x^i} \frac{\partial T}{\partial x'^j}, \quad i = 1, 2, 3. \]

The velocity field transforms similarly,

\[ v'^i = \frac{\partial x'^i}{\partial x'^j} v^j, \quad i = 1, 2, 3. \]

Examples of fields that transform as scalar fields are the density \(\rho\), the temperature \(T\), and the kinetic energy.

A transformation of the Galilei group relates the coordinates of two observers that move relatively to each other with a fixed velocity \(\vec{u}\),

\[ x_i \rightarrow x'_i = x'_i(\vec{x'}) = x_i - tu_i, \tag{3.11.2} \]
with \( \vec{u} \) a constant vector. This is a coordinate transformation in \( \vec{x} \) space, but a complication arises from the dependence of the transformation on the parameter \( t \).

For reasons that are related to the appearance of \( t \) in the transformation (3.11.2), the action of the Galilei group on our fields is not what one could expect. Instead,

\[
\Phi'(x', t) = \Phi(x, t), \quad \partial_i' \Phi'(x', t) = \partial_i \Phi(x, t) + u_i,
\]

and

\[
\dot{\Phi}'(x', t) = \dot{\Phi}(x, t) + \vec{u} \cdot \vec{\nabla} \Phi + \vec{u}^2/2.
\]

At first sight this seems incomprehensible and an explanation within this present context can never remove all doubts. The easiest way to demonstrate that this is the transformation law that we want is to obtain the result by reduction of a Lagrangian that is Lorentz invariant. The reader may not wish to follow the derivation; the alternative is to accept Eq.s (3.11.3-4) on faith. What really matters is to verify that our Lagrangian is invariant. We shall return to show that that is the case below.

The Lorentz group is the group of coordinate transformations of the form

\[
x'^\mu = x^\nu \Lambda^\mu_\nu.
\]

Here the Greek indices run over 1,2,3,0 and \( \Lambda \) is 4-dimensional matrix. The group includes rotations of the spatial coordinates, but the ‘proper’ Lorentz transformations involve one space coordinate and the time. The parameter is a vector \( \vec{u} \); when it points in the \( x \)-direction the transformation is

\[
x' = \gamma (x + ut), \quad t' = \gamma (t + ux/c^2), \quad y' = y, \quad z' = z,
\]

where \( c \) is the velocity of light. Any 4-dimensional, scalar field \( \psi \) transforms as follows,

\[
\psi'(\vec{x}', t') = \psi(x, t)
\]

and the gradient transforms just as expected for 4-dimensional coordinate transformations,

\[
\frac{\partial}{\partial x'} \psi'(\vec{x}', t') = \gamma \left( \frac{\partial}{\partial x} \psi(x, t) - u \dot{\psi}(\vec{x}, t)/c^2 \right), \quad \dot{\psi}(x', t') = \gamma \left( \dot{\psi}(x, t) - u \frac{\partial}{\partial x} \psi(x, t) \right),
\]

\[
\frac{\partial}{\partial y'} \psi'(\vec{x'}, t') = \frac{\partial}{\partial y} \psi(\vec{x}, t),
\]

\[
\frac{\partial}{\partial z'} \psi'(\vec{x'}, t') = \frac{\partial}{\partial z} \psi(\vec{x}, t),
\]

(3.11.6)

The odd elements in (3.11.3-4) come from a simple change of notation. We replace the field \( \psi \) by a new field \( \Phi \) according to the definition,

\[
\psi(x, t) = c^2 t + \Phi(x, t).
\]

70
With this change of notation (3.11.5) takes the form

$$\Phi(x', t') + c^2 t' = \Phi(x, t) + c^2 t$$

from which

$$\Phi(x, t) = \Phi'(x', t') + c^2 (t' - t)$$

$$\frac{\partial}{\partial x} \Phi(x, t) = \gamma \frac{\partial}{\partial x'} \phi'(x', t') + u$$

and

$$\dot{\Phi}(x, t) = \gamma \frac{\partial}{\partial t'} \Phi'(x', t') + \gamma u_i \frac{\partial}{\partial x^i} \Phi(x', t') + c^2 (\gamma - 1).$$

In the non-relativistic theory one ignores terms of order $1/c^2$, hence $\gamma = 1 + \vec{u}^2/2c^2$ and this result is the same as (3.11.3-4).

Now that we are aware of the transformation properties of the velocity we have a good reason to be careful about changing the kinetic part of the Lagrangian density.

Finally, combining (3.11.3-4) we find that $\vec{v}(x) = \vec{v}'(x') + \vec{u}$ and, to first order in $\vec{u}$,

$$\dot{\Phi}(x, t) - \vec{v}^2(x)/2 = \dot{\Phi}'(x', t') - \vec{v}'^2(x')/2;$$

So we see that the Fetter-Walecka Lagrangian is invariant under Galilei transformations; there is no preferred system in conservative hydrodynamics.

Other formulations of hydrodynamics are not Galilei invariant. Attempts to include an energy have not discovered one that is Galilei invariant. Indeed, the Hamiltonian of F-W theory is not Galilei invariant, but the Lagrangian is! Some very well known text books are less than clear about this. See for example Khalatnikov (1956), Landau and Lifshits (1960) page 264, Putterman (1972).

A relativistic version of the Fetter-Walecka model will be presented in chapter X. It is the only indication, in a field theory, that the non-relativistic limit of General Relativity is the Newtonian theory of gravity of fluids.

III.12. Remark concerning the space of variations.

There is a fundamental point to be understood and remembered. In any variational system, every allowed variation of the dynamical variables implies a condition that must be satisfied by the system; every enlargement of the class of variations implies an additional equation of motion, or an additional constraint on the solutions. Of course, there is a risk that admitting more variations may lead to a system of Euler-Lagrange equations that do not allow solutions!

Therefore, let us beware.

According to Gibbs, the ‘variations’ that are to be considered in applications of his energy axiom are “all possible variations of the system”. Elaborating through several pages of text, he insists that constraints of various sorts limit the variations to those that are physically realizable. Now it is possible to imagine a variation of $S_1$ and $S_2$ that keeps
the sum fixed, but it is not physically realizable unless the temperatures are equal. What
we are assured with great emphasis in the textbooks is that entropy is not conserved. When heat is transferred from a system with temperature $T_1$ then this system suffers a change $dQ_1 = T_1 dS_1$ of heat. If this heat is received by another body at temperature $T_2$ then the change of heat of that system is $dQ_2 = -dQ_1 = T_2 dS_2$. The total change of heat of the system as a whole is $0 = dQ_1 + dQ_2 = T_1 dS_1 + T_2 dS_2$. Unless the temperatures are equal, the sum $dS_1 + dS_2 \neq 0$. Consequently, when the temperatures are unequal there are no changes in the individual entropies that keep the total entropy constant. The space of variations remains the same. Prigogine (1949) already reached the same conclusion. He writes, on pages 17-18: *

“We can therefore say that “absorption” of entropy in one part, compensated by a sufficient “production” in another part of the system is prohibited. This formulation implies that in every macroscopic region of the system the entropy production due to irreversible processes is positive. (…) Interference of irreversible processes is only possible when they occur in the same region of the system.”

The importance that Prigogine attaches to this clarification can be judged from the sequel:

“Such a formulation may be called a “local” formulation of the second law in contrast to the “global” formulation of classical thermodynamics. It’s value lies in the fact that it permits a much closer analysis of irreversible processes and, as such, it will constitute the central postulate on which this book is based.”

The central postulate! Apparently, Prigogine goes to some pain to avoid saying that Gibbs erred at this point.

**We do not agree that the principle of minimum energy demands equalization of the temperature. Consequently, we must keep both $S_1$ and $S_2$ fixed for the class of variations considered in the principle of minimum entropy.**

Let us turn to the axiom of maximum entropy. The total entropy is

$$S = S_1 + S_2 = \frac{1}{T_1}(E_1 - F_1 - V_1 P_1) + \frac{1}{T_2}(E_2 - F_2 - V_2 P_2),$$

and the variations of $E_1$ and $E_2$, with $dE_1 + dE_2 = 0$, make a contribution to the variation of the total entropy,

$$dS = \frac{dE_1}{T_1} + \frac{dE_2}{T_2} = dE_1\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \ldots$$

And here it it is clear that, if it is possible to vary the partial energies without changing the values of the other variables, then this contribution to the change in the total entropy

* See also pages 20, 21, where a clear distinction is made between entropy production and entropy convection by mass flow, and page 39.
will vanish (making the total entropy extremal) only if the temperatures are equal. Such changes are said to be physically possible even if not discussed in detail within the present context. Transfer of energy by radiation is often mentioned, but is there any reason to hold that radiation is not another example of heat transfer? In fact, what is required is a variation of the energies that does not affect the other terms in the last equation. This requires additional degrees of freedom, and when these are appropriately included in the expression for the total energy of the theory we find that they must be kept fixed as well. So there is no way to transfer energy without affecting the other terms, and no general conclusion is possible.

**Taking stock**

We have seen that the fundamental relations of thermodynamics, more precisely the thermodynamics of isolated systems, are the variational equations of an action principle. We have defined adiabatic thermodynamics as the mathematical structure defined by this action principle. To use it we need an expression for the free energy and we must learn what values to assign to the specific entropy density. There is a strong indication that, for many homogeneous systems, this density takes the form \( s = \rho S \), \( S \) constant.

But thermodynamics is more than adiabatic thermodynamics, and more than a theory of homogeneous systems. Although we shall postpone the study of dissipative processes, we shall very soon find out that it is essential to be able to determine the final result of entropy producing dissipation. Without formulating general axioms, we shall take up the study of important systems and use experimental input to try to deduce special results that we hope will merge into a general pattern that can be called “theory”.

What does it mean to “find the entropy”. What has already been emphasized deserves to be reiterated here, as we are on the threshold of the applications. There are several separate problems.

To most writers, “finding the entropy” means one of two things: to discover an expression, in terms of density and temperature, that gives the entropy of a configuration where the density and the temperature are known, or to evaluate this expression for a given configuration. There is a third aspect to “determination of the entropy”, one that we consider to be more fundamental because it shall be confronting us at every turn: The more basic problem is to discover the correct value of the assigned, specific entropy density; that is, the off shell expression for the entropy density that is expressed in terms of the mass densities and that appears in the variational principle as the term \( sT \). The first instance of this problem is the case of a pure substance, where in most applications \( s = \rho S \) with \( S \) usually uniform. In the case of mixtures we shall propose that the ‘assigned density’ \( s \) is a linear function of the densities.

This problematics is not part of the traditional treatment; it is a principal innovation presented in this treatise. It is a part of the program to determine the Lagrangians that encode all the properties (or as many as we can) of a given system. The ‘simplest’ example is the program of finding an expression for the interaction between the components of a binary liquid that accounts for the speed of sound as well as the critical behavior. Actually, this is not at all a simple problem!
IV. APPLICATIONS TO SIMPLE SYSTEMS

Recall that a simple system is one for which the dynamical variables are a density, the temperature, the pressure and the entropy, all fields over a subset of $\mathbb{R}^3$, possibly with movable boundaries. The paradigm of a simple system is an ideal gas; in the first application we shall consider the problem of propagation of sound in an ideal gas.

This process is not within the province of thermodynamics as it is usually understood, but it is an important part of a theory of the dynamics of fluids, and of adiabatic thermodynamics. The theory was developed by Laplace (1806).

IV.1. Propagation of sound in an ideal gas

This is the first of several sections devoted to the propagation of sound. We are here dealing with the simplest case, the propagation of a plane pressure wave in an ideal gas.

The difficult part is to know what theory applies to this phenomenon. One starts with a gas at equilibrium, density, pressure and temperature uniform and time independent, and considers a first order perturbation of this system

$$\rho = \rho_0 + \varepsilon \rho_1, \quad T = T_0 + \varepsilon T_1,$$

with harmonic perturbations, e.g. $\rho \propto \exp i(kx + \omega t)$, $k$ and $\omega$ constant.

We may be sure that there will be a fluctuation of density and pressure but it is possible to entertain some doubts concerning the temperature. Newton’s isothermal theory of sound propagation (Proposition 49 of Book II of the Principia) postulates that the temperature is fixed and that the equation of continuity as well as the Bernoulli equation apply. He also needs a relation between density and pressure and for this he uses the ideal gas law.

Here is the detailed paradigm for the use of the Euler-Lagrange equations.

1. Write down the expression for the Lagrangian, with the appropriate formula for $f$:

$$\mathcal{L} = \rho (\dot{\Phi} - \frac{v^2}{2}) - \mathcal{R} T \ln \frac{\rho}{T_n} + \rho ST. \quad (4.1.1)$$

2. Variation of $\Phi$ gives the equation of continuity; to first order in $\varepsilon$,

$$\dot{\rho}_1 = -(\rho_0 v_1).$$

3. Variation of the density gives

$$\Phi = \mathcal{R} T (\ln \frac{\rho}{T_n} + 1) + ST. \quad (4.1.2)$$

In Newton’s theory $T$ is held fixed and the calculation goes as follows, using the last 2 equations. If a prime denotes the spatial derivative in the direction of propagation,

$$\frac{\dot{\rho}_1}{\rho_0} = -\dot{v}'_1 = \dot{\Phi}_1'' = \mathcal{R} T \frac{\rho''_1}{\rho_0}$$

and thus

$$c^2 = \frac{\omega^2}{k^2} = \mathcal{R} T.$$
Using $T = 293$ and $\mathcal{R}_{\text{air}} = 0.8314 \times 10^8/28.96$ gives $c = 290 \text{m/sec}$. The actual value is 343 m/sec.

A better result is obtained with the assumption, first proposed by Laplace (1806), that sound propagation is “adiabatic”. That is to say that it is governed by the Euler-Lagrange equations of our Lagrangian, with a fixed value of $S$. In Laplace’s theory $\rho$ and $T$ are related by the adiabatic condition: it is the third and last of the Euler-Lagrange equations, obtained by variation of $T$,

$$\mathcal{R}_\rho (\ln \frac{\rho}{T^m} - n) + \rho S = 0 \quad (4.1.3)$$

The ratio $\rho/T^m$ is thus fixed and therefore $T_1/T_0 = (1/n)\rho_1/\rho_0$, so the same calculation gives

$$\frac{\ddot{\rho}_1}{\rho_0} = -\dot{v}_1' = \Phi''_1 = (1 + \frac{1}{n})\mathcal{R}T''_1 = \gamma\mathcal{R}T \frac{d\rho''_1}{\rho_0}.$$

and

$$c^2 = \gamma\mathcal{R}T.$$

In this book we shall always assume that the specific entropy is fixed. For this reason it is useful to repeat the last calculation, that of Laplace, in somewhat greater generality.

Let us write the Lagrangian as follows.

$$\int d^3x \mathcal{L} = \int d^3x \left( \rho(\dot{\Phi} - \vec{\nu}^2/2) - W(\rho, T) \right), \quad W = f + sT,$$

The three Euler-Lagrange equations are

$$\dot{\rho} + \vec{\nabla} \cdot (\rho \vec{v}) = 0, \quad \frac{\partial W}{\partial T} \bigg|_\rho = 0, \quad \dot{\Phi} - \vec{\nu}^2/2 = \frac{\partial W}{\partial \rho} \bigg|_T.$$

As we have seen, for this to simplify we need (a) for the entropy density $s$ to be linear in $\rho$, $s = \rho S$ and (b) that the specific entropy $S$ is uniform. The first condition is satisfied by an ideal gas; it is not always pointed out that the second condition (the isentropic assumption) is used as well, to get the formula (see Section III.1)

$$\vec{\nabla} p = \vec{\nabla} \left( \rho \frac{\partial f}{\partial \rho} - f \right) = \rho \vec{\nabla} \frac{\partial W}{\partial \rho} \bigg|_S.$$

$$\frac{\ddot{\rho}_1}{\rho_0} = -\dot{v}_1' = \frac{\partial p'}{\rho} \bigg|_S = \frac{\rho''_1 dp}{\rho \, dp \, \text{adiab}}.$$

$$c^2 = \gamma\mathcal{R}T.$$
For an ideal gas the equations are
\[ \dot{\rho} + \text{div}(\rho \vec{v}) = 0, \quad R(\ln \frac{\rho}{Tn} - n) + S = 0, \quad \dot{\Phi} - \vec{v}^2/2 = \mu + ST = (n + 1)RT, \] (4.1.6)
where \( \mu \) is the chemical potential (Section II.7) and
\[ \frac{dp}{d\rho} \bigg|_{\text{adiab.}} = \gamma RT. \] (4.1.7)

For air \( \gamma = 1.4 \), which gives a speed of sound in air as 343 m/sec. The result is an excellent prediction for air and other gases at atmospheric temperature and pressure. See the web article “Laplace and the Speed of Sound”. * Laplace’s calculation is found in an article by his protege Biot (1802).

**Corollary.** If the adiabatic derivative \( p \) is negative the system is unstable; the perturbation grows exponentially.

**Remark.** It deserves to be emphasized that the adiabatic condition was needed, which would be something of a surprise if it were interpreted as no more than a formula that determines the entropy. We do not need the value of the entropy, but we used the fact that it is uniform (the poltropic condition) and that it is constant in time. In other words, the specific entropy density, not only the total entropy, is an adiabatic invariant. At least, the assumption that it is so, is a successful assumption as far as the propagation of pressure waves is concerned. It should also be emphasized, once again, that this work of Laplace, 200 years old, when translated to the modern idiom, is a successful use of entropy for a system that is not in equilibrium.

**Radial wave**

A radial wave, originating at the center of a Cartesian Coordinate system and propagating in the direction of the radius vector, or else converging on the center, requires a source or an absorber at either end. The propagation of the wave from source to absorber can be discussed without a specification of the emitter or the transmitter; all that is needed is the boundary conditions. We postulate spherical symmetry; the boundaries are spheres of radii \( r_0, r_1 \), with \( 0 \leq r_0 < r_1 < \infty \).

We consider a first order perturbation of a static configuration in which all the field variables are uniform and the flow velocity is zero. The appropriate generalization of (4.1.4) is, for an ideal gas,
\[ \partial_t^2 \delta \rho = \gamma RT_0 \Delta \delta \rho \]
Setting \( \partial_t \delta \rho = i\omega \delta \rho \) we get the radial, 3-dimensional Helmholtz equation
\[ (k^2 + r^{-2} \partial_r r^2 \partial_r) \delta \rho = 0, \quad k^2 = \frac{\omega^2}{\gamma RT_0}. \]

* www.nd.edu/ powers/ame.20231/finn1964.pdf?
It has 2 independent solutions, both singular at the origin,
\[ \delta \rho(t, r) = \frac{1}{r} e^{i\omega t \pm ik r}. \]

With the freedom to choose the sign of \( k \) we can construct a wave traveling into or out of the origin. These solutions will be singular at the origin, evidence of a source or a sink. In the case of a converging wave we can speculate about the mechanism by which the energy can be accounted for; sono-luminescence is one way. We hope to return to this problem, in a discussion of stationery flows.


IV.2. The van der Waals gas
Van der Waals (1873) proposed a physically motivated modification of the ideal gas law. For 1 gram or one mole of gas it takes the form
\[ p = \frac{\mathcal{R} T}{V - b} - \frac{a}{V^2}. \] (4.2.1)

In this section \( V \) stands for \( 1/\rho \). For any amount of gas it is
\[ p = \frac{\mathcal{R} \rho T}{1 - b \rho} - a \rho^2. \] (4.2.2)

The main interest of this formula is that it accounts for the condensation of the gas at low temperatures, but at first we shall examine the pure, gaseous phase only.

The parameter \( b > 0 \) is “the excluded volume”, intended to take into account the fact that the volume available to a particle of the gas is diminished by the fraction of the total that is occupied by the other particles. This arises from the point of view that regards a gas as a collection of classical particles, which is not wholly justified since the particles obey quantum statistics (about which more elsewhere). A dramatic effect of this change in the expression for the free energy density is that, when the gas is strongly compressed, the density increases as before, but now it is limited by the value \( \rho = 1/b \). As this limit is approached the pressure grows without bounds.

The second term is meant to take into account a direct interaction between the particles. This is probably the first example of a suggestion to model an interaction by the addition of a polynomial in the density to the free energy density. It was justified by a study of inter particle interactions, but attempts to predict the values of the parameters by particle dynamics have been unsuccessful, to the point of disfavoring, for a time, the work of van der Waals (Uhlenbeck 19??). In modern times the parameters \( a \) and \( b \) are treated as phenomenological, to be adjusted to a best fit of observed thermodynamical properties, independently for each type of gas. The parameter \( a \) is normally positive, which indicates an attractive force. To make the pressure positive we may restrict the value of \( a \),
\[ \frac{a}{\mathcal{R} T} < 4b, \]
but negative pressures actually occur, as metastable configurations (Ramsey 1956) and the van der Waals theory is successful in that domain as well.

The van der Waals expression has the great merit that it never leads to unreasonable predictions. There have been many proposals to improve the agreement with experiment but here we shall work with the original proposal, Eq.(4.2.2). Generalizations will be considered later in this chapter.

Fig.4.2.1 shows the pressure as a function of the volume for several values of the temperature. At very high temperatures or large volumes the pressure is given fairly accurately by the ideal gas law, and there is just one real value (and 2 complex values) of the volume for each value of \(p,T\). At lower temperatures, when

\[ T < T_c, \]

there are 3 real values of the volume for each value of \(p,T\). This is the domain within which condensation takes place and a liquid phase coexists with the gas. The “critical temperature” \(T_c\) is the highest temperature at which the gas and the liquid can coexist. At this temperature

\[ \frac{\partial p}{\partial V} \bigg|_T = 0, \quad \text{and} \quad \frac{\partial^2 p}{\partial V^2} \bigg|_T = 0. \tag{4.2.3} \]

The critical temperature \(T_c\) and the associated critical pressure and density are

\[ \mathcal{R}T_c = \frac{8}{27} \frac{a}{b}, \quad p_c = \frac{1}{\mathcal{R}} \frac{a}{27 b^2}, \quad \rho_c = \frac{1}{3b}. \]

For \(\text{He}_4\) the experimental values in cgs units are

\[ T_{cr} = 5.19, \quad \rho_{cr} = 0.0696, \quad p_{cr} = 0.227 \times 10^7, \quad V_{cr} = 14.35; \]

and in the same units the parameter values are

\[ a = 2162.5 \times 10^6, \quad b = 5.9. \]

This is not quite right, it improves if we change the critical density to 0.05625, then

\[ p_{cr} = \frac{0.8314 \times 10^8 \times 5.19 \times 0.05625}{4(2/3)} - 2162.5 \times 10^6 \times 0.05625^2 = 2.2596 \times 10^6. \]

* The values of \(T_c\) for real gases range from 5K for helium “... to values well beyond measurement.” (Rowlinson 1959)
Fig. 4.2.1. Loci of constant $T$ in the $V, P$ plane according to van der Waals. The abscissa is the specific volume $V = \frac{1}{\rho}$, the ordinate is the pressure.

In the more popular units,

$$\rho_{cr} = 56.25/4 = 14.0625 \text{ mol/L}, \quad a = 2162.5 \times 16 = 34600 Pa L^2/mol^2,$$

$$b = (3 \times 14.0625)^{-1} = .02370 L/mol,$$

$$T_{cr} = 5.19, \quad \rho_{cr} = 14.0625 \text{ mol/L}, \quad p_{cr} = .227 \times 10^7.$$

Now

$$p_{cr} = \frac{.8314 \times 10^5 \times 5.19 \times 14.0625}{(2/3)} - 34600 \times 14.0625^2 = 2.2596 \times 10^6.$$

Finally, in bars, multiply all three terms by $10^{-5}$.

$$p_{cr} \frac{.8314 \times 5.19 \times 14.0625}{(2/3)} - .3460 \times 14.0625^2 = 22.596 \text{ bar}.$$

The principal application of van der Waals’ formula is to the study of the change of phase. But a relation between pressure, volume and temperature is not sufficient to determine all the thermodynamical properties of the system; in particular, it is not enough information to determine the formula for the free energy, nor the internal energy, and it is not enough to predict the speed of propagation of sound.

Van der Waals’ formula does not determine the free energy. The equation $p = -\partial F/\partial V$ has the general solution

$$F(V, T) = -RT \ln(V - b) - \frac{a}{V} + \psi(T).$$

This can also be expressed as

$$F(V, T) = -RT \ln(V - b)T^n - \frac{a}{V} + \tilde{\psi}(T).$$

This form is suggested by the expectation that the gas becomes an ideal gas in the limit when $a = b = \psi = 0$. If $\tilde{\psi}(T) = 0$ then

$$S = -\frac{\partial F}{\partial T} = \mathcal{R} \ln(V - b)T^n + n\mathcal{R} \quad (4.2.4),$$

79
where $V$ is the molar volume, and if $S$ is uniform this gives a modification of the polytropic relation obeyed by an ideal gas,*

$$k := \frac{1}{(V - b)T^n} = \text{constant}.$$

The internal energy is simply

$$U = nRT - \frac{a}{V},$$

or, in terms of the natural variables,

$$u(\rho, s) = n\mathcal{R}\rho\left(\frac{\rho}{1 - b\rho}\right)^{1/n}k^{-1/n} - a\rho^2, \quad k = e^{S/R-n}. \quad (4.2.5)$$

From now on we shall take $\tilde{\psi} = 0$ as our definition of the van der Waals gas, thus

$$F_{vdW}(V, T) = -RT\ln(V - b)T^n - \frac{a}{V}. \quad (4.2.6)$$

Let us compare this approach with that of Rowlinson (1959). He does not use an expression for the free energy, or the internal energy, but he says (page 71) that $\partial U/\partial V\bigg|_T \propto 1/V^2$ and he reports that this is approximately verified for 5 liquids between the triple point and the critical point. The choice $\hat{\psi}(T) = 0$ is thus strongly indicated for a gas that satisfies van der Waals’ relation while preserving some properties of the ideal gas. We shall refer to this fluid as a van der Waals’ fluid. Later we shall see how Rowlinson gets some of his results by postulating the mere existence of an analytic expression for $F$. The above formula for the free energy is used by Lemmon et al (2000).

See Fig.4.2.1. When the temperature is fixed below the critical temperature, and the pressure is fixed in the interval between the two stationary points, then the relation (4.2.2) allows for 3 values of the density,

$$\rho_1 < \rho_0 < \rho_2,$$

as is illustrated in Fig.4.3.1. The middle value is an unstable equilibrium** and will be ignored from now on. What happens to the gas as the temperature is lowered past the critical point is complicated. But, by action of surface tension and gravity there results, if one waits long enough, a separation of the fluid into two phases, the liquid taking up the lower part of the vessel. We are not equipped to account for this transformation and limit ourselves to describe the result. Note that the separation is observed, not predicted; this is a fact that we shall take up later on, in connection with mixtures.

---

* It will be remembered that the polytropic relation is a special case of the adiabatic relation.

** It is unstable in a mechanical sense (Rowlinson 1959 page 20) and also in the sense of the preceding section.
IV.3. Saturation

Consider a homogeneous body of gas with total mass 1, temperature \( T < T_c \). As the gas is compressed the temperature is maintained by contact with a reservoir, the process carried out slowly so that the system goes through a sequence of equilibria. The pressure increases until the point \( A \) in the Fig. 3.4.1 is reached. One observes that, as the volume is reduced further the gas gradually converts, at constant pressure, to the liquid phase, until the point \( B \) is reached when all the gas has been converted. In the case of steam (water) at normal atmospheric pressure the density increases by a factor of 1 700. *

![Maxwell’s rule](image)

Fig.4.3.1. Maxwell’s rule. The saturation pressure (= vapor pressure) is the value at the horizontal line that makes the two enclosed areas equal. The coordinates as in Fig. 4.2.1.

In what follows we shall make frequent reference to “the temperature”. We know that the Euler-Lagrange equations, for a homogeneous system at rest, demand a uniform temperature. But during condensation the system separates into two parts and we are in a situation that is discussed at length under the heading of “interacting systems”. The experiments are unequivocal: at equilibrium, both phases have the same temperature.

The pressures are also equal at equilibrium. This follows from the action principle, as we have seen in Section III.8.

The van der Waals gas at the point \( A \) is characterized by a uniform, specific entropy density \( S_2 \). The same is true of the van der Waal’s liquid at the point \( B \), though with a different value, \( S_1 \), say. The formula (2.2.3) in Section II.2 tells us that \( S_2 > S_1 \).

* We are ignoring the interesting phenomenon of metastable states. Some catalyst is needed for the process of condensation to begin.Apparently, it is possible to reach the maximum on the pressure curve by increasing the pressure, and the minimum by decreasing it. The pressure at the minimum is not necessarily positive. See Rowlinson (1959) page 21 and Ramsey (1956).
We are considering configurations of adiabatic equilibrium only, so the flow velocity vanishes. The effective Lagrangian is thus

\[ \int d^3 x \left( \rho_\ell \dot{\Phi}_\ell + \rho_g \dot{\Phi}_g - f - sT \right), \]  

where \( \dot{\Phi}_\ell \) and \( \dot{\Phi}_g \) are real numbers. The integrals extend over the region occupied by the liquid and over the region occupied by the fluid. We have here a first example of a rule that we expect to apply universally:

**The Lagrangian of a compound system is,**

**at least in a first approximation,**

**the algebraic sum of the Lagrangians of the components.**

The field \( \dot{\Phi} \) takes different values in the gas and in the liquid. The velocity potential is uniform for equilibrium configurations, except for a possible discontinuity at the meniscus. We consider the equations of motion, restricted to the stationary case, all fields time independent.

Local variation with respect to the density gives, with \( T \) and \( P \) fixed, in either phase,

\[ \dot{\Phi} - ST - \frac{\partial}{\partial \rho} f = 0, \]  

and variation of the temperature gives the adiabatic relation

\[ \frac{\partial}{\partial T} (f + sT) \bigg|_{\rho} = 0. \]  

For a stationary state with \( \vec{v} = 0 \) this implies that all the fields are uniform within each phase and, except for density and entropy, continuous throughout.

This is a complete description of the stationary system, for given values of temperature and pressure. Global variation of both densities leads to the conclusion that both parts have the same temperature and pressure. A complementary global variation of the density will help to specify the coexistent pressure; that is, the location of the point \( A \) in the figure. This point is determined by Maxwell’s rule, that we shall discuss next, before completing the discussion of the equations of motion.

The above Lagrangian also applies to metastable configurations (Reisman 1971).

**Interpretation of the velocity potential**

In a homogeneous fluid at rest the velocity potential fulfills the role of Lagrange multiplier; in a fluid that is separated into a liquid and a gaseous phase it has a more interesting interpretation. The discontinuity in \( \dot{\Phi} \), across a boundary of thickness \( x \); is

\[ \Delta \dot{\Phi} = \dot{\Phi}_1 - \dot{\Phi}_2 = \Delta \vec{x} \cdot \vec{a} = \vec{x} \cdot \vec{F}/\rho; \]
it is the work required to lift one gram of matter out of the liquid. It is equal to $\Delta \bar{v}^2/2$ and we thus have
\[
\Delta \dot{\Phi} = \frac{1}{2} \bar{v}_{\text{esc}}^2, \quad (4.3.4)
\]
where $\bar{v}_{\text{esc}}$ is the escape velocity required to overcome the surface tension. The interpretation of $\rho \Delta \dot{\Phi}$ as the energy of evaporation of one $cm^3$ of the liquid is thus natural. In a famous experiment, designed for education and employing the simplest means, the surface tension was measured and related to the evaporation energy (also measured). From these data Avogadro’s number could be calculated. The value is about $6 \times 10^{23}$. Here are some web posts

1. Surface Tension Ishita Patel, M. S. SURFACE TENSION
   wsimson.tripod.com/OFFLINE/surf-tension.pdf
2. National Physical... resource.npl.co.uk/mtdata/surface tension.htm

Van der Waals has developed a more detailed model for the transition region, the “squared gradient model”, where the above picture is made more explicit (van der Waals 1893).

With two independent densities and associated velocity potentials we have two independent equations of continuity. This is because, in the bulk, whichever component is present is conserved. Conversion takes place only on the phase boundary. That no surface energy is included in the energy density is of course an idealization. In the squared gradient model (op cit), the single field $\dot{\Phi}$ varies continuously from $\dot{\Phi}_1$ to $\dot{\Phi}_2$ in the finite boundary layer.

Because the two spatial divisions of the system each contain only one fluid component, either liquid or gas, the adiabatic condition holds separately in both,
\[
S_1 = -R (\ln \frac{\rho_1}{(1-\rho_1)T^n} - n), \quad S_2 = -R (\ln \frac{\rho_2}{(1-\rho_2)T^n} - n). \quad (4.3.3)
\]
In the pure gas domain, as in the pure liquid domain, there is only one velocity potential and, in particular, in the stationary case, only one independent parameter $\dot{\Phi}$. As the gas condenses, all properties of each component remain constant, except for the total mass of each. Consequently, $\dot{\Phi}_1$ and $\dot{\Phi}_2$ remain constant during isothermal compression. The two parameters are different, because the fixed values of $p$ and $T$ allows for 2 stable values of the density.

IV.4. The dew point and the bubble point, Maxwell’s rule

We turn to the question of predicting the values of the densities and the pressure at $A$ and at $B$ in Fig.4.3.1, the state of equilibrium or coexistence of gas and liquid.

Variation of the density in either region gives the information that the dynamical variables are constant in each; nothing more, since the term $\dot{\Phi}$ in (4.3.2) contains a Lagrange multiplier. Additional information is obtained by the supplemental, piecewise uniform variation with $\delta \rho_1 + \delta \rho_2 = 0$, namely
\[
\text{Disc } \dot{\Phi} = \text{Disc}(\mu + ST). \quad (4.4.1)
\]
Here

\[ \mu = \frac{\partial f}{\partial \rho} \bigg|_T \]

is the chemical potential. This relation is standard thermodynamics. We shall assume that the entropy density is \( s = \rho_1 S_1 + \rho_2 S_2 \) - which is also standard since the two phases are separated. This implies that the specific entropy difference is \( S_1 - S_2 \) and Boltzmann’s theory then identifies \( T(S_1 - S_2) \) with \( \epsilon \) at equilibrium. (De Groot and Mazur).

It remains only to discover the state of lowest ‘energy’. An unequivocal result of 200 years of study is that the ‘energy’ that characterizes the ground state in this isolated system is the free energy \( F = \int d^3 f \), with the caveat that the traditional Lagrange multiplier must be taken into account. The action principle suggests that ‘energy density’ is synonymous with Hamiltonian density, in this case \( f + sT \). To overcome this conflict we have suggested replacing the entropy, so far treated as a mere constant, by \( \dot{\sigma} \), please see Section II.9.

Now Eq. (4.4.1) should better be written

\[ \text{Disc}(\dot{\Phi} - \dot{\sigma}T) = \text{Disc} \mu. \tag{4.4.1'} \]

The principle of maximum entropy at equilibrium implies that for a fixed value of the temperature, the left side vanish, making \( \mu \) continuous. It is nevertheless instructive to work out the implications of the equivalent minimization of the energy. It too implies the continuity of the chemical potential. It remains only to consider the variation of the respective volumes of liquid and gas. The ‘energy’ is the total Hamiltonian

\[ H = V_1 f_1 + V_2 f_2 + \epsilon V_2. \]

The last term, with \( \epsilon \) an arbitrary constant, allows for the normalization of the Hamiltonian. It would be needed to make this expression for \( H \) minimal with respect to variations of the partial volumes, but actually it is irrelevant since the values of the dynamical variables are already fixed by the Euler-Lagrange equations - the state of equilibrium is uniquely determined in terms of the fixed parameters \( S_1, S_2, \Phi_1 \) and \( \Phi_2 \). To alter the relative amounts of liquid and vapor we must change the value of the Lagrange multipliers.

The state of equilibrium is thus characterized by

\[ \text{Disc } \mu = \text{Disc}(\dot{\Phi} - ST) = 0. \tag{4.4.2} \]

Both statements are verified experimentally. Because we’re not aware of any convincing theoretical argument that the free energy must be minimal, and because it can only be proved within the framework of an action principle, or by experience, we prefer to regard this result as an experimental fact. It has been supported by numerous other experiments, and for this reason we have tweaked our action principle so as to identify the free energy, rather than the internal energy, with the Hamiltonian (Section III.9).

The conventional point of view is essentially the same. The on shell value of \( \mu \) is the specific Gibbs potential,

\[ \mu = \frac{\partial f}{\partial \rho} = \frac{f + p}{\rho} = F + VP = G(p,T). \]
Because “this function is a function of $T$ and $p$” it follows that the slope of the free energy density has the same value in either phase. But this statement is not trivial. The familiar argument is

$$d(F + VP) = \frac{\partial F}{\partial T}dT + \frac{\partial F}{\partial V}dV + VdP + PdV = -SdT + VdP.$$ 

This shows only that the value of the function $F + VP$ is defined locally by $T$ and $P$. It does not imply that the value is the same at the points $A$ and $B$.

Callen, in his highly admired text book (Callen 1960), makes the same point. His strategy throughout the book is to invoke maximal entropy to arrive at an operative statement of the principle of minimum energy, with the interpretation ‘energy’ (of an isolated system) = free energy. In this case the axiom of greatest entropy makes the left side of (4.4.1’) equal to zero and this implies that $\mu_1 = \mu_2$. The principle of maximal entropy is thus confirmed by experience.

From Callen’s point of view the statement $\text{Disc}(\dot{\Phi} - ST) = 0$ reflects the fact that the two phases are in a type of diathermal contact where the heat is exchanged by means of transmutation.

It is an experimental fact that $F + VP$ ($F$ if the volume is fixed) does have the same value for both components of the saturated phase. It implies that the horizontal line in Fig.4.3.1 divides the enclosed area in two equal parts and that the slope $\partial f/\partial \rho$ (the chemical potential) has the same value at the points $A, B$. This condition fixes a unique relation between $p$ and $T$. An actual example, with numbers and figures, will be presented later.

![Fig.4.4.1. Coexistence, schematic. The curves are the values of $p$ and $\mu$, plotted against the molar volume.](image)

The difference $\epsilon = \dot{\Phi}_g - \dot{\Phi}_\ell$ is the specific heat of evaporation, or latent heat; for

$$\epsilon = (S_g - S_\ell)T = \Delta Q,$$

(4.4.2)

where $\Delta Q$ is the amount of heat needed, per gram, to convert the liquid to gas. This last equation is sometimes presented without justification. It means that the energy that is
supplied to bring about the evaporation at constant temperature and pressure is entirely
entropic. This is in accord with the principle that the entropy tends to assume the highest
possible value. In the context of the action principle it implies that the free energy is
minimum.

The adiabatic relation
The adiabatic relation is local, so it applies separately in both regions,

\[ S_i = R \ln \frac{\rho_i}{(1 - b\rho_1)T^n} - n, \quad i = 1, 2. \]

Consequently,

\[ S_1 - S_2 = R \ln \frac{\rho_1}{\rho_2} \frac{1 - b\rho_2}{1 - b\rho_1}, \]

which determines the evaporation energy \( \epsilon \). See Saha’s formula in Section V.8.

When applied to the evaporation of water at 373 K this gives a value for the heat of
evaporation that is compared to the actual value of 2260 J/g. *

Finally, since both \( p = \rho \partial f/\partial \rho - f \) and \( \partial f/\partial \rho \) are continuous it follows that

\[ f(\rho_\ell) - f(\rho_g) = (\rho_\ell - \rho_g) \frac{\partial f}{\partial \rho} \bigg|_{\rho = \rho_g}, \quad (4.4.3) \]

so that the two points on the curve \( f(\rho) \) have a common tangent, as illustrated in Fig. 4.4.2.

Conversely, when a straight line is drawn so as to touch the \( f \) locus at two points, then
the pressure has the same value at both points. This could have been predicted on the
basis of the fact that the function \( f + p \) has zeros at both points.

The function \( f(T, \rho) \) thus plays exactly the role that Rowlinson attributes to the free
energy while at the same time giving it a curious twist since he says that there is no
analytic expression for the free energy. Indeed, the free energy is the function

\[ \int_{\text{liq}} d^3x f(T, \rho_1) + \int_{\text{gas}} d^3x f(T, \rho_g) \]

of the 3 variables \( T, \rho_1, \rho_2 \). It depends on the function \( f \) but also on the amount of vapor
that is present. The analytic density \( f(T, \rho) \) is nevertheless the key.

* I used \( R_{\text{air}} = .46 J/g \) and \( V_{\text{liq}}/V_{\text{gas}} = 1700. \)
Fig. 4.4.2. The common tangent. This is a graph showing the free energy density against the density. The common tangent identifies the two coexistent densities. They become minima if a suitable, immaterial linear term is added to the definition of $f$.

The location of the line of condensation, connecting the points $A$ and $B$ in Fig. 4.4.1, cannot be deduced from the expression for the pressure, nor from the variation of the Gibbs function. The principle of maximum entropy or minimum (at least stationary) energy has to be invoked. This conclusion is not novel. What may be new is the perspective that allows to transfer the lesson to other contexts.

Calculating the dew point for Argon.

At the point where the liquid is in equilibrium (coexistence) with the gas the pressure depends only on the temperature; this pressure is the vapor pressure. To find the vapor pressure of Argon as a function of the temperature we must determine the two densities at which both the pressure,

$$P = \frac{RT\rho}{1 - b\rho} - a\rho^2,$$

and the chemical potential

$$\mu = \frac{\partial f}{\partial \rho} = RT\left(\ln\frac{\rho}{(1 - b\rho)T^n} + \frac{1}{1 - b\rho}\right) - 2a\rho$$

have the same values. Data for Argon are:

$$Argon, m = 40, n = 3/2, T_c = 150K, p_c = 4.9MPa.$$

Setting $a = 1.355 \text{ L}^2\text{bar/mol}^2, b = .03201 \text{ L/mol}$ in van der Waals formula gives $T_c = 152.6, p_c = 4.96MPa = .003912 \frac{RT_c}{\rho_c} = .0104$. 

87
The simplest way to determine the dew point; that is, the saturation pressure for a chosen value of $T$, is to plot, in the $x,y$ plane, the loci $p(x) = p(y)$ and $\mu(x) = \mu(y)$, namely, with the densities $x$ and $y$ in $Kg/cm^3$,

$$\ln \frac{x}{1 - 32x} + \frac{1}{1 - 32x} - \frac{16478}{T}(2x) = \ln \frac{y}{1 - 32y} + \frac{1}{1 - 32y} - \frac{16478}{T}(2y),$$

$$\frac{x}{1 - 32x} - \frac{16478}{T}x^2 = \frac{y}{1 - 32y} - \frac{16478}{T}y^2.$$

The dew point is found by inspection of Fig.4.4.3. This figure shows the loci of points $(x,y)$ where $p(x) = p(y)$, resp. $q(x) = q(y)$ for the case that $T = 140$. They intersect at the points where $x,y$ are the densities of the dew point, in grams per liter,

$$\rho_\ell = .01662 \text{ and } \rho_g = .00492.$$

Fig.4.4.3. Argon. The two curves are loci of points $(x,y)$ where $p(x) = p(y)$, resp. $\mu(x) = \mu(y)$. The values of $x$ and $y$ at the intersection of the two curves are the liquid and gas densities at saturation, in grams per liter. Here $T = 140K$.

In Fig.4.4.4. The same information is shown. the abscissa is the density. The two curves are the pressure (purple) and the chemical potential (blue), the latter scaled to pass through the dew point densities. The horizontal line is determined by Maxwell’s rule.
Another way to find the dew point is to plot the free energy and find the two points with a common tangent, see Fig.4.4.5. To read the figure we blow it up, to confirm that two points with a common tangent exist.

Fig.4.4.5. Argon. The common tangent. A plot of the free energy density of Argon at $T = 140K$ against the density. To get an accurate reading of the points of contact add a linear function to make the tangent horizontal.

Here is a table for Argon, based on the van der Waals equation. These values are fairly accurate just below the critical point but by the time we get down to $T = 100K$ they are off by a factor of 2.

<table>
<thead>
<tr>
<th>$T$</th>
<th>$\rho_1$</th>
<th>$\rho_2$</th>
<th>$p/RT_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>145</td>
<td>.0152</td>
<td>.0060</td>
<td>.0038</td>
</tr>
<tr>
<td>140</td>
<td>.0166</td>
<td>.0049</td>
<td>.0033</td>
</tr>
<tr>
<td>135</td>
<td>.0178</td>
<td>.0041</td>
<td>.0030</td>
</tr>
<tr>
<td>130</td>
<td>.0188</td>
<td>.0034</td>
<td>.0027</td>
</tr>
<tr>
<td>125</td>
<td>.0197</td>
<td>.0028</td>
<td>.0024</td>
</tr>
<tr>
<td>120</td>
<td>.0205</td>
<td>.0023</td>
<td>.0020</td>
</tr>
<tr>
<td>110</td>
<td>.0231</td>
<td>.0010</td>
<td>.0011</td>
</tr>
</tbody>
</table>

**IV.5. The critical point**

The nature of the critical point is of great interest. It has been the object of very extensive investigations, most notably with the help of the renormalization group.

The critical point, a fixed point where $\rho_1, \rho_2, T$ and $p$ have well defined values, is the state with the highest value of $T$ at which coexistence occurs.

The van der Waals equation fails to give the correct relation between temperature and pressure in the saturation region. Nevertheless, we begin by studying this equation in the neighborhood of the critical point. We introduce “reduced” variables as follows,

$$RT = RT_c + t, \quad p = p_c + dp, \quad \rho = \rho_c + d\rho,$$
where the critical values are

\[ \mathcal{R}T_c = \frac{8}{27} \frac{a}{b}, \quad p_c = \frac{1}{27} \frac{a}{b^2}, \quad \rho_c = \frac{1}{3b}. \] (4.5.1)

In terms of these variables the van der Waals equation takes the following form (exactly; the reduced variables are not differentials but finite displacements from the critical point)

\[ \frac{1}{3b}(t - 2bdp) + (t + bdp)d\rho + ab\rho^3 = 0. \] (5.5.2)

For fixed temperature and pressure this equation for \( d\rho \) has either 1 or 3 real roots. In the region of one real root this root is the density, and the relation is a true equation of state. In the domain of 3 real roots the temperature and pressure are related and the (average) density is undetermined in the interval between the smallest and the largest roots.

Expanding the equation \( q_A = q_B \), namely

\[
\mathcal{R}T(\ln \frac{\rho_1}{1-b\rho_1} + \frac{1}{1-b\rho_1}) - 2a\rho_1 = \mathcal{R}T(\ln \frac{\rho_2}{1-b\rho_2} + \frac{1}{1-b\rho_2}) - 2a\rho_2
\]

in the neighbourhood of the critical point we find, to lowest order in \( d\rho \), the simple statement that \( d\rho_1^2 = d\rho_2^2 \). If the three real solutions of (5.5.2) are \( d\rho_1 < d\rho_0 < d\rho_2 \), then we have \( d\rho_1 + d\rho_2 = 0 \). In addition,

\[
d\rho_1 + d\rho_2 + d\rho_0 = 0, \quad d\rho_1d\rho_2d\rho_0 = \frac{-1}{3ab^2}(t - 2bdp), \quad (d\rho_1 + d\rho_2)d\rho_0 + d\rho_1d\rho_2 = \frac{t + bdp}{ab}.
\]

This implies that, to lowest order in \( d\rho \), \( t - 2bdp = 0 \), so that only one direction in the \( t, dp \) plane leads from the critical point into the saturation region.

Fig. 4.5.1. The two curves mark the border of the region (above and right) of the pure phase in the reduced variables \( t, dp \).
We obtain direct confirmation of this conclusion by writing down the condition for the existence of three real roots of Eq.(3.2),

\[
\frac{(t + bdp)^3}{3a} + \frac{(t - 2bdp)^2}{4b} < 0. \tag{4.5.3}
\]

This defines a curve with two branches that meet at the origin with a common tangent, the line \( t = -2bdp \).

In the saturation region there is a fixed relation between temperature and pressure, so that there is only one path along which the critical point can be approached. On this path the average density is related to the entropy and varies between \( \rho_1 \) and \( \rho_3 \). Any path that leaves the critical point in another direction begins in the region of a single real root, in the region of a pure phase. There is no condensation in a (sufficiently small) neighborhood of the critical point. The linearized theory and the description of small perturbations around the critical point are therefore unexpectedly simple and regular, to be regarded as problems of a single phase governed by the Lagrangian (4.3.1).

**IV.6. Sound propagation in pure phases and at the critical point**

For a first application, let us calculate the speed of propagation of sound in Helium according to van der Waals. Fig.4.6.1 shows the speed of sound as measured.

![Fig.4.6.1. Helium sound against temperature for fixed pressure, \( p = .01 \ atm \) (red) and \( p = 50 \ atm \) (blue), against temperature, from \( T = 5.19 \) to \( T = 1000 \); it refers to experiments carried out with frequencies between ... ,... and ... ,... herz.](image)

The next figure shows values obtained from van der Waals’ formula with critical parameters

Helium: \( a = 0.0346 \ bar \ Lit^2/mol^2 \), \( b = 017.4 \ Lit/mol \).

The calculation is straightforward (see below), using the equation of continuity and the integrated form of the Bernoulli equation, as in the case of an ideal gas; the square of the speed is the adiabatic derivative of the pressure with respect to the density, where “adiabatic” now means that the temperature is evaluated according to

\[
\frac{\partial (f + \rho ST)}{\partial T} \bigg|_{\rho,S} = 0;
\]
that is, $(V - b)T^n = \text{constant}$. This use of the word adiabatic is standard and explains why the last equation is referred to as the adiabatic relation.

Fig. 4.6.2. Helium sound speed as calculated using Eq. (4.6.1).

The equations that govern a first order, adiabatic perturbation of a pure phase in equilibrium, in which the perturbed fields depend on only one spatial coordinate, are the linearized equations of motion,

$$
\frac{d\dot{\rho}}{\rho} = -\ddot{\rho}' = \frac{\partial^2 \rho}{\partial x^2} \frac{\partial}{\partial \rho} (f + sT)\bigg|_s.
$$

See Section IV.1. The derivative is one of the definitions of the chemical potential. As always, since the specific entropy is uniform, this leads to

$$
c^2 = \left.\frac{\partial p}{\partial \rho}\right|_s.
$$

In the present case

$$
T = \left(\frac{\rho}{(1 - b\rho)k}\right)^{1/n}, \quad p = \frac{\mathcal{R}}{k^{1/n}} \left(\frac{\rho}{(1 - b\rho)}\right)^{1+1/n} - a\rho^2
$$

and

$$
c^2 = \frac{\gamma RT}{(1 - b\rho)^2} - 2a\rho. \quad (4.6.1)
$$

At the critical point this reduces to

$$
c^2 = \frac{.8314 \times 10^8 \times 5.19}{4} \frac{5/3}{(1 - 17.4 \times .0697)^2} - 2 \times .0697^2 \times 2162.5 \times 10^6 \leftrightarrow c = 134.5 \text{m/s}.
$$

The numerical value applies to helium, with $n = 3/2$; it is a small deviation from Laplace’s formula $\sqrt{\gamma RT} = 134.1 \text{ m/s}$. 

92
Table 4.3, at the end of the chapter, gives a range of values. Comparison with Table 4.4 shows little deviation from experiments, or from measured values, at low pressures, but at the highest pressure the fit to experiment is very bad, showing no improvement with respect to the ideal gas model. A better fit is achieved with the general cubic model discussed at the end of the chapter.

IV.7. Refinements of the expression for the internal energy

**The heat capacity**

We consider the region of one phase, at or above the critical point. We shall attempt to account for the anomalies in this region by variation of the heat of evaporation, more precisely the parameter $\epsilon$, with temperature. The potential, with this term now included, is

$$V_1(T, \rho) = \mathcal{R}\rho T \ln \frac{\rho}{(1-b\rho)T^n k_0} - \kappa(\rho) - \rho\epsilon_1(T).$$

The pressure is not affected. We shall assume that the function $\epsilon$ takes the form

$$\epsilon(T) = \alpha(T - T_c)^{1-\beta}.$$

We expect that $\alpha$ is positive and that $\beta$ is small, positive, to make the evaporation energy zero at the critical point. Then

$$C_V = n\mathcal{R} + \alpha\beta(1 - \beta)t^{-\beta}, \quad t := T - T_c$$

infinite at the critical point. Experiments with helium indicate that $\alpha < 0$ and that $\beta \approx .04$.

**The speed of sound**

With $\psi = \epsilon$ there is a correction to Eq. (3.3),

$$\frac{d\dot{\rho}}{\rho} = \frac{T''}{\rho} \frac{\partial p}{\partial T} + \frac{\rho''}{\rho} \frac{\partial p}{\partial \rho} + \epsilon_1''(T).$$

This is supplemented by the on shell condition

$$\ln \frac{\rho}{(1-b\rho)T^n k_0} - n = \epsilon_1'/\mathcal{R}, \quad (4.7.1)$$

which implies that, to first order,

$$(n + \epsilon_1''T/\mathcal{R}) \frac{dT}{T} = \frac{1}{1-b\rho} \frac{d\rho}{\rho}.$$ 

Hence

$$\frac{d\dot{\rho}}{\rho} = \mathcal{R}T'' \frac{1}{1-b\rho} + \frac{\rho''}{\rho} \frac{\partial p}{\partial \rho} + \ldots,$$
which gives for the speed $c$ of sound propagation

$$c^2 = \frac{RT}{n(1-b\rho)^2} + \frac{\partial p}{\partial \rho} + \ldots$$

What follows is the general third order equation of state. Evaluating the second term we find

$$c^2 = \gamma \frac{RT}{(1-b\rho)^2} - \frac{a}{\rho^2} \frac{2(V-b)+x}{((V-b)^2 + x(V-b) + y)^2}.$$ 

Experiment shows a pronounced dip in the speed of sound as a function of density or temperature, in a small region above the critical point. To first order in the perturbation it is

$$\frac{\rho''}{\rho} \left( \frac{RT}{(1-b\rho)^2} - 2a \right) + T'' \frac{R}{1-b\rho}.$$ 

The last term was simplified with the help of the modified shell condition, namely

$$\mathcal{R} \left( \ln \frac{\rho}{(1-b\rho)T^n k_0} - n \right) + \epsilon' = 0.$$ 

This also gives us

$$dT = \frac{1}{1 - Te''/nR} \frac{T}{n} \frac{1}{1-b\rho} \frac{dp}{\rho}.$$ 

Thus

$$c^2 = \frac{d\rho''/\rho}{dT''/T} = \mathcal{R}dT'' \left( n + \frac{1}{1-b\rho} + \frac{\epsilon' - Te''}{R} \right) + d\rho'' \left( \frac{bpT}{(1-b\rho)^2} - 2a \right).$$ 

To first order in $\epsilon$ it gives the squared speed

$$c^2 = \frac{RT}{(1-b\rho)^2} \left( \gamma + \frac{T/\mathcal{R}e''}{1 - T/\mathcal{R}e''} \right).$$

**IV.8. Generalization; the cubic equation of state**

It is sometimes of interest to reduce the errors inherent in the van der Waals expression for the pressure, and many suggestions have been made. A generalization developed by Patel and Teja takes the form

$$p = \frac{RT}{1-b\rho} - \frac{a\rho^2}{(1-c\rho)(1-d\rho)},$$

with a certain relation between the parameters $b, c, d$. The associated free energy density is

$$f(\rho, T) = \rho RT \ln \frac{\rho}{(1-b\rho)T^n} + \frac{a\rho}{c-d} \ln \frac{1-c\rho}{1-d\rho} + \rho \psi(T), \quad k_0 = \text{constant},$$
the function $\psi$ arbitrary so far. There are arguments to show that this function can best be taken to be zero; in that case the internal energy density is

$$U = nRT + \frac{a}{c - d} \ln \frac{1 - c\rho}{1 - d\rho}.$$  

The van der Waals gas is the case in which $c = d = 0$. Provisionally, we shall set $\psi = 0$, deferring refinements until they are needed, as when we take up the study of the neighborhood of the critical point; then

$$f(T, \rho, S) = RT \rho \ln \frac{\rho}{(1 - b\rho)T^n} + \kappa(\rho),$$  \hspace{1cm} (4.8.2)

where

$$\kappa(\rho) = \frac{a\rho}{c - d} \ln \frac{1 - c\rho}{1 - d\rho}.$$  

The adiabatic condition (2.4) (from variation of $T$) is

$$\ln \frac{\rho}{(1 - b\rho)T^n k_0} = n,$$  \hspace{1cm} (4.8.3)

and the on shell internal energy density at equilibrium is

$$u = nR\rho T + \rho\kappa(\rho) + \text{constant} \rho.$$  

We use the expression (4.6.1) for the pressure,

$$p = \frac{RT}{(V - b)} - \frac{a}{(V - c)(V - d)},$$  \hspace{1cm} (4.8.4)

but specialize to the case considered by Patel and Teja (Patel 2004). The calculations are much simplified when we introduce $V' = V - b$, and define $x, y$ by writing

$$p = \frac{RT}{V'} - \frac{a}{V'^2 + xV' + y}.$$  \hspace{1cm} (4.8.5)

The special case considered by Patel and Teja is the case that $y = 2b^2$. An extremum of this function of $V'$ occurs at

$$\frac{RT}{a} = \frac{V'^2(2V' + x)}{(V'^2 + xV' + y)^2},$$

where

$$\frac{RT}{p} = \frac{V'^2(2V' + x)}{V'^2 - y}.$$  \hspace{1cm} (4.8.6)

At the critical point

$$V'^3 - 3yV' - xy = 0, \hspace{0.5cm} x = y^{-1}V'(V'^2 - 3y).$$

95
Finally, at the critical point the value of $b$ is given by the experimental values of the compressibility $Z_{cr} = R T / p$ and the density $\rho_{cr}$ by

$$\frac{R T}{p V} |_{cr} = \frac{(V - b)^3}{y V}.$$ 

For He$_4$ the experimental values are

$T_{cr} = 5.19, \quad \rho_{cr} = .0697, \quad p_{cr} = .227 \times 10^7, \quad Z_{cr} = .301, \quad V_{cr} = 14.35,$

and the parameters are

$a = 2.378 \times 10^9, \quad b = 3.61, \quad x = 15.31, \quad y = 26.06.$

These parameters were used to calculate the speeds given in lines labelled “cubic” in Table 4.3.

**IV.9. Stability**

This is a concept that will become very difficult later, as we come to deal with more complicated problems. We have already studied the van der Waals gas; it will provide the first illustration.

The Bernoulli equation tells us that, to have a stationary state we need to balance the forces. Suppose that the velocity is zero, then the Bernoulli equation tells us that

$$\rho \vec{\nabla} \dot{\vec{v}} = -\vec{\nabla} p.$$ 

In simple systems the temperature can be eliminated with the help of the adiabatic condition; then the pressure is a function of the density and the specific entropy, supposed constant, hence

$$\rho \dot{\vec{v}} + \frac{\partial p}{\partial \rho} |_{S} \vec{\nabla} \rho = 0.$$ 

If the velocity is to the right, say, and the acceleration is in the same direction, then the space between the particles will increase and the density must decrease; this implies that, for stability, $dp/d\rho$ is positive. In more detail, suppose the acceleration is in the positive $x$ direction and imagine a virtual change that makes the acceleration increase. Then by the equation of continuity the gradient of the density must decrease. So again, the coefficient must be positive.

An equivalent argument is to calculate the speed of propagation of sound. We found that its square is the adiabatic derivative of the pressure with respect to the density and learned that if this is positive we will have wave propagation, while if it is negative there will be decay.

In the case of the van der Waals fluid, this condition is violated in the rising part of the curve showing pressure against volume. Where $dp/d(1/\rho)$ is positive, the configuration is unstable. If we approach this region along an isotherm, from right to left, then after passing
the point of coexistence we enter a metastable region. In the absence of a disturbance, as the pressure is increased slowly, condensation can be avoided, but a small disturbance may initiate a catastrophic condensation. If the top of the curve is reached condensation becomes inevitable. Similarly, the region below the bubble point may be entered without actually creating evaporation, even so far as to make the pressure negative, but if the bottom of the curve is reached then evaporation will be rapid.

Table 4.1. Liquid/vapor critical temperature and pressure

<table>
<thead>
<tr>
<th>Substance</th>
<th>Critical temperature</th>
<th>Critical pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon</td>
<td>-122.4 C (150.8 K)</td>
<td>48.1 atm (4,870 kPa)</td>
</tr>
<tr>
<td>Ammonia</td>
<td>132.4 C (405.6 K)</td>
<td>111.3 atm (11,280 kPa)</td>
</tr>
<tr>
<td>Bromine</td>
<td>310.8 C (584.0 K)</td>
<td>102 atm (10,300 kPa)</td>
</tr>
<tr>
<td>Caesium</td>
<td>1,664.85 C (1,938.00 K)</td>
<td>94 atm (9,500 kPa)</td>
</tr>
<tr>
<td>Chlorine</td>
<td>143.8 C (417.0 K)</td>
<td>76.0 atm (7,700 kPa)</td>
</tr>
<tr>
<td>Ethanol</td>
<td>241 C (514 K)</td>
<td>62.18 atm (6,300 kPa)</td>
</tr>
<tr>
<td>Fluorine</td>
<td>-128.85 C (144.30 K)</td>
<td>51.5 atm (5,220 kPa)</td>
</tr>
<tr>
<td>Helium</td>
<td>-267.96 C (5.19 K)</td>
<td>2.24 atm (227 kPa)</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>-239.95 C (33.20 K)</td>
<td>12.8 atm (1,300 kPa)</td>
</tr>
<tr>
<td>Krypton</td>
<td>-63.8 C (209.4 K)</td>
<td>54.3 atm (5,500 kPa)</td>
</tr>
<tr>
<td>CH4 (Methane)</td>
<td>-82.3 C (190.9 K)</td>
<td>45.79 atm (4,640 kPa)</td>
</tr>
<tr>
<td>Neon</td>
<td>-228.75 C (44.40 K)</td>
<td>27.2 atm (2,760 kPa)</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>-146.9 C (126.3 K)</td>
<td>33.5 atm (3,390 kPa)</td>
</tr>
<tr>
<td>Oxygen</td>
<td>-118.6 C (154.6 K)</td>
<td>49.8 atm (5,050 kPa)</td>
</tr>
<tr>
<td>CO2</td>
<td>31.04 C (304.19 K)</td>
<td>72.8 atm (7,380 kPa)</td>
</tr>
<tr>
<td>N2O</td>
<td>36.4 C (309.6 K)</td>
<td>71.5 atm (7,240 kPa)</td>
</tr>
<tr>
<td>H2SO4</td>
<td>654 C (927 K)</td>
<td>45.4 atm (4,600 kPa)</td>
</tr>
<tr>
<td>Xenon</td>
<td>16.6 C (289.8 K)</td>
<td>57.6 atm (5,840 kPa)</td>
</tr>
<tr>
<td>Lithium</td>
<td>2,950 C (3,220 K)</td>
<td>652 atm (66,100 kPa)</td>
</tr>
<tr>
<td>Mercury</td>
<td>1,476.9 C (1,750.1 K)</td>
<td>1,720 atm (174,000 kPa)</td>
</tr>
<tr>
<td>Sulfur</td>
<td>1,040.85 C (1,314.00 K)</td>
<td>207 atm (21,000 kPa)</td>
</tr>
<tr>
<td>Iron</td>
<td>8,227 C (8,500 K)</td>
<td>5,000 atm (510,000 kPa)</td>
</tr>
<tr>
<td>Gold</td>
<td>6,977 C (7,250 K)</td>
<td>217.7 atm (22.06 MPa)</td>
</tr>
<tr>
<td>Aluminium</td>
<td>7,577 C (7,850 K)</td>
<td>217.7 atm (22.06 MPa)</td>
</tr>
<tr>
<td>Water</td>
<td>373.946 C (647.096 K)</td>
<td>217.7 atm (22.06 MPa)</td>
</tr>
</tbody>
</table>

Table 4.2. Some van der Waals parameters

<table>
<thead>
<tr>
<th>Substance</th>
<th>(a(L^2\text{atm/mol}^2))</th>
<th>(b(L/\text{mol}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>17.71</td>
<td>0.1065</td>
</tr>
<tr>
<td>anhydride</td>
<td>20.158</td>
<td>0.1263</td>
</tr>
<tr>
<td>Acetone</td>
<td>16.02</td>
<td>0.1124</td>
</tr>
<tr>
<td>Acetonitrile(=C_2H_3N)</td>
<td>17.81</td>
<td>0.1168</td>
</tr>
<tr>
<td>Acetylene</td>
<td>4.516</td>
<td>0.0522</td>
</tr>
<tr>
<td>Chemical Compound</td>
<td>Mass (amu)</td>
<td>Density (g/cm³)</td>
</tr>
<tr>
<td>------------------------------</td>
<td>------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>Ammonia (= NH₃)</td>
<td>17.03</td>
<td>0.715</td>
</tr>
<tr>
<td>Argon</td>
<td>39.95</td>
<td>0.147</td>
</tr>
<tr>
<td>Benzene</td>
<td>78.11</td>
<td>1.05</td>
</tr>
<tr>
<td>Bromobenzene</td>
<td>169.91</td>
<td>1.073</td>
</tr>
<tr>
<td>Butane (= C₄H₁₀)</td>
<td>58.12</td>
<td>0.691</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>12.01</td>
<td>1.99</td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td>64.14</td>
<td>1.50</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>28.09</td>
<td>1.45</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>194.84</td>
<td>1.62</td>
</tr>
<tr>
<td>Chlorine (= Cl₂)</td>
<td>35.45</td>
<td>1.72</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>150.86</td>
<td>1.52</td>
</tr>
<tr>
<td>Chloroethane</td>
<td>61.51</td>
<td>1.46</td>
</tr>
<tr>
<td>Chloromethane</td>
<td>30.00</td>
<td>1.27</td>
</tr>
<tr>
<td>Cyanogen (= C₄N₂)</td>
<td>100.08</td>
<td>1.40</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>92.14</td>
<td>0.801</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>74.13</td>
<td>0.776</td>
</tr>
<tr>
<td>Diethyl sulfide</td>
<td>86.16</td>
<td>0.907</td>
</tr>
<tr>
<td>Ethane (= C₂H₆)</td>
<td>28.05</td>
<td>1.37</td>
</tr>
<tr>
<td>Ethanol (= C₂H₅OH)</td>
<td>44.09</td>
<td>0.805</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>88.14</td>
<td>0.768</td>
</tr>
<tr>
<td>Ethylamine</td>
<td>58.07</td>
<td>0.773</td>
</tr>
<tr>
<td>Fluorobenzene</td>
<td>116.99</td>
<td>1.70</td>
</tr>
<tr>
<td>Fluoromethane</td>
<td>19.97</td>
<td>1.78</td>
</tr>
<tr>
<td>Freon</td>
<td>28.02</td>
<td>0.773</td>
</tr>
<tr>
<td>Germanium tetrachloride</td>
<td>222.13</td>
<td>1.80</td>
</tr>
<tr>
<td>Helium</td>
<td>39.95</td>
<td>0.147</td>
</tr>
<tr>
<td>Hexane (= C₆H₁₄)</td>
<td>86.18</td>
<td>0.776</td>
</tr>
<tr>
<td>Hydrogen (= H₂)</td>
<td>2.01</td>
<td>0.090</td>
</tr>
<tr>
<td>Hydrogen bromide</td>
<td>80.91</td>
<td>1.92</td>
</tr>
<tr>
<td>Hydrogen chloride</td>
<td>27.98</td>
<td>1.70</td>
</tr>
<tr>
<td>Hydrogen selenide</td>
<td>119.93</td>
<td>1.70</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>34.07</td>
<td>1.70</td>
</tr>
<tr>
<td>Iodobenzene</td>
<td>253.87</td>
<td>1.70</td>
</tr>
<tr>
<td>Krypton</td>
<td>128.37</td>
<td>1.70</td>
</tr>
<tr>
<td>Mercury (= Hg)</td>
<td>200.59</td>
<td>1.80</td>
</tr>
<tr>
<td>Methane (= CH₄)</td>
<td>15.03</td>
<td>0.634</td>
</tr>
<tr>
<td>Methanol</td>
<td>32.04</td>
<td>1.05</td>
</tr>
<tr>
<td>Neon</td>
<td>20.18</td>
<td>1.17</td>
</tr>
<tr>
<td>Nitric oxide</td>
<td>30.01</td>
<td>1.27</td>
</tr>
<tr>
<td>Nitrogen (= N₂)</td>
<td>28.01</td>
<td>1.27</td>
</tr>
<tr>
<td>Nitrogen dioxide</td>
<td>44.01</td>
<td>1.47</td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>30.01</td>
<td>1.27</td>
</tr>
<tr>
<td>Compound</td>
<td>Density</td>
<td>Sound Speed</td>
</tr>
<tr>
<td>----------------------</td>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>Oxygen</td>
<td>1.378</td>
<td>0.03183</td>
</tr>
<tr>
<td>Pentane</td>
<td>19.26(.09)</td>
<td>0.146(.1449)</td>
</tr>
<tr>
<td>Phosphine=PH$_3$</td>
<td>4.692</td>
<td></td>
</tr>
<tr>
<td>Propane=C$_3$H$_8$</td>
<td>8.779(9.39)</td>
<td>0.08445(.0905)</td>
</tr>
<tr>
<td>Silane=SiH$_4$</td>
<td>4.377</td>
<td>0.05786</td>
</tr>
<tr>
<td>Silicon tetrafluoride</td>
<td>4.251</td>
<td>0.05571</td>
</tr>
<tr>
<td>Sulfur dioxide</td>
<td>6.803</td>
<td>0.05636</td>
</tr>
<tr>
<td>Tin tetrachloride</td>
<td>27.27</td>
<td>0.1642</td>
</tr>
<tr>
<td>Toluene=C$_7$H$_8$</td>
<td>7 24.38(.86)</td>
<td>0.1463(.1497)</td>
</tr>
<tr>
<td>Water</td>
<td>5.536</td>
<td>0.03049</td>
</tr>
<tr>
<td>Xenon</td>
<td>4.250(.192)</td>
<td>0.05105(.0516)</td>
</tr>
</tbody>
</table>

Table 4.3. Helium sound speed

<table>
<thead>
<tr>
<th>$T$</th>
<th>$p = .01$</th>
<th>$c$</th>
<th>$T$</th>
<th>$p = .1$</th>
<th>$c$</th>
<th>$T$</th>
<th>$p = 50$</th>
<th>$c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.19</td>
<td>.0001</td>
<td>134.0</td>
<td>5.19</td>
<td>.001</td>
<td>133.3</td>
<td>5.19</td>
<td>.1417</td>
<td>780.0</td>
</tr>
<tr>
<td>10</td>
<td>.5 E-4</td>
<td>186.1</td>
<td>10</td>
<td>.5 E-3</td>
<td>186.1</td>
<td>10</td>
<td>.118</td>
<td>569.5</td>
</tr>
<tr>
<td>20</td>
<td>.23 E-4</td>
<td>263.2</td>
<td>20</td>
<td>.24 E-3</td>
<td>263.4</td>
<td>20</td>
<td>.08</td>
<td>462.5</td>
</tr>
<tr>
<td>50</td>
<td>.1 E-4</td>
<td>416.2</td>
<td>50</td>
<td>.1 E-3</td>
<td>416.5</td>
<td>50</td>
<td>.04</td>
<td>524.7</td>
</tr>
<tr>
<td>90</td>
<td>.55 E-5</td>
<td>558.4</td>
<td>90</td>
<td>.55 E-4</td>
<td>558.5</td>
<td>90</td>
<td>.021</td>
<td>642.4</td>
</tr>
<tr>
<td>140</td>
<td>.34 E-5</td>
<td>696.4</td>
<td>140</td>
<td>.34 E-4</td>
<td>696.5</td>
<td>140</td>
<td>.016</td>
<td>764.5</td>
</tr>
<tr>
<td>200</td>
<td>.24 E-5</td>
<td>832.5</td>
<td>200</td>
<td>.24 E-4</td>
<td>832.5</td>
<td>200</td>
<td>.0113</td>
<td>889.1</td>
</tr>
<tr>
<td>280</td>
<td>.17 E-5</td>
<td>984.9</td>
<td>280</td>
<td>.17 E-4</td>
<td>985.0</td>
<td>280</td>
<td>.0082</td>
<td>1033</td>
</tr>
<tr>
<td>400</td>
<td>.12 E-5</td>
<td>1177</td>
<td>400</td>
<td>.12 E-4</td>
<td>1177</td>
<td>400</td>
<td>.0058</td>
<td>1217</td>
</tr>
<tr>
<td>700</td>
<td>.7 E-6</td>
<td>1557</td>
<td>700</td>
<td>.7 E-5</td>
<td>1557</td>
<td>700</td>
<td>.0034</td>
<td>1589</td>
</tr>
<tr>
<td>1000</td>
<td>.5 E-6</td>
<td>1861</td>
<td>1000</td>
<td>.5 E-5</td>
<td>1884</td>
<td>1000</td>
<td>.00237</td>
<td>1887</td>
</tr>
</tbody>
</table>

Table 4.4. Sound speed in He from Eq.(4.6.1). Conversions.

1 $J m^3 = 10^6 Pa = 10 Lit^2 bar$, 1 $Lit^3 atm = 101.325 J m^3 = 101.325 Pa m^6$, $.986 atm = 1 bar = 10^5 Pa.$
V. A THEORY OF FLUID MIXTURES

The traditional treatment of mixtures often relies on rules concerning the additivity of properties; one of the most important ones is the additivity of the energies of the components of a composite system. Most fundamental of all is the postulate of additivity of Lagrangians;

$$\mathcal{L} = \sum_{i=1,2} \mathcal{L}_i = \sum_i \rho_i (\dot{\phi}_i - \vec{v}_i^2/2) - f - sT,$$

it incorporates the additivity of energies and the additivity of entropies. The algebraic sum of the Lagrangians of two adiabatic systems describes an adiabatic system with two non interacting components. * Realistically, coexistent systems are never non interacting and ways have to be found to take the interaction into account. The strategy will be to begin by adding together the Lagrangians of components, with the expectation that corrective terms, ‘interactions’, will have to be added. The systematic application of this point of view is not wide spread in thermodynamics. (See for example many studies of critical phenomena in mixtures.) But it is a standard, and successful, strategy in more developed branches of theoretical physics - and it incorporates a general concept that helps us understand mixtures:

**In the limit when interactions are weak, each constituent behaves as if the others were absent**

Recall that in unary thermodynamics it is axiomatic that the free energy (or any other fundamental potential expressed in terms of the natural variables) tells us all that we need to know about a substance. It follows that a mixture in which each constituent behaves as if it were alone is described by variables that satisfy the usual equations of motion of a unary system. The natural variables for the mixture is thus the collection of natural variables for the ingredients. And if this mixture is characterized by an action principle, then the action must be a sum of individual actions, in the limit of no interactions.

The persistent use of a Lagrangian does much to distinguish our approach to thermodynamics, the choice of variables is just as important. I confess to being perplexed by the common usage, especially the occasional suppression of degrees of freedom and the preference for molar fractions over partial densities. Here is the addition formula for free energy of a mixture of ideal gases,

$$F = \frac{f_1 + f_2}{\rho} = N_1 F_1 + N_2 F_2 + R T \left( N_1 \ln N_1 + N_2 \ln N_2 \right).$$

In terms of ordinary densities this statement takes the form $f = f_1 + f_2$.

* Literally true, but it overlooks two points: 1. That the two temperatures are taken to be equal and 2. The adiabatic condition, about which much more below.

** Compare the Gibbs-Dalton hypothesis, Section V.4.
Until further notice it will be assumed that no chemical reactions are taking place in the mixtures under consideration, and that the equilibria are uniform. In this case an important idea is the Gibbs-Dalton hypothesis, to be developed in this chapter and used in Chapter VI.

Chemical interactions change the picture materially; they will occupy us for the remainder of this chapter. Immiscible fluids form an other category of mixtures, the subject of Chapter VI.

V.1. Variables and potentials

A description of two non interacting systems requires two sets of variables. In particular, each system has a temperature or a temperature field. This is natural if the two systems occupy different, non overlapping regions of space. Situations exist where two systems occupy the same space and for which it has nevertheless been found useful to maintain a notion of separate temperatures. * But in this book the temperature shall always be taken to be a unique field extended over the total vessel. Two components may be present in the same region but we shall try to get by with only one temperature field. If this strategy fails then it shall be abandoned, reluctantly. That has not come to pass, so far.

Taken for granted is the idea that each distinct component has an independent flow vector field. Otherwise, there would be no way to formulate the separate conservation of masses and separate equations of continuity, for each component (and no way to visualise the ‘mixing’). More precisely, we say that, if two densities are separately conserved, then one needs two independent velocity fields \( \vec{v}_1 \) and \( \vec{v}_2 \) in order to be able to assert that \( \dot{\rho}_1 + \text{div}(\rho_1 \vec{v}_1) = 0 \) and \( \dot{\rho}_2 + \text{div}(\rho_2 \vec{v}_2) = 0 \). ** But if only the total density is conserved then there is only one velocity and only one continuity equation. The analysis becomes simpler if one assumes that the mixture behaves as a one component fluid, *** with properties defined by interpolation between those of the components. This drastic assumption, first used by van der Waals, is tempting in the case of mixtures of many components; it is common, for example, in calculations relating to the interior of the Sun. But it ignores physical degrees of freedom and cannot account for all observed phenomena. Others introduce individual densities and velocities without comment, as in Bois and Kubicki (2000), an NTNU thesis.

By adopting a two-velocity approach to all binary mixtures without chemical reactions we depart in an essential way from what is common practice. The most important 2-fluid theory is Landau’s theory of superfluidity. But Landau’s equations are not derived from an action principle and consequently, even in that case, we shall propose a new direction. See Chapter VIII. For an example of a treatment of mixtures in terms of multiple velocities see Glavatsky (2009).

In the ideal case, when there is no interaction between the components, there can be no objection to two separate and independent velocities; they are unaware of each other and they pass freely through each other. But this transparency will be much affected when we

---

* For example, in plasma physics, and in Cosmology.
** As in Landau’s 2-fluid theory of liquid helium with its 2 equations of continuity.
*** “Air is a mixture that behaves, under normal conditions, like an ideal gas.” Mueller 2009.
allow for an interaction between the components, the simplest being an addition to the total free energy density,

\[ f = f_1 + f_2 + f_{\text{int}}, \quad f_{\text{int}} = \alpha \rho_1 \rho_2, \quad \alpha \text{ constant.} \]

An interaction of this type was used with some success by van der Waals. With \( \alpha \) positive it has the effect of discouraging the overlap of the densities of the two species.

From now on it is taken for granted that the dynamical variables of mixtures at rest are the individual densities \( \rho_i \), individual specific entropies \( S_i \) (next section), and \( T \). The variables chosen by Gibbs, and used almost universally ever since, are the total volume or density and the molar fractions, instead of the individual densities. This leads to a definition of the Gibbs function as a function of pressure, temperature, and molar fractions, related to the free energy by a Legendre transformation, \( G(P, T, x) = F(V, T, x) + VP \).

In our approach, using densities, the Gibbs potential density is not related to the free energy density by a Legendre transformation. The Legendre transformations of densities are natural generalizations of those listed in Section III.7, including the following,

\[ p(T, \mu_1, \mu_2, \ldots) = \sum_i \rho_i \mu_i - f, \quad dp = \sum_i \rho_i d\mu_i + s dT, \quad (5.1.1) \]

with

\[ \mu_i = \left. \frac{\partial f}{\partial \rho_i} \right|_T = \left. \frac{\partial u}{\partial \rho_i} \right|_s. \]

Also

\[ u(\rho_1, \rho_2, \ldots, s) = f(\rho_1, \rho_2, T) + s T, \quad du = \sum_i \mu_i d\rho_i + T ds, \quad df = \sum_i \mu_i d\rho_i - s dT. \]

The interpretation of the pressure as a thermodynamical density potential was stressed in Section III.5.

For a multi component system, with no interaction between the constituents, we shall make the natural assumption that the free energy is

\[ f = \sum_i f_i, \]

where \( f_1, f_2, \ldots \) are the same expressions for the free energy of the components, in terms of their natural variables, that apply when they are by themselves.

The principal density potentials for multicomponent thermodynamics are

\[ p(T, \bar{\mu}) \quad f(T, \bar{\rho}), \quad u(s, \bar{\rho}). \]

The introduction, by Gibbs, of molar fractions as principal variables, the associated approach to chemical potentials and the complications that this brings to analysis (Gibbs - Duhem relation, a separate treatment of open systems) will be eschewed; the variables are \( T \), the densities, and the chemical potentials defined above.
Molar fractions and ‘free energy of mixing’

With the introduction of molar fractions and the associated chemical potentials, Gibbs arrives at expressions for the differentials of thermodynamical potentials. When those relations are rewritten in terms of densities all reference to molar fractions drops out and one ends up with the simpler set of differentials given above. We leave the verification of this to the skeptical reader.

We must not neglect to point out that the above formula for pressure can be expressed in the more familiar fashion as

\[ p(T, \rho, N_1, \ldots) = f - \rho \frac{\partial f}{\partial \rho} \bigg|_{T,N_1,N_2,\ldots}, \]  

(5.1.2)

where \( N_1, N_2, \ldots \) are the molar fractions. However, the formula \( f = f_1 + f_2 \) may seem controversial. The standard approach is to express the free energy for \( N \) moles of the liquid as \( NF \), thus \( F \) is the free energy of one mole of the pure gas when it is alone. Then the usual formula for the mixture is,

\[ F = f / \rho = N_1 F_1 + N_2 F_2 + F_{\text{mix}}. \]

We can compare the two expressions in the case of a mixture of two ideal gases. In terms of molar densities the free energy of an ideal gas is

\[ f(\rho_i, T) = R \rho_i T \ln \frac{\rho_i}{T n_i}. \]

In the mixture, if the molar fraction is \( N_1 = \rho_1 / \rho \), one writes

\[ f_i(\rho_i, T) = \rho_i RT \ln \frac{\rho_i}{T n_i} = \rho N_i RT (\ln \frac{\rho}{T n_i} + \ln N_i). \]  

(5.1.3)

We hold that this separation is wholly unwarranted. It results in the unwieldy expression

\[ F = \frac{f_1 + f_2}{\rho} = N_1 F_1 + N_2 F_2 + RT \left( N_1 \ln N_1 + N_2 \ln N_2 \right). \]  

(5.1.4)

The last term is \( F_{\text{mix}} \); it is regarded as a ‘mixing correction’ and in the general case it is replaced by a phenomenological correction. * When the densities are used as fundamental variables all the awkward mixing terms disappear.

For non interacting gases the more natural formula \( f = f_1 + f_2 \) will be used in this book; there is no mixing term. Interactions will be introduced by adding a term that depends on both sets of variables,

\[ f = f_1 + f_2 + f_{\text{int}}. \]

The same remarks apply to entropy; the concept “entropy of mixing” does not appear again in this book. The densities \( f \) and \( s \) are additive in the absence of interaction.

* See Lemmon and Jacobsen (1968), where we find \( F = N_1 F_1 + N_2 F_2 + F_{\text{mix}} + F_{\text{int}}. \)
Remark. The Gibbs-Duhem relation is the statement that the function \( f \) depends on the \( n + 1 \) variables \( \rho_i = \rho N_i \) and \( T \), and not separately on \( \rho \).

V.2. Entropy and equations of motion

The following expression for the Lagrangian density is appropriate when there are no chemical reactions and all the densities are independent variables. Note that each individual kinetic energy \( -\rho_i \vec{v}_i^2 / 2 \) must be accompanied by the term \( \Phi_i \), for Galilei invariance. See Section III.11. Clearly, this implies a set of canonical pairs of basic variables \( (\rho_i, \Phi_i) \). It was argued, and postulated in the introduction to this chapter, that the action for an ideal composite system - one without interactions between the constituents - must be additive; consequently, before including an interaction term we have the tentative Lagrangian,

\[
\mathcal{L} = \sum_{i=1,2} L_i = \sum_{i} \rho_i (\dot{\Phi}_i - \vec{v}_i^2 / 2) - f - sT. \tag{5.2.1}
\]

with

\[
f = \sum_{i} f_i \quad \text{and} \quad s = \sum_{i} s_i, \quad i = 1, 2.
\]

Variation of the temperature gives the adiabatic condition

\[
s = -\frac{\partial f(T, \rho_1, \rho_2)}{\partial T} = \frac{\partial f_1(T, \rho_1)}{\partial T} + \frac{\partial f_2(T, \rho_2)}{\partial T}; \tag{5.2.2}
\]

in the absence of interactions it expresses a weak form of the Gibbs-Dalton hypotheses, to be discussed below.

The structure of the kinetic term is appropriate in the absence of chemical reactions. It is strongly motivated by the need to preserve the equations of continuity. We are very reluctant to modify the structure of this term; interactions will be taken into account by modifications of the potential. Changes that are appropriate in the case of chemical reactions will be discussed in Section V.6.

We shall suppose that particles of distinct components are distinguishable; whence the additivity of the entropy. More precisely: for the same reasons that have made us limit attention to the case of uniform specific entropy densities in a one component system, we shall assume that, whether interactions are present or not, the entropy density of a multicomponent system, I mean the density \( s \) that appears, multiplied by \( T \), in the last term in the above Lagrangian, is a linear function of the densities, with constant coefficients

\[
s = \sum \rho_i S_i. \tag{5.2.3}
\]

This assures that the identification of the pressure with the on shell value of the Lagrangian density extends to mixtures. That \( S_1 \) and \( S_2 \) are uniform in the absence of interactions has been our working assumptions; no exceptions have been encountered so far. Obedience to this command is presumed to have been achieved during mixing, by a non-adiabatic development, but we are concerned only with the final result, and the adiabatic development that follows. That (5.2.3) remains true when interactions are present is, at the time
of writing, an assumption. It implies the absence of unexpected entropic forces (forces proportional to the gradient of the specific entropies) in the Bernoulli equation, and that all the other fields are also uniform in the absence of external forces.

This is a place to recall what is one of the most important aspects of Gibbs approach, the role of entropy in the formulation of the variation principle. In the case of a simple system the entropy is fixed. In general, it is agreed that an adiabatic system is one with fixed entropy; we have followed the lead of Prigogine in generalizing this:

**A one-component adiabatic system has a fixed entropy distribution; the entropy density is** \( s = \rho S \) **with a fixed, uniform value of** \( S \).

Here we are going further, to postulate, as a working assumption, that

**In an adiabatic Lagrangian the entropy density is a fixed linear function of the densities, with constant coefficients.**

In the case of a binary mixture, \( s = \rho_1 S_1 + \rho_2 S_2 \). Note the inevitable appearance of two entropy parameters; the allocation of entropy between the two components is now a problem. The explicit modeling of the entropy density is an important feature of our procedure; it is not standard. It aims at an improved predictive power and the possibility of doing without the ubiquitous reference state. A little reflection will show that this approach is new. There may be antecedents, but discussions of the structure of the entropy density are extremely rare. We mean by that the proposal of an expression for the entropy density of mixtures in terms of the mass densities, that goes into the formula for \( f + sT \). It is not that the above assumption is inevitable, but that, if there are exceptions then that would be worthy of notice. It is a working assumption.

The appearance of two entropy parameters, adiabatic invariants, in the expression for the total Lagrangian of a 2-component system, invites a re-examination of the concept of two time scales in thermodynamics. Experience shows that the addition of heat to any system eventually leads to an adiabatic system with well defined entropy; so if the formula \( s = \sum \rho_i S_i \) is valid, then the ultimate adiabatic system is characterized by a particular partition of the total entropy among the two components; that is, by a one-dimensional subset of the entropy plane, the plane with coordinates \( S_1, S_2 \). This subspace defines a path along which the system moves as the entropy is changed by the addition of heat. But what determines the path, and how does the system reach a point on this path?
Suppose the system is initially in a state of absolute equilibrium, reached after being isolated long enough for dissipation to have run its course. Suppose further that a manipulation of the system leads to a Lagrangian in which \( s = \sum \rho_i S_i \), with fixed but randomly chosen values of \( S_1, S_2 \). Mathematically, it appears to be a well defined adiabatic system with adiabatic processes that, by definition, do not modify the entropy parameters. The motion that brings the system back to the point of absolute equilibrium is a process of another kind; that is, it is not adiabatic and the most economical standpoint is to characterize it as one of dissipation or degradation driven by a search for maximal entropy. But the choice of the actual path may have a different explanation: It may be driven by the search for maximum entropy, but another factor may be the condition of adiabatic stability. We can offer no general insight into this problem as yet; the best we can do is to examine particular processes and the way that the problem has been solved in the past.

From now on we shall assume that the entropy takes the form (5.2.3) and that the coefficients \( S_i \) are uniform. It is proposed as a useful working assumption; to be honored until it is proved wrong.

Variation of the action with respect to the densities gives, when the entropy parameters are uniform, a pair of Bernoulli equations

\[
\frac{Dv_i}{Dt} = -\mu_i - S_i T \quad \mu_i := \frac{\partial f}{\partial \rho_i}|_T, \quad i = 1, 2.
\]

This too is hardly conventional. Landau’s two-flow theory recognizes two independent velocities and incorporates similar equations, but instead of individual chemical potentials \( \mu_i \) on the right hand side, there appears the gradient of the total pressure \( p \) in both equations. That is, the two fluids interact with each other by an unusual mechanism that is not found in other physical systems. Certainly, mutual interactions must be included. But we shall take a suggestion from the field theories of elementary particles, to introduce the interaction in a different way, by means of an interaction term \( f_{\text{int}} \), a function of
the two densities, in the total Lagrangian density. Landau assumes that each fluid feels
the pressure of the other, and that is reasonable; but we shall obtain the same effect by
including an interaction (attractive or repulsive) in the Lagrangian.

The concept of the entropy of the mixture as a linear function of the densities leads to
a new view of the problem of mixtures and a new way to analyze experiments. A principal
problem is to determine, for any mixture, the path that it chooses as it winds through the
entropy plane.

We may be opening up a new direction of development of thermodynamics. It is based
on what we believe to be the most important concept introduced by Gibbs: the concept of
“assigned entropy”. In global, adiabatic thermodynamics a numerical value is assigned to
the entropy; then the energy functional is minimized. In the local theory of mixtures the
entropy density has to be given as a linear function of the densities, with assigned values
of the coefficients, to define an adiabatic system. Linearity is a working assumption. It is
strange that no previous attempt to model the assigned entropy could be found; perhaps
understanding of the concept is not wide spread.

V.3. Mixture of 2 ideal gases

This example will throw some light on the question of allocation of entropy.

Imagine a vessel, divided into two parts by a wall, the two parts filled with an ideal gas of
type 1 and an ideal gas of type 2, respectively. Assume that the wall is impenetrable
to either gas; but that it admits the transfer of heat. The Lagrangian density for this
system is,

\[ L = \sum_{i=1}^{2} \sum_i \left( p_i (\dot{\Phi}_i - \vec{v}_i \cdot \vec{v}_i / 2) - f_i - s_i T \right), \]

where \( s_i = \rho_i S_i \) and \( S_1, S_2 \), are adiabatic invariants. It is postulated that there is a
unique, continuous temperature field, extending over both vessels, continuous at the wall
(See Section III.8.).

This Lagrangian describes two separate systems that interact with each other solely by
sharing the boundary condition implied by the continuity of the temperature at the wall.
The feasibility of this setup is amply confirmed by experiments.

What happens if the dividing wall is removed? The most common observation is that
mixing takes place, the particles of gas number 1 begin to “diffuse” into the space formerly
reserved for the other gas, and vice versa. If no external forces are acting the mixture
often becomes uniform. At this stage of our study we shall not inquire into the physical,
probably non adiabatic process that causes the mixing, but only try to describe the final
states.

The process aside, we need to find the Lagrangian of the system after mixing. One result
of mixing is a reassignment of entropies. After mixing, each of the originally separated
gases have expanded to a larger volume, with attendant changes in the entropy parameters;
what are the final values? A law discovered by Dalton states as follows:

**Dalton’s law.** At equilibrium, the total pressure of the mixture of two ideal gases (the
pressure against the walls) is the sum of the pressures that would have been obtained if
each gas would have occupied the total volume in the absence of the other, at the same
temperature.

Important as it is, this information is a very small part of what we wish to know: what
are the dynamical properties of this mixture, in short, what is the Lagrangian for this new
gas? This need to know more led some people to overstate Dalton claims. Dalton was said
to have held that each gas in a mixture behaves as if it were alone. He did not. Some of
the controversy is discussed in Dalton’s book (Dalton 18 ).*

If indeed it were so, that each gas in the mixture behaves as if it were alone, then we
should obtain the Hamiltonian density for the mixture by simply adding the two Hamil-
tonian densities and integrating over the vessel filled by both, assigning a different tem-
perature to each gas. This concept of dual temperatures is unphysical except in certain
cases where a method is devised to measure the two separate temperatures. We postulate
a single temperature field and we are led to consider the following Lagrangian density for
the mixture,

\[ \mathcal{L} = \sum_i \left( \rho_i (\dot{\Phi}_i - \mathbf{u}_i \cdot \mathbf{u}_i) - f_i - s_i T \right), \] (5.3.1)

where \( f_1(T, \rho_1) \) and \( f_2(T, \rho_2) \) are the expressions for the free energy appropriate for each
gas when alone. We repeat that this is undertaken merely as a first step towards the
eventual construction of a realistic Lagrangian. The adoption of this Lagrangian is in
accord with the spirit of Dalton’s law. The thermodynamic pressure is

\[ p = \sum \rho_i \frac{\partial f}{\partial \rho_i} - f = \sum \mathcal{R}_i \rho_i T \] (5.3.2)

and the entropy is

\[ s = \sum s_i = \sum \rho_i S_i. \]

The formula for the total pressure expresses Dalton’s law; the inclusion of interactions
will invalidate it, unless it is of total degree one. This suggests that we keep in mind a
particularly interesting interaction,

\[ f_{\text{int}} \propto \sqrt{\rho_1 \rho_2}. \] (5.3.3)

The first question that needs to be discussed arises from the appearance of two entropy
parameters when only one was expected. The total entropy density is a linear function of
the two densities, depending on two parameters \( S_1, S_2 \).

Exploring the merits of any explicit expression for the Lagrangian of a binary or multi
component system is a departure from common practice. Attempts to model the Gibbs
function are common, but they involve a ‘reference pressure’ \( p_0 \) (usually one atmosphere)
and an unspecified Gibbs function \( G(T, p_0) \); consecrated in tables. Confrontation with

---

* Here is a sample statement of the law in a modern textbook: “... the assumption is made
that each gaseous component of the mixture behaves as if it existed at the temperature of
the mixture and filled the entire volume ...” (Holman1980).
observation would seem to point to a determination of the correct form for the unknown function, but we have seen no attempt to do this. The special, linear form that is being postulated for the assigned entropy gives a structure to the modeling that can easily be tested by experiments. The overall plan is to test naive expressions for the Lagrangian, including the entropy, and make improvements as necessary. The most important advantage of this program is that each attempted application will suggest a refinement of the Lagrangian and, especially, the fact that one Lagrangian has to accommodate a variety of effects and experiments. The search is on for a best possible Lagrangian capable of accounting for all properties of the mixture of the two gases.

Additivity of the Lagrangian for a system of two non-interacting components embodies additivity of the Hamiltonians, which is natural, but also additivity of the thermodynamic potentials, even when that is only as a benchmark, subject to modifications as required by observation. Though it seems natural, this attitude is not standard. Consequently, from this point onwards there will be a significant divergence from the usual approach. To defend this deliberate departure from tried and tested methods in the treatment of mixtures it may be said that, certainly, there can be nothing wrong with it in the limit of a very weak interaction between the components. And this cannot be said with as much assurance of some other approaches.* Our reward will be a theory with a very much enhanced predictive power. The predictions are, of course, to be tested.

V.4. The Gibbs-Dalton hypothesis for ideal gases ...

The additivity of energies that is implied by the addition of Lagrangians is an attractive assumption, and probably a must in the absence of interactions, but what can be done about the two entropy parameters? Addition of heat to the system must change the parameters and if the system is to end up in a well-defined configuration then it has to follow a fixed path in the ‘entropy plane’ with parameters $S_1, S_2$. A partial answer to this question is provided by a literal interpretation of the Gibbs-Dalton hypothesis, developed by Gibbs from Dalton’s law, namely

**Gibbs-Dalton hypothesis.** When the mixture of ideal gases reaches a final equilibrium each gas has the entropy that it would have if it were alone.

**Discussion.** In our context Dalton’s law appears to be expressed by Eq.(5.3.2) and to be a direct consequence of the additivity of Lagrangians. But this is not what Dalton’s law means. Dalton’s law $p = \sum p_i$ has content only after we decide what the symbols “$p_i$” stand for. To Dalton they are the pressures of a pure gas with temperature $T$ and density $\rho_i$; in the case of an ideal gas $p_i = R_i \rho_i T$. But the summands $p_i = \rho_i \partial f_i / \partial \rho_i - f_i$ in Eq.(5.3.2) are expressed in terms of the temperature, the densities and the entropy. To define them we need to eliminate the entropy; hence Dalton’s law follows from (5.3.2) only

---

* This criticism, if that is what it is, can be countered, to some extent, by making the observation that, realistically, no interaction implies vanishing density. A problem would arise, however, with the discovery of gases that are ideal at a finite density.
if the entropy is a sum of partial entropies and each partial entropy is related to density and temperature by the same expression as it is in the case of the components in isolation. This is what leads to the Gibbs-Dalton hypothesis.

One interpretation of the Gibbs-Dalton hypothesis is the adiabatic relation that is one of the Euler-lagrange equations,

\[ s = -\frac{\partial f}{\partial T}. \]

We shall call this the weak form of the hypothesis. It is of little use without a prescription for assigning a value to the entropy parameters. We have insisted on maintaining Gibbs’ point of view, that the variational principle minimizes the energy for a fixed value of the entropy. In extended, one component thermodynamics this was interpreted in the sense of the specific entropy density, and the latter has been found to be uniform in a wide context. In the case of a heterogenous system Gibbs does not offer guidance. The last formula serves only to calculate the entropy for a given configuration of the system, which is of little use.

To be useful, the adiabatic relation needs to be supplemented by a rule for assigning entropy. A first step, and a major one, is to demand additivity, in the strong form

\[ s = \sum s_i = \sum \rho_i S_i, \]

with uniform values of \( S_1 \) and \( S_2 \). That leaves only the problem of tracing the path followed by the system through the entropy plane, a problem for the solution of which we defer to experiment.

A stronger interpretation of the Gibbs-Dalton hypothesis is possible, namely

**Strong Gibbs-Dalton hypothesis.** When the mixture of ideal gases reaches a final equilibrium each gas has the entropy that it would have if it were alone at the same density and temperature.

When each gas is alone these relations hold:

\[ S_i = -R_i (\ln \frac{\rho_i}{T n_i} - n_i), \quad i = 1, 2 \quad \text{separated gases}. \]

According to the strong version of the hypothesis it holds for a mixture, but only at equilibrium.

\[ S_i = -R_i (\ln \frac{\rho_i}{T n_i} - n_i), \quad i = 1, 2 \quad \text{at equilibrium}. \]

This is what we are going to mean by ‘the strong Gibbs-Dalton hypothesis’ (for an ideal gas). It is expected to hold in the absence of any chemical reactions. The virtue of this statement is that, as a statement about the value of the entropy, it applies to the adiabatic system in general, not just to equilibrium states; it removes the ambiguity in the Lagrangian by fixing a relation between the two (or several) entropy parameters defined in (5.2.1).
Consider two ideal gases with

\[ f_i + s_i T = \mathcal{R}_i \rho_i T \ln \frac{\rho_i}{T n_i} + \rho_i S_i T, \quad i = 1, 2. \]

If each gas were alone we should have the 2 equations of motion (adiabatic relations),

\[ \mathcal{R}_i \rho_i (\ln \frac{\rho_i}{T n_i} - n_i) + \rho_i S_i = 0, \quad i = 1, 2, \quad (5.4.1) \]

from variation of each Lagrangian with respect to the temperature, but variation of the proposed total Lagrangian (5.3.1) with respect to the common temperature yields only one adiabatic equation: *

\[ \sum_{i=1,2} \left( \mathcal{R}_i \rho_i (\ln \frac{\rho_i}{T n_i} - n_i) + \rho_i S_i \right) = 0. \quad (5.4.2) \]

The strong Gibbs-Dalton hypothesis requires that both of Eq.s (5.4.1) hold for the unified system, but only at equilibrium. If the equilibrium is characterized by uniform densities then this amounts to the required relation between \( S_1 \) and \( S_2 \), a relation that provides the required path in the entropy plane. Suppose that there is a value \( T_0 \) of \( T \) such that both terms vanish, then for all \( T \)

\[ \mathcal{R}_i \rho_i (\ln \frac{\rho_i}{T n_i} - n_i) - \rho_i S_i = n_i \mathcal{R}_i \rho_i \ln \frac{T_0}{T} \]

and the equation of motion Eq.(5.3.2) reduces to

\[ (\sum n_i \mathcal{R}_i \rho_i) \ln \frac{T_0}{T} = 0. \]

This can be true only at \( T = T_0 \). That is, if such a value of \( T \) exists when the densities take the equilibrium values, then the equation of motion implies that this is the value of \( T \) at equilibrium and that both terms vanish separately at equilibrium. The strong Gibbs-Dalton hypothesis can thus be stated within the present context as follow:

Gibbs-Dalton hypothesis, strong version:

For correctly assigned values of the entropy parameters \( S_1 \) and \( S_2 \), the equilibrium temperature is uniquely fixed by the requirement that both terms in (5.4.2) vanish separately.

Away from equilibrium only (5.4.2) holds and each component gas no longer behaves as if the other component were absent! The two gases at equilibrium may not be ‘aware of each other’, but in configurations other than equilibrium the pair of adiabatic conditions that characterize the pure gases is replaced by the single adiabatic condition (5.4.2).

* This is enough to give the formula for the internal energy density, \( u = \sum_i n_i \mathcal{R}_i \rho_i T \).
For a system of ideal gases with fixed total quantities of each component and with uniform equilibrium densities the Gibbs-Dalton hypothesis predicts the following entropy path,

$$\frac{S_1}{n_1 R_1} - \frac{S_2}{n_2 R_2} = \ln \frac{\rho_2^{1/n_2}}{\rho_1^{1/n_1}}, \quad (5.4.3)$$

where $\rho_1, \rho_2$ are the densities at equilibrium. It agrees with Boltzmann’s distribution law if $n_1 = n_2$. See Section V.4.

V.5. ... and what lies behind it

We shall attempt to determine what it is that would drive the mixed gas to satisfy the strong version of the Gibbs-Dalton hypotheses. * Let

$$x = \frac{\rho_1}{k_01(eT)^{n_1}}, \quad y = \frac{\rho_2}{k_02(eT)^{n_2}}, \quad S_i = -R_i \ln k_{0i}, \quad i = 1, 2,$$

so that the Gibbs-Dalton hypothesis makes $x = y = 1$, and the adiabatic relation (5.4.2) takes the form

$$x \ln x + ay \ln y = 0, \quad a = (R_2k_{02}/R_1k_{01})(eT)^{n_2-n_1}. \quad (5.5.1)$$

Let us fix $S_1$ and $S_2$, and consider an equilibrium configuration in which all the fields are uniform. Fig. 5.5.1 shows the locus of points in the $x, y$ plane at which Eq.(5.4.2) holds, for a particular value of $T$. Since the variables $x, y$ are constant multiples of the densities these variables are in fact scaled densities and we may refer to the plane of the figure as the density plane. There is a family of such curves, one for each value of $T$. The figure also shows several lines of constant total pressure,

$$p = (\rho_1 \frac{\partial}{\partial \rho_1} + \rho_2 \frac{\partial}{\partial \rho_2} - 1)(f_1 + f_2) = T(R_1\rho_1 + R_2\rho_2). \quad (5.5.2)$$

The loci of $P$ are straight lines. The isotherm intersects the isobar at 2 points, at one point, or at no point in the $\rho$-plane. If they intersect at no point then there is no such configuration.

If the curves touch at one point then the densities are uniquely determined. The tangents of the two curves at any point are given by

$$R_1 d\rho_1(\ln x + 1) + R_2 d\rho_2(\ln y + 1) = 0, \quad \text{and} \quad R_1 d\rho_1 + R_2 d\rho_2 = 0,$$

respectively; they coincide only if

$$\ln x = \ln y. \quad (5.5.3)$$

* The answer given by Boltzmann to this question is the foundation of statistical mechanics. Here we are looking for an answer within our chosen context of thermodynamic field theory.
By virtue of Eq. (5.4.2) that implies that both logarithms are zero, as required by the Gibbs-Dalton hypothesis.

There remains the possibility of two intersections, at points $A$ and $B$ in the figure. To justify the Gibbs-Dalton hypothesis we have to throw some aspersions on this case. Well, if the gas at equilibrium is homogeneous, then the ratio $r = \rho_1/\rho_2$ is given in advance by the ratio of total masses. This number need not coincide with the value of either of the ratios $r(A)$ or $r(B)$. If it is intermediate between those values then the gas must separate into two parts, one part in which $r = r(A)$ and another part in which it is $r = r(B)$. Later we shall see that mixtures exist, where this does indeed happen, but in the case of ideal gases, or at high temperature or low pressure for most gases, we know that it does not; so there is no stationary state available. That is the same as to say that such states are adiabatically unstable to convection. Flow will develop and eventually the kinetic energy will degenerate to heat. The final state will be stationary but the values of the entropy parameters must have changed.

Fig.5.5.1. GibbsDalton. The coordinates are the (scaled) densities $x$ and $y$. The oval is the locus of (5.4.2) determined by fixing $T, S_1$ and $S_2$. The straight lines are isobars.

The only stable, homogeneous equilibrium available is the point $C$ where the two curves have the same tangent. At that point both terms in (5.4.2) vanish separately, as we have shown.

If the values of the densities and of the temperature are given, then this is a restriction on the values of the two entropy parameters $S_1$ and $S_2$. For a given system with fixed mass and with uniform equilibrium densities, there will be a curve $T \mapsto (S_1(T), S_2(T))$, the image of which is the path followed by the system as the temperature is varied so as to move it through a succession of equilibrium configurations, see Fig 5.5.1.

We seem to be able to conclude that the Gibbs-Dalton hypothesis finds the only stable mixture and that this is what determines how the entropy is apportioned between the two components. An argument based on the maximal entropy principle was expected. Instead we have here an analogue of free expansion; the assumed initial point is unstable and goes into an agitated state, out of equilibrium. The final equilibrium is reached by degradation of the kinetic energy, leading to a state of maximal entropy.
Thus it seems that the Gibbs-Dalton distribution of entropy is not reached by a purely dissipative process but because it is the only one that allows for the existence of equilibrium states, or more generally for any stable adiabatic system. The fact that values of pressure and entropy cannot be assigned at random is easily proved by more elementary examples. See Section III.5 and Fig. 3.5.2. If this conclusion is correct it shows that some important questions about equilibrium thermodynamics are answered only by the extension to hydro-thermo-dynamics.

It seems that the entropy chosen by the Gibbs-Dalton hypothesis is a kind of critical point. Recall that, in general, a critical point in thermodynamics is one in which a Legendre transformation is singular (Tisza 1970). For example, consider the Legendre transformation

\[ p(T, q_1, q_2) = \sum \rho_i \mu_i - f, \quad \mu_i = \frac{\partial f}{\partial \rho_i}, \quad i = 1, 2. \]

An example of a critical point is a point where

\[ \det(\partial^2 p/\partial \rho_i \partial \rho_j) = 0. \]

The critical point at hand is defined by the vanishing of the Jacobean of the transformation \( T, p \rightarrow \rho_1, \rho_2 \),

\[ J = \left| \begin{array}{cc} \frac{\partial T}{\partial \rho_1} & \frac{\partial T}{\partial \rho_2} \\ \frac{\partial p}{\partial \rho_1} & \frac{\partial p}{\partial \rho_2} \end{array} \right|; \]

that is, a point where the two gradients in the density plane

\[ \left( \frac{\partial T}{\partial \rho_1}, \frac{\partial T}{\partial \rho_2} \right), \quad \left( \frac{\partial p}{\partial \rho_1}, \frac{\partial p}{\partial \rho_2} \right) \]

are parallel. The derivations are to be taken with \( S_1, S_2 \) fixed.

With this interpretation we can ask for a generalization of the hypothesis to the case of a mixture of real, interacting gases. This question will be taken up again in Section VI.1.

The suggested form of the Lagrangian for a mixture, with the concept of an entropy space and the need to find the path through this space chosen by the system, is a central feature of the treatment proposed in this book.

**Condensation**

The process of condensation of a van der Waals gas has been treated, formally, as a type of mixture. But we were looking at this “mixture” when the two components were, in fact, separated. The adiabatic condition applies locally, in the gas as in the liquid, hence it gives both relations

\[ S_i = -R \rho_i \ln \frac{\rho_i}{(1 - \rho_i) T_n}, \quad i = 1, 2. \]

Both entropy parameters remain constant during the process of liquefication.
In the case of a mixture of real gases we do not expect the original Gibbs-Dalton hypothesis to apply; this includes van der Waals gases fluids as well as ideal fluids with other types of mutual interaction. Both of these cases will be studied below. It also does not apply to the case of two ideal gases in the case when dissociation and recombination take place. This case shall be studied in Section V.7. The condition for equilibrium, Eq. (5.7.3), is not compatible with the strong Gibbs-Dalton condition, unless \( R_2(n_2 + 1) = R_1(n_1 + 1) \).

V.6. Gibbs-Dalton hypothesis for some real gases

In the case of two fluids of very different nature the Dalton law of partial pressures is not expected to be valid, and the Gibbs-Dalton hypothesis even less. The Gibbs-Dalton hypothesis applies to ideal gases, and real gases are not ideal gases. Can anything be said about the distribution of entropy in a mixture of real gases? We shall answer this question in the affirmative.

One expects that there is an interaction between two dissimilar atoms. As was first shown by van der Waals (1890), this interaction can be simulated by adding an interaction term to the free energy. Because we are interested in the equilibrium states the density gradients will be small and it is enough to consider an interaction energy that is an algebraic function of the densities, not involving their gradients. As a preliminary test of this idea we merely add the following term to the free energy density,

\[
f_{\text{int}} = \alpha (\rho_1 \rho_2)^k,
\]

with \( \alpha \) and \( k \) constant. There is direct experimental evidence in favor of this expression, since the measured “excess free energy” (Rowlinson 1969 page 138) sometimes has exactly this shape, with \( k \) in the region of .5 to 1 or higher. See Fig. 5.6.1. The forces are often repulsive, which makes \( \alpha \) positive. The total free energy is \( f_1 + f_2 + f_{\text{int}} \). For \( f_1 \) and \( f_2 \) we shall use, in a first instance, the expressions that pertain to the one-component ideal gases. Thus, at equilibrium, the Hamiltonian density is

\[
\rho_1 \vec{v}_1^2/2 + \rho_2 \vec{v}_2^2/2 + f + sT, \quad f = f_1 + f_2 + \alpha (\rho_1 \rho_2)^k, \quad s = \sum \rho_i S_i.
\]

\[
f_1 = R_1 T \rho_1 \ln \frac{\rho_1}{T n_1}, \quad f_2 = R_2 T \rho_2 \ln \frac{\rho_2}{T n_2}.
\]

115
Fig.5.6.1.Int. Illustration of the dependence of the excess free energy of a mixture on the concentration, for a fixed value of the total density. It is not always positive.

The Gibbs-Dalton hypothesis specifies a relation between $S_1$ and $S_2$ by focusing on the unique equilibrium configuration. We are not admitting external forces, so the densities are uniform and determined by the total volume and the masses; the temperature is also uniform. The statement of the strong Gibbs-Dalton hypothesis is a relation between the entropy parameters that is related to the equilibrium values of the densities.

Now we ask in what way this rule is expected to be modified by the interaction. A simple and possibly universal hypothesis is available: that the stability interpretation discovered in Section V.2 applies, namely

$$\text{det} \left( \frac{\partial(p,T)}{\partial(\rho_1,\rho_2)} \right) = 0. \quad (5.6.3)$$

The partial derivatives are adiabatic; that is, the entropy parameters are kept fixed. We have

$$dp = [\mathcal{R}_1 T + k(2k - 1)\alpha(\rho_1\rho_2)^k/\rho_1]d\rho_1 + [\mathcal{R}_2 T + k(2k - 1)\alpha(\rho_2\rho_2)^k/\rho_2]d\rho_2$$

and the adiabatic condition

$$\mathcal{R}_1 \rho_1 \ln x + \mathcal{R}_2 \rho_2 \ln y = 0,$$

where

$$x = \frac{\rho_1}{k_01(eT)^{n_1}}, \quad y = \frac{\rho_1}{k_01(eT)^{n_1}},$$

gives

$$dT \propto [\mathcal{R}_1 (\ln x + 1)]d\rho_1 + [\mathcal{R}_2 (\ln y + 1)]d\rho_2.$$
The oval is the locus of solutions of the adiabatic condition for fixed values of $T, S_1, S_2$, the coordinates $x, y$ are the densities, scaled: $x \ln x + y \ln y = 0$. The other curve is a locus of constant pressure, $x + y + (xy)^{1.2} = 3.05$.

The condition for tangency takes the form

$$\frac{1 + \ln x}{1 + \ln y} = \frac{1 + \alpha'(\rho_1 \rho_2)^k / R_1 \rho_1 T}{1 + \alpha'(\rho_1 \rho_2)^k / R_2 \rho_2 T}, \quad \alpha' := k(2k - 1)\alpha.$$  

The Gibbs-Dalton relation $x = y = 1$ is thus modified, unless the molar density is the same for both gases. This is illustrated in Fig. 5.6.1, for $k = 1/2$, $\alpha' > 0$.

There remains an interesting possibility that $\alpha'$ may in special cases be negative. Then the situation illustrated in Fig.5.6.3 may be realized.

Here the generalized Gibbs-Dalton hypothesis is satisfied at two points, with different concentrations. Before we conclude that two different concentrations may coexist we have to investigate the condition of equilibrium.

Fig.5.6.3. Gibbs-Dalton. An interesting possibility. Same as the preceding equation but the pressure is $x + y - .37(2k - 1)(xy)^k$, $k = 1.2$ or $x + y + 2.6(2k - 1)$ with $k = .4$.

V.7. The simplest mixtures. Boltzmann theory

Consider a gas with a ground state with free energy $f = 0$, consisting of molecules with two quantum levels. More precisely, consider a molecule that converts freely between two
energy levels, a lowest level 1 with vanishing free energy \( f_1 = 0 \) and an “excited” level 2 with internal energy density \( f_2 = \epsilon \rho_2 \). Suppose that

\[
\epsilon = (S_2 - S_1)T. \tag{5.7.1}
\]

This is analogous to what we found to be an expression of Maxwell’s rule.

Now let us take a route that may be risky: irrespective of the properties that we have imputed to the gas, assume (with Gibbs-Dalton, strong version) that the familiar expression for the entropy of an ideal gas applies to each component of the mixture:

\[
S_i = -R \ln \frac{\rho_i}{(eT)^{n_i}}, \quad i = 1, 2. \tag{5.7.2}
\]

Thus

\[
\frac{\rho_2}{\rho_1} = (eT)^{n_2-n_1} e^{-\epsilon/RT}. \tag{5.7.3}
\]

This is Boltzmann’s distribution law for the population of the two levels. Both equations (5.7.1) and (5.7.3) are standard lore and not to be tampered with, this in spite of any doubts that may arise concerning the actual direct, experimental verification of Eq.(5.7.3).

Consider now the Lagrangian density

\[
\Phi \rho - f - sT = \Phi \rho - \sum \left( R_i T \rho_i \ln \frac{\rho_i}{T^{n_i}} + \rho_i S_i T \right).
\]

Note that only the total density is conserved; therefore there is only one velocity potential and there is no way to include the binding energy directly, though it is accounted for via Eq.(5.7.1). The new equations of motion are, the adiabatic relation (variation of \( T \))

\[
\sum \rho_i (R_i \ln \frac{\rho_i}{(eT)^{n_i}} + S_i) = 0,
\]

the equation of continuity (variation of \( \Phi \)) and the hydrostatic condition (variation with \( d\rho_1 = -d\rho_2 \))

\[
\ln \frac{\rho_2^{1/n_2}}{\rho_1^{1/n_1}} = -(S_2 - S_1), \tag{\ast}
\]

where, as before, \( S_i \) is the entropy per mol of the \( i \)'th component. I have followed the same method as for saturation. The two cases are very different, for in one case the two components are separated and in the other case they are mixed, so that we cannot be sure that this is right.
V.8. Chemical reactions: Dissociation

We consider the simplest example of a chemical reaction involving ideal gases, the transformation between atomic and molecular hydrogen,

\[ H_2 \leftrightarrow 2H. \]

At sufficiently low temperatures the gas is almost purely molecular, with molecular weight and adiabatic index

\[ m_1 = 2, \quad n_1 = 5/2. \]
At equilibrium we shall have \( \vec{v} = 0 \) and

\[ \rho_1 = \rho = M/V, \quad \ln \frac{\rho}{T^{n_1}} - n_1 = -s_1/R_1. \]

At sufficiently high temperatures the gas is almost purely atomic, with \( m_2 = 1, \quad n_2 = 3/2. \)
At equilibrium,

\[ \rho_2 = \rho = M/V, \quad \ln \frac{\rho}{T^{n_2}} - n_2 = -s_2/R_2. \]

Consider a mixture of two gases, similar in all respects to \( H \) and \( H_2 \), except that the reaction analogous to \( H_2 \leftrightarrow 2H_1 \) does not take place. The Lagrangian density would be

\[
\mathcal{L} = \sum \left( \rho_i \dot{\Phi}_i - \vec{v}_i^2/2 - \phi \right) - \sum \left( R_i T \rho_i \ln \frac{\rho_i}{T^{n_i}} + T \rho_i S_i \right).
\]

A hypothesis that can be tried is that this expression retain some validity for the real hydrogen problem. But it must be changed in essential ways. In \( \mathcal{L}' \) there are two independent velocity fields and therefore two independent potentials \( \Phi_1 \) and \( \Phi_2 \). Variation leads to independent conservation laws, atoms and molecules are independently conserved. The difference between this hypothetical system and real Hydrogen is that in the real system only the total density (grams/cm\(^3\)) is preserved, so we have only one conservation law and we can admit only one variation, hence only one independent potential velocity field,

\[ \vec{v}_1 = \vec{v}_2 = \vec{v}, \quad \dot{\Phi}_1 - \dot{\Phi}_2 = \epsilon = \text{ constant}. \]

The Lagrangian density becomes

\[
\mathcal{L} = \rho_1 \dot{\Phi}_1 + \rho_2 \dot{\Phi}_2 - \rho(\vec{v}^2/2 + \phi) - \sum \left( R_i T \rho_i \ln \frac{\rho_i}{T^{n_i}} + T \rho_i S_i \right),
\]  \( 5.8.1 \)

with \( \rho = \rho_1 + \rho_2 \). The distinction between one molecule and two atoms is not entirely lost, for we are able to maintain two independent densities; indeed this must be so for otherwise the problem of two kinds of gases, atomic and molecular, would not exist. The densities are separately observable and we shall derive a formula for the concentrations in the mixture. Generalisations, to the case of more than two component fluids with chemical interactions, will be considered in the next section.

Let us study the equations of motion in the case that the fluid is at rest, \( \vec{v} = 0 \) everywhere. The effect of gravity is neglected. Variation with respect to \( T \) yields the adiabatic relation

\[
\sum \left( R_i \rho_i \left( \ln \frac{\rho_i}{T^{n_i}} - n_i \right) + \rho_i S_i \right) = 0.
\]  \( 5.8.2 \)
Independent, local variation of the two densities tells us that all the fields are uniform. The actual values of \( \rho_1 \) and \( \rho_2 \) are not obtained, for the variational equations each get a contribution from a \( \rho \dot{\Phi} \)-term. But in variation of the densities with \( \rho \) fixed, \( \delta \rho_1 = -\delta \rho_2 \), the contributions of these terms cancel out and we obtain an additional relation,

\[
R_1 T \left( \ln \frac{\rho_1}{T n_1} + 1 \right) + S_1 T - R_2 T \left( \ln \frac{\rho_2}{T n_2} + 1 \right) - S_2 T = 0, \tag{5.8.3}
\]

Now it is at once clear that the question that has occupied us in the first 4 Sections of this chapter has a different dimension for this, very different, type of mixture. In the condition of equilibrium we have an additional relation, for fixed temperature, between densities and entropies. Eqs (5.7.1) and (5.7.2), together, define a mapping,

\[(\rho_1, \rho_2) \leftrightarrow (S_1, S_2).\]

If this mapping is one - one, is more information needed? Certainly it is locally one-to-one almost everywhere. We may ask if the Gibbs-Dalton hypothesis is valid, if it is compatible with the equation of motion. Contrary to the case of the unary fluid the answer is that it is most likely not, and that if it happens to be then this circumstance gives no useful information.

**Gibbs’ phase rule**

For a binary mixture, this famous rule says that the number of coexistent phases is at most 3. It is based on counting the number of relations at equilibrium and comparing with the number of independent field variables. From our point of view the question takes on a different significance.

In the case of a binary mixture with a single phase we have only one Euler-Lagrange equation, the adiabatic relation. We expect an isolated system to be stable. That would not be the case if the entropy parameters could drift, subject only to the adiabatic condition; so we need an independent mechanism to constrain the choice. The Gibbs-Dalton hypothesis solves this problem for us.

In the case at hand, when there are two phases mixed together, we are presented with two Euler-Lagrange equations and that should be sufficient. The correct apportionment of the entropy between the two components is determined by the equations of motion.

If a third phase is present an extra algebraic condition will single out a point on this line and a fourth will render the system of equations without a solution.

**Solving the equations**

The densities are the normal kind, in grams/cm\(^3\). The particular linear combination that appears here reflects the fact that it is mass that is preserved by the reaction, and not (for example) the number of particles. Since for hydrogen \( R_2 = 2 R_1 \), Eq.(5.5.2) reads

\[
\ln \frac{\rho_1}{\rho_2^2} - (n_1 - 2n_2) \ln T - 1 = \frac{S_2 - S_1}{R_1}. \tag{5.8.4}
\]

In general, with \( R_i = R/m_i \), where \( m_1, m_2 \) are the atomic molecular weights,

\[
\ln \frac{\rho_1^{m_2}}{\rho_2^{m_1}} - (n_1 m_2 - n_2 m_1)(\ln T + 1) = \frac{m_1 m_2}{R}(S_2 - S_1). \tag{5.8.4}
\]
The right hand side is usually expressed in terms of the binding energy, by means of Boltzmann’s formula

$$\epsilon = (S_1 - S_2)T.$$  \hspace{1cm} (5.8.5)

We shall try to derive this formula.

**Minimal energy**

As in the case of condensation, we need to understand what is meant by ‘energy’ in this context. The boundary conditions are the same, the Hamiltonian is still the free energy; we only need to include the binding energy in the Hamiltonian, thus

$$h = \epsilon \rho_1 + f_1 + f_2.$$  

This is in fact standard, see for example Landau and Lifshitz (1965). To do this without affecting the action - we already have the correct equations of motion - all that is needed is a slight change of vocabulary. The Lagrangian density is

$$\dot{\Phi} + \epsilon \rho_1 - sT - h, \quad h = \epsilon \rho_1 + f_1 + f_2,$$

the Euler-Lagrange equations are the same as before and, at equilibrium, minimization of the Hamiltonian implies the Boltzmann relation

$$T(S_1 - S_2) = \epsilon.$$  

What we have gained is the proper definition of ‘energy’ as understood by Boltzmann, and Boltzmann’s formula (5.8.5). This result confirms the validity of our entropy postulate for the mixture,

$$s = \rho_1 S_1 + \rho_2 S_2;$$

compare the discussion that follows Eq. (4.4.1). To sum up, the thermodynamical action principle, knowing nothing about binding energies, gives (5.8.4); at equilibrium the principle of minimum energy, without invoking the concept of entropy, gives the same result but with \((S_2 - S_1)T\) replaced by \(\epsilon\). Together, they yield Boltzmann’s formula.

$$T(S_2 - S_1) = \epsilon,$$  \hspace{1cm} (5.8.5)

This relation is usually taken for granted; see for example Prigogine (1955), page 41. Thus finally

$$\ln \frac{\rho_1}{\rho_2} - (n_1 - 2n_2) \ln T - 1 = \frac{\epsilon}{R_1 T}.$$  \hspace{1cm} (5.8.6)

To compare this with the result of Eckert () that was famously applied by Saha (1921) to stellar atmospheres, we replace the partial densities by the partial pressures, defined here by \(p_i = R_i \rho_i T\), to get

$$\ln \frac{p_1}{p_2} \frac{R_2^3}{R_1^2} - \left( (n_1 + 1 - 2(n_2 + 1) \right) \ln T - 1 = \frac{\epsilon}{R_1 T}.$$  

121
or, finally

\[
\ln \frac{p_1}{p_2^2} = \frac{C_{P1} - 2C_{P2}}{\mathcal{R}} \ln T + \frac{\epsilon}{\mathcal{R}_1 T} + 1 - \ln 2, \\
\text{(5.8.7)}
\]

where \( C_{P_i} = (n_i + 1)\mathcal{R}_i \).

This is the result contained by Saha from kinetic theory.

**Remark.** The Euler-Lagrange equations (5.8.2-3) allow us to determine how the total entropy is distributed among the two species. Both approaches agree that the total entropy density before mixing is

\[
- \sum \mathcal{R}_i \rho_i (\ln \frac{\rho_i}{T^{n_i}} - n_i),
\]

and there may be an expectation that the two summands represent the share of entropy allocated to each species as predicted by the Gibbs-Dalton hypothesis. Instead, from the condition of equilibrium and the adiabatic condition we obtain

\[
S_1 = -\mathcal{R}_1 (\ln \frac{\rho_1}{T^{n_1}} - n_1) - \frac{\rho_2}{\rho} [\mathcal{R}_1 (1 + n_1) - \mathcal{R}_2 (1 + n_2)].
\]

This is not in contradiction with classical theory, since that theory does not deal with the question; this can be understood as follows. ‘Entropy production’ refers to the difference between the entropies in two hypothetical, equilibrium situations, at the beginning and at the completion of a process. During the process the traditional position is that entropy is undefined. Our understanding is that, at equilibrium, the total entropy is determined (in terms of the temperature) by the adiabatic condition and that the allocation of entropies at equilibrium (the difference \( S_1 - S_2 \)) was calculated with the same result as in the classical theory. ‘Entropy production’ can be calculated by comparing the total entropy at final equilibrium with the total equilibrium before mixing, provided that we are given the temperatures. (In the case that no chemical reaction takes place we know that the temperature does not change. We do not try to determine whether this entropy production is due to mixing, to the progress of the chemical reaction or to the removal of the wall of separation. The classical theory does not say, nor does it ask.

De Groot and Mazur (ref) have proposed that, once mixing is complete, entropy production can be understood in terms of the progress of the chemical reaction. In that theory \( \dot{\Phi} \) is the rate of specific heat flow.

**Numerical calculations.** Fig.5.7.1 and Fig.5.7.25 and Fig.5.7.3.

The molecular binding energy is about 4.5 eV, or in relation to the rest energy, in energy units \( \epsilon = (4.5/1876 \times 10^6)c^2 \approx 2.15 \times 10^{12} \). Thus

\[
\epsilon/\mathcal{R}_1 = 4.3 \times 10^{12}/.83214 \times 10^8 = 51674.
\]

Fig.5.7.1 shows \( r \) versus \( T \), for \( n_1 = 5/2, \ n_2 = 3/2 \) with \( 1/\epsilon \rho = 1000 \).
The measurements are usually performed under conditions of constant pressure. Setting \( \rho_1/2 + \rho_2 = p/RT \) we get, when \( n_2 = 5/2 \) and \( n_2 = 3/2 \),

\[
\frac{\rho_2^2}{\rho \rho_1} = \frac{r^2}{1 - r^2} = \frac{R}{2e \rho p} T^{3/2} e^{-\epsilon/RT}; \quad r = \rho_2/\rho. \tag{5.8.8}
\]

This relationship is plotted in Fig.5.7.2. for \( \text{Rep} = 1000. \)

V.9. Other chemical reactions

More complicated reactions raise new questions. Consider the choice of variables, in the slightly more complicated case of a reaction of the type

\[ A \leftrightarrow B + C \tag{5.9.1} \]
where $\nu_A$ molecules of type $A$ changes into $\nu_B$ molecules of type $B$ and $\nu_C$ molecules of type $C$. The densities (in grams) of components $A, B, C$ are $\rho_A, \rho_B, \rho_C$. We shall convey the precise information by writing

$$\nu_A \rho_A - \nu_B \rho_B - \nu_C \rho_C := \bar{v} \cdot \bar{A} = \epsilon, \quad \bar{v} := (\nu_A, -\nu_B, -\nu_C), \quad \bar{A} := (A, B, C).$$

Two densities are independently conserved, for example

$$\nu_A \rho_A + \nu_B \rho_B, \quad \text{and} \quad \nu_B \rho_B - \nu_C \rho_C.$$

We therefore need two Lagrange multipliers and two velocities. The space of conserved densities is a 2-dimensional linear space and these two densities form a basis for it. Any meaningful statement must be independent of the basis chosen. The kinetic part of the Lagrange density can perhaps be expressed as

$$(\nu_A \rho_A + \nu_B \rho_B) \dot{\Phi}_1 + (\nu_B \rho_B - \nu_C \rho_C) \dot{\Phi}_2$$

But the sum of squared velocities is not linear, so what is the correct expression for the kinetic energy? Any attempt to eliminate one of the velocities leads to disorderly formulas; it is better to impose a constraint.

We take the complete Lagrangian density, regardless of interactions, to be, as in the case that there are no chemical reactions,

$$\mathcal{L} = \rho_A (\dot{\Phi}_A - \frac{\bar{v}_A^2}{2}) + \rho_B (\dot{\Phi}_B - \frac{\bar{v}_B^2}{2}) + \rho_C (\dot{\Phi}_C - \frac{\bar{v}_C^2}{2}) - f_A - f_B - f_C - sT, \quad (5.9.2)$$

with

$$s = \rho_A S_A + \rho_2 S_B + \rho_C S_C \quad (5.9.3)$$

and with uniform coefficients $S_A, S_B, S_C$. The densities are in grams per $cm^3$ and the kinetic energies are in common, cgs units.

As a solution to the problem of finding a proper definition of the kinetic energy we propose:

**Conjecture. The effect of the reaction is to impose the linear constraint**

$$\nu_A \dot{\Phi}_A = \nu_B \dot{\Phi}_B + \nu_C \dot{\Phi}_C, \quad (5.9.4)$$

or

$$\bar{v} \cdot \dot{\Phi} = 0.$$

Immediate support for this idea comes from the equations of motion. Variation with respect to the two independent potentials gives the two conservation laws

$$\frac{d}{dt}(\nu_A \rho_A + \nu_B \rho_B) + \text{div}(\nu_A \rho_A \bar{v}_A + \nu_B \rho_B \bar{v}_B) = 0, \quad (5.9.5)$$

124
\[
\frac{d}{dt}(\nu_A \rho_A + \nu_C \rho_C) + \text{div}(\nu_A \rho_A \vec{v}_A + \nu_C \rho_C \vec{v}_C) = 0. \tag{5.9.6}
\]

That is, the flow vectors are just what one could expect; compare Landau’s 2-velocity theory. This account of the independent variables and the conservation laws is an alternative to the treatment by Prigogine (1949) and his school.

The conjecture (5.9.4) is based on the significance of the velocity potential, more precisely the time derivative \(\dot{\Phi}\), as an energy parameter. We have already remarked, in the simpler case of dissociation, as well as in the case of saturation, that it includes the latent heat.

At equilibrium all the fields are uniform and the remaining information that comes from the Euler-Lagrange equations includes the adiabatic relation

\[
\frac{\partial}{\partial T}(f_A + f_B + f_C + sT) = 0 \tag{5.9.7}
\]

and stationarity of (5.8.2) with respect to the local variations of the densities. A principal result is that, at equilibrium, in the absence of external forces, the densities are uniform. We shall assume that each component is an ideal gas, then (5.9.7) takes the familiar form

\[
\sum_{i=A,B,C} \left( R_i \rho_i \left( \ln \frac{\rho_i}{T n_i} - n_i \right) + s_i \rho_i \right) = 0.
\]

Additional information comes from an independent global variations of the densities that leave invariant the constraint (5.9.4), namely

\[
\delta \rho \propto \vec{v} := (\nu_A, -\nu_B, -\nu_C).
\]

Thus

\[
\vec{v} \cdot \vec{\mu} = T \vec{v} \cdot \vec{S}, \quad \vec{\mu} = (\mu_A, \mu_B, \mu_C)
\]

In the case of 3 ideal gases the full expression for this is

\[
\frac{(\rho^\nu/m)_A}{(\rho^\nu/m)_B (\rho^\nu/m)_C} (eT)^{(n/m)_A+(n/m)_B+(n/m)_C} = e^{-\vec{v} \cdot \vec{S}/RT}.
\]

Here \(m_A\) is the molecular weight of fluid \(A\) and \((n/m)_A := n_A/m_A\). The affinity to the Saha equation is evident. For other fluids the right hand side depends on the interaction between the components. It is a function of the densities alone, independent of the temperature. The chemists resort to accumulated tables.

As in the case of dissociation, we claim that maximization of the entropy makes the Hamiltonian stationary or equivalently that

\[
T \vec{v} \cdot \vec{S} = \epsilon,
\]

125
and this leads to the alternative statements

\[
\frac{(\rho^{\nu/m})_A}{(\rho^{\nu/m})_B (\rho^{\nu/m})_C} = (eT)^{(n/m)_A - (n/m)_B - (n/m)_C} e^{-\epsilon/RT}
\]

Either form gives a value for the reaction “constant”

\[
K_c = \frac{(\rho^{\nu/m})_A}{(\rho^{\nu/m})_B (\rho^{\nu/m})_C},
\]

as a function of the temperature. While the specialization to ideal gases limits the practical value of this result it is nevertheless a little strange that this function is always taken from experiment and that no attempt is made to predict it, with the exception of the work of Saha, \textit{op cit}.

Project. Compare with Holman and with an experiment.

V.10. Taking stock.

The approach to binary mixtures through the addition of Lagrangians furnishes a two parameter family of model Lagrangian densities. The two parameters are interpreted in terms of the entropies assigned to each type of molecule. As heat is added to the system the entropy must change and a decision has to be made about the allotment of additional entropy to each gas; this gives us the concept of a 2-dimensional entropy space and the path in this space that is chosen by the system. We had expected that the key to the determination of the path is entropy maximization, but this expectation has not been confirmed.

We have studied some mixtures of gases that are free to transmogrify, and we have seen two examples of a rule that would have the physical path through entropy space reduce to relations of the type \( \epsilon = (S_2 - S_1)T \). In the case of ideal gases that do not make chemical reactions the stronger statement furnished by the strong Gibbs-Dalton hypothesis may apply.

When we begin to consider mixtures of van der Waal’s gases in the next chapter we shall find that condensation is a major part of it, so that both items of insight summarized here will be put to severe tests.

So far, there was no attempt to predict rates of chemical reactions. In the case that the reactions are driven by input of energy the rates will be determined by the rate of input of heat or other forms of energy, as in electrolysis. In the case of spontaneous reactions that produce heat, the difficulty lies in the almost impossible task of preparing suitable initial conditions. A few very special circumstances may offer some hope for fruitful analysis.

1. Many systems have metastable configurations that can be reached with care, such as is the case with supercooled vapors or superheated liquids. Then an initial state can be prepared that is characterized by simple properties, such as uniformity. Possibly, the decay of such states may take place without convection setting in, or with convection with a high degree of symmetry.
2. Solids may offer possibilities for analysis, because of the simplification that is the absence of convection. The simplest instance is offered by the slab, when an initial uniform configuration is disturbed by suddenly bringing one of the bounding plates to a higher temperature. There may be an opportunity of deriving Fourier’s heat transfer law from thermodynamics.

**Stability**

Here we take up the discussion of (mechanical) stability first considered in Section IV.9. To understand the analogous situation in a homogeneous mixture the easiest way is to recall the connection with the calculation of the speed of sound. In Section we found that the square of sound is determined by a matrix $M$ defined by

$$\frac{\tilde{\rho}_i}{\rho_i} = M^i_j \frac{\rho''_j}{\rho_j},$$

where

$$M^i_j = \frac{\partial \mu_i}{\partial \rho_j}.$$

Stability demands that the determinant of this matrix be positive. This turns out to a very weak requirement.
VI. IMMISCIBLE FLUIDS

We shall continue our study of real fluids with an interesting phenomenon that is strangely absent from some textbooks on thermodynamics and the main subject in others. Here, in the first place, we shall introduce interactions between the components of a mixture. After all, the form of the free energy of a real, pure gas reflects the influence that each particle has on its neighbours; so it is reasonable to expect that unlike particles also interact with each other.

VI.1. Ideal gases with mutual interaction

When 2 fluids are mixed, and afforded enough time to settle down, one of two things may happen. (1) The system approaches an equilibrium state in which the mixture is uniform, the concentration \( \frac{\rho_1}{(\rho_1 + \rho_2)} \) having the same value throughout the vessel. Such mixtures are said to be miscible. (2) But sometimes the two fluids may not mix so readily. A small amount of each fluid can be dissolved in the other, either way, within limits. But at a range of temperature and pressure, if the average concentration is too high, then a different type of equilibrium may be observed, typically containing bubbles of one fluid mixture floating in a background of another fluid mixture with very different concentration. Because this chaotic configuration, with variable droplet size and a major influence of surface tension, is difficult to analyze, let us admit the presence of the standard gravitational field. Then a likely result is that the heavier fluid occupies the lower part of the vessel (a small amount of the lighter fluid dissolved in it) while the lighter fluid occupies the rest (a small amount of the heavier fluid dissolved in it).

Examples involving two liquids, a liquid and a gas or a gas and a solid are common, but it is reported that the combination of any pair of ‘gases’ is completely miscible.* The processes by which such things may come about are almost beyond analysis, but we can try to understand the final, equilibrium states. The role of gravity is not taken into account quantitatively; instead it will be regarded as a weak force, easily overcome if there is a tendency for mixing to take place. Gravitation is used only to explain the observation that the fluid separates into distinct regions with smooth boundaries and our studies concern the final, equilibrium configurations.

In the case of two fluids of very different nature the Dalton law of partial pressures is not expected to be valid, and the strong Gibbs-Dalton hypothesis must at least be modified, see Section V.5. One expects that there is an interaction between two dissimilar atoms. As before, in section 5.6.1, we add a van der Waals interaction term to the free energy. Because we are interested in the equilibrium states the density gradients will be small and it is enough to consider an interaction energy that is an algebraic function of the densities, not involving their gradients. We shall include the following term in the free energy density of the mixture of two ideal gases,

\[
 f_{\text{int}} = \alpha (\rho_1 \rho_2)^k, \tag{6.1.1} 
\]

* This is what we read in many places, but if a van der Waals fluid above the critical point is ‘a gas’ then there are numerous cases of immiscible gases (Scott and van Konynenburgh 1980, page 503).
with $\alpha$ and $k$ constant. There is direct experimental evidence in favor of this expression, see Section V.6. The total free energy is $f_1 + f_2 + f_{\text{int}}$. For $f_1$ and $f_2$ we shall use, in a first instance, the expressions that pertain to the respective one-component ideal gases. Thus, at equilibrium, the Hamiltonian density is

$$\rho_1 \vec{v}_1^2/2 + \rho_2 \vec{v}_2^2/2 + f + sT, \quad f = f_1 + f_2 + \alpha(\rho_1 \rho_2)^k, \quad s = \sum \rho_i S_i, \quad (6.1.2)$$

where, for the time being, the individual energy densities are those of ideal gases,

$$f_1 = \mathcal{R}_1 T \rho_1 \ln \frac{\rho_1}{n_1}, \quad f_2 = \mathcal{R}_2 T \rho_2 \ln \frac{\rho_2}{n_2}. \quad (6.1.3)$$

A great deal of attention is paid to the “excess free energy (density)” of a real mixture. It is defined as $f_{\text{excess}} = f - f_1 - f_2$, where $f_1$ and $f_2$ refer to situations where the individual fluids are alone with the same density and temperature. Compare Rowlinson (1959). The densities $f_1$ and $f_2$ are known in the case of ideal gases, and more or less known in other cases; yet the idea of modelling the excess, as a correction to the sum $f_1 + f_2$, is not popular. See however Lemmon (1996), Lemmon and Jacobsen (1998, 1999). For a vast accumulation of free energy functions see Hicks and Young (1975). *

**Fig.6.1.1. Free energy. The function $f$ with $\alpha = .5, .42, .3, k = .56$ and fixed total density, as a function of the concentration of the mixture. The middle curve has the characteristic shape with two extrema. However, they are maxima, not minima, for either sign of $\alpha$. Ideal gases are perfectly miscible and this type of interaction does nothing to alter that property.**

Following van der Waals, an alternative procedure has been to model the mixture as a single component fluid with properties that are a compromise between those of the components, with an explicit dependence of the van der Waals parameters on the molar fractions. **This is true, in particular, of an influential paper by Scott and Van Konynenburg (1968).**

---

* Unfortunately, their definition of free energy excess includes the “free energy of mixing” so that a detailed confrontation could not be made.

** Rowlinson voices some degree of skepticism: “Such attempts rest on the fallacy that the forces $(\alpha - \beta)$ between two molecules of species $\alpha$ and $\beta$ are always determinable from the strengths of the forces $(\alpha - \alpha)$ and $(\beta - \beta)$.” Rowlinson does not offer an alternative but see the quoted papers by Lemmon and Jacobsen.
Note especially an expression for the excess free energy, valid in the limit of infinite pressure (Scott and Van Konynenburg p. 499), that agrees with Eq.(6.1.1), with \( k = 1 \). *

Our point of view is that a mixture, having more degrees of freedom than the one component fluid, must exhibit features that cannot be simulated by a single component, either physically or mathematically. A single-component model uses an incomplete set of dynamical variables and therefore cannot obey the fundamental relations of thermodynamics.

Lemmon and Friend (....) include a factor \( T \) in their expression for the excess free energy, to make it look like a contribution to the entropy. A contribution to the free energy that is linear in \( T \) can always be compensated by a shift in the entropy. We shall make it a working assumption that the interaction strength is independent of the temperature.

Unfortunately, some of the concepts that help us understand non-interacting gases do not apply when interactions are present, and there is no sensible definition of partial pressures. The total pressure is well defined; it coincides with the on shell value of the Lagrangian density,

\[
p = \sum \rho_i \frac{\partial f}{\partial \rho_i} - f \quad (= \mathcal{L} \text{ on shell}). \quad (6.1.4)
\]

In the present case,

\[
p = \sum \mathcal{R}_i \rho_i T + (2k - 1)\alpha(\rho_1 \rho_2)^k. \quad (6.1.5)
\]

This is illustrated in Fig.6.1.2 for the case that \((2k - 1)\alpha > 0\). The dependence of \( p \) on the concentration (at constant temperature and volume) is linear in the absence of interaction; it dips below the straight line when \((2k - 1)\alpha\) is negative and it rises above it if it is positive.

But there is no natural definition of partial pressures and Dalton’s law cannot be formulated; that is one reason why the Gibbs-Dalton hypothesis is preferable; it can be formulated and suitably modified to take the interaction into account, as we have seen in Chapter V. The equations of motion, from variation of the densities, gives (6.1.2), or

\[
-\frac{D\vec{v}_i}{Dt} = \frac{\partial (f + sT)}{\partial \rho_i} \bigg|_T.
\]

In the case of a simple system we can work with the pressure or with the chemical potential as we like, but in the case of mixtures we had better get used to using the latter. In general, the pressure is one of the potentials (potential densities), not a variable.

At constant pressure, the volume as a function of concentration is often less than the sum of the volumes of the separate components. Observation of excess free energy and the deficit of volume are ready sources of information about the parameters \( \alpha \) and \( k \).

* One aspect of this approach is particularly reasonable; it is assumed that the “displaced volume” of gas number 1, represented by the coefficient \( b \) in the expression for the pressure, must be affected by the presence of gas number 2, and vice versa. I have not tried to include this effect in the calculations.
Fig. 6.1.2. Pressure at constant temperature, showing the effect of interaction on the pressure profile. The abscissa is the concentration. When $\alpha$ is positive the upper curve illustrates the case that the exponent $k$ is larger than .5, the lower curve the case that $k < .5$.

We shall consider the possible existence and stability of a two-phase equilibrium. After completing this simplest instance of interacting fluids with a brief Summary we shall have enough confidence to attack van der Waals’ fluids in the next section.

**Data**

There exist collections of experimental data that can be related to the interaction density in mixtures. Before we can use it we must be sure to know what it is that is measured. A large compilation of measured values of excess energies lists the observed values of the enthalpy (density). This choice is based on the idea that the experiments were done under circumstances where the system was in diathermic contact with the surroundings and under constant (atmospheric) pressure. That the pressure rather than the volume was fixed is easy to understand, for pressures equalizes almost instantaneously. Whether there was enough time for changes in the temperature to adjust may seem doubtful, although, if that was the express intention of the experimenters, then there is no reason why it should not be. But the action principle that has been developed, so far, is adiabatic, and we shall continue to apply it to isolated systems exclusively. The fluctuations of shortest time parameter are the adiabatic changes and they are the variations that determine the instantaneous equilibrium configuration. The postulate of minimum energy therefore refers to either the Helmholtz free energy $\int f$ (if the volume is fixed) or the Gibbs free energy $\int f + p$ (if the pressure is fixed). For simplicity we shall deal with the former case only.

The difficulty with direct experimental sources is the telegraphic nature of information. For example “The critical temperatures were observed by allowing the tubes to warm slowly in an environment of measured uniform temperature.” Neither “critical temperature” nor “observed” are defined. Comments provided by the compiler is sometimes useful.

**Conditions for equilibrium**

According to the action principle a static configuration is characterized by the condition that the action must be stationary with respect to variations of the temperature and the densities. Local variations of the temperature gives the adiabatic condition. The principal statement that comes from variation of the densities is that the fields must be piecewise
uniform. If the fluid separates into two parts with different concentrations then additional, global variations that remain to be investigated are variations that hold the total masses fixed, piecewise uniform variations that satisfy

$$\delta \rho_1^u = -\delta \rho_1^v, \quad \delta \rho_2^u = -\delta \rho_2^v,$$

where the superscripts $u, v$ refer to the two parts of the fluid. This implies continuity of the pressure and the temperature and (the Euler-Lagrange equations)

$$\text{Disc}(\dot{\Phi}_i + T S_i) = \text{Disc} \mu_i := \mu_i^u - \mu_i^v, \quad i = 1, 2.$$

The principle of maximum entropy (= minimum free energy) makes both sides equal to zero.

That both chemical momenta are continuous is the condition that a particle, of either type, at the dividing surface is subject to the same mechanical force whether it is considered to belong to one side of the boundary or the other; the continuity of $\dot{\Phi}_i - S_i T$ means that entropic forces are balanced as well.

To sum up, equilibrium of the divided fluid implies continuity of temperature, pressure and $\dot{\Phi}_i + T S_i - \mu_i, i = 1, 2$. Minimum energy implies that $\dot{\Phi}_i + T S_i$ and $\mu_i$ are separately continuous.

To solve these equations several methods can be used.

**The method of the common tangent**

The conditions of equilibrium are

$$T^u = T^v, \quad p^u = p^v, \quad \mu_i^u = \mu_i^v, \quad i = 1, 2. \quad (6.1.6)$$

We shall regard the densities as coordinates in a 2-dimensional Euclidean space and use a geometric notation. The equations of equilibrium tell us that the tangent planes to the equipotential surface $f = \text{constant}$, at the two points, are parallel (See Section IV.4.) Now

$$p = (R_1 \rho_1 + R_2 \rho_2) T + \alpha (2k - 1)(\rho_1 \rho_2)^k, \quad (6.1.7)$$

Since $p = \rho_1 (\partial f / \partial \rho_1) + \rho_2 (\partial f / \partial \rho_2) - f$ it follows that

$$f(\rho_1, \rho_2)^u - f(\rho_1, \rho_2)^v = (\rho_1^u - \rho_1^v) \mu_1^u + (\rho_2^u - \rho_2^v) \mu_2^u.$$

That is, the two tangent planes actually coincide. This is exactly the same situation that occurs in saturation, as illustrated in Fig.4.3.1 and subsequent figures, but in a higher dimension, making illustration more difficult.

As an example we may take $\beta = 2, k = 1$ and thus $\alpha = 2RT/\rho$. The concentrations at the minima of $f$ in Fig.6.1.3 are $x = .24853$ and $y = .75147$. The pressure is $R \rho T + \alpha \rho_1 \rho_2 = R$, so that the excess pressure at fixed volume must be more than twice the pressure of the corresponding ideal, non-interacting mixture. It is likely that, when this condition is met, one or both of the real gases will be in the domain where they must be described by the van der Waals equation of state.
Fig. 6.1.3. Common tangent. Example, \( \beta = 2, k = 1 \); the dependence of \( f \) on the concentration, on the line \( \rho_1 + \rho_2 = 1 \). The free energy density has been re-normalized to give the tangent zero slope.

Fig. 6.1.4. The range of values of the parameters \( k \) (abscissa) and \( \beta \) (ordinate) for which the free energy density exhibits two minima is the interval between the two lines.

For assigned values of the parameters \( \alpha, k \) there is a finite range of values of \( \alpha \); if \( k = 1 \) it is, approximately,

\[
2 < \frac{\alpha}{RT} \rho^{2k-1} < 10.
\]

This is the range of temperatures for which separation occurs. The upper limit is referred to as UCST or upper critical solution temperature. At this temperature any decrease in the temperature converts the system from a homogeneous liquid to a two phase system. The lower limit, L(ower)CST the same transformation takes place when the temperature is increased. (Scott and Van Konynenburg 1968)

**Symmetry**

It happens that the formula for the pressure, when expressed in terms of molar densities, is symmetric with respect to the interchange of the two densities; the fact that \( p^u = p^v \) strongly suggests that we look for solutions that satisfy

\[
(\rho^u_1, \rho^u_2) = (\rho^v_2, \rho^v_1).
\]  

(6.1.8)

For a determination of equilibrium using (6.1.8) see Fig. 6.1.5. This method is seldom applicable.

133
Fig. 6.1.5. Determination of concentrations using symmetry. The curve is the locus of pairs of densities that satisfy the symmetry condition Eq. (6.1.8). The two vertical blue lines mark the values of $x$ with the selected value of the pressure. The coexistent densities are the coordinates of the intersections.

**Direct search**

Both methods used so far to find the coexistent mixtures depend on symmetry, on the assumption that the two coexistent mixtures have conjugate concentrations, $(\rho_1, \rho_2)^u = (\rho_2, \rho_1)^v$. But there are other solutions, and to find them all we know of no method better than the following. We produce plots of the loci defined by the three equations

$$
\mu_1(x, y) = A, \quad \mu_2(x, y) = B, \quad p(x, y) = C,
$$

where $A, B, C$ stand for real numbers. These numbers are adjusted so that the first two curves intersect at 2 points; then they are adjusted further until an isobar passes through both of them. For an illustration, see Fig. 6.1.6.

Fig 6.1.6. A typical determination of co-existence. The ordinates are the two densities. The red lines are loci of the chemical potentials, the green line is an isobar. The two
triple intersections are the densities of two coexistent densities. The geometry is typical of immiscibility, as opposed to condensation of one of the constituents.

This method is the more rewarding, for it will give us a visual representation of the nature of the physical phenomenon. We shall refine this scheme and carry out the calculations in several particular cases later.

Summary.

We have explored a simple phenomenon that involves a mixture of two ideal gases, slightly modified by a simple interaction term added to the free energy. In this case we have verified, under certain circumstances, the separation of the mixture into two parts with quite different concentrations. What makes real gases more complicated, and more interesting, is the fact that interactions between like particles also come into play, in a regime not too far from saturation, where the individual fluid components behave, approximately, like van der Waals fluids. In fact, it is commonly believed that the phenomenon of immiscibility cannot occur in fluids above the condensation point. It is even said that it does not happen with gases; what lies behind this is a too restricted definition of “gas”.

What about the entropies of these mixtures? It would be naive to suppose that the Gibbs-Dalton law applies, since we expect that it is affected by the interaction. Fortunately, as was we have seen, and as we shall confirm below, it is not necessary to know the entropies in the present investigation. What we need to know about the entropy was discussed above; it led to the statement that the chemical potentials are continuous.

VI.2. Mixture of two van der Waals fluids.

The spinodal of unaries

Refer to Fig. 6.2.1; it is the same as Fig.4.3.1, with additions. The curve is the van der Waals potential, the function $p(\rho, T)$ for a fixed value of $T$. This function is sometimes referred to as an equation of state, which is misleading since $\rho, T$ is not the natural set of variables for the pressure - the natural variables are $\mu$ and $T$.

![Image](image.png)

Fig.6.2.1. From Chapter 4; with the points of the spinodal added; it is the manifold that consists of the two points $u$ and $v$ on the density axis defined by (6.2.1). The abscissa is the inverse density. The temperature is fixed below critical.
The points $A$ and $B$ in the figure are the points of coexistence for the chosen temperature; both $p$ and $\mu$ have the same values at both points. They define a pair of stable configurations in equilibrium with each other. A very useful concept is the “spinodal”; in the present case it is the set of densities labelled $u, v$, points at which $\partial p/\partial \rho|_T = 0$. A better characterization of this manifold is,

$$\frac{\partial^2 f}{\partial \rho^2}|_T = 0$$

(note that $\partial p/\partial \rho|_T = \rho \frac{\partial^2 f}{\partial \rho^2}$); it has the advantage of being defined by the free energy as a function of its natural variables and it has a simple and natural generalization to mixtures.

The most important property of the spinodal is the following. The two points are bracketed by the points $A, B$; the unstable point between $A$ and $B$ lies between the spinodal points and this gives a fairly accurate indication of the location of the points of coexistence once the spinodal is known. As the temperature is raised points $A$ and $B$ approach each other and coalesce with the spinodal (points $u$ and $v$) at $T_{cr}$.

The mapping $p \rightarrow \rho$ is 3-valued when the pressure is between the values $p(u)$ and $p(v)$, one-valued when the density is outside this interval.

**The spinodal of binaries**

The set of 2-phase configurations of a typical binary system, for each pair of values $p, T$, is a one-dimensional subset of the density plane. Since, in the case of van der Waals fluids $x = b_1 \rho_1$ and $y = b_2 \rho_2$ take values between 0 and 1 we shall use coordinates $x, y$ with this range, $0 < x, y < 1$ and refer to $\vec{\rho} = (x, y)$ as a point in density space.

For fixed $T$ below a certain limit $T_{max}$, the density space of a typical binary system is divided into 3 or more distinct regions, separated and sometimes bounded by points of the spinodal, the spinodal being the locus of points on which

$$\det \left( \frac{\partial f}{\partial \rho_i \partial \rho_j} \right) = 0,$$

the natural generalization of (6.2.1). These are points where the mapping $\vec{\mu} \rightarrow \vec{\rho}$ is 2-valued. They form lines that separate a single valued domain from a 3-valued domain. The spinodal is not the line of coexistence, but it gives a good indication of where the coexistent mixtures are and it has the advantage of being easy to calculate and to plot.

Here is an example of what is observed in a typical experiment. The experimenter usually begins with a homogeneous mixture at low pressure, a gaseous system with fixed concentration. Because the concentration cannot be easily manipulated it is natural to use the concentration as one of the variables, another being the total density or its inverse, the volume. The temperature may be kept fixed while the pressure is slowly increased to take the system through a sequence of adiabatic equilibria.

As the pressure is increased (with $T$ fixed) the system typically traces a radial line in density space. Eventually, as the density approaches the spinodal, condensation sets in; this point is referred to as the **dew point**. At best, the droplets fall like rain and accumulate at the bottom of the vessel.
The next three diagrams show what happens to a model of an Ethane-Propane mixture in the 2-dimensional density space. The oval (purple) is the spinodal of the mixture. As the temperature is raised the oval contracts and reduces to a point at a temperature \( T_{max} = 370.5 \), above which no phase separation occurs. When \( T \) is reduced to 369.5, which is the critical temperature of Propane, the oval touches the vertical axes; at lower temperatures the oval is a horizontal band across density space.

![Density diagram for the model of the mixture of methane (abscissa) and propane (ordinate) at \( T = 370.5, \alpha = 5 \), showing the spinodal (purple) and two (blue) isobars. The other curves are loci of one of the two chemical potentials. The spinodal is a closed line bordering an oval. Radials indicate critical concentrations for this value of \( T \).](image1)

**Fig. 6.2.2.** Density diagram for the model of the mixture of methane (abscissa) and propane (ordinate) at \( T = 370.5, \alpha = 5 \), showing the spinodal (purple) and two (blue) isobars. The other curves are loci of one of the two chemical potentials. The spinodal is a closed line bordering an oval. Radials indicate critical concentrations for this value of \( T \).

![Density diagram for (the same model of) the mixture of methane and propane at \( T = 370, \alpha = 5 \). If the temperature is lowered to 369.5, which is the critical temperature of propane, then the spinodal reaches the vertical axis and below that temperature it is a nearly horizontal band that reaches across the entire interval \( 0 < x < 1 \). The blue lines are isobars, the red ones and the light blue ones are loci of the chemical potentials.](image2)

**Fig. 6.2.3.** Density diagram for (the same model of) the mixture of methane and propane at \( T = 370, \alpha = 5 \). If the temperature is lowered to 369.5, which is the critical temperature of propane, then the spinodal reaches the vertical axis and below that temperature it is a nearly horizontal band that reaches across the entire interval \( 0 < x < 1 \). The blue lines are isobars, the red ones and the light blue ones are loci of the chemical potentials.
The slope of the radial line in Fig. 6.2.3 is the concentration \( \rho_2/\rho_1 \). In the most standard type of experiment the system moves out along a radial line as the pressure is increased. If the radial line intersects the spinodal oval, then the system moves along the radial until, before quite touching the spinodal, it reaches a point of condensation, the dew point, shown in Fig. 6.2.3 as \( A \), with density \( \vec{\rho}^u = (x^u, y^u) \).

What happens next, as the pressure is further increased, is this. In addition to the gas at the point \( A = \vec{\rho}^u \) there appears a liquid at the point \( B = \vec{\rho}^v \), on the same isobar. Initially the population of this point; that is, the total amount of liquid with this density, is negligible, but with increasing pressure the system gradually transfers, by condensation, from \( A \) to \( B \). To maintain the average concentration of the total sample this transfer is accompanied by a movement of both points towards the right, along “lines of coexistence” at a nearly constant distance from the spinodal. This continues until the upper point reaches the radial of the original concentration (the continuation of the original radial line) at which point the condensation is complete and the whole system is at the point \( B' \), the bubble point. The lower point of coexistence has moved from the original point \( A \) to reach the point \( A' \) (on the same isobar as \( B' \)) with the occupation diminishing to zero. Further increasing the pressure does not lead to any unusual phenomena, the liquid remains homogeneous, moving along the original radial line, upwards from \( B' \).

At lower temperatures the spinodal reaches the vertical axis, at \( T = 369.5 \), the critical temperature of Propane, as well as the vertical line \( x = 1 \). At still lower temperatures it approaches the horizontal axis at \( T = 306 \), the critical temperature of Ethane, as shown in Fig.6.2.4

![Figure 6.2.4](image)

Fig.6.2.4. As the two preceding figures but the temperature is slightly above the critical temperature of Ethane.

Experimental reports often give much less information, most experiments are stopped on reaching the dew point, to record the dew point pressure at the chosen temperature. In a companion experiment one starts with a homogeneous liquid at high pressure and traces out the approach to the point \( B' \), the bubble point. The actual separation is often not observed. Results are presented as a \( T, p \) graph.
Calculation of the line of coexistence

The theoretical calculation of the points of coexistence is painful without the assistance of an appropriate computer. These points are defined by the conditions of equilibrium,

\[ T^u = T^v, \quad p^u = p^v, \quad \vec{\mu}^u = \vec{\mu}^v. \]

The best strategy that was found is the following. Choose a value of \( T \) and an isobar and select a point \( \vec{\rho}_0 \) on it. Experience allows to select a point fairly close to the line of coexistence. Draw the loci (all for fixed \( T \) and \( \vec{\rho}_0 \))

\[ p(\vec{\rho}) = p(\vec{\rho}_0), \quad \mu_1(\vec{\rho}_1) = \mu_1(\vec{\rho}_0), \quad \mu_2(\vec{\rho}) = \mu_2(\vec{\rho}_0). \]

The last two should have two further intersections, one inside the spinodal (ignore it) and one on the upper side. This latter will probably not lie on the same isobar; in that case slide to point \( \vec{\rho}_0 \) along the chosen isobar until the required triple intersection is achieved on the upper side. This locates a pair of co-existent concentrations, the points \( A \) and \( B \). The points \( A' \) and \( B' \) are easily determined since they are known to be on the radial line of the original, average concentration.

VI.3. Sample applications - first example

This is all about mixtures of van der Waals fluids. The experimental literature is vast, but much of it reports only partial results; there is very little observation of actual separation. Theoretical attempts are, for the most parts, applications of van der Waals’ one-fluid method that we have already mentioned; more shall be said about this below. There have been many attempts to account for the data using variations of the van der Waals approach. Because these theories are phenomenological, and consequently subject to few constraints, they are often successful in reproducing selected data. The attempts reported here are also less than completely successful but the work is far from complete.

In this Section we continue to base the approach on the action principle, with a complete set of thermodynamical variables, with the approach to mixtures of Chapter V and with the component unaries modeled as van der Waals fluids. Because we aim at making predictions, we must restrict the number of free parameters; consequently our first attempt uses the following expression for the free energy density,

\[ f = f_1 + f_2 + f_{int}, \quad f_{int} = \alpha \rho_1 \rho_2. \]

There is only one free parameter, \( \alpha \), the van der Waals parameters in \( f_1 \) and in \( f_2 \) are determined by observations of the pure components. The interaction term is of the type used by others, but much more restricted; compare Scott and van Konigenburg’s

\[ f_{int} = Q(c)\rho^2, \]

where \( \rho \) is the total density, \( c \) is the concentration and \( Q \) is a polynomial – and these are not the only adjustable parameters.
Here we shall examine some mixtures of the simplest organic fluids. The critical parameters are

<table>
<thead>
<tr>
<th></th>
<th>(T_{cr})</th>
<th>(p_{cr})</th>
<th>(\rho_{cr})</th>
<th>(a)</th>
<th>(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>190.6</td>
<td>4.63</td>
<td>7.83</td>
<td>.229</td>
<td>.0427</td>
</tr>
<tr>
<td>Ethane</td>
<td>306</td>
<td>4.96</td>
<td>5.21</td>
<td>.550</td>
<td>.0640</td>
</tr>
<tr>
<td>Propane</td>
<td>369.5</td>
<td>4.52</td>
<td>3.95</td>
<td>.877</td>
<td>.0844</td>
</tr>
<tr>
<td>Butane</td>
<td>425.1</td>
<td>3.58</td>
<td>2.72</td>
<td>1.466</td>
<td>.123</td>
</tr>
</tbody>
</table>

Table. Units are MPa for pressure, MPa(Lit/mol)^2 for \(a\) and (mol/Lit) for \(b\). The figures are consistent with van der Waals’ formula within 1 percent.

The vapor pressures of ethane and propane are calculated from the van der Waals formula and collected in the following

<table>
<thead>
<tr>
<th></th>
<th>(T)</th>
<th>(p)</th>
<th>(\text{Exp.})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>306</td>
<td>4.97</td>
<td>4.96</td>
</tr>
<tr>
<td></td>
<td>290</td>
<td>4.00</td>
<td>3.51</td>
</tr>
<tr>
<td>Propane</td>
<td>369.5</td>
<td>4.55</td>
<td>4.09</td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>4.1</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Table. Vapor pressure of Ethane and Propane. “Exp.” stands for ‘Experimental value of the pressure’. For propane, these are very difficult to find; and most of the discrepancy arises from the inconsistency of the few experimental figures. For consistency the numbers 4.55 and 4.09 in the first column should have been equal. Pressure in MPa.

As an approximation to the real, unary fluids, the van der Waals model is successful in the qualitative sense. Quantitatively, it usually reproduces the experimental properties to better than 10 percent accuracy near the critical temperatures, better at higher temperatures but progressively less well at lower temperatures. Our hope is to develop a model of the mixtures with a comparable degree of agreement with experiments.

**Binary van der Waals mixtures. Formulas**

For a mixture of any two van der Waals fluids, the assumed free energy density is

\[ f = f_1 + f_2 + \alpha R (\rho_1 \rho_2)^k, \]

with the constant \(\alpha\) of order unity and \(k = 1\). To simplify we set \(x = b_1 \rho_1, y = b_2 \rho_2\), We also drop the factor \(T^n\) in the logarithm since it makes no contribution to the determination of the equilibrium,

\[ f_1 = \frac{R}{b_1} \left( T x \ln \frac{x}{1-x} - \frac{27}{8} T_1 x^2 \right), \quad f_2 = \frac{R}{b_2} \left( T x \ln \frac{y}{1-y} - \frac{27}{8} T_2 y^2 \right) \]
and
\[ f = \frac{\mathcal{R}}{b_1} \left( T x \ln \frac{x}{1-x} - \frac{27}{8} T_1 x^2 \right) + \frac{\mathcal{R}}{b_2} \left( T y \ln \frac{y}{1-y} - \frac{27}{8} T_2 y^2 \right) + \alpha \mathcal{R} \left( \frac{xy}{b_1 b_2} \right)^k; \]

\( T_1 \) and \( T_2 \) are the critical temperatures of the constituents. The derivatives of the free energy density are, when the exponent \( k \) in (6.2.1) is unity,
\[ \mu_i(x, y) = \mathcal{R} T \left( \ln \frac{\rho_i}{\left(1 - b_i \rho_i\right) T^{n_i}} + \frac{1}{1 - b_i \rho_i} \right) - 2a_i \rho_i + \alpha \mathcal{R} \rho_j, \quad i, j = 1, 2 \text{ or } 2, 1. \]

and
\[ f_{ii} = \frac{\mathcal{R} T}{\rho_i (1 - b_i \rho_i)^2} - 2a_i, \quad i = 1, 2, \quad f_{12} = \alpha \mathcal{R}. \]

The thermodynamic pressure is
\[ \frac{p}{\mathcal{R}} = \frac{1}{b_1} \left( T \frac{x}{1-x} - \frac{27}{8} T_1 x^2 \right) + \frac{1}{b_2} \left( T \frac{y}{1-y} - \frac{27}{8} T_2 y^2 \right) + \frac{\alpha}{b_1 b_2} xy. \]

The spinodal, a two-dimensional manifold in the 3-space with coordinates \( T \) and the two densities, is defined by
\[ \text{det} \left( \frac{\partial^2 f}{\partial \rho_i \partial \rho_j} \right) = 0. \]

In a form suitable for the computer,
\[ f_{11} = \mathcal{R} b_1 \left( T \frac{1}{x(1-x)^2} - \frac{27}{4} T_1 \right), \]
\[ f_{22} = \mathcal{R} b_2 \left( T \frac{1}{y(1-y)^2} - \frac{27}{4} T_2 \right), \]
and \( f_{12} = f_{21} = \alpha \). The spinodal is thus the locus
\[ b_1 b_2 \left( T \frac{x}{x(1-x)^2} - \frac{27}{4} T_1 \right) \left( T \frac{y}{y(1-y)^2} - \frac{27}{4} T_2 \right) = \alpha^2. \]

(6.3.3)

For a fixed value of \( T \) it is empty unless \( T \) is less than a “maximal” value that, for the Ethane/Propane mixture with \( \alpha = 10 \), is
\[ T_{max} = 375.4 K. \]

The variation of this with the strength of the interaction is shown in the Table.

<table>
<thead>
<tr>
<th>( \alpha )</th>
<th>1</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_{max} )</td>
<td>369.6</td>
<td>369.8</td>
<td>371.1</td>
<td>375.4</td>
<td>443.6</td>
</tr>
<tr>
<td>( p/\mathcal{R} )</td>
<td>1661</td>
<td>1685.5</td>
<td>1765</td>
<td>1930</td>
<td>2860</td>
</tr>
<tr>
<td>( p )</td>
<td>13.81</td>
<td>14.01</td>
<td>14.67</td>
<td>16.05</td>
<td>23.78</td>
</tr>
</tbody>
</table>
TABLE. Maximal temperature, being the highest temperature at which separation occurs, for Ethane/Propane with varying interaction strength.

At this value of \( T \) the spinodal is a single point at \( x = y = 1/3 \). Below this value the single point opens to a closed oval, as shown in Fig.6.2.2-3. Both figures also show two isobars, each of which cuts the oval. Straight lines from the origin are lines of constant concentration; in Fig.6.2.2 they are tangent to the ovals.

**Coexistence**

The conditions for coexistence of two mixtures is the continuity of \( T, p \) and

\[
\mu_i(x, y) = \mathcal{R}T \left( \ln \frac{\rho_i}{(1 - b_i\rho_i)T^n_i} + \frac{1}{1 - b_i\rho_i} \right) - 2a_i\rho_i + \alpha\rho_j, \quad i, j = 1, 2 \text{ or } 2, 1.
\]

An efficient way to perform the calculation was already presented.

The dynamical variables have the following values at points \( A, A', B, B' \), in Fig.6.2.3.

<table>
<thead>
<tr>
<th>Point</th>
<th>( x^u )</th>
<th>( y^u )</th>
<th>( p/R )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A )</td>
<td>.3</td>
<td>.3</td>
<td>1658</td>
</tr>
<tr>
<td>( B )</td>
<td>.291</td>
<td>.370</td>
<td></td>
</tr>
<tr>
<td>( A' )</td>
<td>.373</td>
<td>.294</td>
<td>1847</td>
</tr>
<tr>
<td>( B' )</td>
<td>.364</td>
<td>.364</td>
<td></td>
</tr>
</tbody>
</table>

Table. The two pairs of coexistent mixtures for given initial low density, 50-50, gaseous, model mixture of ethane and propane. Most experiments measure only the pressure.

**Points that are critical to the experimenter**

In a region of temperatures just below \( T_{\text{max}} \) the spinodal is an oval, simply connected and convex. In a typical experiment one starts with a low pressure and low densities, \( x \) and \( y \) normalized molar densities less than \( 1/3 \). The mixture is homogeneous. The pressure is increased, or the temperature is increased, or both, but the concentration is kept fixed. One is moving out from the origin of the density diagram along one of the radials. This radial may cross the spinodal or it may pass to the left or to the right of it. In the first case separation will occur at a point below the spinodal; what happens here was described in Section VI.2. Fig.s 6.2.2 and 6.2.3 illustrate this in the case of a model.

As the temperature is changed the intersection of any radial line eventually becomes tangent to the spinodal. The meniscus disappears if this point is very close to the spinodal, as in Fig.6.2.2; at that point the densities of liquid and gas become equal; these are the critical points reported by the experimenter. As the temperature descends to \( T_2 \), the critical temperature of the least volatile gas, the oval reaches the vertical axis. Below this temperature there is an interval of temperatures where the oval still may have a radial tangent at the high end, at very high pressures, then this also disappears. At still lower temperatures, as we approach the critical point of the other gas, it returns. See Fig.6.2.4.

This behavior of the model is in contradiction with experiments. We must conclude that our first choice of \( f_{\text{int}} \) is inappropriate, but before looking for alternatives we shall look briefly at another example, the Argon-Oxygen system.

142
The critical points to the experimenter are the configurations at which the radials determined by the concentration are tangent to the spinodal oval. They are uniquely determined by the temperature, at least for temperatures close to $T_{\text{max}}$. Figs. 6.2.2-4 show the shape of the spinodal for a descending series of temperatures, for a model that has $f_{\text{int}} \propto \rho_1 \rho_2$.

**Remark.** The study of mixtures in terms of expressions for the free energy are legion in the literature. It is unexpected, however, to encounter an approach that is phenomenological to the point that additional input, an “equation of state” or more precisely an expression for the pressure, is needed (Hicks and Young 19); this even in the case that the inspiration comes from van der Waals and the free energy had already been used. In thermodynamics, the pressure is determined by the free energy density, $p = \bar{\rho} \cdot \nabla f - f$. But the ‘free energy’ of the one-fluid model is not the thermodynamic free energy and the one field model is not thermodynamics. Consequently, the formula that is used to calculate the critical points is without justification. Separate phenomenological input (with additional adjustable parameters) is invoked in the form of an independent relation between pressure and temperature.

**VI.4. Mixture of two van der Waals fluids. Second example**

The plan for this section is not just to study another mixture, but to consider another type of interaction.

Here we examine mixtures of Argon and Oxygen. These two gases have approximately the same van der Waals parameters.

**Gas number 1, Argon,** $\mu_1 = 40$, $n_1 = 3/2$, $T_1 = 150K$, $p_1 = 4.9MPa$, $a_1 = 1.355$, $b_1 = .03201$.

and

**Gas number 2, Oxygen,** $\mu_2 = 32$, $n_2 = 5/2$, $T_2 = 155K$, $p_2 = 5MPa$, $a_2 = 1.382$, $b_2 = .03186$.

The units are bar liter$^2$/mol$^2$ for $a$ and liter/mol for $b$.

We begin by examining the spinodals isobars, Eq. 6.4.1:

$$b_1 b_2 \left( \frac{T}{x(1-x)^2} - \frac{27}{4} T_1 \right) \left( \frac{T}{y(1-y)^2} - \frac{27}{4} T_2 \right) = \alpha^2. \quad (6.4.1)$$

this relates $\alpha$ directly related to $T_{\text{max}}$, the highest temperature at which separation can occur at any concentration, the critical temperature We should like to begin by choosing the best value of the coupling strength $\alpha$. Unfortunately, this is rarely measured. Jones and Rawlinson (196) tell us only that $T_{\text{max}}$ is higher than 149.4K; our model says that it is higher than 155. the Table relates $T_{\text{max}}$ to $\alpha$. 

143
$T_{max}$ $\alpha$

155.2 .001
156.0 .0032
160.0 .0098
164.2 .0160
171.2 .0260
179.6 .0380
186.7 .048

TABLE. The highest temperature at which separation occurs, as a function of the strength of the interaction $f_{int} = \alpha \rho_1 \rho_2$.

Fig 6.4.1 shows the spinodal for $\alpha = .016$, $T = 160K$. In Fig.6.4.2 $T = 155K$, which is the critical temperature of Oxygen, the spinodal oval has grown to reach the vertical axis. In Fig. 6.4.3 the temperature is 149.4K, the highest temperature recorded by Jones and Rawlinson. The blue line is the locus of the concentration, value .202 as in the experiment. According to observation, this is a critical point so we expect it to be nearly tangent to the spinodal. Since the temperature is below the critical temperature (155K) of oxygen, this is in clear disagreement with the model.
Later we shall attempt to understand the propagation of sound in mixtures, with the same model and the same interaction as we have used here, $f_{\text{int}} = \alpha \rho_1 \rho_2$, to find that it cannot account for sound propagation either. Instead, what works very well for the speed of sound is

$$f_{\text{int}} = \alpha \sqrt{\rho_1 \rho_2}.$$  

Although the success of this model in accounting for the speed of sound refers to experiments at room temperature, it is natural to ask what it can do for the critical phenomena being discussed here. Indeed, our approach obbliges us to use the same Lagrangian for both phenomena. As we have stressed, this is an essential feature of our method, the main source of a greatly enhanced predictive power.

**The square root interaction density for mixtures**

It was natural to expect that the expression for the interaction energy take the same form as the self-interaction energy in van der Waals formula. That is why we have given this idea a fair hearing, to see it fail. We already had some experience with sound propagation that suggested a different form for $f_{\text{int}}$ (Fronsdal 2011). To test the idea that the same Lagrangian density must serve for both phenomena we now investigate the viability of

$$f_{\text{int}} = \mathcal{R} \alpha \rho_1 \rho_2 + \mathcal{R} \alpha' \sqrt{\rho_1 \rho_2},$$

with $\alpha$ provisionally equal to zero. The chemical potentials

$$\mu_1 = f_1 = \mathcal{R} T \left( \ln \frac{\rho_1}{(1 - b_1 \rho_1) T^{m_1}} + \frac{1}{1 - b_1 \rho_1} \right) - 2 a_1 \rho_1 + \mathcal{R} \frac{\alpha'}{2} \sqrt{\rho_2 / \rho_1},$$

$$\frac{f_{11}}{\mathcal{R}} = b_1 \left( \frac{T}{x(1 - x)^2} - \frac{27}{4} T_1 \right) - \frac{\alpha'}{4} \sqrt{b_1^3 / b_2} \sqrt{y / x^3},$$

$$\frac{f_{12}}{\mathcal{R}} = \frac{\alpha'}{4} \sqrt{b_1 b_2 / \sqrt{xy}}.$$
and the spinodal is the locus

\[ f_{11}f_{22} = \left( \frac{\alpha'}{4} \right)^2 \frac{b_1 b_2}{xy} \]

or

\[
\left( \frac{T}{x(1-x)^2} - \frac{27}{4} T_1 - \sqrt{\frac{b_1}{b_2}} \frac{\alpha'}{4} \sqrt{\frac{y}{x^3}} \right) \left( \frac{T}{y(1-y)^2} - \frac{27}{4} T_2 - \sqrt{\frac{b_2}{b_1}} \frac{\alpha'}{4} \sqrt{\frac{x}{y^3}} \right) = \left( \frac{\alpha'}{4} \right)^2 \frac{1}{xy}.
\]

To interpret it we need isobars. The pressure is independent of the interaction, simply

\[
p = \frac{1}{\mathcal{R}} \left( \frac{x}{1-x} T - \frac{27}{8} T_1 x^2 \right) + \frac{1}{\mathcal{R}} \left( \frac{y}{1-y} T - \frac{27}{8} T_2 x^2 \right).
\]

The expression for the \( \mu_i \) are

\[
\frac{\mu_1}{\mathcal{R}T_1} = \frac{T}{5.19} \left( \ln \frac{x}{1-x} + \frac{1}{1-x} \right) - \frac{27}{4} x + 36.0321 \sqrt{\frac{20}{50} y} + 0.3112 \alpha' \sqrt{\frac{y}{x}}
\]

\[
\frac{\mu_2}{\mathcal{R}T_2} = \frac{T}{290} \left( \ln \frac{y}{1-y} + \frac{1}{1-y} \right) - \frac{27}{4} y + 1.38765 \sqrt{\frac{20}{50} x} + 0.0133 \alpha' \mathcal{R},
\]

The formulas that we need are the free energy,

\[
\hat{f} = \frac{f b_1}{\mathcal{R}T_{c1}} = T_r x \ln \frac{x}{1-x} - \frac{27}{8} x^2 + b \left( T_r y \ln \frac{y}{1-y} - c \frac{27}{8} y^2 \right) + \beta xy,
\]

the chemical potentials,

\[
\mu_x(x,y) = T_r \left( \ln \frac{x}{1-x} + \frac{1}{1-x} \right) - \frac{27}{4} x + \beta y,
\]

\[
\mu_y(x,y) = b T_r \left( \ln \frac{y}{1-y} + \frac{1}{1-y} \right) - b c \frac{27}{4} y + \beta x,
\]

the second derivatives,

\[
f_{xx} = \frac{T_r}{x(1-x)^2} - \frac{27}{4}, \quad f_{yy} = b \frac{T_r}{y(1-y)^2} - b c \frac{27}{4}, \quad f_{xy} = \beta,
\]

and the pressure,

\[
p b_1 = T_r \left( \frac{x}{1-x} + b \frac{y}{1-y} - \frac{27}{8} (x^2 + b c y^2) \right) + \beta xy.
\]

Reasonable with the observations of Jones and Rowlinson is obtained with \( \alpha = 120 \), as shown in the Table and in Fig.s 6.4.4-7.
<table>
<thead>
<tr>
<th>$T$</th>
<th>$p$</th>
<th>$c$</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>132.0</td>
<td>520</td>
<td>.77</td>
<td>.798</td>
</tr>
<tr>
<td>138.0</td>
<td>760</td>
<td>.70</td>
<td>.599</td>
</tr>
<tr>
<td>143.8</td>
<td>865</td>
<td>.34</td>
<td>.401</td>
</tr>
<tr>
<td>149.4</td>
<td>1100</td>
<td>.19</td>
<td>.202</td>
</tr>
</tbody>
</table>

**TABLE.** The square root model with $\alpha = 120$. The third column is the (molar) concentration $c = x/(x+y)$. The temperatures are those of the experiment and the last column are the experimental concentrations. Experimental values of the pressure are not available.

The 4 experiments are illustrated by the plotting of the spinodal (purple) and the relevant isobar (blue) in the density plane, in Figs 6.4.4-7. Each radial (green) line is the path followed during one of the experiments, in which the concentration is constant. The experiment started at low density and pressure and was terminated at the dew point.

Quantitatively, the model agrees very well with the measurements. The shape of the spinodal is quite different in this model and this is the type of structure that is needed to account for the experiment of Jones and Rowlinson. It may be noted that the geometry exhibited at the first two points is quite different from the last two points; something that cannot be revealed by the experiment.

**Fig. 6.4.4.** Here $T = 149.4$.

**Fig. 6.4.5.** Here $T = 143.8$.  

147
Fig. 6.4.6. Here $T = 138K$.

Fig. 6.4.7. Here $T = 132K$.

**Nitrogen and Argon**

This case is very similar but there is less experimental information available.

**Gas number 1, Nitrogen**, $\mu_1 = 34$, $n_1 = 5/2$, $T_1 = 126.3$, $b_1 = .03913$.

**Gas number 2, Argon**.

Taking $\alpha' = 100$ we get a good fit to 3 out of four experimental points.

<table>
<thead>
<tr>
<th>$T$</th>
<th>$p$</th>
<th>$c$</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>131.0</td>
<td>580</td>
<td>.58</td>
<td>.8</td>
</tr>
<tr>
<td>134.5</td>
<td>600</td>
<td>.42</td>
<td>.6</td>
</tr>
<tr>
<td>141.0</td>
<td>865</td>
<td>.4</td>
<td></td>
</tr>
<tr>
<td>146</td>
<td>1100</td>
<td>.30</td>
<td>.2</td>
</tr>
</tbody>
</table>

TABLE. Nitrogen and Argon. The first 3 column gives the result of our model; the last is experimental.

These bare numbers do not give an idea of the complicated picture that is illustrated in Figs 6.4.8-10. The picture changes very rapidly with the input parameters, so that experimental uncertainties play a role.

We conclude that the Lagrangian with a square root interaction is in qualitative agreement with measurements if the interaction strength $\alpha'$ is near $100(cm/sec)^2$. Later we shall see that the same Lagrangian can account for the speed of sound in the mixture.
Fig. 6.4.8. The singular point for $T = 146$ and $\beta = \pm 3$.

Fig. 6.4.9. The singular point for $T = 134.5$ and $\beta = \pm 3$. 

149
Fig. 6.4.10. The singular point. for $T_r = 146$ and $\beta = \pm 3$.

Fig 6.1.6 is a clear example to show what happens near a critical point. We plot loci of $\mu_1$ (red curves) and $\mu_2$ (blue curves), for the same value of $T$, $\alpha$ and densities $(x, y) = (a, .6a)$. This is the value of $x$ at the point where the line $y = .6x$ nearly touches the closed line. This is the case shown in Fig.6.1.6, where the three loci of $\mu_1, \mu_2$ and $p$ are seen to touch, and in Fig.6.4.3. This is a critical point of the set of configurations that is projected out by fixing the relative concentration to $y/x = .6$.

This scenario is close to the experimental situation. One begins with a homogeneous mixture at the higher temperature and reduces the temperature very slowly. At the critical temperature condensation sets in, the 10-to-6 homogeneous mixture seizes to be stable.
VI.5. Helium and Xenon

Critical parameters:

He: \( T_{cr} = T_1 = 5.19 K, \quad p_{cr} = 2.24 \text{atm} = 227 kPa, \)

\( \text{Xe: } T_{cr} = T_2 = 289.8 K = 16.6^C, \quad p_{cr} = 57.6 \text{atm} = 5840 kPa. \)

Van der Waals parameters:

He: \( a_1 = .0346 \text{bar}\text{Lit}^2/\text{mol}^2, \quad b_1 = .0237 \text{Lit}/\text{mol} \)

\( \text{Xe: } a_2 = 4.250 \text{bar}\text{Lit}^2/\text{mol}^2, \quad b_2 = .05105 \text{Lit}/\text{mol} \)

Interaction \( f_{int} = \mathcal{R}\alpha \rho_1 \rho_2 \)

This is a mixture that has been difficult to deal with; the van der Waals approach has not been successful. We begin by briefly confirming this within our framework.

The free energy density is thus \( f = f_1 + f_2 + \mathcal{R}\alpha \rho_1 \rho_2 \).

**The maximal (critical) temperature**

The maximal temperature of the mixture is the lowest temperature for which the determinant of the matrix of second partial derivatives of the free energy is positive definite, at this point

\[
\begin{align*}
&b_1 b_2 \left( \frac{T}{x(1-x)^2} - \frac{27}{4} T_1 \right) \left( \frac{T}{y(1-y)^2} - \frac{27}{4} T_2 \right) = \alpha^2. \\
\end{align*}
\]

(6.5.1)

We list the critical temperature for some values of the coupling strength.

\[
\begin{align*}
&\alpha^2 = 507, \quad T_{cr} = 340 \\
&\alpha^2 = 50, \quad T_{cr} = 295.7 \\
&\alpha^2 = 40, \quad T_{cr} = 294.6 \\
&\alpha^2 = 30, \quad T_{cr} = 293.5 \\
&\alpha^2 = 20, \quad T_{cr} = 292.3 \\
&\alpha^2 = 8.5, \quad T_{cr} = 291
\end{align*}
\]

**TABLE**

These values are taken from a graph, more accurate values can be obtained digitally, for example, at \( \alpha^2 = 50, \ T_{cr} = 295.686 \). From now on this is the value of \( \alpha \) that have been used. The associated value of the normalised densities are 1/3; this gives the exact expression

\[
T_{cr} = \frac{T_1 + T_2}{2} + \sqrt{\frac{4}{27} \alpha^2 T_1 T_2 + \left( \frac{T_1 - T_2}{2} \right)^2}. \\
\]

(6.5.2)

For \( \alpha^2 = 50 \) it gives \( T_{cr} = 295.686 \), both Mathematica (File Untitled-2) and Graphing Calculator.

The densities are molar, so \( \mathcal{R} \) is the universal gas constant.
In a series of illustrations we show the spinodal for $\alpha^2 = 50$ and temperatures ranging from 292.5K to 150K. As expected, the spinodal oval exists for $T \leq 295K$ and reaches the vertical axis when $T = 289.8K$. Sample coexistent points are shown in each figure, again as expected each pair of coexistent densities bracket the spinodal at a distance is nearly constant except when the isobar is tangent to the spinodal; these are the configurations that are labelled “critical” in the sense of the experimenter.

Confrontation with experiments makes it very clear that this model is not realistic. Comment on individual experiments?

We plot loci of the chemical potentials and the pressure for this temperature, 

$$\frac{\mu_1}{RT_1} = \frac{T}{T_1} \left( \ln \frac{x}{1-x} + \frac{1}{1-x} \right) - \frac{27}{4} x + \frac{\alpha}{b_1 RT_1} y - \frac{T}{T_1} \ln(b_1 T^{3/2}),$$

$$\frac{\mu_2}{RT_2} = \frac{T}{T_2} \left( \ln \frac{y}{1-y} + \frac{1}{1-y} \right) - \frac{27}{4} y + \frac{\alpha}{b_1 RT_2} x - \frac{T}{T_2} \ln(b_2 T^{3/2}),$$

Finally, for He-Xe,

$$\frac{\mu_1}{RT_1} = \frac{T}{5.19} \left( \ln \frac{x}{1-x} + \frac{1}{1-x} \right) - \frac{27}{4} x + 36.0321 y - \frac{T}{T_1} \ln(b_1 T^{3/2})$$

$$\frac{\mu_2}{RT_2} = \frac{T}{290} \left( \ln \frac{y}{1-y} + \frac{1}{1-y} \right) - \frac{27}{4} y + 1.38765 x - \frac{T}{T_2} \ln(b_2 T^{3/2}),$$

We also plot the pressure

$$p = \frac{T}{R} \left( \frac{x}{1-x} - \frac{a_1}{R b_1^2} x^2 + \frac{1}{54 b_2} \frac{y T}{1-y} - \frac{a_2}{R b_2^2} y^2 + \frac{\alpha}{R b_1 b_2} x y \right)$$

$$p = \frac{299 T}{.0237 (1-x)} - \frac{a_1}{R b_1} x^2 + \frac{299 T}{.051} \frac{y}{1-y} - \frac{a_2}{R b_2^2} y^2 + 7890 x y$$

We plot all three curves.

This gives, at the critical point, for the above functions, $p/R = 7773.53$ and

$$\frac{\mu_1}{RT_1} + \frac{T}{T_1} \ln(b_1 T^{3/2}) = \frac{T}{T_1} \left( \ln \frac{x}{1-x} + \frac{1}{1-x} \right) - \frac{27}{4} x + \sqrt{\frac{b_1 T_2}{b_2 T_1}} \beta y = 55.72893$$

$$\frac{\mu_2}{RT_2} + \frac{T}{T_2} \ln(b_2 T^{3/2}) = \frac{T}{T_2} \left( \ln \frac{y}{1-y} + \frac{1}{1-y} \right) - \frac{27}{4} y + \sqrt{\frac{b_2 T_1}{b_1 T_2}} \beta x = -964777.$$
\[ \frac{\mu_2}{RT_2} = -.957782 - 5.72823 = -6.68601. \]

All three curves intersect at \( x = y = 1/3 \) with a common tangent when \( T = T_{cr} = 295.2K \).
See file Singular10.

When we lower the temperature we get triple intersections as in the earlier case treated, where the gases were similar. If we increase the temperature we get only a simple intersection. See Fig.s Singular4,5 where the temperature is 298.2.

I have repeated this and, most important, the triple intersections appear just as expected. The two intersections between the \( \mu_i \) curves do not automatically have the same pressure. I find that the pressure must be lowered to bring it about. This is all as expected, but there is something to understand.

There is no concentration separation for high temperature, and in order to enter a region in which such separation exists it is necessary to open the oval. Once the oval is open; that is when \( T < T_{max} \), the fluid separates into two parts, either as a fog in a background or, with the help of time and gravity, into two separated mixtures. When it does separate it finds on each isobar, two compatible densities, on either side of the oval, outside the oval. As we continue to lower the temperature the oval grows but the coexistent posts continue to keep clear. They move south from the critical point \((1/3,1/3)\) and we must try to trace out their paths, these are the lines of coexistent mixtures.

A large part, with figures is missing. The figures should be recovered with little comment.

Preliminary results for coexistence. \( T_{cr} = 295.686, \mu_1 = 55.72893, \mu_2 = -.964777, \rho = 7695.844 \). Files Singular10 and singularjfc2.

\[
\begin{align*}
T = 295, \mu_1 = 55.7293, \mu_2 = -.9662, p = 7690(7675), \delta y = .002. \\
T = 295, \mu_1 = 50, \mu_2 = -.9874, p = 7250, 7235 \\
T = 295, \mu = 30, \mu_2 = -1.06, p = 5845, 5835 \\
T = 295, \mu = 20, \mu^2 = -1.095, p = 5230, 5220, \rho = (-.090, -.023)(-.095, .022) \\
T = 295, \mu_1 = 10, \mu_2 = -1.096 \\
T = 295, \mu_1 = 0, \mu_2 = -1.161
\end{align*}
\]

At these points there is no longer a triple intersection. I have gone too far.

\[
\begin{align*}
T = 294, \mu_2 = -.9684, p = 7675(7650), \delta y = .005. \\
T = 294, \mu_1 = 0, \mu_2 = -1.1637, p = 4150, 4140, \rho = (-.137, -.035)(-.143, .036) \\
T = 293, \mu_1 = 0, \mu_2 = -.9705, p = 7660(7630), \delta y = .006. \\
T = 293, \mu_1 = -40, \mu_2 = -1.2748, p = 2610, 2606, \rho = (-.217, -.017), (-.219, .017). \\
\end{align*}
\]

Too far?
Try to change $\mu_1$ to get a smaller spread of pressures,

$T = 292, \mu_1 = 50, \mu_2 = -.992, p = 7220(7180)$ no improvement.

$T = 292, \mu_1 = 60, \mu_2 = -.957, p = 8000(7995)$ much better, $\rho = (.02, -.07), (.0056, .076)$

$T = 292, \mu_1 = 0, \mu_2 = -1.17, p = 4110, 4090, \rho = (-.135, -.067), (-.145, .063)$

$T = 280, \mu_1 = 60, \mu_2 = -.957, p = 7970(7910), \delta y = -.075, +.1.$

$T = 280, \mu = -200, \mu_2 = -1.465, p = 8000, 686.2, \rho$

All lie outside the oval.
The adiabatic condition

So far we have not used the Euler-Lagrange equations, only the axiom that two compatible mixings can occur. The main Euler-Lagrange equations are

\[ \dot{\Phi}_i^a - \mu_i^a - S_i^a T = 0, \quad i = 1, 2, \quad a = u, v. \]

Here the index \( i \) stands, as always, for He and Xe, while \( a \) stands for the two phases. This is nothing unless we know something about the constants \( \dot{\Phi}_i^a \). Before we get into that let us see what we get from the adiabatic condition.

Above the critical point we have a normal mixture of van de Waals gases. Let us lower the temperature slowly, so that over short times both \( S_1 \) and \( S_2 \) are fixed, and that over a longer time they have time to adjust to the Gibbs-Dalton hypothesis. Thus at equilibrium

\[ R \ln \frac{\rho_i^a}{(1 - b_i \rho_i)(eT)^n_i} + S_i = 0, \quad i = 1, 2, \quad a = u, v. \]

At equilibrium, the upper index on the densities, and therefore also on the specific entropies are redundant. So we can let \( \rho_i \) and \( S_i \) denote the values of these quantities at the critical point. More simply

\[ S_i/R = -n_i \ln(2b_i \ln eT_{\text{crit}}), \]

Next, we combine this with the result of the calculations,

\[ \frac{\mu_1}{RT_1} + S_1/RT_1 = -211.931T_1 - \frac{3/2}{T_1} \ln(2b_1 eT_{\text{crit}}) \]

\[ = -211.931 + (1.5/5.19) \ln 5.19 = 211.931 + .909 = 212.84. \]

\[ \frac{\mu_2}{RT_2} + S_2/RT_2 = -211.931T_2 - \frac{3/2}{T_2} \ln(2b_2 eT_{\text{crit}}) \]

\[ = -8.16574 + (1.5/290) \ln 290 = 8.16574 + .03709 = 8.20299. \]

Here we are in the same position as in the case of normal saturation of a uniform van der Waals fluid. We can change the volume, isothermally, then the volumes \( V^u \), \( V^v \) alone can change, until one or the other disappears. A further change in volume must lead to a change in pressure or in temperature.

Nothing dramatic happens as the temperature is reduced to the critical point; there is no discontinuity in the concentration, just a bifurcation. The mixtures differ infinitesimally at first and it will take time for the new equilibrium to be reached. If we lower the temperature only a milli-Kelvin below critical, then there will be time for the new equilibrium to be reached.

This result stands by itself, without any discussion of the entropy. However, our main purpose is to find a Lagrangian that accounts for both sound speeds and immiscibility.

To establish the sound speeds we had to make some assumption about the distribution of
entropy among the two gases. We chose to apply the Gibbs-Dalton hypothesis, so now we must verify that it is compatible with the result obtained for immiscibility.

The adiabatic condition is

\[
\frac{x}{3b_1} \left( \ln \left( \frac{x}{3b_1} \right) - 3/2 \right) + \frac{x}{3b_1} \frac{S_1}{R} + \frac{1}{3b_2} \frac{S_2}{R} + \frac{y}{3b_2} \left( \ln \left( \frac{y}{3b_2} \right) - 3/2 \right) = 0.
\]

We have two parameters to satisfy this last condition and at the same to make the curve tangent to the isobar. This works very well to give

\[
\frac{S_1}{R} = 7.525, \quad \frac{S_2}{R} = 6.645.
\]

Taking these values of the entropy parameters we can calculate \( \dot{\Phi}_1 \) and \( \dot{\Phi}_2 \) at the critical point and that completes the determination of the mixture. File Gibbs-D We still have to verify what happens as we move to substantially lower temperatures. See file SingularG-D and repeat the calculation a correlation between pressure and densities.

**Summary**

1. We found the critical point, \( T_{cr} = 299 K, x = y = 1/3 \).
2. We verified the behaviour in the neighbourhood of the critical point, not yet very far below.
3. We cannot yet calculate the entropies, but we find that it is consistent to make them satisfy the Gibbs-Dalton hypothesis.
4. Unique values are obtained for \( S_1 \) and \( S_2 \).
5. We need experimental information about miscibility of Helium and Xenon. What is the experimental critical point and what are the densities at that point?
6. It turns out that the interaction has very little effect on the Gibbs-Dalton mechanism.

More accurate results. I measured, for several temperatures, the coexistent densities, then calculated the corresponding pressures. The strategy was to assume that \( \mu_1 \) would change little. The first step consisted of choosing a \( \mu_2 \) locus that would intersect the \( \mu_1 \) locus symmetrically, see Fig and reading the densities at the two intersection own interest, ignoring the one in the middle. Then I calculated the pressures of these two densities; if they differed I adjusted \( \mu_1 \), only a small adjustment was necessary, as seen in the Table.

Useful? Skip to page 169

The density data is in file coexist. The spinodal are in files 295-270.
To finish the calculation of the chemical potentials at the critical point.

\[
\frac{\mu_1}{R T_1} = \frac{T}{5.19} \left( \ln \frac{x/b_1}{1-x} + \frac{1}{1-x} \right) - \frac{27}{4} x + 910 y = 320 - \frac{T}{T_1} \ln b_1,
\]

\[
\frac{\mu_2}{R T_2} = \frac{T}{295} \left( \ln \frac{y/b_2}{1-y} + \frac{1}{1-y} \right) - \frac{27}{4} y + 0.088 x = -1.395 - \frac{T}{T_2} \ln b_2,
\]

(When plotting we do not use the values indicated for the constant terms.) Next we must interpret the last term on the left side as \(\alpha/3b_2 R T_1\). Here

\[
\frac{\alpha}{R} = \sqrt{\beta T_1^2 T_2} = \sqrt{50 \times 5.19 \times 290} = 274.3,
\]

\[
\frac{\alpha}{3b_2 R T_1} = \frac{274.3}{.1503 T_1} = 743
\]

\[
\frac{\alpha}{3b_1 T_2 R T_2} = \frac{274.3}{.0711 T_2} = 6.28
\]

Figure Singular 4 shows that the loci of \(\mu_1, \mu_2\) and the pressure are tangent at this point. At a slightly lower temperature they all cross at 3 points. This is clear indication that two compatible mixtures are being created. We find that this is in fact the point where the two loci touch; at a slightly lower temperature they cross three times.

This calculation is sensitive to terms like \(\rho T\) in the free energy, so we cannot determine immediately whether the two chemical potentials are equal or not. For this we have to take into account that the complete formula is. For this reason, the last terms in the figure are phenomenological.

To interpret this in terms of meaningful quantities we must express it in terms of \(\mu_1\) and \(\mu_2\).

The entropy

\[
\mu_1 = RT \left( \ln \frac{\rho_1}{(1-b_1 \rho_1)T^{3/2}} + \frac{1}{1-b_1 \rho_1} \right) - 2a_1 \rho_1 + \alpha \rho_2 - S_1 T.
\]

note. The vdW parameters are given in molar densities so we have to use the same; hence there is no index on \(R\). Here appears the specific entropy \(S_1\). Up to now, when the question was to determine the critical temperature, there was no need to discuss the entropy. In the traditional approach the expression used for the free energy includes phenomenological parameters referred to as free energy of mixing. Instead, we shall use the condition of equilibrium, \(\mu_1 = \mu_2\) to determine a relation between \(S_1\) and \(S_2\), expecting that they are constant. More precisely, we shall determine the quantity

\[
(S_1 - S_2) T,
\]
expecting a linear function of $T$. This will be derived within the theory, without any experimental input. To do this we use the fact that we know the values of the variables at the critical point,

$$
\mu_1 = R 259 \left( \ln \frac{1/3b_1}{(2/3)(259)^{3/2}} + \frac{1}{2/3} \right) - 2 \frac{a_1}{3b_1} + \frac{\alpha}{3b_2} - 259 S_1,
$$

with $b_1 = .0237$,

$$
\frac{\mu_1}{R} = 259 \left( \ln \frac{14.065}{2778.8} + 1.5 \right) - 2 \frac{a_1}{3b_1R} + \frac{\alpha}{3b_2R} - 5.19 \frac{S_1}{R},
$$

Here,

$$
\frac{a_1}{b_1 R} = \frac{27}{8} T_1
$$

and

$$
\frac{\alpha}{R} = \sqrt{T_1T_2} = \sqrt{5.19 \times 290 \times 50} = 274.3.
$$

Thus

$$
\frac{\mu_1}{R} = -980.60 - \frac{27}{4} \times 5.19 + \frac{1}{3 \times .0237} \times 259.25 - 259 \frac{S_1}{R}
$$

Next

$$
\frac{\mu_2}{R} = 5.19 \left( \ln \frac{1/3b_2}{(2/3)(5.19)^{3/2}} + \frac{1}{2/3} \right) - 2 \frac{a_2}{3b_2R} + \frac{\alpha}{3b_1R} - 5.19 \frac{S_2}{R},
$$

with $b_2 = .051$,

$$
\frac{\mu_2}{R} = R 5.19 \left( \ln \frac{6.536}{7.882} + 1.5 \right) - 2 \frac{a_2}{3b_2R} + \frac{\alpha}{3b_1R} - 5.19 \frac{S_2}{R},
$$

Here

$$
\frac{a_2}{b_2 R} = \frac{27}{8} T_2, \quad \frac{\alpha}{3b_2 R} = \beta_2
$$

VI.8. The square root interaction density This section is not finished.

We have used a square root for the interaction to calculate sound speeds and the bilinear interaction suggested by van der Waals for the investigation of miscibility. This is against common sense, for there should be a universal Lagrangian to cover both. To achieve reconciliation we shall now begin with another review of critical phenomena, using a compromise,

$$
F_{\text{int}} = \alpha \rho_1 \rho_2 + \alpha' \sqrt{\rho_1 \rho_2}.
$$
The spinodal line is now defined as the locus of
\[
\left( \frac{T/5.19}{x(1-x)^2} - \frac{27}{4} - \beta_1^1 \sqrt{\frac{y}{x^3}} \right) \left( \frac{T/290}{y(1-y)^2} - \frac{27}{4} - \beta_2^2 \sqrt{\frac{x}{y^3}} \right) = \left( \sqrt{\beta} + \frac{\beta_1^2}{\sqrt{xy}} \right) \left( \sqrt{\beta} + \frac{\beta_2^1}{\sqrt{xy}} \right)
\]
with
\[
\beta := \frac{\alpha^2}{b_1 b_2 T_1 T_2 R^2}
\]
and
\[
\beta_1^1 = \frac{\alpha'}{4RT_1} \sqrt{\frac{b_1}{b_2}} = .01556\alpha'/R, \quad \beta_1^2 = \frac{\alpha'}{4RT_1} \sqrt{\frac{b_2}{b_1}} = .03727\alpha'/R,
\]
\[
\beta_2^1 = \frac{\alpha'}{4RT_2} \sqrt{\frac{b_1}{b_2}} = .0002786\alpha'/R, \quad \beta_2^2 = \frac{\alpha'}{4RT_2} \sqrt{\frac{b_2}{b_1}} = .0006670\alpha'/R,
\]
Example: \( \beta = 20, \alpha'/R = 23 \) gives similar result with narrow spnod.

The expression for the pressure is not changed except for the value of \( \beta \). The expression for the \( \mu_i \) are
\[
\frac{\mu_1}{RT_1} = \frac{T}{5.19} \left( \ln \frac{x}{1-x} + \frac{1}{1-x} \right) - \frac{27}{4} x + 36.0321 \sqrt{\frac{20}{50} y} + .03112 \frac{\alpha'}{R} \sqrt{\frac{y}{x}}
\]
\[
\frac{\mu_2}{RT_2} = \frac{T}{290} \left( \ln \frac{y}{1-y} + \frac{1}{1-y} \right) - \frac{27}{4} y + 1.38765 \sqrt{\frac{20}{50} x} + .001334\alpha'R,
\]
Some preliminary calculations show that, qualitatively, the result is not much different.
VII. SPEED OF SOUND IN MIXTURES

VII.1. Propagation of sound in Gibbs-Dalton mixtures

In a mixture of two ideal gases, without mutual interaction, two sets of degrees of freedom are excited and two normal modes of propagation will appear. The formula for the value of $c^2$ ($c$ is the velocity of propagation) is replaced by a propagation matrix; the two possible speeds are the eigenvalues of this matrix.

For the propagation of sound in air, approximated by the ideal gas model, it was found (first by Laplace) that a crucial condition for a successful prediction is the assumption that the specific entropy density $S = s/\rho$ is uniform. It is evident that, as we approach the problem of sound propagation in a mixture of gases, the entropy needs to be taken into account, and appropriately.

Equations of motion for ideal gases

We shall do the calculation under the assumption that the equilibrium state satisfies the strong Gibbs-Dalton hypothesis

$$\mathcal{R}_i \rho_i (\ln \frac{\rho_i}{T n_i} - n_i) + \rho_i S_i = 0, \quad i = 1, 2, \quad (7.1.1)$$

with $S_1, S_2$ constant. Linear perturbations are introduced by substitutions

$$T \rightarrow \hat{T} = T + \delta T, \quad \rho_i \rightarrow \hat{\rho}_i = \rho_i + \delta \rho_i, \quad i = 1, 2. \quad (7.1.2)$$

The perturbations are subject only to the adiabatic condition

$$\sum_i \left( \mathcal{R}_i \hat{\rho}_i (\ln \frac{\hat{\rho}_i}{T n_i} - n_i) + \hat{\rho}_i S_i \right) = 0. \quad (7.1.3)$$

In the expansion of this according to (7.1.2) the term of order zero vanishes by hypothesis and the first order term simplifies, with the help of (7.1.1), to

$$\frac{\delta T}{T} \sum n_i \mathcal{R}_i \rho_i = \sum \mathcal{R}_i \delta \rho_i. \quad (7.1.4)$$

I repeat that the perturbation does not obey the Gibbs-Dalton hypothesis; if it did it would reduce the number of degrees of freedom and the result would be very different. The Gibbs-Dalton hypothesis serves only to constrain the entropy. With that, the Lagrangian is fixed and the only dynamical equations used are the Euler-Lagrange equations, including the relation (7.1.3) in the linearized form (7.1.4). That we have such a relation is due to the fact that we have modeled the entropy of the mixture as a linear function of the densities,

$$\hat{s} = \hat{\rho}_1 S_1 + \hat{\rho}_2 S_2.$$

The other linearized equations of motion are the equation of continuity and the Bernoulli equation

$$\frac{\delta \hat{\rho}_i}{\hat{\rho}_i} = -v_i' = \partial^2 \hat{s}_i \frac{\partial W}{\partial \rho_i} \bigg|_{T}, \quad (7.1.5)$$
with
\[ W = \sum_i \mathcal{R}_i \rho_i T \ln \frac{\rho_i}{T_{n_i}} + sT. \] (7.1.6)

and
\[ \frac{\partial W}{\partial \rho_i} \bigg|_T = R_i T (\ln \frac{\rho_i}{T_{n_i}} + 1) + S_i T. \]

To evaluate (7.1.5) we use the Gibbs Dalton condition (7.1.4) on the equilibrium state (on the coefficients),
\[ \delta \frac{\partial W}{\partial \hat{\rho}_i} \bigg|_{\hat{T}} = \mathcal{R}_i \delta T + \mathcal{R}_i T \frac{\delta \rho_i}{\rho_i}, \quad i = 1, 2, \]

but only the linearized adiabatic condition (7.1.4) on the variations \((\delta T, \delta \rho_i)\), namely
\[ \frac{\delta T''}{T} = \frac{R_1 \delta \rho''_1 + R_2 \delta \rho''_2}{n_1 \mathcal{R}_1 \rho_1 + n_2 \mathcal{R}_2 \rho_2}, \] (7.1.7)

Let
\[ \kappa = \frac{\mathcal{R}_2}{\mathcal{R}_1} = \frac{\mu_1}{\mu_2}; \quad \tau = \frac{\rho_1}{\rho_2}, \]
\[ A = n_1 \tau + n_2 \kappa. \]

then
\[ \frac{\delta T''}{T} = \frac{\delta \rho''_1}{\rho_1} \frac{\tau}{A} \frac{A}{\kappa} + \frac{\delta \rho''_2}{\rho_2} \frac{\kappa}{A}. \] (7.1.8)

Next
\[ \frac{\delta \hat{\rho}_1}{\rho_1} = \frac{\mathcal{R} T}{\mu_1} \frac{\tau}{A} \frac{\delta \rho''_1}{\rho_1} + \frac{\mathcal{R} T}{\mu_1} \frac{\kappa}{A} \frac{\delta \rho''_2}{\rho_2} + \frac{\mathcal{R} T}{\mu_1} \frac{\delta \hat{\rho}_1'}{\rho_1}, \] (7.1.9)
\[ \frac{\delta \hat{\rho}_2}{\rho_2} = \frac{\mathcal{R} T}{\mu_2} \frac{\tau}{A} \frac{\delta \rho''_1}{\rho_1} + \frac{\mathcal{R} T}{\mu_2} \frac{\kappa}{A} \frac{\delta \rho''_2}{\rho_2} + \frac{\mathcal{R} T}{\mu_2} \frac{\delta \hat{\rho}_2'}{\rho_2}. \] (7.1.10)

**The propagation matrix**

The matrix of squared velocity is the matrix of coefficients in these equations,
\[ \frac{\mathcal{R} T}{\mu_1} \begin{pmatrix} 1 + \frac{\tau}{A} & \kappa \frac{\kappa}{A} \\ \kappa \frac{\kappa}{A} & \kappa + \kappa^2 \frac{\kappa}{A} \end{pmatrix}, \quad A = n_1 \tau + n_2 \kappa. \]

For mixtures we define the reduced speed \(c\) in terms of the Newtonian speed of the first component, \(v = c \sqrt{\mathcal{R}_1 T}\). This reduced speed is a zero of the determinant of the matrix
\[ M = \begin{pmatrix} 1 + \frac{\tau}{A} - c^2 & \frac{\kappa}{A} \\ \frac{\kappa}{A} & \kappa + \kappa^2 - c^2 \end{pmatrix} \] (7.1.11)

The density fluctuations satisfy
\[ M \begin{pmatrix} \delta \rho_1 / \rho_1 \\ \delta \rho_2 / \rho_2 \end{pmatrix} = 0. \] (7.1.12)
The theory predicts two modes, with speeds that vary with the concentrations. Experimenters report a single mode.

We shall see that the disagreement with experiment can be overcome, but it is of interest to begin by describing the predictions of the naive Gibbs-Dalton model in some detail. There is a surprise: two different types of mixtures must be distinguished.

**Two types of mixtures**

There will be reference to the figures. In all the figures the abscissa is the natural logarithm of the ratio of densities, \( \tau = \rho_1/\rho_2 \). Gas number 1 dominates on the right where \( \tau \to \infty \); gas number 2 dominates on the left where \( \tau \to 0 \). The vertical coordinate is \( c/\gamma_1 \), the unit is thus the Laplacian speed of sound in gas number one, approached asymptotically in the region marked \( C \) in Fig.7.1.1.

In the limit \( \tau = 0 \) the first solution is

\[
c^2 = 1, \quad M = \begin{pmatrix} 0 & 1/n_2 \\ 0 & \kappa \gamma_2 - 1 \end{pmatrix}, \quad \gamma_i = 1 + \frac{1}{n_i}, \quad i = 1, 2. \tag{A}\]

The speed is the Newtonian speed of gas number 1, \( d\rho_2 = 0 \) and the energy is carried by \( d\rho_1 \). The fluctuations are in equal or in opposite phase. To determine which, we have the matrix equation

\[Md\rho = 0.\]

In particular,

\[
\frac{\kappa \tau}{A} d\rho_1 + (\kappa + \frac{\kappa^2}{A} - c^2) d\rho_2 = 0. \tag{7.1.9}\]

When \( \tau \approx 0 \) the second coefficient is \( \kappa \gamma_2 - 1 \). The two coefficients have the same sign if \( \kappa \gamma_2 > 1 \), so in that case the phases are opposed. This may be important for it may make it difficult to excite this mode. The relative phase does not change as the concentration is varied. (Note that \( M_{22} \) has the same sign for all values of the concentration.)

The second solution is

\[
c^2 = \kappa \gamma_2, \quad M = \begin{pmatrix} 1 - \kappa \gamma_2 & 1/n_2 \\ 0 & 0 \end{pmatrix}. \tag{B}\]

The speed is the Laplacian speed of gas number 2 and the energy is shared. The phases are equal if \( \kappa \gamma_2 > 1 \), so the two solutions are different in this respect.

In the limit \( \tau = \infty \) the first solution is

\[
c^2 = \gamma_1, \quad M = \begin{pmatrix} 0 & 0 \\ \kappa/n_1 & \kappa - \gamma_1 \end{pmatrix}. \tag{C}\]

The speed is the Laplacian speed of gas number 1 and the energy is shared. The fluctuations are in opposite phase if if \( \gamma_1/\kappa < 1 \). The second solution is

\[
c^2 = \kappa, \quad M = \begin{pmatrix} \gamma_1 - \kappa & 0 \\ \kappa/n_1 & 0 \end{pmatrix}. \tag{D}\]
The speed is the Newtonian speed of gas number 2, \( d\rho_1 = 0 \) and the energy is carried by \( d\rho_2 \). The fluctuations are in opposite phase if \( \gamma_1/\kappa > 1 \).

It may be expected that the excitation with opposite phases will be very difficult to achieve.

The solution that is Newtonian at one end will connect to whatever solution has the same relative phase at the other, thus if

\[
\kappa \gamma_2 - 1, \quad \gamma_1/\kappa - 1
\]

have the same sign, then the speed of one mode will be Newtonian and that of the other will be Laplacian. While if the signs are opposite each solution will be Newtonian at one end and Laplacian at the other.

**Summary,**

The letters A,B,C,D refer to the four regions of Fig.7.1.1. The phases of the two modes are opposed in these cases

A, the Newtonian mode, if \( \kappa \gamma_2 = (\mu_1/\mu_2)\gamma_2 > 1 \).
B, the Laplacian mode, if \( \kappa \gamma_2 < 1 \).
C, the Laplacian mode, if \( \gamma_1/\kappa < 1 \).
D, the Newtonian mode, if \( \gamma_1/\kappa = (\mu_2/\mu_1)\gamma_1 > 1 \).

These excitations are difficult to excite and they may not have been observed.

**Type 1 mixture, “similar” gases**

This is the case when \( \kappa \gamma_2 - 1 \) and \( \gamma_1/\kappa - 1 \) have the same sign, for example:

\[
\text{Gas 1/ Gas 2} = \text{Nitrogen/Argon: } \kappa = 28/40, \ n_1 = 5/2, n_2 = 3/2,
\]

with \( \kappa \gamma_2 = 7/6 \) and \( \gamma_1/\kappa = 2 \). There is a ‘Newtonian mode’ that interpolates between case (A) and case (D) with a speed that interpolates between the Newtonian (isothermal) speeds of the two pure gases. See the lower curve in Fig. 4. The two amplitudes are in opposite phase and the amplitude of the dominant gas tends to zero in the limit when this gas is alone. This mode is almost irrelevant since it is very difficult to excite it. A ‘Laplacian mode’ mode interpolates between case (B) and case (C) (upper curve) with a speed that interpolates between the Laplacian (adiabatic) speeds of the two pure gases. The two amplitudes are in opposite phase. The dominant gas carries most of the energy but the amplitudes are comparable. A simple oscillator will excite this mode only. The success of the Laplacian assumption of fixed entropy is assured in this case.

All this tends to be confirmed by experiment. The experiment, by Lofqvist, was done under approximately “normal” conditions, where both gases can be treated as ideal gases with small error. The first mode cannot be excited mechanically * and there are other

* Compare the fruitless attempts to excite second sound in superfluid Helium (Peshkov 1946)
reasons why it may be expected to be unobservable, or at least to justify the fact that
it has escaped detection. The prediction of the Gibbs-Dalton model needs only a minor
correction to agree with experiment. See Fig.7.1.1).

![Fig.7.1.1](image)

Fig.7.1.1. The upper and lower curves show the calculated speeds (actually $c/\sqrt{\gamma_1}$) of
the two modes of sound in $N_2/Ar$, a type 1 mixture, from the Gibbs-Dalton model, plotted
against $\ln(\rho_1/\rho_2)$. The curve below the data points is from Eq.(7.1.10). The abscissa is
$\ln(\rho_{N}/\rho_{Ar})$, pure Nitrogen on the right, pure Argon on the left. Data by Lofquist et
al(2003). The unit of speed that is used as vertical coordinate is the Laplacian speed of
sound in Nitrogen.

**Type 2 mixture, “disparate” gases**

It is the case when $\kappa\gamma_2 < 1$ and $\gamma_1/\kappa > 1$, for example, Helium/Xenon, $\kappa = 4/131.3$,
$n_1 = n_2 = 3/2$.

There is a mode, with speed that approaches the adiabatic speed of sound in the lighter
gas in the limit when this gas is alone (C), but in the opposite limit it approaches the
Newtonian value of the same gas (A). The amplitudes are in equal phase.

A second mode has a speed that approaches the Newtonian speed of sound of the heavier
gas in the limit when this gas is alone (B) and the Laplacian speed of of the same gas in
the opposite gas when that is alone (D). The amplitudes are in the same phase.

Experiment yields a single mode with a speed that varies with concentration and that
approaches the expected Laplacian values in the limits of either pure gas. See Fig.7.1.2. It
appears that a cross-over takes place; in fact, there is evidence of a “critical” concentration.
There are frequent hints that there are other, less prominent modes, about which little
information is given.
Fig. 7.1.2. The upper and lower curves show the 2 calculated speeds of sound in $He/Xe$, a type 2 (disparate) mixture. Coordinates as in Fig. 7.1.1. The interpolating curve is from Eq. (7.4.10). Data points from delo Mora and Puri (1985). Pure Helium at right, pure Xenon at left. The high datum point is from Schmorenburg (1996). At A,C the asymptotes are the Newtonian, resp. the Laplacian, speeds in Helium.

The reason for this disagreement was at first attributed to the fact that no account had been taken of any kind of damping, and for high frequencies the importance of damping has been confirmed. But at low frequencies the loss of energy to absorption is not thought to be important. Indeed, the measured rates of absorption are extremely low. (Holmes 1960)

An alternative explanation is much more appealing. The calculations were made on the assumption that there is no interaction between the two gases. This makes it possible for a signal to be transmitted by either component without involving the other. In the solution represented by the upper line in Fig. 7.1.2 the signal is carried by Helium even in the limit when the mixture consists entirely of Xenon. In the other case the signal is carried by Xenon even in the limit when this gas is absent. This is clearly unreasonable and we expect that even a weak interaction must result in a cross over.

Plotting these functions, we want to compare with experiments, but besides the data we shall use a well known analytic fit. The formula that fits the observations, and much better than could be expected, is (Lofqvist et al 2003)

$$c^2 = \frac{\tau + \kappa}{\tau + 1} \left(1 + \frac{\tau + \kappa}{n_1 \tau + n_2 \kappa}\right). \quad (7.1.10)$$

The origin of this prediction is not thermodynamic field theory but calculations of particle dynamics and the Boltzmann scattering equations. For a brief account of the calculation see de la Mora and Puri (1986). It is predicted to hold in the limit when the effect of diffusion is so strong as to force the two velocities to be nearly equal. That is the key feature of the formula, and that must be the basic fact that is responsible for its success:
apparently something forces the two velocities to be nearly equal. This must be explained in terms of an interaction between the two components, but the conclusion that it is due to strong diffusive damping is not compelling.

The explanations that have been offered to explain the success of (7.1.10) are equations for the two velocities and, some times, two temperatures. We have noted that the introduction of two temperatures may be interpreted in terms of a deviation from Gibbs-Dalton equilibrium conditions. But we are strongly constrained by the need to retain the standard equations, continuity and Bernoulli. Indeed, any modification of the kinetic part of the Lagrangian tends to cause a loss of mass conservation: that is, of particle number conservation. It is therefore of interest to explore alternatives.

In the special case that \( \kappa = 1 \) the value given by (7.1.10) is one of the two eigenvalues of the matrix \( M \); the other one is \( c^2 = 1 \). As the van der Waals expression for the free energy of a gas was intended as a phenomenological expression of the inter particle interactions, so the interaction term \( \alpha \sqrt{\rho_1 \rho_2} \) seems to be a means of introducing the interaction between two dissimilar atoms into the thermodynamical formulation.

The data quoted are from experiments at room temperature, at frequencies around 1 MHz. More data is needed, over a wide range of frequency and temperature.

**VII.2. A simple model of interactions**

Let us add the following “interaction term” to the potential; that is, to the hamiltonian,

\[
\alpha \sqrt{\rho_1 \rho_2},
\]

(7.2.1)

with \( \alpha \) constant. It turns out that \( \alpha \) has to be positive, which means that the interaction is repulsive. The reason for this choice will become clear almost immediately. Such a term will affect the formula for the internal energy, but it is a correction to the free energy density and it does not change the formula for the entropy. The hypothesis of Gibbs and Dalton can be maintained and we shall do so. The formula for the pressure is not affected.

The equation of motion

\[
\frac{D\vec{v}_j}{Dt} + \text{grad} \left( W + \frac{\alpha}{2} \sqrt{\frac{\rho_i}{\rho_j}} \right) = 0, \quad i, j = 1, 2 \text{ or } 2, 1
\]

no longer suggest a useful definition of individual pressures. The acceleration of the molecules of each gas is strongly dependent on the configuration of the other.

Again we consider first order perturbations of the equilibrium configuration. The linearized equations (7.1.5) are modified:

\[
\frac{d\rho_i}{\rho_i} = -\dot{v}'_i = \partial^2_x \left( \frac{\partial W}{\partial \rho_i} \right) + \frac{\alpha}{2} \sqrt{\frac{\rho_j}{\rho_i}}, \quad j \neq i.
\]

Eq.s (7.1.5) and (7.1.6) gain additional terms,

\[
\alpha \frac{4}{\sqrt{\rho_1}} \left( \frac{d\rho_2''}{\rho_2} - \frac{d\rho_1''}{\rho_1} \right) \quad \text{and} \quad \frac{\alpha}{4} \sqrt{\frac{\rho_1}{\rho_2}} \left( \frac{d\rho_1''}{\rho_1} - \frac{d\rho_2''}{\rho_2} \right).
\]

166
What makes the choice (7.2.1) special is the fact that, for a monochromatic wave, these additions are proportional to the difference $v_1 - v_2$ of the velocities. When the interaction is strong it will favor equalization of the velocities. Our brief analysis of the standard theory shows that this is the feature that accounts for its success. *

The reduced speed of propagation is now obtained by setting to zero the determinant

$$\left( 1 + \frac{\tau}{A} - \beta \tau^{-\frac{1}{2}} - c^2 \right) \left( \kappa + \frac{\kappa^2}{A} - \beta \tau^{\frac{1}{2}} - c^2 \right), \quad \beta := \frac{\alpha}{4R_1T}. \tag{7.2.2}$$

In the limit of large $\beta$ the only eigenvector has $d\rho_1/\rho_1 = d\rho_2/\rho_2$, or $\vec{v}_1 = \vec{v}_2$, and the eigenvalue $c^2$ is precisely as in (7.1.10). This very curious mathematical result is overshadowed by the fact that, as already noted, when $\kappa = 1$ and $\beta = 0$ there is perfect coincidence between the two formulas, except that the vanishing of the determinant of (7.2.2) has the additional solution $c^2 = 1$.

Numerical results for a type 1 mixture are in Fig. 7.2.1. It may be seen that a value $\beta = .3$ is sufficient to bring the theory into substantial agreement with the experiment. Higher values of $\beta$ improves the agreement for low frequencies but tends to spoil it when compared with the few data that are available for the highest frequencies. Negative values of $\alpha$ do not give reasonable results.

Fig.7.2.1. The effect of the interaction (7.2.1) on sound speed in $N_2/Ar$. The blue curve on top (purple curve middle) is obtained with $\beta = 0$ ($\beta = .3$). Higher values of $\beta$ gives even better agreement with experiment. The unphysical mode has disappeared. The lower (black) curve is the prediction of Eq.(7.1.14).

The case of type 2 mixtures (Fig.7.1.2) is more dramatic. Very small values of $\beta$ are enough to eliminate the isothermal modes in the SE and NW corners of the figure. The

* In the presence of the interaction we are not justified to use the Gibbs-Dalton hypothesis. It would be interesting to use the modification proposed in Section VI.1. We have not done the calculation.
former disappears and the latter drops down to join the Laplace branch at the lower left. Agreement with experiment requires a value of $\beta$ at least equal to 1, near perfect agreement is gotten with $\beta = 5$, and larger values of $\beta$ only improve the fit, except for the data at the highest frequencies. Lower temperatures, near the critical point, have not been studied.

\[ \text{Fig. 7.2.2. Effect of the simple interaction term on the speed of sound in He/Xe. From top to bottom: } \beta = 0 \text{ (black), } 0.01 \text{ (blue), } 0.1 \text{ (purple) and 1 (red). The green line is from (7.1.10). Additional data points from Bowler and Johnson (1986), at higher frequencies.} \]

\section*{Variants}

1. In Chapter VI we have followed custom in using an interaction of the form $\alpha \rho_1 \rho_2$ ($k = 1$ instead of $k = 1/2$). Since we are bound to use the same interaction Lagrangian we are compelled to use the same value of $k$ in both cases. But this is not a critical test. The quadratic interaction energy ($k = 1$) used to study critical mixing is numerically insignificant at the temperatures and densities at which we have examined sound speeds. When an interaction of the form $\alpha \rho_1 \rho_2$ is included the linearized equations take the form

\[ \frac{d\hat{\rho}_i}{\rho_i} = -v'_i = \partial_x^2 \left( \frac{\partial W}{\partial \rho_i} \bigg|_T + \alpha \rho_j \right), \ j \neq i. \]

This, as an attempt to improve the agreement with experiment, is a total failure. A small amount of this type of interaction can be allowed, but it does nothing to improve the agreement with experiment.

We have tried to include a coupling of the form $\alpha \sqrt{\rho_1 \rho_2}$ in the calculation of critical mixtures and find that the predictions are reasonable. See Chapter VI.

2. The variation of the speed of sound with the frequency is another challenge. It can be modeled with interactions of the squared gradient type (van der Waals)

\[ \alpha \int d^3x \left( \sum \partial_i \rho_1 \partial_i \rho_2 \right)^k. \]

It is necessary to collect much more experimental information, at a wide range of temperatures, at appropriate frequencies.
VII.3. Two van der Waals gases. Sound speed

This Section and the next studies the gaseous Helium-Xenon mixture. the treatment is new in the sense that it is a test of a new model of the entropy of mixtures. This does not contradict the usual treatment, it just aims to reduce the number of phenomenological parameters.

The Lagrangian for a mixture of two non interacting van der Waals gases is

\[ \sum_i \left( \rho_i (\dot{\Phi}_i - \vec{v}_i^2 / 2) + \mathcal{R}_i \rho_i T \ln \frac{\rho_i}{(1 - b_i \rho_i) T_{n_i}} - a_i \rho_i^2 + \rho_i S_i T \right) \]. \tag{7.3.1}

This formula presents our model for the entropy of a mixture of two van der Waals gases, as a linear function of the two densities. The usual treatment avoids introducing the entropy but the formula used for the free energy density contains phenomenological terms, linear in the densities, to make up for it.

To this we shall have to add an interaction term.

As usual, we shall consider, in first order perturbation theory, a traveling wave on a uniform background at rest,

\[ \rho_i \rightarrow \rho_i + \delta \rho_i, \quad T \rightarrow T + \delta T, \quad \vec{v}_i \rightarrow \delta \vec{v}_i. \]

The direction of the velocity is fixed and taken to coincide with that of the x-axis.

The equations of continuity are

\[ \delta \dot{\rho}_i = -\rho_i \frac{d}{dx} \delta v_i, \]
\[ \frac{\delta \ddot{\rho}_i}{\rho_i} = - \frac{d}{dx} \delta \dot{v}_i = \frac{d^2}{dx^2} \delta \dot{\Phi}_i. \]

The Bernoulli equations are, to first order,

\[ -\dot{\Phi}_i = \mathcal{R}_i T \left( \ln \frac{\rho_i}{(1 - b_i \rho_i) T_{n_i}} + \frac{1}{1 - b_i \rho_i} \right) - 2a_i \rho_i + S_i T =: \mu_i(\rho_1, \rho_2, T), \quad i = 1, 2. \tag{7.3.2} \]

We need the coefficients in

\[ -\delta \dot{\Phi}_i = \sum_j \frac{\partial \mu_i}{\partial \rho_j} \delta \rho_j + \frac{\partial \mu_i}{\partial T} \delta T. \]

To lowest order the partial derivatives are

\[ \frac{\partial \mu_i}{\partial \rho_j} = \left( \frac{\mathcal{R}_i T}{\rho_i(1 - b_i \rho_i)^2} - 2a_i \right) \delta_{ij}, \quad \frac{\partial \mu_i}{\partial T} = \frac{\mathcal{R}_i}{1 - b_i \rho_i}. \tag{7.3.3} \]
To derive this simple expression for $\partial \mu / \partial T$ we have used the Gibbs-Dalton condition for the equilibrium state. The perturbed state is subject to the adiabatic condition only. This is because we are committed to using the Euler-Lagrange equations of our action principle and nothing else. It gives us one relation between the three variables and allows us to express $\delta T$ in terms of $\delta \rho_1$ and $\delta \rho_2$. To lowest order,

$$\sum \frac{R_i \delta \rho_i}{1 - b_i \rho_i} = \sum R_i \rho_i n_i \frac{dT}{T}. \quad (7.3.4)$$

Finally, the squared-speed matrix is given by

$$\frac{\delta \rho_k}{\rho_i} = \left( \frac{R_i T}{(1 - b_i \rho_i)^2} - 2a_i \rho_i \right) \frac{\delta \rho'_{i}}{\rho_i} + \frac{R_i T}{1 - b_i \rho_i} \frac{1}{\sum_k n_k R_k \rho_k} \sum_j \frac{R_j \delta \rho''_j}{1 - b_j \rho_j}.$$

$$= \sum_j (c^2)_{ij} \frac{d^2}{dx^2} \frac{\delta \rho_j}{\rho_j}. \quad (7.3.5)$$

The van der Waals formula is not enough to calculate the speed of sound, even in a unary system. More information is needed and one way to introduce it is to define the van der Waals fluid by specifying the formula for the internal energy density. When instead we specify the Lagrangian density there still remains to choose the values of the two entropy parameters. One way to do that is to apply the Gibbs-Dalton hypothesis to the unperturbed configuration. This is what leads to the simple result (7.3.3).

So far, the formulas had involved only the ratio $\tau = \rho_1 / \rho_2$ of the two densities. To draw curves of sound speed versus concentration we need to hold something fixed. In most experiments, the temperature and the pressure of the unperturbed states are kept fixed. The temperature, where it appears explicitly in our calculation was fixed at 293 K. The pressure may be taken to be 1 atmosphere and

$$p = \sum \frac{R_i \rho_i T}{1 - b_i \rho_i} - a_i \rho_i^2.$$

To show the sound speeds as functions of the concentration we shall draw curves for fixed values of the pressure. Note that the fixed pressure refers to the sequence of equilibrium states that serve as zeroth order of the perturbations; the perturbed configurations do not have fixed pressure.

We reduce (7.3.5) to

$$\frac{d \rho_i}{\rho_i} = \left( \frac{R_i T}{(1 - b_i \rho_i)^2} - 2a_i \rho_i \right) \frac{\delta \rho'_{i}}{\rho_i} + \frac{R_i T}{1 - b_i \rho_i} \frac{1}{\sum_k n_k R_k \rho_k} \sum_j \frac{R_j \delta \rho''_j}{1 - b_j \rho_j}$$

$$= \sum_j (c^2)_{ij} \frac{d^2}{dx^2} \frac{\delta \rho_j}{\rho_j}.$$
or

\[ c^2 = R_1 T \left( B_1^2 + \frac{B_1^2}{R_1} + B_2^2 \frac{R_2}{R_1} \right) \Sigma \left( B_2^2 - \frac{B_1 B_2 \kappa_2}{R_1} \right) \].

Here

\[ A = n_1 \kappa_2 + n_2 \tau_1, \quad B_i = \frac{1}{b_i \rho_i} \].

Treating Helium at normal temperature as an ideal gas we simplify this,

\[ c^2 = R_1 T \left( \frac{1}{A} + \frac{B_2 \kappa_2}{A} \right) \Sigma \left( B_2^2 - \frac{2 \phi \rho_2}{R_2 \kappa_2} \right) \].

We wish to compare these curves with experimental values; alternatively we may compare with the phenomenological formula from Section VII.1,

\[ c^2 = \frac{\tau + \kappa}{\tau + 1} \left( 1 + \frac{\tau + \kappa}{n_1 \tau + n_2 \kappa} \right). \quad (7.1.10) \]

Our formula for the sound speed does not involve the temperature except in the definition of the coupling strength \( \beta \), and as an overall factor that we have factored out. But it does contain the densities through \( \rho \) and \( \tau \)

\[ \rho_1 = \frac{\rho}{1 + 1/\tau}, \quad \rho_2 = \frac{\rho}{1 + \tau}. \]

We must have more data, especially near condensation. (Johnson et al?)

Apply to He/Xe to refine earlier calculation.

We need to include the effect of our interaction. See the Mathematica files.

Numerical results?
VIII. SUPERFLUID HELIUM. Part A

VIII.1. Experiments and interpretation

Here is a very brief summary of the first important experiments on superfluid Helium, the development that culminated with Landau’s two fluid theory. It is natural that we should take a special interest in this system, for it stands alone as the only important example of two fluid thermodynamics. The matter of rotational motion and (quantized) vortices can not be taken up at this point. See Chapter X.

A. The fountain experiment

Liquid Helium is cooled in vessels $A$ and $B$; initially the levels are equal. A capillary that connects this vessel to the vessel $B$ is very fine and no significant amount of liquid gets through, until the temperature descends below 2.19K. Both vessels are then thermally isolated. If a temperature difference is established, with $T_A > T_B$, then the level in vessel $A$ will rise due to a flow through the tube, Fig. 8.1.1, until the pressure due to gravity provides a counter-force and an equilibrium is established. The mass flows toward the higher temperature in order to reduce the temperature difference.

The effect is quite dramatic: The flow is independent of the pressure and, what is more, it is independent of the diameter of the tube though this be varied as much as by a factor of 50!

Reference

This highly unusual behavior led F. London (1938) to suggest that liquid Helium below 2.19 degrees Kelvin is a mixture of two components or phases, a normal component and a superfluid component with vanishing viscosity, and that the liquid that gets through (the superfluid component) carries no entropy with it. The capillary, with its capacity for denying passage to the normal component, plays the part that is taken by gravitation in the case of saturation; that is, it separates the two components. The two-components model was developed by Tisza.

Note: We shall see that the two densities at equilibrium are determined by the temperature, so we should understand that the super fluid in $B$ is just a little richer in the super component than in $A$. Perhaps we have to suppose that only the liquid in the tube is pure superfluid.

That the entropy of the super fluid component is near zero (supposing that it is) is a reflection of the excitation spectrum of the Helium atom; this information can be used but not justified within our context. It suggests that the free energy of the super fluid component is independent of the temperature, which makes sense when the total free energy is regarded as a sum $f_1 + f_2$ of those of the two separate gases. A reasonable inference is that the temperature of the liquid in equilibrium cannot be lowered without converting some of the liquid from normal fluid to superfluid. And this is what is observed.

The underlying, atomic description of what may be going on will not be discussed in this book. The (by now) standard explanation is that the individual Helium atom has a single, isolated ground state of very low energy. When the temperature is lowered the atoms, being bosons, all seek the lowest level, and since there is only one isolated level
at this lowest energy, the effective number of degrees of freedom is zero and there are, effectively, no populations of the higher energy levels. (Bose-Einstein Condensation.) The fluid divides into two parts, with the atoms of one, the ‘superfluid’, condensing into the lowest level. London speaks of a phase separation in momentum space and Landau later advanced the same concept, as we shall see later.

This behavior does not by itself imply that liquid Helium is governed by a different kind of thermodynamics; we shall see, in Section 8.2.3, that London’s intuition about the entropy is sufficient to explain the unusual behavior of this liquid, so long as we limit our attention to quasi-static phenomena.

Fig. 8.1.1. The fountain effect. The central portion (light blue) is filled with a fine powder that is impermeable to the normal form of liquid helium.

B. The entropy

We have proposed the representation

\[ s = \rho_1 S_1 + \rho_2 S_2, \]  

of the entropy functional (density) of a mixture. The specific entropies \( S_1 \) and \( S_2 \) are adiabatic invariants. In the analogous case of saturation, heating results in an increase of the amount of gas while the specific entropies \( S_1 \) and \( S_2 \) remain fixed or almost so. The fountain effect can be similarly understood as resulting from the fact that \( S_1 \) and \( S_2 \) in He II vary but slowly with the temperature and that \( S_2 \ll S_1 \).

Very precise measurements of the entropy density \( s \) are available. In the upper half of the temperature interval, where the normal gas dominates, the first term is expected to make the larger contribution and on this assumption it is seen that the specific entropy \( S_1 \) varies only slowly with the temperature, which confirms the view that the lowering of entropy takes place, mainly, through conversion of the normal fluid to superfluid.
### Table 8.1.1

<table>
<thead>
<tr>
<th>Pressure (atm)</th>
<th>Entropy Density (J/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>$s = 1.59 \rho_1 + .0058 T^3 \rho_2,$</td>
</tr>
<tr>
<td>0.05</td>
<td>$s = 1.45 \rho_1 + .0042 T^3 \rho_2,$</td>
</tr>
<tr>
<td>1.00</td>
<td>$s = 1.36 \rho_1 + .0025 T^3 \rho_2,$</td>
</tr>
<tr>
<td>1.50</td>
<td>$s = 1.289 \rho_1 + .0025 T^3 \rho_2,$</td>
</tr>
<tr>
<td>2.00</td>
<td>$s = 1.18 \rho_1 + .0020 T^3 \rho_2,$</td>
</tr>
<tr>
<td>2.50</td>
<td>$s = 1.129 \rho_1 + .0017 T^3 \rho_2.$</td>
</tr>
</tbody>
</table>

Table 8.1.1. Relation between measured entropy density and the equilibrium values of densities and temperature, covering the whole interval from .1K to 2.1K. Note that entropies given by Brooks and Donnelly (1977) are specific densities. Our “s” is density in $J/cm^3$; the entropy quoted by Brooks and Donnelly multiplied by mass density. In the table the pressure is given in atmospheres.

There is no significant dependence of the specific entropy $S_1$ on the temperature when $1 < T < 2$. Towards lower temperatures, when the normal gas is absent, the entropy of the super fluid becomes dominant and there is no way to go except to reduce the specific entropy $S_2$. We see from the Table that it is proportional the third power of the temperature.

### C. The equilibrium configuration

A relation between the basic variables $\rho_1, \rho_2$ and $T$ defines the equilibrium configurations of the system. Using data found in Putterman’s book we plot all available physical points in the interval $1.3 < T < 2.1$ in Fig.8.1.2 and find that the following equation describes it well, *

\[
X(\rho_1, \rho_2, T) := (\rho_1 + a \rho_2 + b)(\rho_1 + c \rho_2 + d) + 10^{-4} = 0,
\]

with

\[
a = -.15, \quad b = .014 - .21(T - 1.3)^2, \quad c = 1.86 - .31T, \quad d = -.398 + .113T.
\]

Using data collected by Brooks and McConnelly we get a slightly different result, see Fig.8.1.3. A more convenient expression for the equilibrium relation between $\rho_1, \rho_2$ and $T$ will be found later.

---

* See however recent experimental work on superfluid Helium at negative pressure.
Fig. 8.1.2. The set of equilibrium configurations as given by Putterman. The ordinates are the two densities. The color goes with the pressure; $p = 0$ for the left most purple dots and $p = 25\text{atm}$ for the (also purple) dots at the right end. The lines connect points with the same temperature, 1.3 K for the outer line and 2K for the inner line. The extrapolation from the purple dots to the origin (negative pressure) is not justified by the experimental data.

Fig. 8.1.3. The set of equilibrium configurations according to Brooks and Donnelly. Blue lines are loci of equal pressure.

The data points used are tabulated at the end of this chapter.
Values of the two densities can be represented with high precision as follows, for each of six values of the pressure, the densities in $mg/cm^3$ and the pressure in atmospheres. The variation with pressure, though relatively weak, makes this representation inconvenient.

**TABLE 8.1.2**

\[
\begin{align*}
\text{p} &= 00, & \rho_1 &= 1.90 \ T^{5.5}, & \rho_2 &= 145.0 - 1.74 \ T^{5.6}, \\
\text{p} &= 05, & \rho_1 &= 2.17 \ T^{5.6}, & \rho_2 &= 152.5 - 1.86 \ T^{5.8}, \\
\text{p} &= 10, & \rho_1 &= 2.56 \ T^{5.7}, & \rho_2 &= 159.0 - 2.20 \ T^{5.9}, \\
\text{p} &= 15, & \rho_1 &= 3.03 \ T^{5.8}, & \rho_2 &= 164.0 - 2.65 \ T^{6.0}, \\
\text{p} &= 20, & \rho_1 &= 3.70 \ T^{5.9}, & \rho_2 &= 168.5 - 3.20 \ T^{6.1}, \\
\text{p} &= 25, & \rho_1 &= 4.40 \ T^{6.0}, & \rho_2 &= 172.5 - 4.00 \ T^{6.2},
\end{align*}
\]

Table 8.1.2. This representation of the concentration is valid over the whole temperature interval, from .1K to 2.1K.

Later we shall see how was it measured.

Fig.8.1.4. Sketch of the concentrations of the normal fluid (increasing) and the superfluid component (decreasing) between $T = 1K$ and $T = \lambda$, for fixed pressure. The actual measurements are indirect, by an interpretation of the cross section for neutron scattering. The proportion of superfluid even quite close to the $\lambda$ point seems to give a tentative answer to the question posed in the Note at the opening of this Chapter.
D. Second sound

Landau’s theory is distinguished by the fact that it treats the two components of a mixture as independent degrees of freedom. It predicted the existence of two kinds of sound, a normal mode (first sound) in which both oscillations are in phase and another, second sound, in which they are in opposite phase. This was a real prediction, made before any experiments confirmed the existence of two sounds in liquid Helium.

With the advantage of already knowing the existence of two sound modes we can affirm with some assurance that there must be two densities and two velocities. With the limitation to irrotational vector fields the kinetic part of the Lagrangian density is

\[
\rho_1 (\dot{\Phi}_1 - \vec{v}_1^2/2 - \phi) + \rho_2 (\dot{\Phi}_2 - \vec{v}_2^2/2 - \phi).
\] (8.1.2)

The gravitational potential \(\phi\) will be neglected. The appearance of an additional degree of freedom naturally implies that two sound modes are likely to exist; the surprise is not the existence of two sounds in liquid Helium but the fact that the observation of a similar phenomenon is rare in other mixtures. The reason, as was seen, is that most mixtures are characterized by a strong interaction between the components, interactions that effectively quash the mode in which the two fluctuations are in opposite phase. Other materials do not exhibit these special features because at comparable temperatures they are in a solid state.

Unless strong interactions between the two components prevent it, two sounds come naturally. *

An implication of this is that we shall have two equations of continuity,

\[
\dot{\rho}_i + \text{div}(\rho_i \vec{v}_i) = 0, \quad i = 1, 2.
\] (8.1.3)

The observation that only the total mass is conserved suggests that there can be only one equation of continuity. But we remember that conservation of mass is not an automatic consequence of the equation of continuity; it only follows when, in addition, one imposes the condition that the boundary velocity be tangential to the boundary. We follow Landau in that we shall impose this boundary condition on the total flow

\[
\vec{j} = \sum_i \rho_i \vec{v}_i,
\]

but not on the individual velocities. Both mass densities are conserved in the bulk but only the total mass is preserved in the interaction with the boundary. The variations of the densities under which the action is extremal are constrained by the fixing of the total mass, but not the individual masses.

In the bulk, away from the boundary, and in the absence of external manipulation of the system such as irradiation, the two liquids flow past each other, conserving their respective

* We have included the gravitational potential \(\phi\) in order to make a point. According to General Relativity, this potential is a natural companion to the operator \(d/dt\). We are therefore very reluctant to include a time derivative anywhere else, which makes us skeptical of Landau’s theory, especially its kinetic elements.
identities. That this is the usual interpretation is seen by comments in the literature; see for example Khalatnikov (1965 page 93).

The kinetic terms in our model, including the terms $\rho_i \dot{\Phi}_i$, are chosen so as to make possible a Lagrangian formulation. Recall, from Section III.11, that the inclusion of the velocity potential helps to make the Lagrangian invariant under Galilei transformations. Khalatnikov, in a book that has become a classic reference (Khalatnikov 1965) also aimed at a Lagrangian formulation, but without the help of the velocity potentials he was constrained to reduce the kinetic energy to the invariant expression $\rho (\vec{v}_1 - \vec{v}_2)^2 / 2$. According to Putterman (1975), there is an analogous contribution to the pressure. Our Lagrangian is Galilei invariant and we do not adopt these measures.

E. Thermodynamic pressure and the pressure on the walls

The thermodynamic pressure is defined as

$$p = \rho_1 \frac{\partial f}{\partial \rho_1} + \rho_2 \frac{\partial f}{\partial \rho_2} - f.$$  \hspace{1cm} (8.1.4)

The free energy is a function of the three independent variables $\rho_1, \rho_2$ and $T$. It is common usage in thermodynamics of mixtures since Gibbs, and especially so in Landau’s treatments of liquid Helium, to reduce the concentration to the role of a parameter, denying it the respect that it deserves as a thermodynamic variable. Such treatments are dynamically incomplete, being partially on shell.

The pressure on the wall has an additional contribution whenever the wall is maintained at a temperature that is different from the fluid. In the case of a heated wall, heat is transmitted to the liquid by the conversion of superfluid to normal fluid. This upsets the balance and, to compensate, normal fluid flows away from the wall and super fluid flows toward the wall. The additional pressure has been measured (Hall, 1954). The standard interpretation of this effect gives results that are in qualitative agreement with experiment. We have nothing to add to it, except this: We stick to the thermodynamic relation (8.1.4); there is no additional term proportional to $(\vec{v}_1 - \vec{v}_2)^2$.

Fig.8.1.5. Hall’s experiment.
The on shell pressure can be expressed in terms of $T, \rho_1$ and $\rho_2$, this relation is found by measurements at equilibrium to take the following form; for example,

$$T = .1 : \quad p = 25 - 1360(0.17246 - \rho) + 14300(0.17246 - \rho)^2.$$  (8.1.5)

The derivative,

$$\frac{dp}{d\rho} = 28600\rho - 3.6384 = c^2$$

varies from 526.7 at $p = 0$ to 1308.8 at $p = 25$. The unit of pressure is one atmosphere. To convert to cgs units multiply by $10^5$ to obtain the square of isothermal velocity of normal sound in cm/sec. At $T = .1$, $c = 229 m/sec$ at $p = 0$ and $c = 362 m/sec$ at $p = 25$. At higher temperatures much the same. The quasi independence of the speed on the temperature is significant.

F. Critical behavior

According to Arp (1989), all singular features of the thermodynamic functions can be fitted with a specific heat that is singular at $T = \lambda$. A term like

$$(T - \lambda) \ln(1 - \frac{T}{\lambda})$$

in the free energy will produce just such a term in the heat capacity.

Although we shall use a similar phenomenological function, we are not going to take the point of view of Arp, who emphasized this singular behavior in a trial function with 41 adjustable coefficients. Arp’s very thorough work suffers from an important omission: it deals with a single fluid. There is no account of the separate densities of the two components, consequently no mention of second sound. All thermodynamic relations ignore the concentration.

Let us remember that van der Waal’s highly successful modeling of a gas near and above the critical gas/liquid point did not predict the “correct critical behavior”. This refers to a very small region that involves altogether different concepts. We do not attempt to achieve agreement with experiment in this small neighborhood.

VIII.2. First analytic models

We shall construct idealized Lagrangian models, with features that resemble those of He II, but simplified and, in one respect, exaggerated.

A. Thermodynamic variables. We postulate that the correct choice of thermodynamic variables are $T$, the densities $\rho_1, \rho_2$ and the individual, specific entropies $S_1, S_2$. It is by far the most convenient choice though others are of course possible. In what follows we are concerned almost exclusively with equilibrium configurations; with no flow ($\vec{v}_1 = \vec{v}_2 = 0$) and all fields uniform.
B. Structure of the Lagrangian.

Landau’s equations for the two fluid model was constructed as a set of equations, without a Lagrangian variational structure, with a Galilei invariant expression for “the energy density” (Putterman 1974, Khalatnikoff 1956). As we know, it is the Lagrangian that is Galilei invariant, not the energy. Imposing Galilei invariance on the energy led to the introduction of terms of the kind \((\vec{v}_n - \vec{v}_n)^2\) that will not be needed here.

It is expected that the Lagrangian density, in a first approximation, is a sum of three kinds of contributions, the kinetic terms (8.1.2), minus the free energy, and the entropy term \(-sT\) with the entropy density in the form (8.1.1). Principal terms in the free energy are associated with each component separately,

\[ f = f_1(T, \rho_1) + f_2(T, \rho_2) + \ldots, \]

but additional terms will be needed to take interactions into account.

An adiabatic system is defined by fixing the specific entropies \(S_1, S_2\) and the pressure (or the volume). How the total entropy is apportioned between the two species can be understood in terms of an underlying atomic theory; for He II it can be determined experimentally and for our model it must be freely invented. In the event that a successful model is found it should be reconciled with atomic theory.

C. The pressure. The term attributed to \(f\) so far, the kinetic part in Eq.(8.1.2), being linear in the density, does not contribute to the pressure (8.1.4). In He II a good approximation is (8.1.5), with variations of \(c^2\) of up to 5 percent over the range of temperatures. Our first model, before necessary improvements, has pressure

\[ p = c^2(\rho - .1455), \quad (8.2.1) \]

with \(c^2\) constant. This pressure implies another term to be included in the free energy, for example

\[ c^2(\rho_1 \ln \rho_1 + \rho_2 \ln \rho_2 + .1455). \quad (8.2.2) \]

(This is appropriate for two non interacting components; the alternative \(c^2(\rho \ln \rho + .1455)\) makes the same contribution to the pressure.) The absence of any dependence on the temperature in the expression (8.2.1) for the pressure ensures that the velocity of propagation of ordinary (first) sound in the models has no direct dependence on the temperature, although it may depend on the concentration. In He II at equilibrium it varies from 227 to 366 m/sec. We are attempting to construct a simple model with properties that are similar to those of Helium, not one to be identified with it.

D. Entropy. The distribution of the entropy between the two species, as a function of pressure and temperature, must be determined from experiments. For liquid Helium, what is known is summarized in Table 8.1.1. Any model must make some assumption, to be justified either by experiment or by atomic theory, preferably by both. Our experience
with phase transitions, dissociation and immiscible fluids is not very helpful in the present instance. The only reliable guide is observation.

We take as a principal feature of our idealized model the axiom that the measured entropy is carried by the normal component; that is,

\[ s = \rho_1 S_1. \]  

(8.2.3)

This defines a family of adiabatic systems, parameterized by a single parameter \( S_1 \). The value of \( S_1 \) determines the adiabatic system and its equilibrium configuration, just as is the case for unary systems. This feature emulates one of the most dramatic aspects of He II, in an extreme form, by setting \( S_2 = 0 \), while experimentally it is non-zero but insignificant except at the very lowest temperatures.

For this reason it is natural to take the temperature dependent terms in the model free energy to be independent of \( \rho_2 \). We make this another postulated property of our model. The simplest possibility is that the \( T \) dependence of \( f \) is confined to a term

\[ a(T) \rho_1. \]  

(8.2.4)

Taking a clue from the ideal gas may work better.

Linearity in \( \rho_1 \) implies that this term makes no contribution to the pressure. The adiabatic condition is

\[ S_1 = -\partial a/\partial T. \]  

(8.2.5)

It is a feature of most familiar systems that the internal energy is first order in \( T \). To achieve this, \( a(T) \) must include terms of the type \( T \ln T \). Since a singularity is expected at \( T = \lambda \) we may be tempted to follow Arp, including a term \( b(\lambda - T) \ln(\lambda - T) \), with \( b \) and \( \lambda \) constant. We leave the function \( a(T) \) undetermined for the present, but notice that the adiabatic condition makes \( T \) uniform for all adiabatic processes.

E. Sound speeds. So far our partial expression for \( f \) contains no coupling between the two fluid components. This implies two sound modes, one in which the super fluid remains at rest, another where the normal component is quiet. This is, of course, very different from what is observed. We need to include an interaction term in the free energy.

Guided by our previous experience with sound propagation in mixtures we would add a term \( \alpha \sqrt{\rho_1 \rho_2} \) or \( \alpha \rho_1 \rho_2 \) to the free energy density, but let us make the more general assumption that the interaction takes the form

\[ f_{\text{int}} = \alpha(\rho_1, \rho_2). \]  

(8.2.6)

For a small deviation from an equilibrium mode we have the following equations

\[ \frac{\ddot{\rho}_i}{\rho_i} = -\ddot{v}_i = \frac{\partial^2}{\partial x^2} \frac{\partial}{\partial \rho_i} (f + sT), \]
where $f$ is the sum of the three terms (8.2.2), (8.2.4) and (8.2.6), $\partial/\partial \rho_i$ are adiabatic derivatives - at constant $S_1, S_2$. Ignoring an additive constant,

$$\frac{\partial}{\partial \rho_1}(f + sT) = a(T) + c^2 \ln \rho_1 + S_1 T + \alpha_1,$$

(8.2.5)

$$\frac{\partial}{\partial \rho_2}(f + sT) = c^2 \ln \rho_2 + \alpha_2,$$

(8.2.6)

where suffixes on $\alpha$ stand for derivatives. The adiabatic condition (8.2.4) makes $T$ constant and the $T$ dependent terms do not contribute. Hence

$$\ddot{\rho}_1 \rho_1 = c^2 \rho_1'' + \rho_1 \alpha_{11} \rho_2'' + \rho_2 \alpha_{12} \rho_1'' / \rho_2,$$

$$\ddot{\rho}_2 \rho_1 = c^2 \rho_2'' + \rho_2 \alpha_{22} \rho_1'' + \rho_1 \alpha_{21} \rho_2'' / \rho_1.$$

The squared-speed matrix is

$$c^2 + \left( \begin{array}{cc} \rho_1 \alpha_{11} & \rho_2 \alpha_{12} \\ \rho_1 \alpha_{21} & \rho_2 \alpha_{22} \end{array} \right).$$

The determinant of the matrix (without the $c^2$ term) is

$$\rho_1 \rho_2 \det(\alpha_{ij}).$$

The case that the function $\alpha$ is everywhere singular; that is, when this determinant vanishes identically, is especially easy to analyze, for in that case the eigenvalues are

$$c_1^2 = c^2, \quad c_2^2 = c^2 + \rho_1 \alpha_{11} + \rho_2 \alpha_{22}.$$

If $\alpha$ is zero either component moves independently, with the same speed. If instead we had replaced the pressure potential $c^2(\rho_1 \ln \rho_1 + \rho_2 \ln \rho_2)$ by the expression favored by Arp and others, namely $c^2 \rho \ln \rho$, then only the total density would oscillate; that is, one of the speeds would be zero.

For a simple example, consider

$$\alpha(\rho_1, \rho_2) = \beta \rho \ln \rho.$$

Then the speed-squared matrix is

$$c^2 + \frac{\beta}{\rho} \left( \begin{array}{cc} \rho_1 & \rho_2 \\ \rho_1 & \rho_2 \end{array} \right).$$

The eigenvectors are: (1, 1) with eigenvalue $c_1^2 = c^2 + \beta$ and $(-\rho_2, \rho_1)$ with eigenvalue $c_2^2 = c^2$. The first is ordinary sound, both components oscillating in phase, the other is second sound with the components in opposite phase.
With a slight change of notation, the complete expression for \( f \) takes the form

\[
f = A + B, \quad A = a(T)\rho_1,
\]

\[
B := (c_1^2 - c_2^2)\rho \ln \rho + c_2^2(\rho_1 \ln \rho_1 + \rho_2 \ln \rho_2) + C(\rho_1 - \rho_2),
\]

where \( c_1(c_2) \) are the constant speeds of the two kinds of sound in the model. Other forms of interaction will give us speeds that vary with the concentration. The pressure is

\[
p = c_1^2\rho.
\]

The last term in \( B \) makes no contribution to the pressure or to the speed of sound.

**F. Equilibrium.** This is a state of rest, with both velocities equal to zero. It is determined by equalizing the chemical potentials

\[
\mu_i = \frac{\partial}{\partial \rho_i} (f + sT) \bigg|_{\rho,T}.
\]

The relation that determines the concentration at equilibrium is \( \mu_1 = \mu_2 \) or

\[
\tilde{a}(T) + c_2^2 \ln \frac{\rho_1}{\rho_2} + 2C = 0,
\]

where the function \( \tilde{a} \) is

\[
\tilde{a}(T) = T \frac{da}{dT} - a.
\]

The model is thus characterized by a fixed relationship between concentration and temperature, independent of \( \rho \) and \( p \).

In liquid Helium below the \( \lambda \) point the concentration is often quoted as a fixed function of the temperature. In the model this relationship between concentration and temperature is determined by the choice that we make of the function \( a(T) \), and we may choose this function so as to further enhance the similarity of the model to He II.

The experimental temperature profile for Helium shown in Table 8.1.2 is approximately

\[
\frac{\rho_1}{\rho} = \left( \frac{T}{2.19} \right)^6, \quad T < 2.19.
\]

Thus, for our model to have similar properties we should take, for \( T < 2.19 \),

\[
\tilde{a}(T) = -2C - c_2^2 \ln \left( \frac{T}{2.19} \right)^{-6} - 1
\]
G. The heat capacity

In the case of a heterogeneous system without chemical reactions or phase changes, what is measurable and usually quoted as \( C_V \) is

\[
C_{p_1,p_2} = C_{\rho,x} = \left. \frac{\partial}{\partial T} U(S,T) \right|_{p_1,p_2},
\]

where \( U \) is the specific internal energy density. It is measureable and well defined because it is possible to raise the temperature without affecting the values of the two densities.

But in the case of He\(_\text{II} \) and other systems with two mixed phases it is not possible to keep the concentration fixed. Heating takes the system through a sequence of equilibrium states in which the concentration is determined by \( \rho \) and \( T \). What can be defined, and measured, is

\[
C_{p_1,p_2} = C_{\rho,x} = \left. \frac{\partial}{\partial T} U(S,T) \right|_{\rho},
\]

The full expression for the free energy density of the model is (8.2.8). The internal energy density, expressed in terms of the variables \( p_1, p_2 \) and \( T \),

\[
u(s,T) = \tilde{a}(T)p_1 - B
\]

and the specific internal energy density is

\[
U(p,\frac{p_1}{p_2},T) = \tilde{a}(T)\frac{p_1}{\rho} - \frac{B}{\rho},
\]

The specific heat at constant volume is

\[
C_V = \frac{d}{dT} U(p,\rho_1,T) \bigg|_{\rho} , \quad \rho_1 = (\frac{T}{2.19})^6.
\]

The relevant total derivative is

\[
\frac{d}{dT} = \frac{\partial p_1}{\partial T} \frac{\partial}{\partial p_1} + \frac{\partial}{\partial T}
\]

and

\[
C_V = \frac{\partial \tilde{a}}{\partial T} \frac{p_1}{\rho} + \frac{\tilde{a}}{\rho} \frac{\partial p_1}{\partial T} - \frac{1}{\rho} \frac{\partial B}{\partial p_1} \frac{\partial p_1}{\partial T}
\]

at equilibrium the second and third terms cancel and

\[
C_V = \frac{6c_2^2}{t} \frac{1}{t^{-6} - 1} , \quad t := \frac{T}{2.19}.
\]

This is in close agreement with the observed specific heat for Helium II for temperatures below the \( \lambda \) point, if \( c_2^2 = 1/10 \). (In Joules/mol.)

We must redo the last figures.

184
8.4. Dynamical equations of the model

Since Landau’s theory can be presented as a collection of formulas, let us list the equations of the model. All are derived from the Lagrangian density

$$\mathcal{L} = \sum_{i=1,2} \left( \rho_i (\dot{\Phi}_i - \vec{\nabla} \Phi^2 / 2) \right) - f - sT,$$

with

$$f = a(T)\rho_1 + B(\rho_1 \rho_2) s\rho_1 S_1 T.$$

- Two equations of continuity, derived from variation of the action with respect to the velocity potentials.

- An adiabatic condition, from variation of $T$, one of the fundamental relations of thermodynamics. In the simplest model it fixes the temperature in terms of the specific entropies.

- Variation of the densities gives the Bernoulli equations

$$-\frac{D\vec{v}_1}{Dt} = \text{grad}(\frac{\partial f}{\partial \rho_1} + S_1 T) = 0, \quad -\frac{D\vec{v}_2}{Dt} = \text{grad}\frac{\partial f}{\partial \rho_2}.$$

Finally, at equilibrium,

$$\frac{\partial f}{\partial \rho_1} + S_1 T = \frac{\partial f}{\partial \rho_2}.$$

this from variation of the densities holding $\rho$ fixed. That is all.

8.5. Rotational flow

An complete description of superfluids must deal with “rotons”, rotational flow, beyond the reach of Fetter-Walecka theory. We shall see, in Chapter X, that the required generalization involves two kinds of flows. This theory is not yet capable of dealing with mixtures and the correct approach to superfields is far from clear: 2 fluids and 1 or 2 kinds of flow? Or 1 fluid and two flows? For this reason it is not of interest to carry the present investigation any further at this time.

but i should explain the fountain effect.
TABLE 8.1.3

Pressure = 0. $s_{BC}$ from Brooks and Donnelly. My $s$ is to be compared to $\rho s_{BC}$.

<table>
<thead>
<tr>
<th>$T$</th>
<th>$\rho_2$</th>
<th>$\rho_1$</th>
<th>$\rho$</th>
<th>$C_V$</th>
<th>$\rho_2/\rho_1$</th>
<th>$s_{BC}$</th>
<th>$s_{BC}/\rho$</th>
<th>$C_V/\rho_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>.1</td>
<td>.14513</td>
<td>.17497E-8</td>
<td>.14513</td>
<td>.20597E-4</td>
<td>829E + 5 .68889E-5</td>
<td>.1E-5</td>
<td>1.2056E-8</td>
<td></td>
</tr>
<tr>
<td>.5</td>
<td>.14513</td>
<td>.11607E-5</td>
<td>.14513</td>
<td>.23749E-2</td>
<td>125030 .80709E-3</td>
<td>.117E-3</td>
<td>.8E-5</td>
<td></td>
</tr>
<tr>
<td>.8</td>
<td>.14513</td>
<td>.11607E-5</td>
<td>.14513</td>
<td>.21058E-1</td>
<td>1250.4 .42709E-2</td>
<td>.6202E-3</td>
<td>.8E-5</td>
<td></td>
</tr>
<tr>
<td>.9</td>
<td>.14473</td>
<td>.37579E-3</td>
<td>.14511</td>
<td>.47598E-1</td>
<td>385.145 .8084E-2</td>
<td>.2596E-2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>.14415</td>
<td>.95892E-3</td>
<td>.14511</td>
<td>.10504</td>
<td>150.32</td>
<td>.15562E-1</td>
<td>.00226</td>
<td>.8E-5</td>
</tr>
<tr>
<td>1.2</td>
<td>.14107</td>
<td>.40407E-2</td>
<td>.14511</td>
<td>.33523</td>
<td>1250.4 .42709E-2</td>
<td>.6562E-2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.4</td>
<td>.13403</td>
<td>.11109E-1</td>
<td>.14513</td>
<td>.80923</td>
<td>12.0649</td>
<td>.13301</td>
<td>.0193</td>
<td>.8289E-1</td>
</tr>
<tr>
<td>1.6</td>
<td>.12090</td>
<td>.24307E-1</td>
<td>.14520</td>
<td>.5506</td>
<td>4.97407 .28431</td>
<td>.0413</td>
<td>.20105</td>
<td></td>
</tr>
<tr>
<td>1.8</td>
<td>.098205</td>
<td>.47147E-1</td>
<td>.14535</td>
<td>.29278</td>
<td>2.08299</td>
<td>.54155</td>
<td>.0757</td>
<td>.4801</td>
</tr>
<tr>
<td>2.0</td>
<td>.060925</td>
<td>.84682E-1</td>
<td>.14561</td>
<td>.80923</td>
<td>12.0649</td>
<td>.13301</td>
<td>.0193</td>
<td>.8289E-1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$T$</th>
<th>$\rho_2$</th>
<th>$\rho_1$</th>
<th>$\rho$</th>
<th>$C_V$</th>
<th>$\rho_2/\rho_1$</th>
<th>$s_{BC}$</th>
<th>$s_{BC}/\rho$</th>
<th>$C_V/\rho_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>.1</td>
<td>.15284</td>
<td>.87476E-9</td>
<td>.15284</td>
<td>.12912E-4</td>
<td>$\infty$</td>
<td>.43073-5</td>
<td>3937.19</td>
<td>.5723E-9</td>
</tr>
<tr>
<td>.5</td>
<td>.15282</td>
<td>.95820E-6</td>
<td>.15283</td>
<td>.16557E-2</td>
<td>159491</td>
<td>.53774E-3</td>
<td>561.198</td>
<td>.6275E-5</td>
</tr>
<tr>
<td>.8</td>
<td>.15263</td>
<td>.18344E-3</td>
<td>.15283</td>
<td>.22425E-1</td>
<td>832.043</td>
<td>.37520E-2</td>
<td>20.453</td>
<td>.1202E-2</td>
</tr>
<tr>
<td>1.0</td>
<td>.15148</td>
<td>.13510E-2</td>
<td>.15284</td>
<td>.11564</td>
<td>112.12</td>
<td>.16276E-1</td>
<td>12.047</td>
<td>.8191E-2</td>
</tr>
<tr>
<td>1.2</td>
<td>.14765</td>
<td>.52329E-2</td>
<td>.15287</td>
<td>.35856</td>
<td>34.912</td>
<td>.55231E-1</td>
<td>10.554</td>
<td>.7E-2</td>
</tr>
<tr>
<td>1.4</td>
<td>.13902</td>
<td>.13998E-1</td>
<td>.15296</td>
<td>.86374</td>
<td>9.324</td>
<td>.14263</td>
<td>10.189</td>
<td>.1007</td>
</tr>
<tr>
<td>1.6</td>
<td>.12315</td>
<td>.30126E-1</td>
<td>.15313</td>
<td>1.6423</td>
<td>4.08776</td>
<td>.30331</td>
<td>10.068</td>
<td>.2446</td>
</tr>
<tr>
<td>1.8</td>
<td>.095685</td>
<td>.57957E-1</td>
<td>.15345</td>
<td>3.1132</td>
<td>1.65273</td>
<td>.57448</td>
<td>9.912</td>
<td>.60588</td>
</tr>
<tr>
<td>2.0</td>
<td>.049022</td>
<td>.10553</td>
<td>.15405</td>
<td>5.4286</td>
<td>2.46536</td>
<td>1.0145</td>
<td>9.61338</td>
<td>2.1527</td>
</tr>
</tbody>
</table>

Pressure = 5

<table>
<thead>
<tr>
<th>$T$</th>
<th>$\rho_2$</th>
<th>$\rho_1$</th>
<th>$\rho$</th>
<th>$C_V$</th>
<th>$\rho_2/\rho_1$</th>
<th>$s$</th>
<th>$s/\rho_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>.1</td>
<td>.15892</td>
<td>.53584E-9</td>
<td>.15892</td>
<td>.92471E-5</td>
<td>$\infty$</td>
<td>.30835-5</td>
<td>5757.27</td>
</tr>
<tr>
<td>.5</td>
<td>.15891</td>
<td>.12284E-5</td>
<td>.15892</td>
<td>.12825E-2</td>
<td>1293.56</td>
<td>.39716E-3</td>
<td>323.315</td>
</tr>
<tr>
<td>.8</td>
<td>.15862</td>
<td>.29087E-3</td>
<td>.15892</td>
<td>.26776E-1</td>
<td>545.33</td>
<td>.38804E-2</td>
<td>14.3347</td>
</tr>
<tr>
<td>.9</td>
<td>.15809</td>
<td>.8369E-3</td>
<td>.15892</td>
<td>.6383E-1</td>
<td>188.9</td>
<td>.89332E-2</td>
<td>10.6742</td>
</tr>
<tr>
<td>1.0</td>
<td>.15701</td>
<td>.19438E-2</td>
<td>.15893</td>
<td>.13393</td>
<td>80.7728</td>
<td>.18815E-1</td>
<td>9.67949</td>
</tr>
<tr>
<td>1.2</td>
<td>.15220</td>
<td>.6862E-2</td>
<td>.15899</td>
<td>.41524</td>
<td>22.1766</td>
<td>.62507E-1</td>
<td>9.10809</td>
</tr>
<tr>
<td>1.4</td>
<td>.14167</td>
<td>.17631E-1</td>
<td>.15911</td>
<td>.99358</td>
<td>8.035</td>
<td>.15848</td>
<td>8.98871</td>
</tr>
<tr>
<td>1.6</td>
<td>.12221</td>
<td>.37530E-1</td>
<td>.15938</td>
<td>.19024</td>
<td>3.25641</td>
<td>.33491</td>
<td>8.9303</td>
</tr>
<tr>
<td>1.8</td>
<td>.088137</td>
<td>.72376E-1</td>
<td>.15991</td>
<td>3.5295</td>
<td>1.21774</td>
<td>.63384</td>
<td>8.75833</td>
</tr>
<tr>
<td>1.95</td>
<td>.046985</td>
<td>.11446E-1</td>
<td>.16059</td>
<td>5.246</td>
<td>.481813</td>
<td>.97517</td>
<td>8.51974</td>
</tr>
<tr>
<td>2.0</td>
<td>.027802</td>
<td>.13405</td>
<td>.16091</td>
<td>5.9711</td>
<td>.207394</td>
<td>1.1252</td>
<td>8.39388</td>
</tr>
</tbody>
</table>

186
### Pressure = 15

<table>
<thead>
<tr>
<th>$T$</th>
<th>$p_2$</th>
<th>$p_1$</th>
<th>$\rho$</th>
<th>$C_V$</th>
<th>$p_2/p_1$</th>
<th>$s$</th>
<th>$s/p_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>.1</td>
<td>.16403</td>
<td>.36709E-9</td>
<td>.16403</td>
<td>.71329E-5</td>
<td>$\infty$</td>
<td>.23779-5</td>
<td>64777.69</td>
</tr>
<tr>
<td>.5</td>
<td>.16402</td>
<td>.18453E-5</td>
<td>.16403</td>
<td>.10838E-2</td>
<td>88887.9</td>
<td>.31462E-3</td>
<td>170.498</td>
</tr>
<tr>
<td>.8</td>
<td>.1636</td>
<td>.424E-3</td>
<td>.16403</td>
<td>.32024E-1</td>
<td>.99742</td>
<td>.42917E-2</td>
<td>170.498</td>
</tr>
<tr>
<td>.9</td>
<td>.16289</td>
<td>.11714E-2</td>
<td>.16404</td>
<td>.75851E-1</td>
<td>139.056</td>
<td>.10319E-1</td>
<td>8.80912</td>
</tr>
<tr>
<td>1.0</td>
<td>.16147</td>
<td>.26347E-2</td>
<td>.16405</td>
<td>.10950</td>
<td>61.2859</td>
<td>.21955E-1</td>
<td>8.333024</td>
</tr>
<tr>
<td>1.2</td>
<td>.15540</td>
<td>.88647E-2</td>
<td>.16412</td>
<td>.44072</td>
<td>17.5302</td>
<td>.71957E-1</td>
<td>8.11725</td>
</tr>
<tr>
<td>1.4</td>
<td>.14242</td>
<td>.22080E-1</td>
<td>.16429</td>
<td>.86039</td>
<td>6.45712</td>
<td>.17897</td>
<td>8.10553</td>
</tr>
<tr>
<td>1.6</td>
<td>.11839</td>
<td>.46810E-1</td>
<td>.16465</td>
<td>2.0192</td>
<td>2.5292</td>
<td>.37664</td>
<td>8.04614</td>
</tr>
<tr>
<td>1.8</td>
<td>.74742E-1</td>
<td>.16536</td>
<td>3.7607</td>
<td>.816794</td>
<td>.71670</td>
<td>7.83219</td>
<td></td>
</tr>
<tr>
<td>1.95</td>
<td>.17795E-1</td>
<td>.14971</td>
<td>.16641</td>
<td>6.2825</td>
<td>.118869</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Pressure = 20

<table>
<thead>
<tr>
<th>$T$</th>
<th>$p_2$</th>
<th>$p_1$</th>
<th>$\rho$</th>
<th>$C_V$</th>
<th>$p_2/p_1$</th>
<th>$s$</th>
<th>$s/p_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>.1</td>
<td>.16849</td>
<td>.26997E-9</td>
<td>.16849</td>
<td>.57664E-5</td>
<td>$\infty$</td>
<td>.19223-5</td>
<td>7120.42</td>
</tr>
<tr>
<td>.5</td>
<td>.16848</td>
<td>.29171E-3</td>
<td>.16849</td>
<td>.99665E-3</td>
<td>57755.7</td>
<td>.26359E-3</td>
<td>90.3603</td>
</tr>
<tr>
<td>.8</td>
<td>.16791</td>
<td>.59442E-3</td>
<td>.16849</td>
<td>.38572E-1</td>
<td>88887.9</td>
<td>.49635E-3</td>
<td>170.498</td>
</tr>
<tr>
<td>.9</td>
<td>.16695</td>
<td>.15873E-2</td>
<td>.16850</td>
<td>.89913E-1</td>
<td>88887.9</td>
<td>.1216E-1</td>
<td>170.498</td>
</tr>
<tr>
<td>1.0</td>
<td>.16512</td>
<td>.34758E-2</td>
<td>.16852</td>
<td>.18135</td>
<td>47.506</td>
<td>.25837E-1</td>
<td>7.4334</td>
</tr>
<tr>
<td>1.2</td>
<td>.15750</td>
<td>.11308E-1</td>
<td>.1861</td>
<td>.50271</td>
<td>13.9287</td>
<td>.83426E-1</td>
<td>7.37761</td>
</tr>
<tr>
<td>1.4</td>
<td>.14159</td>
<td>.27633E-1</td>
<td>.16883</td>
<td>1.1844</td>
<td>5.12395</td>
<td>.20455</td>
<td>7.40238</td>
</tr>
<tr>
<td>1.6</td>
<td>.11154</td>
<td>.58433E-1</td>
<td>.16931</td>
<td>2.2859</td>
<td>1.90884</td>
<td>.42826</td>
<td>7.32908</td>
</tr>
<tr>
<td>1.8</td>
<td>.54659E-1</td>
<td>.11660</td>
<td>.17028</td>
<td>4.4834</td>
<td>.816794</td>
<td>.82223</td>
<td>7.05172</td>
</tr>
</tbody>
</table>

### Pressure = 25

<table>
<thead>
<tr>
<th>$T$</th>
<th>$p_2$</th>
<th>$p_1$</th>
<th>$\rho$</th>
<th>$C_V$</th>
<th>$p_2/p_1$</th>
<th>$s$</th>
<th>$s/p_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>.1</td>
<td>.17246</td>
<td>.22085E-9</td>
<td>.17246</td>
<td>.4815E-5</td>
<td>.78E-9</td>
<td>.16053-5</td>
<td>7268.73</td>
</tr>
<tr>
<td>.5</td>
<td>.17245</td>
<td>.18453E-5</td>
<td>.17246</td>
<td>.10069E-2</td>
<td>88885</td>
<td>.23324E-3</td>
<td>126.40</td>
</tr>
<tr>
<td>.8</td>
<td>.17425</td>
<td>.8335E-3</td>
<td>.17247</td>
<td>.47252E-1</td>
<td>209</td>
<td>.59974E-3</td>
<td>48.32898</td>
</tr>
<tr>
<td>.9</td>
<td>.17166</td>
<td>.21514E-2</td>
<td>.17248</td>
<td>.10767</td>
<td>88887.9</td>
<td>.14726E-2</td>
<td>170.498</td>
</tr>
<tr>
<td>1.0</td>
<td>.16803</td>
<td>.45751E-2</td>
<td>.17251</td>
<td>.21193</td>
<td>36.7273</td>
<td>.30896E-1</td>
<td>6.75308</td>
</tr>
<tr>
<td>1.2</td>
<td>.15847</td>
<td>.14396E-1</td>
<td>.17262</td>
<td>.58045</td>
<td>11.0077</td>
<td>.97621E-1</td>
<td>6.78112</td>
</tr>
<tr>
<td>1.4</td>
<td>.13868</td>
<td>.34682E-1</td>
<td>.17291</td>
<td>1.3577</td>
<td>8.994</td>
<td>.23620</td>
<td>6.81045</td>
</tr>
<tr>
<td>1.6</td>
<td>.99891E-1</td>
<td>.74342E-1</td>
<td>.17356</td>
<td>2.635</td>
<td>1.34368</td>
<td>.49733</td>
<td>6.668976</td>
</tr>
<tr>
<td>1.8</td>
<td>.17527E-1</td>
<td>.15821</td>
<td>.17512</td>
<td>5.4955</td>
<td>.11079</td>
<td>.99186</td>
<td>6.26926</td>
</tr>
</tbody>
</table>

Table 1.8.3. Experimental data from Brooks and McConnelly. Corrected only for $p = 0$.  

187
IX. Atmospheres

We attach great significance to the early work of Newton and Laplace on sound propagation in the atmosphere, for it showed, at a very early date, that thermodynamics is more than a science of equilibria. The study of the atmospheres in themselves, even when limited to stationary phenomena, is of course the most important scientific endeavor of our time. They too take us beyond equilibria, and indeed adiabatic thermodynamics, but not so far that careful application of the Gibbsian variational principle becomes irrelevant. We shall undertake a study of atmospheres in Section IX.2. There is yet another reason to study atmosphere, for they are defined by gravitation and ultimately, in the astrophysical context, they require a fusion of thermodynamics with General Relativity.

IX.1. Introducing gravitation

Gravitation enters as a component of most, if not all applications of physics. There is a set and tested procedure for introducing the gravitational field into any dynamical context. In classical, non-relativistic physics it consists of adding the gravitational potential energy to the Hamiltonian. For an isolated, ideal gas one adds

$$ \int_{\Sigma} d^3x \rho \phi, $$

where $\rho$ is the mass density and $\phi$ is the Newtonian potential. The adiabatic Lagrangian becomes

$$ \int L = \int_{\Sigma} d^3x \left( \rho(\dot{\Phi} - \vec{v}^2/2 - \phi) - f - sT \right). $$

In the case of an ideal gas,

$$ \int L = \int_{\Sigma} d^3x \left( \rho(\dot{\Phi} - \vec{v}^2/2 - \phi) - \mathcal{R}T \rho \ln \frac{k}{k_0} \right), \quad k := \frac{\rho}{T^n}. \quad (9.1.1) $$

This prescription for including the effect of gravity has its ultimate justification in General Relativity. The most important effect of gravity is contained in the time component of the metric and it usually appears in connection with time derivatives, thus as an extra term in the Hamiltonian and added to the velocity potential.

In this section the constant $k_0$ stands for the specific entropy,

$$ S/\mathcal{R} = n - \ln k_0, \quad (9.1.2) $$

assumed constant, and $k := \rho/T^n$ is sometimes referred to as the adiabatic temperature. The gravitational field appears in the equation of motion,

$$ \dot{\Phi} - \vec{v}^2/2 - \phi = \mathcal{R}T(\ln \frac{k}{k_0} + 1). $$
When the effect of gravity is taken into account in the dynamics we get a theory of atmospheres. In the case of terrestrial gravity \( \phi = gz \), where \( g \) is a constant and \( z \) is the elevation. The adiabatic condition makes \( k = k_0 \), constant, and the equation

\[
\dot{\Phi} - gz = \mathcal{R} T (\ln x + n + 1), \quad x := \frac{k}{k_0}.
\]  

(9.1.3)

predicts a constant temperature gradient (lapse rate) for an isolated atmosphere that consists of an ideal gas. The effect has never, to our knowledge, been tested in the laboratory, (but see Liao (2008) and Graeff (2009)), but the constant lapse rate is a feature that is observed in the earth’s atmosphere, in the oceans and in the internal structure of stars (Lane 1870, Ritter 1880, Emden 1908, Eddington 1926, Levy 19). For the earthly troposphere this formula actually gives a value of the temperature gradient that is close to observation, at low atmospheric humidity. This successful application of a theory originally constructed to account for laboratory experiments where gravitational effects are insignificant, modified in standard fashion to include gravity, does not attribute the observed temperature gradient to the radiation from the Sun or to any external source other than gravity (Fronsdal 2011). The actual atmosphere is close to isentropic, not because of the effect of convection and radiation but in spite of it. The effect of humidity on the lapse rate will be examined below. currently, this is the attitude adopted in the context of planetary atmospheres.

It is evident that, in the absence of the Sun, the present state of the earthly atmosphere could not endure. The extinction of the sun would lead to a general cooling of the atmosphere. This cooling is not described by any process encompassed by adiabatic Lagrangian dynamics. Instead, another external agent enters the picture, the spontaneous emission of infrared radiation. As this is a slow effect we can regard the cooling as a sequence of equilibria of adiabatic dynamics, a slow loss of entropy and an increase in the value of \( k_0 \) (Section II.3). The reverse effect is also possible and if the terrestrial atmosphere is found to be stable over long times then we must conclude that spontaneous cooling by emission is balanced by the heating that is indirectly provided by the sun (the greenhouse effect).

The problem of the gravitation induced temperature gradient can be debated within the framework laid out in the Appendix to this chapter. Important aspects of historical atmospheric science, including the popular polytropic atmospheres and Emden’s stability theorem are also relegated to that Appendix.

**The van der Waals atmosphere**

As far as the atmosphere of the earth is concerned, the van der Waals modification of the ideal gas may seem to be of little interest, since the excluded volume factor \( (1 - bp) \) differs from unity by about one part in 1000. Nevertheless, we shall find a useful application of the van der Waals model to study the humidity of our atmosphere, see below. Applications to stellar atmospheres are interesting but they must be done within the framework of General Relativity.

**IX.2. Mixed, isentropic atmospheres**
At one time it was believed that, in an atmosphere consisting of several components with different molecular weights, the lighter gas would float on top, contrary to the popular idea that all gases are miscible. This was surely based on observation, since cooking gas, entered at ground level, tends to remain there; however, it does so only for a short time. Dalton made the radical proposal that each gas behaves as if the other were absent. This was an overstatement and led to much misunderstanding and debate, some of it recorded in Dalton’s book (Dalton 1806). In the case of gases that have had time to settle, Dalton’s prediction had some initial success, but the most recent observations indicate that the concentrations tend to be nearly independent of elevation.

A complete investigation of the atmosphere must recognize that it involves a dissipative process, but if the problem that concerns us is the density and temperature profile of a final, stationary state of the mixed atmosphere then it begs the question. If an equilibrium is ultimately reached, then we are mainly interested in the end result, and less in describing the process that leads to it. The process is dissipative but the net entropy of the atmosphere is preserved by radiation. We shall assume that it can be ignored in the study of the final, stationary configuration, and in the adiabatic perturbations of it.

We have embraced the Gibbs-Dalton hypothesis and we have used it for mixtures that are not under the influence of gravity. But for a mixture of ideal gases in the gravitational field it leads to a contradiction. Namely, since the hydrostatic conditions for the individual gases also remain valid in the mixture (assuming no mutual interaction), we would deduce that

\[ \dot{\Phi}_i - \phi = R_i (n_i + 1)T, \quad i = 1, 2, \]

from which two expressions for the lapse rate:

\[ gz = R_1 (n_1 + 1)T = R_2 (n_2 + 1)T, \]

which is contradictory whenever \((n_1 + 1)/m_1 \neq (n_2 + 1)/m_2\). In this section the mass densities are in g/cm\(^3\), not molar, and the constants \(R_1 = R/m_1, R_2 = R/m_2\).

In what follows we shall take the Lagrangian for the mixture to be the sum of the Lagrangians for the two pure gases, eventually to be corrected by an interaction term. The original form of the Gibbs-Dalton hypothesis is not satisfied.

**IX.3. Nitrogen and Oxygen**

We begin by examining the atmospheric concentration of Nitrogen and Oxygen, ignoring the rarer components. According to a number of sources, the relative concentration does not vary with altitude, but no authoritative scientific information was found. (?)

Consider a vertical column of air consisting of nitrogen and oxygen and confined to the range \(0 < z < z_1\) of elevation. The equations of motion that determine the equilibrium configurations are, if entropic forces and other interactions are ignored,

\[ \dot{\Phi}_1 - gz = \mathcal{R}_1 T (\ln x + 1 + n_1), \quad x := \frac{\rho_1}{T^{m_1} k_{01}} = \frac{k_1}{k_{01}}; \quad (9.3.1) \]

\[ \dot{\Phi}_2 - gz = \mathcal{R}_2 T (\ln y + 1 + n_2), \quad y := \frac{\rho_2}{T^{m_2} k_{02}} = \frac{k_2}{k_{02}}; \quad (9.3.2) \]
and

\[ R_1 \rho_1 \ln x + R_2 \rho_2 \ln y = 0. \]  

(9.3.3)

The last equation is the adiabatic condition. The adiabatic parameter \( k_0 \) and the “adiabatic temperature” \( k \) were defined in Eq.s (9.1.1) and (9.1.2). In the case of pure gases without gravity \( x = y = 1 \); the Gibbs-Dalton hypothesis would assign the same values in the mixture. The concentration would be constant and related to the specific entropies. This would be possible if nothing linked the two systems, but not here, for the adiabatic condition, and the gravitational terms \( -gz \), amount to indirect forms of interaction.

The fixed parameters are

\[ R_1 = R/28, \quad R_2 = R/32, \quad R = 8.314 \times 10^8, \quad n_1 = n_2 = 5/2. \]

The two \( \dot{\Phi} \)'s are constant, determined by the boundary conditions. The most interesting question concerns the adiabatic parameters \( k_{01} \) and \( k_{02} \); that is, the specific entropies \( S_1 \) and \( S_2 \). We harbor a strong prejudice for taking them to be uniform, independent of \( z \); the first question is whether this allows for a solution. We shall show that, when \( n_1 = n_2 \), the answer is affirmative.

The data at ground level \( z = 0 \) are,

\[ T(0) = 293.159, \quad \rho(0) = .0012, \quad \rho_1(0) = .9184 \times 10^{-3}, \quad \rho_2(0) = .2816 \times 10^{-3} \]

and \( \rho_1(0)/\rho_2(0) = 3.2614 \). This gives us the predicted pressure at sea level,

\[ p(0) = [R_1 \rho_1(0) + R_2 \rho_2(0)]T = 1.0139 \times 10^6, \]

against the experimental value that ranges from 1 to 1.05 million ergs.

We shall look for a solution with \( x, y \) both uniform. The specific entropies \( S_1 \) and \( S_2 \) are also uniform, though not with the same values as for the separate gases. In that case the concentration is also constant, by (9.3.3).

Combining the three equations of motion to eliminate the logarithms we find, since the concentration is uniform,

\[ \left. \frac{T(0) - T}{z} \right|_{z=0} = \frac{g}{\sum (n_i + 1)R_i \rho_i/\rho} \]

(9.3.4)

which gives a constant temperature lapse rate of 9.715 degrees Kelvin per kilometer. Consequently Eq.s (9.3.1-2) are equivalent to

\[ \frac{-g}{RT'} = \frac{\ln x + 3.5}{28} = \frac{\ln y + 3.5}{32}. \]

(9.3.5)

Combining this with Eq. (9.3.3) we find that, if \( x, y \) are constant, the unique solution is

\[ x = .902428, \quad y = 1.4662, \quad \frac{x}{y} = .61240, \quad \frac{\rho_1}{\rho_2} = 3.2614, \quad \frac{k_{01}}{k_{02}} = 5.2988. \]
The densities for the pure gases at standard conditions are: Nitrogen .0001251, Oxygen .0001429.

For any set of values of $k_{01}$, these figures fix the densities in terms of $T$, which is in turn determined by the elevation $z$. Thus $k_{01}$ is unrestricted and can be taken to be uniform. Using the data at ground level we obtain

$$k_{01} = \frac{.9184 \times 10^{-3}}{.902428} (293.159e)^{-2.5} = 5.6771 \times 10^{-11}, \quad k_{02} = 1.0714 \times 10^{-11}$$

and

$$S_1 = -R \ln(xk_{01}) = 23.6947R/\text{mol}, \quad S_2 = 24.8768R\text{mol}.$$ 

Note that, because $x$ and $y$ are not equal to 1, these differ from the entropy of the corresponding pure ideal gas with the same density and temperature. The deviation of $x$ and $y$ from unity is a measure of the effect of mixing; Nitrogen effectively passes some of its entropy to Oxygen. The adiabatic parameter for pure Nitrogen under normal conditions * is $6.58 \times 10^{-11}$; for Oxygen it is $7.52 \times 10^{-11}$; that is,

$$S_N = -R \ln(5.6771 \times 10^{-11}) = 23.44R/\text{mol}, \quad S_O = 23.31R/\text{mol}.$$ 

These values are not normalized to agree with the third law, but the difference $S_N - S_O = 1.12J/mol$ compares well with the measured value reported as $1J/mol$.

The difference from the values that apply to pure gases is of course greater for the minor component of the mixture.

A misprint here.

**Discussion.** We justify taking $x, y$ uniform as follows. Consider the mixture without the presence of gravity. Then, surely all variables are uniform. The effect of mixing is merely to change the values of the entropy parameters $k_{01}, k_{02}$. These values may conform to the Gibbs-Dalton hypothesis or they may not. The variables $\Phi_1, \Phi_2$ play their limited role as constants of integration. What happens as we turn on gravity? Only one thing is changed: we are to add the term $-gz\rho$ to the Lagrangian density. Nothing suggests a direct effect of gravitation on the entropy distribution, so the assigned specific entropy densities should not change, so long as the equations of motion have a solution. But the equations of motion demand that the entropy parameters allow for the existence of solutions, and this dynamical requirement is inconsistent with the Gibbs-Dalton hypothesis. Although turning on gravitation does not involve a change in entropy, the entropies have to have values that allow for the existence of solutions of the equations of motion, and that is the requirement that we are using to determine these parameters, pending more data.

* “Standard conditions”: $T = 0^\circ C = 273.16K$, the density of N is .001251 and .001251/(300e)^{5/2} = 6.587 \times 10^{-11}$. This was my original number. “Normal conditions”: $T = 293.15K$. I should have used .00125′/(273.16e)^{5/2} = 8.2368 \times 10^{-11}$. Change later.
IX.4. Air and Argon

The densities for the pure gases at standard conditions are: Air .00012, Argon .0001784. The adiabatic parameters for pure Air: 6.32 E-11, Argon: 7.66 E-8; that is,

\[ S_{Air} = 23.48 \mathcal{R} / \text{mol}, \quad S_{Ar} = 16.38 \mathcal{R} / \text{mol}. \]

where do these values come from?

This case is different since the two gases have different adiabatic index; see (9.3.1-2). By “Air” we mean an ideal gas with \( n = 5/2 \) and atomic weight 29. Eq.s (10.3.1-3) apply, but the data are different.

The fixed parameters are

\[ \mathcal{R}_1 = \mathcal{R}/29, \quad \mathcal{R}_2 = \mathcal{R}/40, \quad \mathcal{R} = .8314 \times 10^8, \quad n_1 = 5/2, \quad n_2 = 3/2. \]

The data at ground level, \( z = 0, \)

\[ T = 293.159, \quad \rho_1(0) = 1.2 \times 10^{-3}, \quad \rho_2(0) = 1.116 \times 10^{-5}, \quad \frac{\rho_1}{\rho_2} = 107.527. \]

Should this be for “Normal conditions”, \( T = 293.15K? \)

This case is more difficult, chiefly because there are fixed parameters to be chosen. Observations seem to indicate that the ratio \( \rho_1/\rho_2 \) varies slowly, but there is no solution that makes \( \rho_1/\rho_2 \) independent of altitude. Because Air is very dominant we expect it to be only a little perturbed by the presence of Argon; that is, the specific entropy is likely to have a value close to what would be observed in the absence of Argon. In other words, the variable \( x \) is likely to be close to 1 under normal conditions at ground level. Taking \( x = .99 \) we get from (9.3.3) the value \( y = 4.68249. \)

Eq.s (9.3.1-2) tell us that

\[ c := T \left( \frac{\ln x + 3.5}{29} - \frac{\ln y + 2.5}{40} \right) \]

must be uniform. Setting \( x = .99, y = 4.44 \) at sea level we get the value, \( c = 7.0462. \) Also at sea level

\[ \frac{k_{01}}{k_{02}} = \frac{\rho_1}{\rho_2} e^{T x} = .68249. \]

Having thus obtained good trial values of the parameters we calculate \( x, y \) and \( T \) by

\[ T^{-1} = \frac{1}{e} \left( \frac{3.5 + \ln x}{29} - \frac{2.5 + \ln y}{40} \right) = -e \frac{k_{01} x \ln x 40}{k_{02} y \ln y 29} \]

and finally the altitude by

\[ g(z - z_0) = \mathcal{R}_1 T (\ln x + 3.5) \]

obtain values from zero to +11 km. The results are in Fig. and in the table. The lapse rate is steady at 10 K/km.
The theory predicts a small reduction in the concentration of Argon at high altitudes.

Since the values of \( x \) and \( y \) are determined we can calculate the adiabatic parameters; at ground level

\[
k_{01} = \rho_1 \frac{(eT)^{n_1}}{x} = 8.485 \times 10^{-14}, \quad k_{02} = \rho_1 \frac{(eT)^{n_2}}{y} = 1.6735 \times 10^{-13}
\]

Then we are free to fix these parameters independent of the elevation and use them to evaluate the individual densities. Calculate entropies. Apply the same method to the case that \( n_1 = n_2 \).

Fig.9.4.1 shows the temperature profile and the line \( T = 300 - 10z \); the lapse rate is very close to uniform.

The significance of a constant lapse rate

must be explained. So far, we have made no reference to Fourier’s heat equation, namely

\[
\dot{T} \propto \Delta T,
\]

If this venerable relation is to be respected, then any stationary atmosphere must have \( \Delta T = 0 \). This property is met by the polytropic atmosphere and that is indeed a principal reason why it is of interest, as emphasized by Emden in 1908. Here, as in the following example, this property is satisfied, to a very good approximation, but not exactly. That the linear relation between the temperature and the altitude is satisfied in the present example is explained by the small amount of Argon in our atmosphere.

The presence of water vapor in our atmosphere has a pronounced effect on the measured lapse rate; we shall try to calculate this effect later.

IX.5. Air and water. Introduction

This is the mixture that controls life on earth. We shall take up the study with respect for generations that have studied it before us and conscious of the special difficulties that characterize \( H_2O \).

Water presents a problem in that we know of no simple, analytic equation of state. The classical van der Waals equation was developed to account for the domain near the critical temperature of \( T= 647K \). To agree with the measured values of the critical temperature and the critical pressure, the density predicted is off by nearly a factor of two, giving 10.95 mol/Lit instead of the measured value 17.87. Conversely, the density of water in normal
conditions is 998.2 g/Lit or 54 mol/Lit, which would imply that \( b\rho = 1.6 > 1 \). In the van der Waals model this parameter varies from 0 to 1.

Data for water. The measured values are, molecular weight 18.015,

\[
T_{cr} = 647 K, \quad p_{cr} = 220 \text{atm}, \quad \rho_{cr} = 17.87 \text{mol/Lit}
\]

Standard van der Waals parameters

\[
a = 5.536 \text{atm(Lit/mol)}^2, \quad b = 0.03049 \text{Lit/mol}
\]

Check, the function

\[
p(\rho) = \frac{0.08314 \times 647\rho}{1 - 0.03049\rho} - 5.536\rho^2
\]

has the value 220.45 at the inflection point \( \rho = 11.069 \).

Our study will be directed at near-normal conditions. Much work has been done to create an accurate equation of state for water, over a very wide range of temperatures, but they lack the attractive feature of the van der Waals model where the coexistence of liquid and water is built in. The solution is to use a van der Waals model specifically adapted to near normal conditions.

At \( T = 293 \text{ K} \) the experimental data are as follows. Vapor pressure 2.3 kPa, densities

\[
\rho_{liq} = 998.2 \text{g/Lit} = 55.4 \text{mol/Lit}, \quad \rho_{vap} = 17.3 \text{g/m}^3 = 0.0096 \text{mol/Lit}
\]

and the ratio of densities is

\[
\frac{\rho_{vap}}{\rho_{liq}} = 1.73285 \times 10^{-5} = \frac{y^u}{y^v}.
\]

We shall construct a van der Waals model on these data.

The van der Waals formula can be written

\[
\frac{p}{p_{cr}} = 8 \frac{T}{T_{cr}} \frac{y}{1-y} - 27y^2
\]

and the free energy density can be expressed as

\[
\frac{f}{p_{cr}} = \frac{8T}{T_{cr}} y \ln \frac{y}{1-y} - 27y^2 + ..., \quad (9.4.3)
\]

where \( y = b\rho \) and +... stands for a term that is linear in \( y \) and that does not affect our calculations of the equilibrium. Because both expressions involve only one parameter, the
The common tangent method allows to calculate $T_{cr}$ from (9.4.2). We find that $T_{cr}$ must have a value near 1178.55.

The two normalized densities and the associated pressure, calculated with the common tangent method using (9.4.4), are:

$$y_{liq} = b' \rho_{liq} = .9199258777 = 55.4b' \text{ mol/Lit}, \quad y_{vap} = 1.59401 \times 10^{-5} = .00096b' \text{ mol/Lit},$$

where $a', b'$ are the new van der Waals parameters required. Both data give the same value for $b'$. To sum up, our modified van der Waals model, chosen to represent the data near normal conditions, is

$$T'_{cr} = 1178.6, \quad b' = .016605, \quad a' = 5.5382.$$ (9.4.6)

The value of $a'$ was obtained from $647(a'/b'^2) = 1187.55(a/b^2)$. We drop the primes from now on. The units are molar densities in $g/Lit$, and atmospheres.

The many significant figures in some of these numbers bespeaks the low compressibility of the liquid, $xdp/dx \approx 6.8 \times 10^{-3}$; the compressibility is the inverse, the experimental value is $4.6 \times 10^{-10}/Pa$.

Finally, the following formula was used for the pressure of the liquid-vapor equilibrium at near-normal conditions

$$p = \frac{.08314 \times T \rho}{1 - .0166 \rho} - 5.5382 \rho^2$$ (9.4.7)

The model of water determined we easily calculate, using the common tangent method, the equilibrium configuration for a modest range of temperature.

<table>
<thead>
<tr>
<th>$T$</th>
<th>$p$ (9.4.4)</th>
<th>$p$ exp.</th>
<th>$y^u$ (9.4.4)</th>
<th>$y^u$ exp.</th>
<th>$y^v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.5040E-3</td>
<td>1.2281E-3</td>
<td>1.0243E-5</td>
<td>0.866E-5</td>
<td>.922908668</td>
</tr>
<tr>
<td>20</td>
<td>2.3389E-3</td>
<td>2.3388E-3</td>
<td>1.5940E-5</td>
<td>1.594E-5</td>
<td>.919925878</td>
</tr>
<tr>
<td>30</td>
<td>3.7790E-3</td>
<td>4.2455E-3</td>
<td>2.4056E-5</td>
<td>2.801E-5</td>
<td>.91692</td>
</tr>
<tr>
<td>50</td>
<td>8.4718E-3</td>
<td>1.2344E-2</td>
<td>5.0605E-5</td>
<td>7.372E-5</td>
<td>.9108489</td>
</tr>
<tr>
<td>70</td>
<td>1.7280E-2</td>
<td>3.1176E-2</td>
<td>9.7250E-5</td>
<td>1.86E-4</td>
<td>.904682723</td>
</tr>
<tr>
<td>90</td>
<td>3.2519E-2</td>
<td>7.0117E-2</td>
<td>1.7304E-4</td>
<td>3.85E-4</td>
<td>.898422971</td>
</tr>
<tr>
<td>110</td>
<td>9.24309E-2</td>
<td>8.4277E-2</td>
<td>2.8904E-4</td>
<td>5.25E-4</td>
<td>.892034</td>
</tr>
</tbody>
</table>

Table. Pressure in atm, temperature in degrees Celcius, $y = bp$ dimensionless.

**Standard method**

It is common to invoke the ideal gas law. If we replace the parameters $a$ and $b$ by zero our formula for the vapor pressure pressure takes the form

$$p = RT \rho = \frac{RT}{.0166} y^u = 5T y^u$$

This does not differ significantly from (9.4.7).
IX.5. Phase separation in a mixture of Air and Water

Data, for “Air” I used Nitrogen, molecular weight 29,

\[ T_{cr} = 128K, \quad p_c = 34\text{atm}, \quad \rho_c = 0.044\text{mol/Lit} = 0.0012754\text{gr/cm}^3, \]

\[ a = 1.408, \quad b = 0.03913. \]

For \( H_2O \) we use the van der Waals model constructed above.

We shall test the merit of regarding the atmosphere as a two-phase mixture of 2 fluids. The influence of gravity will be ignored but we shall nevertheless assume that the two phases separate.

We take the free energy density of this system to be

\[ f = f_1 + f_2 + \alpha \rho_1 \rho_2. \]

To discover the spinodal line we use the formula from Section VI.3 with a slightly different notation.

\[
\left( \frac{T/T_1}{x(1-x)^2} - \frac{27}{4} \right) \left( \frac{T/T_2}{y(1-y)^2} - \frac{27}{4} \right) = \beta := \frac{\alpha^2}{b_1 b_2 T_1 T_2 R^2}. \tag{9.6.1}
\]

Here \( T_1, T_2 \) are the two critical temperatures. When \( \beta = 0 \) there are only the spinodals of each separate fluid. For small, positive \( \beta \) there appear ovals, below 210K for \( \beta = 1 \), below 1149 K when \( \beta = 10 \). These oval quickly grow to the limits of the domain \( 0 < x, y < 1 \) for lower temperatures.

We know the saturated state of water at normal conditions. We now increase the pressure by admitting air, and calculate the coexistent 2-phase configurations for a range of values of the pressure. this is easy, for the water densities do not change.

Calculation

See files AirWater 1a, 1b

Having established a pair of coexistent modes of water,

\[ y^u = 1.59405, \quad y^v = 0.919926, \]

it is easy to include air into the mixture, at least so long as the interaction strength \( \alpha \) is zero. We just choose a value of \( p \) and adjust the parameters \( p \) and \( p \). The result is in the following Table
Table, saturation densities for the system of Air and Water. The density ratios are $c = .01$ (humidity in the air) and $c' = .0017$ (air dissolved in water in water).

At the lowest pressure we have the ideal-gas approximation

$$p \approx .02323 + 622.5x = .02323 + 21.5\rho_1.$$  

Here $\rho_1$ is the molar density of water, in mol/Lit as usual and the pressure is in bars. The first term is the contribution of water vapor, the other is $R\rho T$. In fact, this approximation is valid over the whole range, the partial pressure of water being fixed. The result concerning the saturation density of water in air is somewhat model independent, yet it is off by several orders of magnitude.

At normal conditions the mass ratio water/air in the atmosphere, is

$$\frac{\rho_2}{\rho_1_{molar}} = c\frac{b_1}{b_2} = .0236 \quad \text{or} \quad \frac{\rho_2}{\rho_1_{mass}} = c\frac{29b_1}{18b_2} = .0380.$$  

This within a factor of two of measured values for saturated air. The ratio of air to water in the ocean is,

$$\frac{\rho_1}{\rho_2_{molar}} = c'\frac{b_2}{b_1} = .000721 \quad \text{or} \quad \frac{\rho_1}{\rho_2_{mass}} = c'\frac{18b_2}{29b_1} = .001166.$$  

This results is a prediction for the solubility of water in air that is very different from what is observed. We take this to mean that a form of interaction is needed.

**Interaction**

We try $k = 10$ and $k = 25$. The last row in the table changes to,

<table>
<thead>
<tr>
<th>$p$</th>
<th>$\rho^u$</th>
<th>$c$</th>
<th>$\rho^v$</th>
<th>$c'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>(.00156992, 1.5925 E-5)</td>
<td>.01014</td>
<td>(.00023688, .919929)</td>
<td>.0002575</td>
</tr>
</tbody>
</table>

and when $k = 25$,

<table>
<thead>
<tr>
<th>$p$</th>
<th>$\rho^u$</th>
<th>$c$</th>
<th>$\rho^v$</th>
<th>$c'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>(.0015699, 1.58971 E-5)</td>
<td>.010126</td>
<td>(.1.388E-5, .919931)</td>
<td>1.509E-5</td>
</tr>
</tbody>
</table>
The humidity in air does not budge, the ratio $c$ does not change, but we observe reduction of $c'$, and the specific proportion of air in water that, for $k = 25$, is a factor of $1/100$, and this brings the prediction in line with observation.

We end our investigation of the earth’s atmosphere at this point, for others to finish.

We have chosen to use the confrontation of theory with experiment to discover useful formulas for the internal energies of mixtures, formulas from which all properties of the mixtures can be calculated. This allows for very little freedom and, consequently, strongly enhanced predictive power. Our first attempt at constructing a model for water does not aim at a detailed agreement with experiment, but only, by experience, to see if a simple and partly justified expression for the free energy density reproduces general features, as was the case with the van der Waals formula.

**The standard approach**

There is no standard approach to constructing the thermodynamic potential for mixtures. The general condition for equilibrium is that

$$
\mu_1^u = \mu_1^v, \quad \mu_2^u = \mu_2^v. \tag{9.6.2}
$$

Remember that this comes from minimizing the energy. The chemical potentials can be expressed as derivatives of the free energy, the enthalpy or the Gibbs energy. Using the enthalpy for illustration, we have

$$
(h_1 - S_1T)^u - (h_1 - S_1T)^v = 0, \quad (h_2 - S_2T)^u - (h_2 - S_2T)^v = 0,
$$

see Section IV.3. The first equation is often ignored if only the vapor is subject of interest. The value of $h_2^u - h_2^v$ is taken from tables. Then follows a step that I do not understand. It is averred that the total differential

$$
d \left[ (h_2 - S_2T)^u - (h_2 - S_2T)^v \right] = 0,
$$

but this can be justified only when projected on a tangent that points along the manifold of coexistent configurations. The completion of the calculation involves additional reference to tables. Tables are useful for engineers who do not have to review the theory in order to get information. But physicists prefer to use the accumulation of experimental results to gradually pin down a useful formula for the free energy density, one that contains the information assembled in all the tables.
IX.7. Polytropic atmospheres

Emden’s book of 1907 laid the foundations for 100 years of astrophysics and it had a profound effect on atmospheric science as can be verified by a modern web survey. It is concerned with the stability of a polytropic atmospheres.

A polytropic atmosphere is one in which the pressure and the density are related this way:

\[ p = a \rho^\gamma, \quad \gamma > 1, \]

with \( a \) and \( \gamma \) constant, independent of the altitude. An isentropic atmosphere that consists of an ideal gas is polytropic with \( \gamma = 1 + 1/n \). We shall consider an atmosphere that consists of an ideal gas, polytropic but not isentropic, with the constant \( \gamma \) unrelated to the adiabatic index \( n \).

**Emden’s theorem**

The polytropic atmosphere is stable to convection if and only if

\[ \gamma < 1 + 1/n, \]

The most stable among polytropic atmospheres is the isothermal atmosphere with \( \gamma = 1 \).

More precisely, the expectation is that, if the polytropic relation is satisfied as initial conditions at \( t = 0 \) then the inequality determines what will happen later: a small convective perturbation will grow unless it is satisfied. (It is assumed that there is no flow at \( t = 0 \).)

The proof offered by Emden in 1907 and repeated in today’s textbooks is the same. Suppose that a small volume of gas is displaced upwards adiabatically; that is, without any heat transfer. The pressure in the displaced gas will adjust, adiabatically, to the new environment, almost immediately. Suppose the inequality is satisfied, then the displaced volume will have a larger density than the gas nearby and it will therefore revert downwards. If instead the small volume is displaced downwards then it will become thinner and again it will rebound.

This arguments is an account of the balance of forces: pressure against gravity. This implies that there is a dynamical theory behind the argument. The number \( n \) is the adiabatic index, hence the fluid is an ideal gas. Ideal gases have been extensively studied and the only known dynamical theory is the thermodynamics developed over many years and reported in this book.

As we have seen in Section III.1, the forces are the pressure, gravitation and, unless the specific entropy is uniform, the entropic gradient. The latter is zero in the isentropic case, when \( \gamma = 1 + 1/n \). The “proof” has no weight because entropic forces are not taken into account.

**The effect of entropic forces**

The paradigm of the type of stability argument offered in the “proof” of Emden’s theorem is this. A ball resting on top of a cylinder is subject to no forces because the contact
force is balanced by gravitation; this is true if the position of the ball is precisely at the highest point, where the energy is stationary to first order of perturbations. This is first order equilibrium. To decide whether the equilibrium is stable or not one carries the calculations to second order. The initial conditions envisaged in the proof do not define an equilibrium because the effect of the entropy gradient has not been included; the forces are not balanced and the argument cannot proceed.

When the gravitational force is included, and \( s = \rho S \) Eq. (3.1.6), the hydrostatic condition, becomes
\[
\nabla p = -\nabla (gz) - \rho T \nabla S.
\]

In accordance with the Gibbsean variational principle the entropy is a given, fixed function of position; suppose we have solved this differential equation for the density (after elimination of the temperature by the adiabatic relation.

To study stability of this point of equilibrium we must study second order perturbations. Turning once more to Gibbs (and our own experience) we do not vary \( S \) but keep it fixed. The required calculation is the same as for sound propagation and the answer is the same, real number, \( c = \sqrt{\gamma RT} \). The equilibrium is stable.

**IX.8. The isentropic atmosphere.**

A famous controversy concerns the temperature profile of an isolated atmosphere in a constant gravitational field. A pillar of statistics proclaims that, at equilibrium, the temperature of any extended system is uniform, and more, that this statement remains true in the presence of a gravitational field. One of the first to voice disagreement with this dictum was Loschmidt, who was crushed by the united authority of Boltzmann and Maxwell. A steady flow of papers have been published over a period of more than 100 years, all proving that there can be no temperature gradient. A few papers have managed to get past editors and referees with proofs of the contrary. Taking up the question again at this time seems almost redundant, and yet.....

It must be said that the belief in the isothermal atmosphere is, in many cases, just that, a belief or conviction, unsupported or contradicted by the evidence. That said, what would qualify a scientist to issue an expert opinion?

**What physics is involved?**

1. Gravitation. What is absolutely clear, yet frequently overlooked, is that it is futile to try to make a decision without a deep knowledge of gravitation. That the controversy involves gravitation is in fact fortunate, for no force is better understood. At the deepest level we have General Relativity with its Equivalence Principle. It tells us that gravitation is a force that resides in the space time metric and that the interaction is strongly restricted by invariance under general coordinate transformations. An intimate knowledge of General Relativity is probably not required, but one should know that, in non-relativistic physics the only component of the metric that is needed is the time-time component \( g_{00} \) and that it takes the form
\[
g_{00} = c^2 - 2\phi.
\]
Here $c$ is the velocity of light and $\phi$ is the Newtonian gravitational potential. In field theories, this component of the metric appears in conjunction with a time derivative, and that is the origin of the following rule:

**To introduce the effect of gravitation in any dynamical framework, simply add the Newtonian potential to the energy density.**

In some less developed contexts this prescription fails to be meaningful, or insufficiently precise, but then there is no alternative. I think that it may be agreed that, in any context in which it cannot be applied, we lack enough knowledge about gravitation to have a meaningful discussion about the influence of gravitation on an atmosphere.

2. Thermodynamics. This word is frequently taken to refer to the study of equilibria exclusively. But that is not enough. There are several cogent reasons why a dynamical theory is needed. In the first place, any discussion of equilibria *per se*, without a description of the systems of which they are the equilibria, is likely to be inconclusive. The concept of equilibrium is, in my opinion, meaningful only in the context of a dynamical system. And again, without a dynamical theory we shall not know how to introduce the gravitational field or to determine its effects.

Any discussion that restricts the input of thermodynamics to statements about abstract equilibria is not likely to be useful. That leads us to:

3. Non-equilibrium thermodynamics. Under this banner there has been a great deal of activity in the last half-century. This point of view is probably not going to be of much help, for the following reason. The term non-equilibrium strongly suggests that any attempt to get away from the equilibrium is an exploration of the unknown. For example, it is widely held that there is not, until now, a reliable account of entropy. But without an understanding of the role of entropy we are lost, just as we should be lost without an understanding of gravitation.

4. Adiabatic thermodynamics. Actually thermodynamics is advanced well beyond the study of equilibria. Already in 1825 Laplace formulated a successful theory of sound propagation, based in part on the postulate that this phenomenon is isentropic; that is, that the entropy per particle does not change when the density and the temperature are executing the motion that is sound. Furthermore, the calculation is done within a dynamical framework, involving the equation of continuity and the Bernoulli equation. Finally, this is an apt example, for it is very close to the issue at hand. So let us examine the calculation in a little more detail.

There is nothing controversial about the equation of continuity; nothing needs to be said about it. When Laplace postulates that sound propagation is isentropic he refers to the fact that the entropy of an ideal gas is related to the temperature and the density by the polytropic relation,

$$\frac{\rho}{T^n} = \text{constant},$$

where $n$ is a constant that is characteristic of the gas. That is; this combination of density and temperature is a constant of the motion. The value of the constant is directly related to the entropy per particle; that is, to the specific entropy.
This dynamical calculation of the speed of sound, and many others, demonstrates that something is in fact known about entropy away from equilibrium. Furthermore, it strongly suggest that a reliable dynamical framework is available that may serve to investigate the effect of gravitation on an isolated atmosphere that consists of an ideal gas.

The theory of ideal gases has been around for more than 150 years. Let us use it.

IX.9. Reply to Maxwell

It has to be maintained that the existence of isentropic atmosphere in a gravitational field is in contradiction with the second law of thermodynamics. If that were so the second law would share the faith of all other laws that have been formulated by scientists over the ages.

The existence of the isentropic atmosphere is a matter for experimental science; unfortunately a decisive experiment would be very difficult. Besides, scientists with enough reputation to be respected seem not to be enthusiastic about investing either their time or their reputation on this problem. The evidence presented by our actual atmosphere has not proved convincing.

The experiment should certainly be done, and with the astounding advance in technology it shall eventually lead to a conclusion. And then what? What should we do if the conclusion is that the isentropic atmosphere exists?

It is unlikely, even in that case, that thermodynamics, or even just the second law, would become obsolete; for the arguments advanced by Maxwell and others is far from conclusive, as will be shown.

Maxwell. Two tubes are filled by two different gases, placed vertically next to each other and isolated from each other and from the environment, except for being connected to a reservoir at the top. At equilibrium: that is, after some time, if no further changes are taking place, the temperatures at the bottom of the two tubes will be different. A heat engine can be installed two exploit this difference and energy can thus be extracted from the heat bath.

Student But that would not be very shocking, not like constructing a perpetuum mobile, since the energy is supplied by the heat bath; any real heat reservoir will eventually get cold.

Maxwell. Granted that the intervention of the infinite heat bath makes it difficult for our discussion to advance, consider instead the following system.
The $U$.

Imagine a tube, in the form of the letter $U$, upright, divided into two parts in the middle (the low end), containing two different ideal gases, gas $A$ on the left, gas $B$ on the right, the whole in complete isolation except for terrestrial gravity, the two gases in thermal contact at the dividing wall. The tubes are closed at the top; the volume and the geometry are fixed. This is ‘the open $U$’. There is no heat bath. for the sake of the argument, assume that the equilibria, in the terrestrial gravitational field, is isentropic.

The tubes are thermally connected only at the bottom. Wait for equilibrium to be established; then the temperatures will be equal there, but different at the top. Now connect the tops of the $U$ with a heat conducting wire, thus creating ‘the closed $U$’. We are going to neglect the heat loss in the wire as well as its heat capacity. The temperature will eventually equalize at the top, finding a new equilibrium at which the temperatures at the top are equal. This means that there has been a flow of heat and, because the change is spontaneous, involving no heat transfer from the environment, there has been a net increase of the total entropy. The process that has just taken place is therefore irreversible.

Next, disconnect the wire and let the system return to the original configuration. But this is impossible, for it would require a decrease in the entropy. Therefore the isentropic equilibrium does not exist.

**Student.** Let us examine the process in a little more detail, starting with no thermal connection at the top, and different temperatures $T_1$, $T_2$ there. Let $S_0$ be the total entropy of the system. Now two things will happen in succession.

First, the thermal connection at the top is connected. This constitutes a change of the system by external interference. It leaves the system out of equilibrium. If the entropy of this new configuration can be defined, call it $S_1$.

Second, the system, left out of equilibrium, will find a new equilibrium, with entropy $S_2$. Given the properties of each gas we can calculate both $S_2$ and $S_0$, but what is the value of $S_1$.

**Maxwell.** Because the system, after the end of the first stage, is out of equilibrium, the entropy that you call $S_1$ is not defined.

**Student.** In that case I may make a suggestion. Is it not possible to assign the value $S_2$ to $S_1$? I may perhaps propose this as the definition of $S_1$. by this definition the change in entropy is due to the interference with the system (the establishment of the thermal connection) and the subsequent establishment of the new equilibrium would be adiabatic since there is no interference from the outside during the second stage.

**Maxwell.** I do not like that definition of $S_1$ but I admit that my argument has been dealt a severe blow.

**Student.** Thank you professor.
X. ROTATIONAL FLOW

Fetter and Walecka (1980) have provided us with an efficient and elegant action principle for hydrodynamics. It applies in the case when the velocity field is irrotational, when it can be expressed as

\[ \vec{v} = -\vec{\nabla} \Phi. \]  

(10.1.1)

This is a strong limitation. There have been many attempts to lift it, especially in dealing with superfluids, and some have come very close to formulating an action principle. (Hall and Vinen.)

Traditional hydrodynamics has 4 independent variables, the density and the 3 components of the velocity. The action principle of Fetter and Walecka has only 2 independent variables, so two more are needed. But it will not do to seek a generalization of Eq.(10.1.1).

X.1. Why the scalar velocity potential is essential

In the first place, the Euler-Lagrange equation

\[ \frac{\delta}{\delta \Phi} A = \dot{\rho} + \vec{\nabla} \cdot (\rho \vec{v}) = 0 \]

is the equation of continuity, the very essence of hydrodynamics.

Second, even though the equations of hydrodynamics are Galilei invariant, only the Fetter-Walecka action principle, with velocity potential, offers an invariant action. The Hamiltonian is not Galilei invariant; the search a Galilei invariant expression for the energy is mis-directed.

As important is the tradition that incorporates gravitation into field theories, especially into hydrodynamics, by including the Newtonian potential into the Hamiltonian density, when this is available. We regard hydrodynamics as a non-relativistic approximation to General Relativity but is there any generally relativistic field theory that has the expected non-relativistic limit? Granted that it is suggested by the correspondence between hydrodynamics and particle mechanics, but our subject is field theories.

Gravitation is represented by the metric, in the non relativistic limit by the time-time component. Consider the generally relativistic field theory with Lagrangian density

\[ \mathcal{L} = \int d^4x \sqrt{-g} \left( \rho (g^\mu\nu \psi_{,\mu} \psi_{,\nu} - c^2) - W[\rho] \right). \]

To explore the non relativistic limit set

\[ g_{00} = c^2 + 2\phi, \quad g_{11} = g_{22} = g_{33} = -1, \]  

(10.1.2)

other components zero, expand in powers of \((1/c)\) and take the limit \(c \to \infty\). To ensure the cancellation of the terms of lowest order we need to set

\[ \psi = c^2 t + \Phi, \]  

(10.1.3)

then terms of order \(c^2\) cancel and we are left with the Fetter-Walecka Lagrangian density

\[ \mathcal{L}_{FW} = \rho (\dot{\Phi} - \vec{\nabla} v^2/2 - \phi) - W[\rho]. \]  

(10.1.4)
In the context of field theories this is the only confirmation that we have of the expectation that Newtonian hydrodynamics, with the inclusion of the gravitational potential, is the non-relativistic limit of General Relativity. As we have already seen, in Section III.11, Eq. (10.1.3) leads to the correct transformation law for the field $\Phi$ under Galilei transformations. But it is not enough, because it is limited to irrotational flows.

We conclude that the required generalization of (10.1.1) must include additional fields with 2 degrees of freedom, with an action that reduces to (10.1.1) by projection. Two additional dynamical variables are needed, one additional pair of canonical variables, either an additional scalar field or else some gauge field with only one propagating component.

The simple introduction of another scalar velocity potential would not lead to rotational flow, and gauge theories with just one propagating mode are few: the Majorana neutrino field and the antisymmetric 2-form field ($Y_{\mu\nu}$) of Ogievetskij and Polubarinov. This is a topic that shall be taken up below.

The connection of potential flow to an action principle is intimately related to the fact that the velocity is a gradient of a more basic field, a scalar potential. The principal field of an ‘alternative’ choice for hydrodynamics, usually denoted $\vec{x}$ is also a derivative and also a natural candidate for an action principle. We shall call this other potential $\vec{X}$, to distinguish it from the coordinates. Since the equations of motion are second order in the time derivative this field appears to have 6 independent degrees of freedom. We already have 2 degrees of freedom with $\rho$ and $\Phi$, conventional hydrodynamics has 4, so this appears to be far too much. It will be seen, however, that it is possible to impose a constraint that reduces the number of degrees of freedom of the new field to 2.

Anticipating that, we add an additional kinetic term $\rho \dot{\vec{X}}^2 / 2$ to our Lagrangian,

$$L = \rho(\dot{\Phi} + \frac{\dot{\vec{X}}^2}{2} + \kappa \rho \dot{\vec{X}} \cdot \vec{\nabla} \Phi - \frac{\vec{\Phi}^2}{2} - \phi) - W[\rho].$$  \hspace{1cm} (10.1.5)

The aptness of this addition, including the third term, will be confirmed in the next section, by comparison with Navier-Stokes theory. The mixing term (with constant coefficient $\kappa$) is included because of several interesting applications. It is gauge invariant, as will be seen in Section X.6.

The genesis of this proposal; that is, the idea that (10.1.5) is a proper generalization of the Fetter-Lagrange Lagrangian to include rotational flows, will come below in the context of an important application: cylindrical Couette flow. The relativistic generalization is needed to discover the gauge theory constraint of this non-relativistic gauge theory; it will be developed in Section X.5. In the next section we shall anticipate, by introducing the constraint without explanation.

X.2. The constraint and the Euler-Lagrange equations

The constraint comes from variation of the gauge field (Section X.5),

$$\vec{\nabla} \wedge \vec{m} = 0, \quad \vec{m} := \rho \vec{w}, \quad \vec{w} := \dot{\vec{X}} + \kappa \vec{\nabla} \Phi.$$  \hspace{1cm} (10.2.1)
This is the constraint that reduces the number of additional degrees of freedom carried by the field $\vec{X}$ to 2. The Euler-Lagrange equations are as follows.

Variation of $\Phi$ gives the equation of continuity,

$$\dot{\rho} + \vec{\nabla} \cdot \rho \vec{v}, \quad \vec{v} := \kappa \vec{X} - \vec{\nabla} \Phi.$$ (10.2.2)

The flow vector is thus $\rho \vec{v}$. Variation of $\vec{X}$ leads to

$$\frac{d}{dt} \vec{m} = 0.$$ (10.2.3)

Finally, variation of the density gives

$$\dot{\Phi} + \dot{\vec{X}} \frac{\rho}{2} + \kappa \rho \vec{X} \cdot \vec{\nabla} \Phi - \vec{\nabla} \Phi \frac{\rho}{2} - \phi = \mu.$$ (10.2.4)

The significance of the parameter $\kappa$ will become clear as we study the applications. Galilei invariance of this non-relativistic, gauge-fixed Lagrangian is an issue; it will be studied later (Section X.6).

The Euler-Lagrange equations of the proposed Lagrangian, Eq. (10.2.2-4), have much in common with modern theories of rotational flow; they all involve potential flow plus additional velocity fields. To initiate a close comparison, and a confrontation with experiment, we note the following. From Eq.s(1.2.1-4) we easily deduce that the vorticity field

$$\vec{\nabla} \wedge \vec{v} = \kappa \vec{\nabla} \wedge \vec{w} = \kappa \frac{1}{\rho} \vec{\nabla} \wedge \vec{m} = (\vec{\nabla} \frac{\kappa}{\rho}) \wedge \vec{w}.$$ (10.2.5)

It follows that the gradient of the density is orthogonal to the vorticity:

$$\vec{\nabla} \rho \cdot (\vec{\nabla} \wedge \vec{v}) = 0.$$ (10.2.6)

A theory of incompressible fluids can be developed only as the limit of compressible fluids.

**III.3. Cylindrical Couette flow**

Couette flow has been been studied for 200 years, with the main focus on the spontaneous onset of turbulence. The experiment has a homogeneous fluid contained in the space between two concentric cylinders, as in Fig.(10.2.1), both cylinders turning independently.

The pioneering series of experiments, by Couette and Mallock, were followed by a paper by Taylor. This work included new experiments but also a pioneering interpretation, the main impact of which was the vindication of the non slip boundary condition. Though it is in need of refinement, this boundary condition is still being used and it will be used here. It is the statement that the limit of the flow velocity, at the material boundary of the containing vessel, is the same as the local velocity of the container at the same point.
Laminar couette flow

The simplest type of flow velocity is horizontal, stationary and circular, in cylindrical coordinates,

\[
\dot{X} = \omega(r)(-y, x, 0), \quad r := \sqrt{x^2 + y^2}
\]  

(10.3.1)

The boundary conditions are “no-slip”, meaning that the velocity of the flow, at the cylindrical boundaries, are the same as the velocity of the walls. To simplify the analysis one thinks of the cylinders as being long, and ignore end effects. The particular case

\[
\dot{X} = b(-y, x, 0), \quad b \text{ constant}
\]  

(10.3.2)

208
is the flow of a solid body. It gives rise to a kinetic potential

\[ K = -\dot{X}^2 \propto -r^2, \] (10.3.3)

(all proportionalities with positive coefficients) and a centrifugal force \(-\nabla K \propto r\) that is balanced by a pressure (constant + \(r^2\)) that presents a force \(-\nabla p \propto -r\). It follows, for ordinary fluids with a positive adiabatic derivative \(dp/d\rho\), if there are no other forces acting, that \(K + p\) is stationary and that the density must increase outwards. See Fig 2.1.

*Fig. 10.3.3. The kinetic potentials, \(1/r^2\) (irrotational flow) and \(-r^2\) (solid-body flow).

Disturbing question: what is the expression for the ‘kinetic potential’ when the velocity has 2 parts, one rotational and one solid-body type?

**The Navier-Stokes equation**

is the basis for every traditional analysis of Couette flow:

\[ \frac{D}{Dt}\vec{u} = -\frac{1}{\rho}\nabla p + \bar{\mu}\rho\Delta \vec{u}. \] (10.3.4)

Here \(\bar{\mu}\) is the viscosity of the fluid, in the simplest case a constant parameter. This equation agrees with (10.2.4) in the special case that \(\vec{u} = -\nabla \Phi\) and \(\dot{X} = 0\). It also agrees with (10.2.4) in the complimentary case, when \(\nabla \Phi = 0\) and \(\vec{v} = \dot{X}\).

* When the dynamical field \(\dot{X}\) in (10.2.4) is replaced by the fixed field (10.3.2), and \(\kappa = 0\), we get a Lagrangian proposed by Hall and Vinen (19) in a much quoted paper on superfluids. We shall see that this is appropriate in the limit of incompressible fluids. For a modern version of this theory see Fetter.
The velocity field in (10.3.4) is denoted \( \vec{u} \) to emphasize that it should not be identified with either \( -\vec{\nabla}\Phi \) or \( \vec{X} \) or \( \vec{v} \).

Stationary flow is possible only if the effect of viscosity is negligible, this requires that \( \bar{\mu} = 0 \) or else that **

\[
\Delta \vec{u} = 0. \quad (10.3.5)
\]

When the flow is stationary, as postulated (and as observed at low speeds), this condition allows the general solution

\[
\vec{u} = \frac{a}{r^2}(-y, x, 0) + b(-y, x, 0), \quad a, b \text{ constant.} \quad (10.3.6)
\]

the parameters \( a, b \) to be determined by the non-slip boundary conditions. The first is irrotational for \( r > 0 \),

\[
\frac{a}{r^2}(-y, x, 0) = a\vec{\nabla}\theta, \quad \theta = \arctan\frac{y}{x}.
\]

This gives rise to a kinematical potential

\[
K \propto \vec{\nabla}\Phi^2 \propto 1/r^2 \quad (10.3.7)
\]

and a centrifugal force

\[
-\vec{\nabla}K \propto \vec{r}/r^4,
\]

and in this case too the force points outwards. Both of these types of flow are of great interest, especially so in connection with superfluid Helium. The second term in (10.3.6) is the flow of a solid body, see Eq.s (10.3.1), (10.3.2). We observe that \( dK/dr \) is negative in both cases and that \( K \) is proportional to \( u^2 \) in one case and to \( -u^2 \) in the other (all proportionalities with positive coefficients).

These elementary considerations already suggest that there are difficulties ahead. What is the kinetic potential when the velocity field is of neither type, but a combination of both, as in (10.3.6)?

In experiments the rotation speeds of the two cylinders are increased slowly from zero, these types of flow are observed at low speeds. We shall describe this regime.

This type of potential flow is of great interest; especially so in the case of superfluid Helium. The second type is the flow of a solid body.

The boundary conditions will be analyzed below.

This prediction of the Navier - Stokes equation is a brilliant success, being in very good agreement with experiments, at low speeds of rotation. The only difficulty is that there is no clear guide to constructing an expression for the energy density, or a kinetic potential. It would be natural to expect that the expression

\[
\rho \vec{u}^2/2, \quad \text{resp.} \quad \vec{u}^2/2,
\]

** The usual justification for this restriction is more involved: With the hypothesis of circular flow the density can only depend on the coordinate \( r \) and the same is true of the pressure; hence the pressure term is a radial force and the projection of the last term along the direction of motion must also be zero; hence \( \bar{\mu}\Delta \vec{u} = 0 \).

210
might be an important part of it, serving as a kinetic energy resp. potential and the latter giving rise to the centrifugal acceleration; we have seen that this not the case in general, though it is true in the case of irrotational flow, as we shall now show, again.

**The question of sign, again**

Consider the simplest cases. The total derivative in (10.3.4) is

\[
\frac{D}{Dt} \vec{u} := \frac{d}{dt} \vec{u} + (\vec{u} \cdot \nabla) \vec{u}.
\]

the last term is (minus) the centrifugal force. When the flow is of the solid body type, Eq.(2.2),

\[
(\vec{u} \cdot \nabla) \vec{u} = b^2 (-y \partial_x + x \partial_y)(-y, x, 0) = -b^2 (x, y, 0) = -\nabla \vec{u}^2 / 2.
\]

That is, the acceleration is outwards and the centrifugal potential \( K \) is \( -\vec{u}^2 / 2 \). In the complimentary case of potential flow,

\[
(\vec{u} \cdot \nabla) \vec{u} = \frac{a^2}{r^2} (-y \partial_x + x \partial_y) \frac{1}{r^2}(x, y, 0) = -\frac{a^2}{r^4}(x, y, 0) = \nabla (\vec{u}^2 / 2);
\]

it is in the same direction, hence correct, but now the centrifugal potential is \( \vec{u}^2 / 2 \). The difference in sign between the two cases means that

One can not, in general, associate the Navier Stokes equation with an energy density \( E[\rho, \vec{u}] \) or with a kinetic potential \( K[\vec{u}] \).

This conclusion is long overdue.

**A classical mistake and what it tells us**

To theorists the principal aim has been to understand the limits on the stability of the laminar flow that was described above and the first notable attempt to do so was that of Rayleigh (1889, 1916) who concluded that the laminar flow should be stable if and only if

\[
\omega_o > \omega_i \quad \text{(approximately)}.
\]

Here \( \omega_o(\omega_i) \) is the angular velocity of the outer (inner) cylinder and \( \omega_i \) is positive by convention. In particular, this implies that the laminar flow would be unstable whenever the two cylinders rotate in opposite directions. The result of observation was different: the condition for stable Couette flow is, approximately,

\[
\omega_o^2 > \omega_i^2;
\]

which allows for stable flow for either sign of \( \omega_o / \omega_i \). Raleigh’s reaches his conclusion twice.

1. Angular momentum (about the axis of rotation) is conserved, the angular momentum is \( L = vr \), “... so that the centrifugal force acting on a given portion of the fluid is \( L^2 / r^3 \).
That is, \(-L^2/r^2\) is regarded as a kinetic potential. But this is without justification and, as it happens, actually wrong; if there is any kinetic potential \(K\) in the context of the Navier-Stokes equation it must satisfy
\[
(\vec{u} \cdot \vec{\nabla})\vec{u} = \vec{\nabla}K.
\] (10.3.8)

2. We quote (Rayleigh 1916): “We may also found our argument upon a direct consideration of the kinetic energy of the motion......”. He concludes that stability requires that this function increase outwards. This is the same argument and here we see more clearly what the difficulty is: There is no justifiable way to introduce the energy concept, or to choose an expression to serve as energy, except in the context of an action principle.

Since the Navier-Stokes equation is an expression of the balance of forces one must ask if there is an additional force that must be taken into account. Yes, there is; but what is without justification is the claim that there is an ‘energy density’ proportional to \(L^2/r^2\) and that it functions as a kinetic potential.

We have seen (1) that any valid expression for ‘kinetic potential’ must have opposite signs for the two types of flow and that (2) if there is a suitable expression for a kinetic potential in the context of the Navier-Stokes equation, then it is not the energy density.

Rayleigh’s choice of ‘energy’ leads to conclusions that are contradicted by experiment. If we merely restrict ourselves to the two special cases examined in the preceding section we see that there is, in either case, an effective kinetic potential, proportional to \(\vec{u}^2\), but with a positive coefficient in one case and a negative coefficient in the other; this disqualifies it from being interpreted as an energy in the general case and blocks Rayleigh’s argument.

During the 100 years that followed the publication of Rayleigh’s paper the calculation has been repeated in numerous textbooks, including these: Chandrasekhar (1955 and 1980), Landau and Lifshitz (1959), Drazin and Ried (1981), Tilley and Tilley (1986), Koshmieder (1993) and Wikipedia (2017).

That Rayleigh’s prediction was contradicted by experiments must have been known to himself in 1916; that it was known to the other authors mentioned is not in doubt. Yet there is no suggestion in the later literature that Rayleigh’s argument is faulty!

Landau and Lifshitz (1959, page 100) claim that viscosity makes Rayleigh’s argument invalid if the cylinders rotate in opposite directions! Chandrasekhar (1981, page 275) argues that the criterion is inconsequential because the region in which it is violated is small, Drazin and Ried (1981, page 79) repeat Chandrasekhar’s argument. Koschmieder (\textit{op cit} Chapter 11) offers the most comprehensive discussion of traditional methods but he too finds no fault with Rayleigh’s argument (\textit{op cit} Chapter 10). Finally, Wikipedia repeats Rayleigh’s argument but offers no clue to why the criterion fails when the cylinders are rotating in opposite directions.

The Navier-Stokes equation by itself does not imply, and in general it does not allow, the existence of an expression with the attributes of energy. But a kinetic potential can be constructed in the special case of stationary, laminar Couette flow, when the velocity field is of the form (10.3.6); it is (Fronsdal 2014)
\[
-K = \frac{b^2}{2}r^2 + ab \ln r^2 - \frac{a^2}{2r^2}, \quad (\vec{u} \cdot \vec{\nabla})\vec{u} = \vec{\nabla}K.
\] (10.3.9)
By the Navier-Stokes equation, this makes a contribution $-\nabla K$ to the acceleration. Therefore, this function is the only kinetic potential that is consistent with the Navier-Stokes equation in the simplest case when the velocity is of the form (2.5). It is not $(1/\rho$ times) the kinetic energy. *

**X.4. The action principle includes a kinetic potential**

The Hamiltonian density is

$$h = \rho (\ddot{X}^2/2 + (\nabla \Phi)^2/2 + \phi) + f + sT.$$  (10.4.1)

Instead of the expected square of the ‘total velocity’ we have the sum of two squared velocities. But the equation of motion, obtained by taking the gradient of (10.1.9), is

$$\nabla \Phi - \nabla \left(-\ddot{X}^2/2 - \kappa \dot{X} \cdot \nabla \Phi + (\nabla \Phi)^2/2 + \phi \right) = \frac{1}{\rho} \nabla p,$$  (10.4.2)

where $p$ is the thermodynamic pressure. Equations (10.4.1-2) both have the correct signs, the first gives the Hamiltonian density with the correct, positive sign for both terms, the second equation agrees with the Navier-Stokes equation (when applicable) with the two different signs. The expression in the large parenthesis is a kinetic potential, but it is not simply related to an energy density.

The Navier-Stokes equation combines the two types of flow in a single velocity field and deals correctly with both of them, but that is as far as one can go with a single velocity field, for the irrotational flow is Eulerian and the solid-body flow is Lagrangian.

We conclude that the action principle is not in conflict with the traditional treatment of this type of flow, but it completes it by giving us the equation of continuity, as well as an energy density; the Hamiltonian is a first integral of the motion and the Lagrangian, not the Hamiltonian, contains the kinetic potential.

With a Hamiltonian and a kinetic potential in hand we can apply standard methods. The first result is, of course, that a stable configuration must satisfy the Euler-Lagrange equations, making the energy stationary with respect to all perturbations. A deeper analysis studies harmonic perturbations to first and second order of perturbation theory, as in Chandrasekhar (1955 and 1980), Landau and Lifshitz (1959), Drazin and Ried (1981) and Koshmieder (1993).

* In the highly regarded book *Stellar Structure and Evolution*, by Kippenhahn, Weigert and Weiss (2012), we find definitions of normalized gravitational, internal and total energies. Then they take it for granted that the name given to the expression for the ‘total energy’ endows it with physical properties. In this manner is reproduced a correct result previously proved by Chandrasekhar (1935). Other examples of such shortcuts are legion, See e.g. Eddington (1926, page 142). Here is different type of example. Arnold and Khesin in their book (1998, pages 2, 19, 37, 75, 119) lay down axioms that, for them, define Hydrodynamics. They always use the standard definition of ‘energy’, $E = v^2/2$. 213
In the presence of viscosity there can be no energy conservation and no action principle. But there is a standard and natural way to modify the Euler-Lagrange equations. Instead of (2.3) one poses
\[ \frac{d}{dt} \vec{m} = \bar{\mu} \rho \Delta \vec{v}. \quad (10.4.3) \]
We have limited our attention to stationary flows, with \( \Delta \vec{v} = 0 \), taking our inspiration from the traditional point of view.

**X.5. Stability of laminar Couette flow by the action principle**

According to (3.2), the kinetic potential is the function
\[ K = -\dot{\vec{X}}^2 /2 - \kappa \rho \dot{\vec{X}} \cdot \vec{\nabla} \Phi + \vec{\nabla} \Phi^2 /2. \quad (10.5.1) \]

By the gauge constraint, for horizontal, circular flow there are constants \( a, b \) such that
\[ -\vec{\nabla} \Phi = \frac{a}{r^2} (-y, x, 0), \quad \vec{m} = -\vec{\nabla} \tau = \frac{b \kappa}{r^2} (-y, x, 0). \quad (10.5.2) \]
The second formula solves the gauge constraint (10.1.6). The velocity of mass transport is
\[ \vec{v} = \frac{\kappa}{\rho} \vec{m} - (1 + \kappa^2) \vec{\nabla} \Phi = \left( \frac{\kappa^2 b}{r^2 \rho} + (1 + \kappa^2) \frac{a}{r^2} \right) (-y, x, 0) = \frac{1 + \kappa^2}{r^2} \left( \frac{c^2 b}{\rho} + a \right) (-y, x, 0), \quad (10.5.3) \]
with \( c^2 := \kappa^2 / (\kappa^2 + 1) \). The only constraint on the field \( \vec{v} \) is that it must be harmonic - see Eq.10.5.3; thus
\[ \frac{1}{\rho} = 1 + \alpha(1 - r^2), \quad \alpha \text{ constant.} \quad (10.5.4) \]

This density profile implies that the vorticity - Eq. (1.10) - is uniform, value \( 2\alpha \kappa b \).

We have referred to the classical intuitive feeling that the pressure must increase outwards. For any normal fluid, for which the adiabatic derivative \( dp/d\rho \) is positive, this implies that the density must increase outwards, so the constant \( \alpha \) must be positive. (We have normalized the density at the outer boundary to unity.) This relates \( \alpha \) to \( \rho_i \),
\[ \alpha = 4.54 (1/\rho_i - 1). \quad (10.5.5) \]

In terms of these vector fields
\[ -K = \frac{\vec{m}^2}{2 \rho^2} - (\kappa^2 + 1) \vec{\nabla} \Phi^2 /2 = \frac{1 + \kappa^2}{2 r^2} \left( \frac{b^2 c^2}{\rho^2} - a^2 \right), \quad c^2 := \frac{\kappa^2}{1 + \kappa^2}. \quad (10.5.6) \]
By (10.5.5),
\[ -K = \frac{1 + \kappa^2}{2} \left( \frac{b^2 c^2 (1 + \alpha)^2}{r^2} - 2 \alpha (\alpha + 1) + \alpha^2 r^2 \right) - \frac{a^2}{2 r^2} \quad (10.5.7) \]
and
\[ -K' = \frac{1 + \kappa^2}{r} \left( \frac{a^2}{r^2} + b^2 c^2 (\alpha^2 r^2 - \frac{(1 + \alpha)^2}{r^2}) \right). \] (10.5.8)

Now that we have a kinetic potential we can apply Rayleigh’s criterion, \( K' < 0 \).

Fig.10.5.1. A pair of straight through the origin is the best possible fit of a locus \( K' = 0 \) to the “hyperbolic” curve that has been observed.

**Boundary conditions**

The walls of the two cylinders move with angular velocities

\[ \omega_i \hat{\theta} = \frac{\omega_i}{r}(-y, x, 0), \quad \omega_o \hat{\theta} = \frac{\omega_o}{r}(-y, x, 0) \quad \omega_i, \omega_o \text{ constant.} \] (10.5.9)

The velocity of mass transport is \( \vec{v} \), Eq.(4.3), this is the velocity that must satisfy the no-slip boundary conditions, whence

\[ \frac{1 + \kappa^2}{r_i^2}(a + \frac{b c^2}{\rho_i}) = \omega_i, \quad \frac{1 + \kappa^2}{r_o^2}(a + \frac{b c^2}{\rho_o}) = \omega_o, \] (10.5.10)

and

\[ a = \rho_o \rho_i \omega_o - r_i^2 \rho_i \omega_i \quad b = \rho_o \rho_i \frac{r_i^2 \omega_i - r_o^2 \omega_o}{\rho_i (\kappa^2 + 1)}, \] (10.5.11)

When these quantities are expressed in terms of the angular velocities we see that the locus \( K' = 0 \) consists of 2 straight lines through the origin of the angular velocity diagram. The best result that can be obtained with the assumption that \( K' \) must be negative, is for the lines \( K' = 0 \) to coincide with the ‘asymptotes’ of the experimental curve, as in Fig. 4.1. That would leave a substantial region that is stable, although \( K' \) is positive.

But even that is not be possible.

The zero locus of (10.5.8) consists of the two lines

\[ \frac{a}{bc} = \pm \beta, \quad \beta = \sqrt{(1 + \alpha)^2 - \alpha^2 r^4}, \]
or
\[ \frac{\omega_i}{\omega_o} = \frac{1 \pm c/\beta r^2 \rho_i}{1 \pm c/\beta r^2}. \]  

(10.5.12)

If the two asymptotes are in the first and fourth quadrant it follows that either
\[ c < \beta < c/\rho_i, \quad \text{or else} \quad c > \beta > c/\rho_i. \]

In the first case \( \rho_i < 1 \). Then \( \alpha > 0 \). At the outer boundary
\[ \beta^2 = 1 + 2\alpha = 1 + 2\frac{1/\rho_i - 1}{1 - r_i^2} < 1/\rho_i^2. \]

By (10.5.12), \( \beta^2 = 1 + 2\alpha < c^2/\rho_i^2 < 1/\rho_i^2 \), which reduces to \( 2/(1 - r_i^2) < 1 + 1/\rho_i \), which is false since the density is very close to 1. At the inner surface, \( \beta \) is even larger. In the second case \( \rho_i > \rho_o \), which is anti-intuitive.

This suggests that the criterion \( K' < 0 \) cannot be made to account for observations, for any choice of the parameters. Later we shall find that that this condition is satisfied almost everywhere; it is not sufficient and it does not relate to the observed boundary of stability, in all but a very limited sense.

X.6. A proposal

It is known that some types of instability are accompanied by bubble formation. (As in the wake of propellers.) We suggest that this may be related to local evacuation (or more generally to a physical breakdown of the laminar nature of the flow) and that it happens at a particular value of the chemical potential, the density and of the corresponding value the kinetic potential \( K \).

We shall test this hypothesis. We are not rejecting the idea that \( K' \) must be negative; it turns out that it is negative almost everywhere.

Let us subtract the constant term from \( K \) in (10.5.7). As we see from that equation, the locus of \( K = 0 \) consists of two straight lines. At the inner boundary,
\[ \frac{\omega_i}{\omega_o} = \left( \frac{r_o}{r_i} \right)^2 \frac{1 \pm c}{1 \pm c(\rho_i/\rho_o)} \]

and these must have opposite signs, hence \( 1 > c > \rho_o/\rho_i \). At the outer boundary,
\[ \frac{\omega_i}{\omega_o} = \left( \frac{r_o}{r_i} \right)^2 \frac{1 \pm c(\rho_o/\rho_i)}{1 \pm c} \]

and \( 1 > c > \rho_i/\rho_o \). This implies that, as the velocity is increased, the instability first manifests itself at the boundary with the higher density.

The value of \( K \) varies with the radius \( r \). If, as the velocity is increased, the instability makes a first appearance at the boundary \( B \), the inner or the outer cylinder, then we expect that the parameters can be tweaked to make a locus \( K(r_i) = A \) or \( K(r_o) = A \) an adequate approximation to the experimental limit curve and that the family of loci,
\( K(r) = A, r_i < r < r_o \) displace upwards as we move away from the boundary \( B \).

We first examined the possibility that the instability first manifests itself at the outer boundary, which would imply that the density is higher there, as had been expected. This resulted in a failure; no more need be said. Then we examined the alternative, that the instability first manifests itself at the inner boundary, in which case the density is higher there, against expectations. This calculation will now be described in detail.

**Main results**

Assume that \( \rho_i > \rho_o \). Fig. 5.1, taken from Andereck *et al* (1883, 1986) is a summary of their results, the lowest line, resembling a hyperbola, is the upper limit of observed, basic Couette flow.

Fig 5.2 shows a \( K \) locus that best fits the experimental curve, with \( \rho_o/\rho_i = .9, \kappa = 5.3 \) and \( R = r_i \). Identical curves are obtained with \( \rho_o/\rho_i = .99, \kappa = 17.5, \rho_o/\rho_i = .999, \kappa = 55 \) and so on, calculated up to \( \rho_o/\rho_i = 1 - 10^{-6} \). The slope of the right asymptote is predicted without ambiguity to be very close to \( (r_o/r_i)^2 \), – a bullseye for the theory. See Eq. (5.3). The slope on the left is very sensitive to the value of \( \kappa \); this too can be seen by inspection of (5.3).

---

**Fig. 10.6.1.** Experimental results of Andereck *et al* (1983, 1986). The abscissa (ordinate) is the angular velocity of the outer (inner) boundary. The lower ‘hyperbola’ is the upper limit of stability of laminar Couette flow.

**Fig. 10.6.2.** A locus \( K(r_i) = A_+ > 0 = \text{constant} \). The lines \( K = 0 \) lie below.
The subsequent figures show the result of repeating the calculation, with the same values of the parameters and the same value of \( A \), at several points in the interval \( r_i < r < r_o \).

Fig.10.6.3. Loci \( K = A_+ < 0, A_+ > 0 \) at the inner boundary, \( r = r_i = .883 \). The three curves are drawn for the same values of \( K \) in all the diagrams that follow.

Fig.10.6.4. The locus \( K = A \) with the same values of \( A \) at \( r = .888 \).

Fig.10.6.5. At \( r = .893 \), the locus is moving upwards, almost everywhere.
In each of these diagrams two straight lines through the origin make up the $K = 0$ locus. The hyperbola that lies between them is a locus $K = A_+ > 0$. The two lines that lie outside form a locus $K = A_- < 0$. All these figures have the same parameters and the same values of $A_+$ and $A_-$. The series start at the inner boundary and proceeds to the outer boundary.

The crucial question is what happens to the locus $K(r) = A$ as $r$ is increased from $r = r_i$
towards $r = r_o$, for fixed values of the parameters and for a fixed value of $A$. Comparing Figures 5.5-10 it can be seen that, almost everywhere, the locus moves upwards with increasing radius; hence at any point in the diagram, the value of $K$ decreases. Only the region near the right asymptotes is difficult to assess. Diagrams 5.3 - 5.8 show that the domain of stability gradually expands as we move outwards, $K'$ is negative almost everywhere and this function does not provide a criterion for stability.

To get a different view of the situation we next plot a zero locus of $K'$, with the same parameters. As the result is virtually independent of the radius in the range $r_i < r < r_o$; we show only the case $r = r_i$. It is seen that $K'$ is negative everywhere except in a small region on the right, which confirms what we concluded by visual inspection of the $K$ loci.

![Graph showing loci of the derivative of the kinetic potential.](image)

Fig. 10.6.9. These are loci of the derivative of the kinetic potential. It is zero on the two straight lines through the origin and it is positive between them, everywhere else it is negative.

That is reassuring, except for the fact that the pressure gradient has the 'wrong' sign since, to balance it, the centrifugal force it should have the wrong sign as well. Instead of two forces balancing each other, the centrifugal force and the pressure gradient reinforce each other!

The next two illustrations are flow lines, in this sense. If at some instant we drop a line of saw dust on the horizontal straight line that connects the two cylinders on the right side (on the positive “x”-axis), then this is what we shall see at some future instant. One gets the impression that the volume elements are being dragged along by the ones closest to the walls, and perhaps this suggests an increased pressure near the inner cylinder.

If the behavior of the system seems to be contrary to our intuition, then one thing that can be done is to educate our intuition.

Are we forgetting a third force? Yes, and perhaps a fourth.
The success of the no-slip boundary condition is witness to a considerable surface tension, to a strong adhesion of the fluid to the walls. Directly, this affects only the first layer of molecules near the walls, but water has a great tensile strength, as is known from the ease at which it withstands negative pressure. See Fig 5.10.

At the beginning of the experiment the fluid is at rest and the density is uniform. There is no pressure gradient and no centrifugal force. Then, as we begin to rotate the cylinders the adhesion of the fluid to the wall exerts a force within the fluid. By the principle of Le Chatelier, the reaction of the system is always to resist; hence, at least at first, the pressure and the centrifugal effect must cooperate against the effect of the adhesion. The non-slip boundary condition is not just a mathematical rule; it speaks for the action of a third
force. In our model, the kinematic potential and the pressure continue to act together in most of the stable configurations. Perhaps Fig.s 5.11 and 5.12 may help to bring this interpretation in line with intuition.

Consider two volume elements, one on the inner cylinder and the other at the outer cylinder, and a thin smooth tube connecting the two points. Make this more precise by assuming that the tensile strength of the fluid is transmitted along the tube. Then there is one case when this force is constant, when the instantaneous, linear velocity of the two end-points are equal. In that case $\omega_i/\omega_o = r_o/r_i$. At that point the centrifugal force has to cancel the force produced by the gradient of the pressure; the pressure increases outwards.

Perhaps that is what we see in Fig. 5.9 when we notice that $K'$ turns positive in a narrow, radial area on the right of the diagram.

**Entropic forces**

The Lagrangian (1.5), in the full thermodynamic setting, is

$$L = \rho(\dot{\Phi} + \ddot{X}^2/2 + \kappa \rho \dot{X} \cdot \dddot{\Phi} - \dddot{\Phi}^2/2 - \phi) - f - sT,$$

where $f(\rho, T)$ is the free energy density. The Bernoulli equation becomes

$$\nabla(\dot{\Phi} + \ddot{X}^2/2 + \kappa \rho \dot{X} \cdot \dddot{\Phi} - \dddot{\Phi}^2/2 - \phi) = \nabla p - (s - \rho \frac{\partial s}{\partial \rho}) \nabla T - \rho T \nabla \frac{\partial s}{\partial \rho}.$$

With the usual assumptions, $s = \rho S$, the specific entropy $S$ uniform, both terms after $\nabla p$ drop out. The result is the familiar hydrodynamic equation; making use of it implies that the specific entropy is assumed to be uniform. The two additional terms have been systematically ignored until now, in obedience to a popular and successful strategy: If an entropy gradient is not needed, ignore it.

In case of difficulties, one may make a different assumption about the entropy density. Allowing the specific entropy $S$ to be non-uniform gives life to the last term. To invigorate the $\nabla T$ term it is necessary to expand the expression $s = \rho S$ with a term that is not linear in $\rho$, as in Landau and Lifshitz (1956).

In the present case we have followed the usual protocol and it has not led to any difficulties, the experimental data having been explained to surprising accuracy given the speculative nature of (3.3). This may be less due to a correct theory than to the paucity of experimental data, which may change when the experiment is repeated with a range of different fluids. The system is not at equilibrium; some energy is being supplied; there is likely to be a temperature gradient and there may be some heat flow. Our model calculations depend only on the density and the chemical potential, only experiments can determine the pressure and the entropy distribution. See caption to Fig. 10.6.10.
X.7. Conclusions

Energy, with associated conservation laws, is the very soul of theoretical physics. It is entirely natural that, in the many contexts where an expression for it is not available, attempts are made to invoke it anyway. But our efforts are better spent if we strive to formulate all of physics in terms of action principles. The difficulty, of course, is to determine the action or, before that, to find the variables that make it possible.

The quest for action principles for hydrodynamics and thermodynamics was pursued most vigorously during the late 19’th and early 20’th century, by some of the most important physicists of that pioneering age: Helmholtz, Maxwell, Cartan, Einstein and others. In a memorandum to O. Veblen, dated March 26, 1945, John von Neuman (1945) laments the fact that “hydrodynamical problems, which ought to be considered relatively simple, offer altogether disproportionate difficulties”; he says that “the true technical reason appears to be that variational methods have ... hardly been introduced in hydrodynamics.” And he adds: “It is well known that they could be introduced, but what I would like to stress is that they have not been used to any practically important scale for calculations in that field”.

The reason that they had not been used is to some extent explained by the internal inconsistencies related to the use (or misuse) of the energy concept.

A viable action principle for rotational Hydrodynamics, Thermodynamics and General Relativity has been proposed (Fronsdal 2014, 2017). It is not unique, but it is the most economical; complicated systems require more variables. This paper offers a first instance of an application, to a system that has resisted a complete development even in the special case of incompressible flows. An application to planetary systems, in the Newtonian approximation, is in the works and the lifting of this model to General Relativity needs only dedication.

Future experiments

In the present contexts of elementary hydrodynamic systems much work has been done on incompressible flows. The more challenging problem of compressible flows require measurements of temperature and pressure profiles, which are difficult. We need more measurements of this type and we need experiments with wider horizons. Andereck and others have explored the full range of flow regimes in the Couette problem, we need to vary the fluid (even going as far as using gases) as well as the density of absorbed air, ambient temperature and pressure and, especially, surface tension; that is, the surface of the cylinders. The theory presented here predicts that the slope of the left asymptote in Fig. 5.1 is sensitive to the compressibility of the fluid.

X.8. A theory of incompressible fluids

We set

\[ \frac{\rho_i}{\rho_o} = 1 + \xi, \quad c = 1 - \psi, \quad 0 < \psi < \xi \]

and obtain, on the asymptotes \( C = 0 \), in the first quadrant,

\[ \frac{\omega_i}{\omega_o} = \left( \frac{r_o}{r_i} \right)^2 \frac{2 - \psi}{2 - \psi + \xi} \approx 1.28 \]
and in the fourth quadrant,

\[ \omega_i/\omega_o = \left( \frac{r_o}{r_i} \right)^2 \frac{\psi}{\psi - \xi} = -1.28 \frac{1}{\xi - 1} < -1.28. \]

In the best fit \( \xi/\psi \approx 5 \).

We get a model of an incompressible gas by taking the limit of large \( \kappa \). In this case it is better to renormalize the field \( \vec{X} \) by absorbing a factor \( \kappa \), to express the Lagrangian density (10.1.5) as

\[ \mathcal{L} = \rho (\dot{\Phi} + \vec{X}^2/2\kappa^2 + \rho \vec{X} \cdot \vec{\nabla} \Phi - \vec{\Phi}^2/2 - \phi) - W[\rho] \quad \text{(10.6.1)} \]

and neglecting the second term in many applications including the present one. The important fields are the velocity of mass flow

\[ \vec{v} = \dot{\vec{X}} - \vec{\nabla} \Phi, \]

and the renormalized vector field

\[ \vec{w} = \frac{1}{\kappa^2} \dot{\vec{X}} + \vec{\nabla} \Phi. \]

In the limit \( 1/\kappa \to 0 \) the field \( \vec{X} \) becomes a non-dynamic field, as in the approach initiated by Hall and Vinen \textit{op cit}.

The interpretation of this theory is difficult. In the first place, if the density is fixed then the canonical structure is lost; we should expect that it reduce to a single canonical pair of field variables. Another difficulty is that the singularity of \( \Delta \Phi \) at the center of whirls can no longer be mitigated by assuming that the density vanish there. In an attempt to solve both problems we may agree to retain \( \rho \) as a dynamical variable, though one that appears in the applications as essentially constant. The equation of continuity then reduces to

\[ \vec{\nabla} \cdot \vec{X} = \Delta \Phi. \]

Since \( \vec{X} \) is a non-dynamical (external) field we can consider the case that it is a point source,

\[ \dot{\vec{X}} = a\delta(\vec{x})\delta(y) \]

and make contact with the string theories of Lund and Regge and of Kalb and Ramond.

Another problem is the determination of the limiting thermodynamics, more precisely the limit of the thermodynamic contribution \( f - sT \) to the action.

224
X.6. Vortices

From the fact that large and beautiful eddies readily appear in the wakes of ships, in the Sun and in the gaseous planets we can conclude that they are energetically favored. We shall study the phenomenon in the context of cylindrical Couette flow.
XI. Astrophysics

There is a limit to how far one can develop astrophysics as an application of non relativistic hydrodynamics; here is an attempt that pushes that limit.

Rotating planets

ABSTRACT Variational techniques have been used in applications of hydrodynamics in special cases but an action that is general enough to deal with both potential flows and solid-body flows, such as cylindrical Couette flow and rotating planets, has been proposed only recently. This paper is one of a series that aims to test and develop the new Action Principle. We study a model of rotating planets, a compressible fluid in a stationary state of motion, under the influence of a fixed or mutual gravitational field. The main problem is to account for the shape and the velocity fields, given the size of the equatorial bulges, the angular velocity at equator and the density profiles. The theory is applied to the principal objects in the solar system, from Earth and Mars to Saturn with fine details of its hexagonal flow and to Haumea with its odd shape. With only 2 parameters the model gives a fair fit to the shapes and the angular velocity field near the surface. Planetary rings are an unforeseen, but a natural and inevitable feature of the dynamics; no cataclysmic event need be invoked to justify them. The simple solutions that have been studied so far are most suitable for the hard planets, and for them the predicted density profiles are reasonable. The effect of precession was not taken into account, nor were entropic forces, so far. There has not yet been a systematic search for truly realistic solutions. The intention is to test the versatility of the action principle; the indications are are very encouraging.
XI.1. Introduction

The ultimate aim of our work is to learn how to deal with a compressible, rotating fluid in General Relativity. Because much important work has been done in the past, we must emphasize the novelty of our work: We approach hydrodynamical problems within the framework of a general Action Principle. In the context of General Relativity this means selecting an adequate relativistic action $A_{\text{matter}}$ for fluid dynamics in an arbitrary metric background and adding it to Einstein’s action for the metric. The energy momentum tensor of $A_{\text{matter}}$ becomes the source of Einstein’s field equations. This is the natural way to ensure that the source of Einstein’s field equations satisfy the integrability conditions (the Bianchi constraint).

Our action principle incorporates traditional hydrodynamics, including the equation of continuity. It generalizes a well known action principle for irrotational hydrodynamics by including rotational velocity fields. It extends to Thermodynamics where it has been extensively applied to mixtures (Fronsdal 2018), to Special Relativity (Ogievetskij and Polubarinov 1964), and most recently to stability of cylindrical Couette flow (Fronsdal 2018). It provides the first field theoretic model of rotating fluids that respects the Bianchi identity and includes the equation of continuity. Previous attempts to formulate an action principle for General Relativity (Hartle 1967, Bardeen 1970, Schutz 1970 and Taub 1954) have not been developed to a stage where applications could be undertaken, but all the ideas of the older work resonate in the present one.

The principal feature of this paper is the action principle; in other respects it is far less complete than earlier models of planetary dynamics. See for example Beauvalet, Lainey, Arlot and Binzel (2012) or Stute, Kley and Mignone (2013). Another feature that is not always included in planetary dynamics is the requirement that the mass flow velocity field be harmonic, as it needs to be for all stationary flows. (See below.) Most important, the action principle is a framework with a greatly improved predictive power, as this paper demonstrates.

Before attacking this problem in the full, Generally Relativistic setting, it is good strategy to study the problem in Newtonian Gravity. The system is a compressible fluid in hydrodynamics; the forces arise from a fixed, central Newtonian potential, or from the mutual, gravitational interaction between the fluid elements and the pressure. Because the new Action Principle is a departure from the past, we present a summary account of it, before applying it to the principal components of the solar system. Harmonic expansions of the dynamical fields will include only the first three terms, except in a study of the hexagonal flows in Saturn.

The gauged-fixed, non-relativistic action is

$$A = \int dtd^3x \mathcal{L}, \quad \mathcal{L} = \rho(\dot{\Phi} - \nabla^2 \Phi^2/2 + \dot{X}^2/2 + \kappa \dot{X} \cdot \vec{\eta} - \Phi^2/2 - \varphi) - W[\rho]. \quad (1.1)$$

The variables are the density $\rho$ and two velocity potentials, the scalar velocity potential $\Phi$ and the vector potential $\vec{X}$. (Compare Schutz 1970.) Projected on the theory of rotational flows, the special case $\dot{X} = 0$, it becomes the Lagrangian that was discovered by Lagrange himself (1760) and brought to our attention by Lamb (1932) and by Fetter and Walecka (1980). Gravity is represented by the Newtonian potential $\varphi$; it can be a fixed, central
potential or the mutual energy of interaction between fluid elements. The action \( (1.1) \) is the non relativistic limit of a generally relativistic action and the potential \( W[\rho] \) is the thermodynamic internal energy density for a system with fixed, uniform specific entropy density. The on-shell value of the Lagrangian density is the thermodynamic pressure; as prophesized with rare insight by Taub (1954).

The Euler-Lagrange equations are: the equation of continuity (from variation of the velocity potential \( \Phi \)),
\[
\dot{\rho} + \mathbf{\nabla} \cdot (\rho \mathbf{v}) = 0, \quad \mathbf{v} := \kappa \mathbf{X} - \mathbf{\nabla} \Phi,
\] (1.2)
the wave equation (from variation of \( \mathbf{X} \))
\[
\frac{d}{dt}(\rho \mathbf{w}) = 0, \quad \mathbf{w} := \mathbf{\dot{X}} + \kappa \mathbf{\nabla},
\] (1.3)
and the Bernoulli equation (from variation of \( \rho \)),
\[
\mathbf{\dot{\Phi}} + \frac{\dot{X}^2}{2} + \kappa \mathbf{\dot{X}} \cdot \mathbf{\nabla} - \mathbf{\nabla}^2/2 - \varphi = \frac{\partial}{\partial \rho} W[\rho].
\] (1.4)

The incorporation of two velocity fields is an essential feature of the theory; what is both novel and effective is that they contain the correct (minimal) number of dynamical variables: 4 for hydrodynamics including the density. The Lagrangian has one free parameter \( \kappa \); it is related the compressibility of the fluid.

The complete theory is a relativistic gauge theory; here we are working in the physical gauge and in the non relativistic limit. There are two velocity fields, \( \mathbf{v} \) represents mass flow; \( \mathbf{w} \) allows for vorticity. A key feature of the theory is the constraint
\[
\mathbf{\nabla} \wedge (\rho \mathbf{w}) = 0,
\] (1.5)
derived by variation of the full Lagrangian with respect to a vector gauge field. (The gauge field is fixed at zero and does not appear in this paper.) It implies that the vector field \( \mathbf{w} \) - defined in (1.3) - can be expressed in terms of a scalar field,
\[
\mathbf{w} = \frac{-1}{\rho} \mathbf{\nabla} \tau.
\] (1.6)
(Of course, we cannot replace \( \mathbf{w} \) by \( \tau \) in the action.) The limit of an incompressible fluid is approached as \( \kappa \to \infty \). It is this constraint that connects the velocity and the density: in the context of the action principle harmonicity of \( \mathbf{\dot{v}} \) becomes a constraint on \( \rho \), solved by Eq.(2.8) below.

We have given a brief account of the theory in the physical gauge; the full gauge theory is described in two papers (Fronsdal 2014 and 2017).

What does the most to validate this theory is that it is formulated as an action principle. To account for rotational motion it includes the velocity field \( \mathbf{\dot{X}} \), as in ‘Lagrangian hydrodynamics’, but as this would seem to add 3 additional degrees of freedom, we need a constraint that effectively reduces this number to 1, as is accomplished by Eq.(1.5).
relation of the field $\dot{X}$ to vorticity, and to a relativistic gauge theory, was proposed, in the special case of incompressible flows, by Lund and Regge (1976). In string theory it is the Kalb-Ramond field (Kalb and Ramond 1974).

The action is not completely new; it appeared in a classical paper by Hall and Vinen (1956) on superfluids and in a more recent review by Fetter (2009) on rotating Bose-Einstein condensates (Fetter 2009). * In those papers $\dot{X}$ is not a local, dynamical field variable but a fixed background feature that accounts for a rigid rotation of the whole system. Although the dynamical, irrotational velocity was seen as insufficient and another degree of freedom was needed, the way to avoid an excessive number of degrees of freedom, by means of the constraint (1.5), was not widely known. The field components $\dot{X}^i$ appear in Bardeen (1970), they are the classical ‘Lagrange parameters’.

A stationary flow is one that evades the dissipating effect of viscosity. In traditional hydrodynamics viscosity is included as an additional term in the Navier-Stokes equation,

$$\dot{v} + (\vec{v} \cdot \vec{\nabla})\vec{v} = \frac{-1}{\rho} \vec{\nabla}p + \bar{\mu} \rho \Delta \vec{v}, \quad (1.7)$$

where $\bar{\mu}$ is the kinematical viscosity, usually a constant. Viscosity cannot be accommodated within an action principle, but its effect can be acknowledged by replacing the conservation law (1.3) by

$$\frac{d}{dt}(\rho \vec{w}) = \bar{\mu} \rho \Delta \vec{v}.$$  

In this way a theory based on conservation laws is distorted to include a type of dissipation, precisely as is done in the familiar approach with Eq.(1.7). In both theories, stationary motion is possible only when the field $\vec{v}$ is harmonic.

The biggest surprise to emerge from this work is the natural and spontaneous appearance of planetary rings. Rings are predicted, not just accommodated. The simplest solutions studied in this paper predict a single ring (or none) for each planet. It is suggested that the parameter $N$ in Eq.(1.9) is related to evolution, that all the planets may have had rings at one time, that the planet Mars, in particular, may have had a ring at relatively recent times and that all the planets will eventually lose their rings. The observed hexagonal rotation pattern of Saturn is useful data that reveals the presence of higher harmonics. The observation of 1-6 internal whorls is a prediction of the theory.

A brief digression on the cylindrical Couette problem

The most familiar systems treated in Newtonian gravity as well as in General Relativity have spherical symmetry. But most heavenly bodies are rotating around an axis that is more or less fixed, with approximate cylindrical symmetry. Much of the inspiration for our work comes from a study of cylindrical Couette flow. Following the advice of Homer Lane (1870), as is traditional in astrophysics, we apply to astrophysics what we

* The equations of motion in the paper by Hall and Vinen (1956) are widely quoted; the action principle not at all.
have learned in terrestrial laboratories. The problem examined by Couette (1888-1890) and Mallock (1888, 1896) is a fluid confined between two concentric cylinders that can be rotated independently around the vertical axis. In classical hydrodynamics the balance of forces is expressed by the Navier-Stokes equation. Boundary conditions, validated by the analysis of Taylor (1923), is assumed to be non-slip and the fluid is compressible. At low speeds any stationary motion is found to be described by the following harmonic vector field

\[ \vec{v} = \frac{a}{r^2}(-y, x, 0) + b(-y, x, 0), \quad r := \sqrt{x^2 + y^2}, \quad a, b \text{ constant.} \quad (1.8) \]

The first term is irrotational for \( r \neq 0 \) and both are harmonic.

The new action principle was used to account for the stability of basic, cylindrical Couette flow (Fronsdal 2018). One feature of the model is that the density profile is subjected to a strong condition that originates in the demand that \( \vec{v} \) be harmonic.

### XI.2. A compressible fluid rotating in a fixed, central gravitational field

Our model of a planet is an isolated system with a liquid or solid core in thermodynamic equilibrium with a gaseous atmosphere, in a stationary, rotating state and described by the action (1.1). In the simplest case it consists of a single substance in two phases. The condition of thermodynamic equilibrium at the phase boundary is that the pressure \( p \), the temperature and the chemical potential \( \mu \) be continuous across the surface. In the case of a thin atmosphere this implies that the pressure and the chemical potential are constant on the surface. The surface is thus a locus of the function - see Eq.(1.4) -

\[ C(x) := \ddot{X}^2/2 + \kappa \dot{X} \cdot \nabla \Phi - \nabla \Phi^2/2 - \frac{GM}{R}, \quad R = \frac{r}{|\sin \theta|} = \sqrt{x^2 + y^2 + z^2}. \quad (2.1) \]

We have chosen the Newtonian expression for the attractive gravitational potential. It is an expedient shortcut of the present treatment, as in the simplest version of the traditional approach, and one that we hope to remove later. It is a valid approximation so long as the departure from spherical symmetry is small.

This model should be appropriate for Earth and Mars and possibly for the frozen planets Neptune and Uranus, less so for the gaseous planets. To determine the appropriate velocity fields we begin by examining the simplest solutions.

If the velocity is irrotational, and \( \ddot{X} = 0 \); then the shape is determined by

\[ -\frac{a^2}{2} \frac{1}{r^2} + \frac{GM}{R} = \text{constant}, \quad r := R|\sin \theta| = \sqrt{x^2 + y^2}. \]

We plot the loci of this expression and vary the parameter \( a^2 \). Instead of an equatorial bulge there is a polar sink-hole, see Fig.3.1. This attempt evidently fails.
Fig. 2.1b. Showing the ‘equatorial bulge’, or rather the polar depression, that would be the effect of pure, irrotational flow.

Fig. 2.2. The more physical locus predicted by solid body flow. (The non compact branch is not part of the traditional theory.)

Solid-body flow is the complementary case in which $\nabla \Phi = 0$ and the angular velocity $\omega = b$. As in the traditional approach; the condition of equilibrium is

$$\frac{\omega^2}{2} r^2 + \frac{GM}{R} = \text{constant.}$$

There is a bulge, see Fig. 2.2. The number usually quoted is

$$\epsilon := \frac{R_{eq.}}{R_{pole}} - 1 = \frac{\omega^2}{2MG} R_{eq.}^3,$$

where, to a good approximation, $R_{eq}$ can be replaced by 1 on the right hand side. For Planet Earth the number is $MG = R^2 g$, $g = 998 \text{cm/sec}^2$, and the approximate value of $\epsilon$ is predicted by this model to be

$$\frac{\omega^2 R^3}{2MG} = \frac{R \omega^2}{2g} = \left( \frac{2\pi}{24 \times 3600} \right)^2 \frac{6.357 \times 10^8}{2 \times 998} = .0016. \quad (2.2)$$

Solving Eq.(2.1) for the azimuthal angle we find that $(b^2/2)R^2 \sin^2 \theta = C - GM/R$ and we conclude that, with the solid body hypothesis the radius is minimal at the poles and the locus of (3.1) always has a non-compact branch, as in Fig. 2.2.
The observed value of $\epsilon$ for Earth is $0.00335$, more than twice the prediction (2.2). The classical theory can be improved by taken into account the effect of the bulge on the potential; for example, by assuming that the shape is an ellipsoid, and that the density is uniform. That results in a value for $\epsilon$ of $0.0042$, which is too large (Fitzpatrick 2018).

A further improvement results from taking the partly known density distribution into account; this has the effect of diminishing the effect of the shape on the potential.

**The general case**

We look for the general solution of the equations of motion. Again

$$\varphi = -\frac{GM}{R}, \quad R := \sqrt{x^2 + y^2 + z^2}, \quad G = \text{constant.}$$

(2.3)

The full set of equations includes the equation of continuity and

$$\ddot{v} := \kappa \dddot{X} - \nabla \dot{\Phi}, \quad \Delta \ddot{v} = 0, \quad \ddot{w} := \dot{X} + \kappa \ddot{\Phi} - \frac{1}{\rho} \nabla \tau,
\dot{\Phi} + \frac{\ddot{X}^2}{2} + \kappa \dddot{X} \cdot \nabla \dot{\Phi} - \frac{\dddot{\Phi}^2}{2} + \frac{GM}{R} = \mu[\rho],$$

(2.4) (2.5)

All the vector fields can be expressed in terms of the two scalar fields $\Phi$ and $\tau$ and the density. The most naive assumption is that the two scalar fields are the same as those that appear in Couette flow, proportional to the azimuthal angle, thus

$$-\nabla \Phi = \frac{a}{r^2}(-y, x, 0), \quad -\nabla \tau = \frac{b}{r^2}(-y, x, 0).$$

(2.6)

These are gradient-type vector fields for circular flows in the horizontal planes, with angular momentum $L_z = \pm 1$. They would not be sufficient for an ambitious attempt to construct realistic models, but they may be enough for our main purpose, which is to establish the versatility of the action principle.

Eq.s (2.4) and (2.6) give

$$\ddot{v} = \kappa \ddot{w} - (\kappa^2 + 1) \nabla \Phi = \omega(-y, x, 0), \quad \omega := \frac{1}{r^2} \left(\frac{\kappa b}{\rho} + a(\kappa^2 + 1)\right).$$

(2.7)

The most general harmonic vector field of this form is a series of spherical functions with higher angular momenta. There is evidence of higher angular momenta in the flow velocities of Venus, Pluto and, most notably, Saturn. In this paper we reduce the series to the simplest terms, the normalized inverse density taking the form

$$\frac{1}{\rho} = 1 + NR + \eta r^2 + \nu \frac{r^2}{R^3}, \quad N > 0, \quad \eta > 0,$$

(2.8)

with constant coefficients $N, \eta, \nu$. The first two terms have $\ell = -1$, the others $\ell = 1$. The introduction of a non-integrable representation of the rotation group ($\ell = -1$) should
be noted. Higher harmonics are needed in the case of Saturn, since this planet shows a distinct, hexagonal flow pattern.

A non-zero value of the last term in (2.8) gives rise to a central hole, shaped like a donut, near the center of the planet; see Fig.(2.3). A very small value of \( \nu \) results in a very small hole; it may serve as a regularizing device, but it is hardly relevant for the evaluation of the shape of the surface. We adopt the expression (2.8), with \( \nu = 0 \), as a plausible first approximation to the density profiles of Earth and Mars and, very tentatively, to those of the other planets.

This is our simplest model planet. It is intended, in the first place, to serve as a model for Earth and Mars and perhaps for Uranus and Neptune. A complete calculation would need a general harmonic expansion for the flow vector field \( \vec{v} \).

**Regularity at the poles**

Take the polar radius to be the unit of length and let the central density be the unit of density. Both \( N \) and \( \eta \) have to be positive, as we shall see.

Let us begin with a star that is spherically symmetric (\( \eta = 0 \)) with polar radius 1 and density ratio

\[
\frac{\rho_{\text{center}}}{\rho_{\text{pole}}} = N + 1;
\]

then we allow for a modest violation of spherical symmetry by increasing the parameter \( \eta \) from zero.

The equation for the surface takes the form,

\[
\frac{1}{2r^2} \left( b^2(1 + NR + \eta r^2)^2 - a^2(1 + \kappa^2) \right) + \frac{GM}{R} = \text{constant.}
\]

In order to avoid getting a dip at the poles (from the denominator \( r^2 \)) we must have

\[
a^2(1 + \kappa^2) = b^2(N + 1)^2.
\]

Then the equation takes the form

\[
\frac{b^2}{2r^2} \left( (1 + NR + \eta r^2)^2 - (N + 1)^2 \right) + \frac{GM}{R} = \text{constant.}
\]
With this constraint the angular velocity - see Eq.(2.7) - is
\[
\omega = \frac{\kappa b}{r^2} \left( \frac{1}{\rho} \pm \frac{N + 1}{c} \right), \quad c := \frac{\kappa}{\sqrt{1 + \kappa^2}}. \tag{2.11}
\]
The visible angular velocity at the equator is
\[
\omega_{eq.} = \kappa b \left( 1 + N + \eta \pm \frac{N + 1}{c} \right). \tag{2.12}
\]
The mass transport velocity can change sign within the star.

The Earth has a small equatorial bulge. To estimate the visible angular velocity we approximate \(\eta\) by zero. With these approximations we obtain, using the lower sign, for the visible angular velocity of Earth, the value
\[
\omega = \frac{b N + 1}{2\kappa} = \frac{a}{2}. \tag{2.13}
\]

Finally the shape is determined by
\[
f(R, r) := \frac{(1 + NR + \eta r^2)^2}{r^2} - (N + 1)^2 + \frac{\xi}{R} = \text{constant}, \tag{2.14}
\]
where \(\xi\) is the constant
\[
\xi = \frac{2GM}{b^2}. \tag{2.15}
\]

Solutions of (2.14) extend to very large \(R\) only if there is an effective cancelation between the terms of highest power, in \(NR + \eta r^2\). If \(\eta N\) is positive there can be no cancellation, at any azimuth; hence all the solutions are compact when we pose
\[\eta N \geq 0.\]

**Overview of results**

The two parameters \(N\) and \(\xi\) form a 2-space with the latter as abscissa; it divides into a lower region (roughly \(N < 1\)) where the planets have a ring, and a complementary upper region where they do not, separated by a “ring-no-ring” boundary. See Fig. 2.4, where three versions of this dividing line are shown, for \(\epsilon = 1/300\) and with \(\eta = .01, .05\) and \(.1\) from high to low. In the same figure we have shown nearly vertical lines of dots, a “trajectory” for each of four planets. The coordinates of the dots on each of the planetary trajectories give a near-perfect fit to the measured ellipsoid of the respective planet.

Fig.2.4. The abscissa is the parameter \(\xi\) and the ordinate is \(N\).
Fig. 2.4 shows the result of calculations as points in the plane of the parameters $\xi$ and $N$, each dot representing a near perfect fit to the ellipsoid. The near vertical lines of dots consist of points all of which give perfect fits to the shape of the respective planet, without rings on the upper part. Results of the calculation are tabulated in the Appendix.

It may be permissible to think of this diagram as an *evolution diagram*, each planet evolving upwards towards a state of greater compression, and loosing its rings as it crosses the ring-no-ring dividing line. Earth lost its rings long ago; it is to be placed on the upper part of its trajectory, well above the $\eta = .1$ line.

Increasing $N$ means higher compression at the center; Earth may have $N$ as high as 2 while Mars is less compressed and may have $N = 1$ or less. Since planets are likely to become more compressed over time we expect planets to evolve upwards. This is in accord with speculations that Mars may have had a ring in the evolutionary recent past. Uranus and Neptune still have rings and must have $N \leq .3$ if our model is applicable to them.

The rings will be discussed below. Other aspects of the model, including the equation of state, will be taken up in the connection with the gaseous planets, in Section V.

I.3. Earth and Mars

The polar radius is our unit of length and remains fixed at unity. The equatorial radius is determined by a 4’th order algebraic equation that is obtained from (3.9) by setting $r = R$. We are mostly interested in shapes that are almost spherical (leaving aside the planetary rings for the moment), with a small equatorial bulge. To find surfaces that include a point on the equator with radius $s = 1 + \epsilon$ we write (2.14) in the form

$$B(R, r) := f(R, r) - f(s, s) = 0,$$

(3.1)

Note that $f(s, s)$ is a constant. The equatorial radius is a zero of the function $B(r, r)$ and after division by $r - s$ this equation reduces to a cubic. For planets without rings this cubic does not have positive roots. If a ring is about to disappear at a distance $s'$ from the center there will be a double zero at $r = s'$.

The measurable parameter $\epsilon$ has replaced the value of the function $f$. However, there are still 3 parameters left, $N, \eta$ and $\xi$, and it is difficult to survey all possibilities. We shall try to find our way around this difficulty as we look at individual planets.

If Earth is an ellipsoid with eccentricity $\epsilon$ and the polar radius is normalized to unity, then the shape is

$$R - 1 = \epsilon \sin^2 \theta; \quad R_{eq} = 1 + \epsilon,$$

with $\epsilon = .00335$. With $s = 1.00335$, the locus $B(R, r) = 0$ passes through the equator at $R = r = s$, and through the pole. Fittings of shapes are relative to this ellipsoid, with the appropriate value of $\epsilon$.

The quality of the fits, examples

Very good fits to the ellipsoid are achieved with $N = 2$ and both of the following $\eta = .092$, $\xi = 3$, and $\eta = .1$, $\xi = 3.5$. The value $N = 2$ was suggested by the measured density profile shown below, in Fig.3.5.
We tried $\eta = .1$ and $N = 2$, leaving only $\xi$ to be varied. The locus is a curve that, at a small scale, resembles the geoid, the fit is perfect at the pole and at the equator. We examined the error at nine intermediate azimuths and found that a perfect fit would require $\xi$ to vary from 0 to 3. But if we fixed $\xi = 3$ the relative error was never larger than $10^{-4}$.

The conclusion is that the identification of the planetary shape with a locus of $C$ through the pole and the equator appears to be natural and that the precise determination of the parameters applicable to each planet requires efficient use of more data. In other words, there still remains considerable flexibility to be used as more data is taken into account.

**Density profile, range of $N$**

Our own planet is unique among the planets in that the density profile has been reliably estimated, see Fig.3.1. A good fit to the central core is not possible since both $N$ and $\eta$ must be positive. This can be understood since the constitution of the earth is far from uniform; the model assumption that the interior is a single phase is an over-simplification. A fair approximation to the observed density suggests that $N$ lie in the interval

$$1.5 < N < 2.5 \quad \text{(Earth)}$$

Fig.3.1. Observationally estimated density profile of Earth.

![Fig.3.1](image)

Fig.3.2. Model equatorial density profile of Earth, for 2 values of the principal parameter $N$. Heavy lines $\eta = .01$, lighter lines, $\eta = .2$. 

![Fig.3.2](image)
Rings, or not

Random sampling of the parameters of the theoretical configurations reveal that the expected, nearly spherical shape of the body is not always realized. For example, in the case that $\eta = .1, N = 1.2$ we get a good approximation to the ellipsoidal shape of the Earth with $\xi = 3.3$. But if the value of $\xi$ is increased to 3.525, then a planetary ring appears, as shown in Fig.3.3. We have crossed the ring-no-ring divider in Fig.2.4, moving horizontally towards the right. For still larger values of $\xi$ the ring eventually dwarfs the planet.

Fig.3.3. Ring around the Earth; about to disappear. Parameters $N = 1.2, \xi = 3.525$.

Nothing in our model relates to the hemispheric asymmetry of Mars; that is, the depression of the northern hemisphere. But we do know the bulge ratio, $\epsilon = 1/135$, and elaborate models of the planet suggest a plausible density profile, shown in Fig. 4.1. We obtain excellent fits to the ellipsoid from $N = .7, \xi = 1.5$ to $N = 3, \xi = 1.75$.

Fig.3.4. Density profile of Mars, with a very thick mantle and a metallic core. Fig.3.5. Density profile for Mars from Eq.(2.8), with $N = 1.7$.

The idea of a ring around Earth can not be entertained, but the planet Mars is another matter. The trajectory for Mars was calculated with the equatorial bulge ratio $\epsilon = 1/135$. We fixed the value of $\eta$ at .1 as for earth and for each of a sequence of values of $N$ we searched for the value of $\xi$ that gives the best approximation to the idealized shape of planet Mars. The lowest value of $N$ for which such a fit exists is $N = .8$.  

237
It is notorious that Mars shows clear evidence of having once been furrowed with large gullies by the action of water (on the southern hemisphere). It has been widely interpreted in terms of a cataclysmic event, eons past. Our calculations suggest that the value of $N$ was once lower, that a ring actually did exist around Mars, and that the ring, consisting mostly of water or ice, disappeared as a result of the increase in $N$. The alternative, that the ring may have fallen as the result of a passage very close to Earth, is less appealing, since we regard the ring as natural and expect it to resume its original shape after a shock. If it did not, then it means that the property $N$ has evolved and that the equations of motion no longer support the ring.

IV. Neptune and Uranus. Venus and Pluto

The shapes of Uranus and Neptune are quoted in the literature but actually they are poorly known (Bertka and Fei 1990). If we treat them as close analogues of Earth and Mars, then they would appear far to the left in Fig.2.4, as shown. The progression of values of the parameter $N$ from Neptune to Earth suggests increasing compression.

Pluto is far out among the outer planet but its small mass is a more relevant parameter (Hellled, Anderson and Schubert 2010). Venus has a complicated structure and winds that are not parallel to the equatorial plane. Both are essentially spherical but Venus has a small bulge that is believed to be induced by winds. Venus also has a very dense atmosphere with a pressure of about 92 Earth atmospheres. For all these reasons neither Venus nor Pluto should be included in this study. Nevertheless, we assigned very small bulges and got good fits to the ellipsoid shape, some of which are recorded in Table 1 and plotted in Fig.4.2.

![Fig.4.2. This would show why Venus and Pluto do not have rings.](image)

While $\eta \approx 0.1$ works well for most of the planets, Venus and Pluto require a value closer to 0.01. In this figure both are plotted with this value of $\eta$. All planets except Saturn and Jupiter have “trajectories” determined by a best fit to the ellipsoid.


The search for a simple model for Saturn, initially with no expectation of accounting for anything more than the equatorial bulge revealed that rings are a dominant feature of our model. The existence of rings gives us an additional measurable parameter, the mean radius standing in for the parameters of a complicated ring system. The radius and the width of the ring can be chosen within wide limits, but the model does not account for the
flat ring system that is actually seen. The radius of the ring is closely related to the value of $\eta$.

In the case of Saturn attempts to fit the model to ellipsoids with an equatorial bulge ratio of 1:10 failed. We did not persist in this, because: 1. Observation of the gaseous giants does not favor our model of a phase transition at the surface. 2. The surface of a gas sphere is not well defined, experimental data usually refer to isobars. See for example Lindal, Sweetnam and Esleman (1985).

Saturn offers an interesting hexagonal flow pattern around the North Pole. A photograph taken above the North Pole of Saturn, shows a hexagonal flow.

![Fig.5.1. Photograph taken by Voyager of the North pole of Saturn.](image1)

![Fig.5.2. Flow lines of the function (6.2) with $a = k = 1, A = .5$.](image2)

The photograph reveals a local, inner whirl, with a remarkable similarity to the six pools that are present in the symmetric model.

A fair mathematical representation of the flow is

$$\Phi = \Im \left(a \ln z + \frac{A}{1 + (kz)^6}\right), \quad A = \text{constant.} \quad (6.2)$$
The flow lines are shown in Fig. 5.2. The gradient of $\Phi$ is

$$\vec{\nabla}\Phi = \left(a + \frac{A(kr)^6}{D^2} \left(1 + (kr)^{12}\cos(6\phi) + 2(kr)^6\right)\right)d\phi + \frac{A\sin(6\phi)}{D^2}(1 - (kr)^{12})(kr)^5kdr.$$ 

For the square we get the surprisingly simple formula

$$(\vec{\nabla}\Phi)^2 = \frac{a^2}{r^2} + 2\frac{A(kr)^6}{D^2} \left(1 + (kr)^{12}\cos(6\phi) + 2(kr)^6\right) + \frac{(kA)^2(kr)^{10}}{D^2}.$$ 

We have calculated only the first order perturbation, then the modified expression for the function $\tilde{f}$ in Eq.(2.14) becomes, for some constant $\alpha$,

$$f(R,r) := \frac{(1 + NR + \eta r^2)^2 - (N + 1)^2}{r^2} + \frac{kA^2}{D^2} \left(1 + (kr)^6\cos(6\phi) + 2(kr)^6\right) + \frac{\xi}{R}.$$

The result has been disappointing. It turns out to be possible to produce hexagonal rings, but no further contact with observation was discovered, so far. A more positive result: With the extra term it becomes possible to imitate the ellipsoidal shape. Jupiter presents some of the same difficulties for analysis, but lacks the interesting hexagonal feature of Saturn. We have not constructed a model for the largest of all the planets.

The Sun is still further from our present objective, and so are galaxies. We present, however, in Fig. 5.3, an object that recalls, by its flatness, the shape of some galaxies; the aspect ratio is about $10^9$.

Fig.5.3. A shape produced by the model, suggesting an application to galaxies. (The full figure extends equally in both directions.)

Finally, here is a portrait of one of the smallest object in the solar system, Haumea is a small moon or mini-planet in the outer Kuiper belt, remarkable for its odd shape.
XI.6. Summary and conclusions

The most significant result of this paper is that an action for hydrodynamics actually provides an effective approach to real problems. The discovery that planetary rings are natural within the formalism is a real surprise and source of encouragement. Rather than a need to invent a special historical event sequence for each ring system, we can now expect that they will emerge naturally from solutions of the equations of motion. That goes a long way towards explaining their amazing stability.

This paper is to be regarded as a first step, to be followed by much more detailed calculations. The equatorial bulge of a planet changes the gravitational field and this affects the calculations, though often to a minor degree. For each of the objects in the solar system it is important to consider other complications that have hardly been mentioned in this paper, including the following.

Replace the fixed gravitational field by the solution of Poisson’s equation. Include more terms in the harmonic expansion of the density, in the hope of creating more elaborate ring systems. The atmosphere was treated as empty, that leaves room for improvement. For the gaseous planets another model, without a surface discontinuity, is indicated. The effect of magnetic fields and radiation must be included.

All these complications have already been taken into account in the literature; we think that the calculations should be repeated within the framework of the action principle, where the energy is conserved and where the number of free parameters is very much
reduced. That should result in a greatly increased predictive power and, perhaps, a better understanding of the fascinating planetary rings. A separate problem that can be approached in the same spirit: the shape of galaxies.
XII. Special and General Relativity

We have already shown that irrotational hydrodynamics is the non relativistic limit of a relativistic field theory, see Section X.1. Here we shall examine the full, relativistic gauge theory of the 2-form field ($Y_{\mu\nu}$) that was introduced in Section X.4.

XII.1. Special Relativity. The Notoph gauge theory

As with all non-relativistic vector fields the problem of a Lorentz covariant generalization is urgent. The idea that every 3-vector, non-relativistic field should grow a fourth component has been popular and in particle mechanics one replaces

$$\dot{X}^i \rightarrow \left( \frac{d}{d\tau} \vec{X}, X^0 \right), \quad X^0 = \sqrt{c^2 + \vec{X}^2}.$$

But the proper time $\tau$ has no place in a theory of fields and, besides, the vector field contains three pairs of presumptive canonically conjugate variables. (Two if massless.) Instead, the relativistic 2-form has just one propagating mode.

The relativistic, antisymmetric tensor field ($Y_{\mu\nu}$) was first studied by Ogievetskij and Palubarinov (1964). One of its remarkable properties is that it mixes with the electromagnetic field, making the photon massive. Its role in string theory was discovered by Lund and Regge and by Kalb and Ramond and further developed by Zelhutin and others.

The relativistic Notoph Lagrangian includes the Maxwell Lagrangian and a coupling term

$$L_{OP} = dY^2 + \frac{1}{8\pi}F^2 + \gamma YF.$$  (11.2.1)

We must include an interaction with the fields $\rho$ and $\Phi$; the most natural way is to set the total Lagrangian matter density to be

$$L_{\text{matter}} = L_{FW} + \rho \frac{1}{2}dY^2 + \frac{1}{8\pi}F^2 + \gamma YF + \frac{\kappa \rho}{\sqrt{-g}}d\psi \wedge dY.$$  (11.2.2)

The last term is included since it is gauge invariant, but the electromagnetic terms will be neglected in the present context. The coefficients $\gamma$ and $\kappa$ are constants.

The “Notoph” field has six components,

$$Y_{ij} = \epsilon_{ijk}X^k, \quad Y_{0i} = \eta_i, \quad i, j = 1, 2, 3.$$  

The gauge group consists of the transformations

$$\delta Y = d \wedge \xi,$$

with an arbitrary one-form $\xi$; by this means the field $\vec{\eta}$ can be reduced to zero, leaving the field $\vec{X}$ that has been associated with fluid flow since antiquity.

Written out in full, our present relativistic Lagrangian density is

$$L = \frac{\rho}{2}(g^{\mu\nu}\psi_{,\mu}\psi_{,\nu} - c^2) + \frac{\rho}{2}dY^2 + \kappa \rho \frac{c^2}{2}e^{\mu\nu\lambda\rho}Y_{\mu\nu,\lambda}\psi_{,\rho} - f - sT.$$  (11.2.3)
A full examination of this relativistic field theory is planned; here we shall limit our study to the non-relativistic version. See Ogievetski and Palubarinov (1964), Kalb and Ramond ( ), Lund and Regge ( ), Fronsdal, (2011).

XII.2. Non-relativistic limit and Galilei transformations

A concept of a non-relativistic limit of a relativistic field theory can be envisaged if each of the dynamical variables can be represented as a power series in \(1/c\), beginning with a term of order zero; that is, \((1/c)^0\), or higher, \((1/c)^1, (1/c)^2, \ldots\). In the case of the model considered we must assume that this is the case for the variables \(\rho, Y, \psi\). We neglect the coupling to the electromagnetic field for the moment. The non-relativistic limit of the Lagrangian exists if every term is of positive or zero order. Dropping all terms of positive order we may ask about the physical meaning of the remainder, including transformation properties.

Taking the basic variables to be \(\rho, Y\) and \(\psi\) we find, with the normalization

\[
dY_{\mu\nu\lambda} = \sum_{\text{cyclic}} Y_{\mu\nu,\lambda}, \tag{11.3.1}
\]

that

\[
\frac{c^2}{24} dY^2 = \frac{1}{2} (\dot{X} + \vec{\nabla} \wedge \eta)^2 - \frac{c^2}{4} (\vec{\nabla} \cdot \vec{X})^2, \tag{11.3.2}
\]

\[
\frac{k}{2} \epsilon^{\mu\nu\lambda\rho} Y_{\mu\nu,\lambda,\rho} = \kappa (\dot{X} + \vec{\nabla} \wedge \eta) \cdot \vec{\nabla} \Phi - \kappa c^2 \vec{\nabla} \cdot \vec{X}
\]

There are terms of order \(c^2\) and to overcome this obstruction we must postulate the boundary condition

\[
\vec{\nabla} \cdot \vec{X} = c^{-2} \Theta + o(c^{-3}), \tag{11.3.3}
\]

with the field \(\Theta\) of order 0. We conclude that the existence of a non-relativistic limit of the Lagrangian depends on the validity of (11.3.1).

Galilei invariance

The subgroup of ‘proper’ Galilei transformations derives from Lorentz transformations of the form

\[
\delta \vec{x} = t \vec{u} \gamma, \quad \delta t = (\vec{u} \cdot \vec{x}/c^2) \gamma, \quad \gamma = \frac{1}{\sqrt{1 - (u/c)^2}}.
\]

Infinitesimal Galilei transformations are related to first order Lorentz transformations. It is enough to retain terms linear in \(\vec{u}\), replacing \(\gamma\) by unity. Infinitesimal Galilei transformations are defined as the ‘contraction’ that consists of taking the limit \(c \to \infty\). But it would be imprudent to take that limit already at this stage, as we shall see. So the transformations to be considered are first order or infinitesimal Lorentz transformations,

\[
\delta \vec{x} = t \vec{u}, \quad \delta t = \vec{u} \cdot \vec{x}/c^2.
\]
In what we shall call a physical gauge the field $\vec{\eta}$ vanishes. The Lorentz group acts on the antisymmetric field in the manner that is indicated by the indices, in particular

$$\delta Y_{ij} = t\vec{u} \cdot \vec{\nabla} Y_{ij} + tu_i Y_{0j} + tu_j Y_{i0}, \quad \delta Y_{0j} = t\vec{u} \cdot \vec{\nabla} Y_{0j} + u_i Y_{ij}/c^2.$$ 

The terms that involve the operator $\vec{u} \cdot \vec{\nabla}$ are generic for scalar fields and they do not contribute to the action. The other terms that are linear in $t$ vanish in a physical gauge, so the component $Y_{ij}$ and the component $\vec{X}$ transform as scalar fields under Galilei transformations. The last term is another matter; its presence shows that the transformed field is not in the physical gauge, since $\delta Y_{0j} \neq 0$. So we have to make a gauge transformation

$$\delta Y_{ij} = \partial_i \xi_j - \partial_j \xi_i, \quad \delta Y_{0j} = \partial_0 \xi_j - \partial_j \xi_0,$$

such that $d\xi = 0$ and

$$\partial_0 \xi_j - \partial_j \xi_0 = -u_i Y_{ij}/c^2.$$

The very existence of a non relativistic limit implies that the basic variables can be represented as power series in $1/c$. So even if this implies a change in $Y_{ij}$, that will be a change of order $1/c^2$ and we can be fairly confident that this is enough that this change can be ignored. We shall see below that great caution is necessary and it is worth while to point out that if $\vec{\nabla} \cdot \vec{X}$ is of order $1/c^2$ then the change $\delta Y_{ij}$ will be of order $1/c^2$. To see this take the curl of the last equation to get

$$\partial_0 \vec{\nabla} \times \vec{\xi} = \vec{u}(\vec{\nabla} \cdot \vec{X})/c^2.$$ 

If we suppose, as we must, that $\vec{\nabla} \cdot \vec{X}$ is of order $1/c^2$ then this makes $\xi$ of order $1/c^3$. We conclude that Galilei transformations affect the field $\vec{X}$ only the way that it affects scalar fields, by the argument shift $\delta \vec{x} = \vec{u}t$.

Dropping terms of order $1/c^2$ we find that the transformation properties of the fields are

$$\delta \Phi = t\vec{u} \cdot \vec{\nabla} \Phi + \vec{u} \cdot \vec{\nabla} \Phi, \quad \delta \vec{\nabla} \Phi = t\vec{u} \cdot (\vec{\nabla} \Phi) + \vec{u}$$

and, with

$$\Theta := c^2 \vec{\nabla} \cdot \vec{X},$$

$$\delta \vec{X} = (t\vec{u} \cdot \vec{\nabla}) \vec{X} + (\vec{u} \cdot \vec{\nabla}) \vec{X}, \quad \delta \Theta = t\vec{u} \cdot \vec{\nabla} \Theta + \vec{u} \cdot \vec{X},$$

while $\Phi$, the components of $\vec{X}$ and those of its spatial derivatives transform as scalar fields with the generator $t\vec{u} \cdot \vec{\nabla}$.

A reason for proceeding cautiously is that there are terms in the Lagrangian of apparent order $c^2$, see (11.2.1-3),

$$-\frac{c^2}{4}(\vec{\nabla} \cdot \vec{X})^2 - \kappa \vec{\nabla} \cdot \vec{X} c^2$$

(11.3.4)

The first is not a problem, since the variation is of order $1/c^3$. This term can be ignored in the non-relativistic limit. But

$$\delta \left(-\kappa \vec{\nabla} \cdot \vec{X} c^2\right) = -\kappa \delta \Theta.$$ 

245
We can complete the definition of the physical gauge by setting $\Theta = 0$, loosing the Galilei invariance of the action, or we can retain the the term $-\kappa \Theta$; in the Lagrangian density and preserve Galilei invariance by setting

$$\delta \Theta = \vec{u} \cdot \dot{\vec{X}}.$$ 

**XII.3. General Relativity.**

The original impetus for developing an action principle for hydrodynamics and thermodynamics was to prepare for a study of astrophysics, the structure of stars and galaxies. The relation of these fields of science to each other is less than evident. However, already in 1870 the physicist Homer Lane published a paper with the following title:

“On the Theoretical Temperature of the Sun, under the Hypothesis of a gaseous Mass maintaining its Volume by its internal Heat and depending on the laws of gases as known to terrestrial Experiment” (Lane 1870)

Half a century later Eddington marveled at the success of a theory that treated the interior of the Sun as if it consists of an ideal gas. And even today the best that can be done to describe the interior structure of stars is to apply the experience that has been gained by terrestrial experiments.

We are going to consider the hydrodynamics of self gravitating fluids by means of Einstein’s equations for the metric, in the context of the General theory of Relativity. Stars and galaxies tend to rotate, in some it may be said that rotation is their dominant characteristic; this has been the principal difficulty for some time. It is a problem that the preceding chapter has already prepared us for, but more preparation is needed: we can approach General Relativity only after promoting our theory to a relativistic, Lagrangian field theory in the sense of the Special Theory of Relativity.

This sketch of an introduction to General Relativity divides naturally into several parts:


**Introduction to General Relativity. Part 1. The metric.**

Here is a very compact summary of the first stage of General Relativity. Special relativity was created in 1905. It arose from the demand that the laws of mechanics have the same invariance group as Maxwell’s theory of electromagnetism, the Poincaré group or the inhomogeneous Lorentz group. It became necessary to formulate physical laws in a language that makes Lorentz invariance manifest, in order that the attention could be directed to physics without the need to worry about consistency with
the new principles at each stage. This had the effect of introducing the Lorentzian metric into all the equations of fundamental physics. For example, Maxwell’s field equations now take the form

$$g^{\mu\nu}\partial_\mu F_{\nu\lambda} = J_\lambda. \quad (11.3.1)$$

The prominence of the metric led Einstein to seek a larger role for it, and this resulted in the idea of geodesic motion. The next great leap forward was the realization that Newton’s equations for the motion of a particle in a gravitational field could be interpreted as geodesic motion in the special metric

$$ds^2 = (1 - \frac{2\phi}{c^2})(c dt)^2 - d\vec{x}^2, \quad (11.3.2)$$

where $\phi$ is the Newtonian gravitational potential. The distance between two points in space time is

$$\int_a^b ds = \int_a^b \sqrt{g_{\mu\nu}dx^\mu dx^\nu} \int_a^b \sqrt{g_{\mu\nu}\dot{x}^\mu\dot{x}^\nu} d\tau, \quad \dot{x}^\mu := \frac{dx^\mu}{d\tau},$$

and the equation that minimizes the value of this expression is

$$\ddot{x}^\mu - \Gamma_{\nu\lambda}^{\mu} \dot{x}^\nu \dot{x}^\lambda = 0, \quad (11.3.3)$$

where the dots stand for derivatives with respect to $s$ and $\Gamma$ is the metric connection,

$$\Gamma_{\nu\lambda}^{\mu} = \frac{1}{2}g^{\mu\rho}(g_{\nu\rho,\lambda} + g_{\rho\lambda,\nu} - g_{\rho\lambda,\rho}). \quad (11.3.4)$$

The proliferation of indices is frightening, but most of the coefficients of $\Gamma$ are zero and a little work leads to the revelation that Eq. (12.3.3) is precisely the Newtonian equations of motion for a particle with unit mass in the field $\phi$ defined in Eq. (11.3.2).

**Introduction to G.R. Part 2. The dynamical metric**

The recognition of geodesic motion was not just an interpretation of Newton’s equations of motion; it was a major discovery with important experimental consequences. But the theory needed further development. In Newtonian theory the potential was determined by solving the Poisson equation with the mass distribution as a source,

$$\Delta \phi = -4\pi G\rho, \quad (11.3.4)$$

with $G$ a universal constant. It relates the field $\phi$ to the source, the matter distribution. The search for a suitable generalization would take 10 years of labor by Einstein, Hilbert, Poincaré and others. The answer is as this. A covariant derivative is defined with the help of the metric connection (12.3.5),

$$D_\mu := \partial_\mu - \Gamma_\mu, \quad 247$$
The Gaussian curvature tensor is

\[ [D_\mu, D_\nu] = R_{\mu\nu} = R_{\mu\nu}^b L^b_a, \]

where the \((L^b_a)\) are matrices, the generators of ‘local Lorentz transformations’. Alternatively, if \(A\) is any co-vector field,

\[ [D_\mu, D_\nu] A_\rho = (R_{\mu\nu})^\lambda_\rho A_\lambda. \]

Two contractions leads to the curvature scalar \(R = g^{\mu\rho}(R_{\mu\nu})^\nu_\rho\) and this scalar field, by virtue of being the only candidate with required characteristics, is the Lagrangian density for the metric field.

Variations of the action

\[ A_{\text{metric}} = \int d^4x \sqrt{-g} R \]  

with respect to the metric,

\[ \delta A_{\text{metric}} = \int d^4x \sqrt{-g} \delta g^{\mu\nu} G_{\mu\nu} = 0. \]

gives a unique field equation

\[ G_{\mu\nu} = 0. \]

When the variation \(\delta g^{\mu\nu}\) in Eq. (11.3.3) is specialized to the type of variation that results from a change of coordinates,

\[ \delta g_{\mu\nu} = D_\mu \xi_\nu + D_\nu \xi_\mu, \]

one finds by means of an integration by parts the identity

\[ G^{\mu\nu};\nu = 0. \]

This is the famous Bianchi identity; it is indeed satisfied identically, for it merely expresses the invariance of the action under coordinate transformations. The simplest way to write this equation is

\[ \frac{\partial}{\partial x^\mu} \sqrt{-g} G^{\mu\nu} + \sqrt{-g} G^{\lambda\rho} \Gamma^\nu_{\lambda\rho} = 0. \]

Eq. (11.3.8) is Einstein’s field equation for the metric field in vacuum; that is, the field equation for ‘empty space’ ... space-time devoid of matter.

A special solution to equation (11.3.4), stationary and spherically symmetric, was found very soon by Schwarzschild (1917); it has an interesting topological structure and led to the concept of Black Holes. But our interest is in space with matter, as a star or a galaxy, not empty space.
Introduction to G.R. Part 3. Sources for Einstein’s equations

In the presence of matter the metric field equation is expected to take the form

\[ G_{\mu\nu} = T_{\mu\nu}. \]  

(12.3.9)

Instead of zero, characteristic of vacuum, it has something on the right hand side that represents matter, the source of the gravitational metric field. An integrability condition arises from the fact that the left side satisfies the Bianchi identity, consistency demands that the source tensor \( T \) must satisfy the same condition, the Bianchi constraint,

\[ T^{\mu\nu}_{\ ;\nu} = 0. \]  

(11.3.10)

The key to satisfying this condition is that the Bianchi identity is derived from invariance under coordinate transformations. A whole class of models that satisfy this last condition is found by taking the matter tensor to be the energy momentum tensor of a coordinate invariant, Lagrangian field theory, with action

\[ A_{\text{matter}} = \int d^4x \sqrt{-g} \mathcal{L}, \]

and energy momentum tensor

\[ T_{\mu\nu} = 2 \frac{\delta}{\delta g^{\mu\nu}} \mathcal{L} - \mathcal{L} g_{\mu\nu}. \]

The constraint is not satisfied identically, but on shell, by virtue of the matter equations. It is a gift to us, offered by any relativistic field theory. This is the result discovered by Noether, that we have reviewed in Section III.8.

This was indeed the method by which the first consistent field theories with a matter-metric interaction were constructed, first of all the so called Maxwell-Einstein theory that unites electromagnetism and General Relativity. The Maxwell Lagrangian density is

\[ -\frac{1}{4} g^{\mu\nu} g^{\lambda\rho} F_{\mu\lambda} F_{\nu\rho}, \]

and the energy momentum tensor (verify this)

\[ T_{\mu\nu} = g^{\lambda\rho} F_{\mu\lambda} F_{\nu\rho} - g_{\mu\nu} \mathcal{L}. \]

But this theory does not involve the theory of fluids or other types of matter. Similar field theoretic models are plentiful, but they do not describe extended distributions of matter. No relativistic field theory of fluids has been available.

Lacking a dynamical matter model suitable for stellar structure, Tolman, in 1934, proposed a phenomenological expression for the matter tensor,

\[ T_{\mu\nu} = (\rho + \frac{p}{c^2}) U_\mu U_\nu - pg_{\mu\nu}. \]  

(11.3.8)
Here $\rho$ is a scalar density field possibly associated with the distribution of mass, $p$ is an isotropic pressure density and $U$ is a four vector field. Tolman interpreted the space components in terms of matter flow and imposed the normalization

$$g^{\mu\nu}U_\mu U_\nu = 1. \quad (11.4.2)$$

The expression for the source in (11.3.8), and the constraint (11.4.2) were inspired by the model of non interacting particles. The model does not have a conserved current, the condition of continuity of classical hydrodynamics is abandoned. Nevertheless, faute de mieux., Tolman’s suggestion has been used in almost all investigations of stellar structure, from Eddington and Chandrasekhar forward.

The most obvious objection to Tolman’s formula is that it fails to incorporate an equation of continuity, a defect that is significant in a theory that aspires to be a generalization of hydrodynamics.

Even more important is the fact that Tolman’s matter tensor is not directly related to a matter model and it has no dynamical content. There are no matter equations of motion that could be used to verify the Bianchi identities. Instead, the suggestion is to regard the condition (12.3.4),

$$T^{\mu\nu;\nu} = 0$$

as a substitute for dynamics. Thus matter has no intrinsic properties; instead it is subject to the consistency conditions that allow it to appear as a source for the gravitational field. In this sense it is like the Navier Stokes equation that simply defines the the acceleration of particles in the fluid in terms of unspecified force fields.

An analogy will help put the right accent on this, and is of great interest by its own rights. Maxwell-Dirac electrodynamics couples to field theories, mainly by introducing an interaction term of the form $eA_\mu J^\mu$ in the Maxwell Lagrangian. Maxwell’s equations now take the form

$$\partial_\mu F^{\mu\nu} = eJ^\mu.$$  

The left side is evidently divergence less, so the right hand side must be divergenceless as well; that is, conserved. And this condition, $J^{\mu;\mu} = 0$, must be satisfied by virtue of the Dirac field equations for the matter field.

It will be objected that, though this is true in Maxwell-Dirac theory, and though it is true that it is a requisite for perturbation theory, it is not satisfied in the theory of electromagnetic fluids. Indeed that is so, and as we have said, Minkowski’s treatment of electrodynamics leaves a lot to be desired.

“To include rotating bodies in General Relativity, we must upgrade every 3-vector field to a relativistic 4-vector field.” This simplistic rule has been dominant since Einstein used it in his relativistic theory of particles, where the prescription was completely successful, as it led to relativistic concepts of mass, energy and momentum, combined to a 4-dimensionsal energy-momentum vector

$$(cp^1, cp^2, cp^3, p^0 = E), \quad E^2 - c^2p^2 = c^4m^2,$$
where the constant \( c \) is the velocity of light. Unfortunately the same idea was applied to the velocity fields of liquids.

First, already in 1908, Minkowski used it in the context of electromagnetism. As Minkowski was aware, and as all modern textbooks tell us, the electromagnetic interactions of a fluid at rest give rise to contributions \( \epsilon \mathbf{E}^2 - \mu \mathbf{B}^2 \) to the energy density. To find the appropriate generalization to the case that there is motion in the fluid he first performs a Lorentz transformation to a reference frame that is moving with constant velocity \( \mathbf{v} \); then he promotes \( \mathbf{v} \) to a four-vector with components

\[
(v^\mu) = (\vec{v}, v^0).
\]

To this we must already object, but there is more to come. Having thus gotten a ‘velocity’ (actually a parameter of the Lorentz group) into his formalism Minkowski simply assumes that the expression that he has obtained is valid as it stands, for arbitrary motions of the liquid. This is what passes as electromagnetism of fluids to this day. Perhaps we should try to do better, in some future chapter of this book.

Of more immediate interest to us is that the approach taken by Minkowski to electrodynamics was adopted without change by Tolman in 1934. We shall have much to say about that.

It is evident that we cannot adopt this approach; the velocity potential can be promoted to a relativistic scalar field, and the gradient to a 4-vector velocity field, but the velocity field \( \dot{\mathbf{X}} \) is another matter. An objection: Is it not true that one often promotes this vector field to a 4-vector by replacing the time derivative by the proper time derivative? This proper time is the time as recorded by a “co-moving” clock. It is a concept that is useful to help explain the relative nature of time in the special theory of relativity, and it may be appropriate in the case of the motion of particles, but proper time has no place in a theory of fields, which is what hydrodynamics is.

Tolman’s formula for the energy momentum tensor is based on the idea of a single, timelike 4-vector velocity field. It cannot accommodate rotating matter, which is fatal since most heavenly bodies are rotating.

**XII.4. Variational principles in Special and General Relativity**

**Gravity waves**

Formulating an action principle for a metric in interaction with a number of particles has been attempted in connection with the recent observation of Gravity Waves. A finite number of point particle models of Black Holes, are moving in a fixed metric field. The matter action is a sum of contributions, one from each particle,

\[
A_{\text{matter}} = \int d^4x \sqrt{-g} \mathcal{L} = \sum_a \int d\tau_a \int d^4x \sqrt{-g} \mathcal{L}_a \delta^4(x - x_a).
\]
Each term is the familiar geodesic action. The dynamical variables are the four-dimensional positions $x^\mu_a$ of the objects, paths in 4-space, each parameterized by its own “proper time” $\tau_a$. So far, when this action is considered on its own, the metric is fixed, not yet a dynamical variable.

We have two ways to obtain the energy momentum tensor. The result is, of course, exactly the same. If we make the usual choice of the parameter, then each of the big square roots is equal to 1 and Noether’s formula gives

$$T^{\mu\nu} = \sum_a \dot{x}_a^{\nu} \dot{x}_a^\mu \sqrt{-g} \delta^4(x - x_a) - \frac{1}{2} g^{\mu\nu} \mathcal{L} \sqrt{-g} \delta^4(x - x_a).$$

This is like Tolman’s formula with

$$\rho = p = \sum \sqrt{-g} \delta^4(x - x_a)$$

except that the term $p/c^2$ in the term $(\rho + p/c^2)U^\mu U^\nu$ is missing. A recent Wikipedia article still has it; I find no support for this extra term and I cannot see how Tolman could justify this relativistic term when all that he does is based on non relativistic particles.

Finally, let us return to our subject, hydrodynamic field theory.

**Relativistic Hydrodynamics**

We have seen that, in the context of special Relativity, the scalar velocity potential becomes a scalar field in the 4-dimensional sense, and that $\Phi, \nabla \Phi$ combine to a four-vector. The relativistic upgrade of the Fetter-Walecka Lagrangian is easy to construct (Fronsdal 2007); we have already seen it in Section X.1.

The first guess is successful; just consider the Lorentz invariant action

$$\int d^3x dt \left( \frac{\rho}{2} (g^{\mu\nu} \psi_{,\mu} \psi_{,\nu} - c^2) - W[\rho] \right). \quad (12.1.1)$$

The metric tensor is Lorentzian, diagonal with components $(-1, -1, -1, c^2)$. The tensor $(g^{\mu\nu})$ is the inverse matrix. The fields $\rho$ and $\psi$ are four-dimensional scalar fields. In flat space, with the Lorentzian metric it is

$$2 \int d^3x dt \left( \frac{\rho}{2c^2} \dot{\psi}^2 - (\nabla \psi)^2 - c^2 - W[\rho] \right).$$

To take the non-relativistic limit it is tempting to drop the first term. The trouble is that, in spite of the factor $1/c^2$, the variation of both terms under an infinitesimal Lorentz transformation,

$$\delta \dot{\psi} = c \vec{u} \cdot \vec{\nabla} \psi, \quad \delta \psi^* = \vec{u} \dot{\psi},$$

are comparable; of course, for they cancel in this Lorentz invariant combination. To arrive at a non-relativistic theory that is invariant to first order in $\vec{u}/c$ we need to retain this contribution to the variation under Lorentz transformations. This was done by expanding

$$\psi = tc^2 + \Phi, \quad \frac{1}{c^2} \dot{\psi}^2 = c^2 + 2\dot{\Phi} + ...$$

252
where the elided terms are of order $1/c^2$. These can be safely dropped, for the necessary contribution to the Lorentz transformation is provided by the variation of the linear term,

$$\delta \Phi = \vec{u} \cdot \vec{\nabla} \Phi.$$

The result is the Fetter-Walecka action; it is invariant under Galilei transformations, as we have seen in Section III.11. This is the simplest way to be convinced that the non-relativistic theory is invariant under Galilei transformations.

Going on to the second vector field $\dot{X}$, we have already studied the complete, special-relativistic gauge theory in X.5. The complete matter action is given in Eq. (11.2.3),

$$\mathcal{L} = \frac{\rho}{2} (\mathcal{L}^{\mu\nu}_{\psi,\mu} \psi_{\nu} - c^2) + \frac{\rho}{2} dY^2 + \kappa \rho \frac{c^2}{2} \epsilon^{\mu\nu\lambda\rho} Y_{\mu\nu,\lambda} \psi_{\rho} - f - sT, \quad (11.2.3)$$

This is the moment of truth; all preparation is complete. We are challenged to produce solutions to the equations of motion.
XI.7 Sources for Einstein’s equations.

More generally, when the field $\vec{X}$ is included,

$$T^0_0 = \rho \dot{\Phi} + \rho \dot{\vec{X}}^2 - \mathcal{L} = h,$$

$$T^i_0 = -\dot{\Phi} \rho \Phi_i + \dot{\Phi} \kappa \rho \vec{X}_i, \quad T^0_k = \Phi_k \rho + X_{i,k} m_i, \quad i = 1, 2, 3$$

and

$$T^j_k = -\Phi_k \rho \Phi_j + \Phi_k \kappa \rho \dot{X}_j - \delta^j_k \mathcal{L}.$$

The energy conservation law (10.3.3) retains its form, with an extra term in $h$ as in (10.2.9), while the law of momentum conservation becomes

$$\frac{d}{dt} T^0_k + \partial_j T^j_k =$$

$$\partial_0 (\Phi_k \rho) + \partial_0 (\rho X_{i,k} \vec{X}_i) + \partial_0 (\kappa \rho X_{i,k} \Phi_i)$$

$$+ \partial_0 (\rho \Phi_k \vec{X}_j) + \partial_0 (\kappa \rho \vec{X}_j \dot{\Phi} + \kappa \Phi_k \vec{X}_j - \partial_k p.$$

With the help of the equation of continuity,

$$1 + 4 + 5 = \partial_0 (\rho \Phi_k) + \partial_j (\rho \Phi_k v_j) = \rho \dot{\Phi} k + \rho v_j \Phi_{kj} = \rho \partial_k \left( \dot{\Phi} - (\nabla \Phi)^2 / 2 + \kappa \dot{\vec{X}} \cdot \nabla \Phi \right)$$

and the field equation $\ddot{\vec{m}} = 0$,

$$2 + 3 = \partial_0 (X_{i,k} m_i) = m_i \dot{X}_{i,k} = \rho \dot{X}_i \dot{X}_{i,k} + \kappa \rho \dot{\Phi}_i \dot{X}_{i,k}.$$

$$5 + 6 = \kappa \rho \Phi_{jk} \dot{X}_j + \kappa \Phi_k \partial_j (\rho \dot{X}_j) - \partial_k p.$$

Combining everything we get

$$\frac{d}{dt} T^0_k + \partial_j T^j_k = \rho \partial_k \left( \dot{\Phi} - (\nabla \Phi)^2 / 2 + \dot{\vec{X}}^2 / 2 + \kappa \dot{X} \cdot \nabla \Phi \right) - \partial_k p,$$

which is zero by virtue of the Bernoulli equation. Hence, once again (10.4.2) is a consequence of the Euler-Lagrange equations.

To discover the underlying conservation law we must go back, to undo the use that was made of the equation of continuity and the equation $(d/dt)\vec{m} = 0$. Then instead of (10.4.10)

$$\frac{d}{dt} (\rho \Phi_k + X_{i,k} m_i) = \text{boundary terms},$$

the expression for the “conserved momentum” is unexpected.

This is the meaning of (10.4.2) but actually the full set of field equations tells us that both $\rho \nabla \Phi$ and $\vec{m}$ are conserved.
IX. Non equilibrium thermodynamics.
   1. Introduction
   2. The entropy profile according to statistical theory
   3. The $U$
   4. Free expansion revisited
   6. Thermodynamics for a system that is not isolated, the slab
   7. Speed of sound. the larger picture
   Atmospheres. Copy? Old
   6. the isothermal atmosphere, confrontational
   7. introduction
   8. Experiments of Graeff, 20 page 266
Non equilibrium thermodynamics

IX.1. Introduction

We shall venture into the no mans land of “non equilibrium thermodynamics”. This expression, as commonly used, refers to systems that are out of equilibrium and not specifically to the problem of the approach to equilibrium. Prigogine has led a vigorous advance in this area but we shall be much less ambitious. As we stated in the foreword to this work, we have chosen to reverse, with respect to tradition, the order in which we apply the two principal ideas of thermodynamics: the action principle and the second law. This puts us in a better position to move out of the context in which the entropy is understood; the Lagrangian and the minimum energy principle remain for our use, not only to equilibria but to the entire field of adiabatic dynamics, provided that it is used with some circumspection. It is a much wider platform from which to make forays into the field of dissipative thermodynamics.

The action principle must be understood, in the first place, as a means to predict the properties of a system as they are implied by a specific choice of the free energy functional, and the assigned entropy, though ultimately by experiments. We have warned against the opposite attitude in which the expression for the entropy in terms of the dynamical variables is viewed merely as a means to evaluate it. But as we approach problems in which the entropy is much less understood, it is appropriate to be less dogmatic; after all, we can derive information about the entropy from observation of adiabatic behavior. This is a very profitable thing to do, for this knowledge is coded into the Lagrangian and affects all subsequent applications to the system.

This chapter tests the limits within which the thermodynamic action principle can be used profitably; where the real limits are cannot be foreseen.

X.2. The entropy profile according to statistical theory

Statistical physics suggests that the isolated atmosphere, at equilibrium, is isothermal. This has led Landau and Lifshitz to state that the entropy distribution, in the case of an ideal gas, at equilibrium, is as follows,

\[
\frac{ds}{dz} = -g \rho_0 / T_0,
\]

(10.2.1)

where \( \rho_0 \) and \( T_0 \) are the density distribution (uniform or not) and the temperature (uniform) at equilibrium and \( g \) is the gravitational acceleration. Since this formula is central to the subsequent development it is important to clarify what it means.

The following formula for the specific entropy density of an ideal gas was deduced by Sackor and Tetrode from kinetic theory,

\[
S = T \ln \frac{\rho}{T_n} + \text{constant}.
\]

(2.2)

Here \( \rho \) is the density in g/cm\(^3\) and \( T \) is the temperature. The same formula can be deduced from classical laboratory experiments. The most direct way to define an ideal gas is to specify the free energy density,

\[
f(T, \rho) = R \rho T \ln \frac{\rho}{T_n}.
\]
The formula for $S$ is the adiabatic condition
\[
\frac{\partial}{\partial T} |_{S,\rho} (f + sT) = 0, \tag{2.3}
\]
where $s = \rho S$ is the entropy density. An “adiabatic system” is defined by the expression for the free energy density, the adiabatic condition (2.3), the definition of the pressure,
\[
p = \rho \frac{\partial f}{\partial \rho} |_T - f \tag{2.4}
\]
and, very important, a fixed choice of the specific entropy distribution $S$.

It will be recalled that, in the successful calculation of the speed of sound in an ideal gas, by Laplace, the essential premise is that $S$ is fixed. In the context, where the effect of gravity is neglected, $S$ is a constant, but the term “adiabatic” refers to a general dynamical system, at equilibrium or not, in which the distribution $S$, uniform or not, is fixed.

This brings us to the interpretation of Eq.(2.1): When it refers to an adiabatic system it is a formula for $\partial s/\partial z$, expressed in terms of the equilibrium properties of the system, independent of $\rho$ and $T$. This value is chosen to make the stationary state isothermal, a central tenet of statistical theory.

We shall see that, in order to accommodate the formula (2.1) into the action principle we need to replace the familiar formula for the assigned entropy ($s = \rho S$) by one that is more general,
\[
s = \rho S + s_{\text{ex}}, \quad s_{\text{ex}} = -g\rho_0.
\]
The adiabatic relation now takes the form
\[
\frac{\partial}{\partial T} |_{S,\rho} (f + sT) = \mathcal{R} \rho (\ln \frac{\rho}{T^n} + 1) + \rho S + s_{\text{ex}} = 0. \tag{2.5}
\]
For a stationary state the principal equation of motion reads
\[
\frac{\partial}{\partial \rho} |_{S,T} (gz\rho + f + sT) = 0, \tag{2.6}
\]
where now the gravitational potential energy has been included. Explicitly,
\[
-gz + \mathcal{R} T (\ln \frac{\rho}{T^n} - n) + ST = 0. \tag{2.7}
\]
Eliminating the logarithm between Eq.s (2.5) and (2.7) we get the required result,
\[
gz + \mathcal{R} (n_i + 1) T + s_{\text{ex}} T / \rho_0 = \text{constant}.
\]
If the atmosphere is isothermal then the formula (2.1) results.

No assumptions was made with respect to the possible spatial variation of the specific entropy $S$, and no assumption about the spatial dependence of $S$ has a bearing on the final
conclusion. That is, the formula (2.1) cannot be interpreted in terms of a variation of the specific entropy density. What is needed to accommodate the isothermal atmosphere is a fixed contribution $s_{ex}$ to the entropy. It is independent of the density, we may refer to it as ‘space entropy’ or ‘geometric entropy’.

This generalization is in full accord with the statistical interpretation of entropy, as will be shown below.

It should be emphasized that the introduction of geometric entropy into the thermodynamic theory of atmosphere came from the need to accommodate the isolated, isothermal atmosphere into non equilibrium thermodynamics. The isentropic, isolated atmosphere is simpler in that it does not seem to have any need for this concept. But we shall see that this last conclusion is premature; it will turn out that the geometric component of the entropy density is needed in any case, though not, so far, to describe the atmosphere.

IX.8. Reply to Maxwell

It has to be maintained that the existence of isentropic atmosphere in a gravitational field is in contradiction with the second law of thermodynamics. If that were so the second law would share the faith of all other laws that have been formulated by scientists over the ages.

The existence of the isentropic atmosphere is a matter for experimental science; unfortunately a decisive experiment would be very difficult. Besides, scientists with enough reputation to be respected seem not to be enthusiastic about investing either their time or their reputation on this problem. The evidence presented by our actual atmosphere has not proved convincing.

The experiment should certainly be done, and with the astounding advance in technology it shall eventually lead to a conclusion. And then what? What should we do if the conclusion is that the isentropic atmosphere exists?

It is unlikely, even in that case, that thermodynamics, or even just the second law, would become obsolete; for the arguments advanced by Maxwell and others is far from conclusive, as will be shown.

Maxwell. Two tubes are filled by two different gases, placed vertically next to each other and isolated from each other and from the environment, except for being connected to a reservoir at the top. At equilibrium: that is, after some time, if no further changes are taking place, the temperatures at the bottom of the two tubes will be different. A heat engine can be installed two exploit this difference and energy can thus be extracted from the heat bath.

Student But that would not be very shocking, not like constructing a perpetuum mobile, since the energy is supplied by the heat bath; any real heat reservoir will eventually get cold.

Maxwell. Granted that the intervention of the infinite heat bath makes it difficult for our discussion to advance. consider instead the following system.
The $U$.

Imagine a tube, in the form of the letter $U$, upright, divided into two parts in the middle (the low end), containing two different ideal gases, gas $A$ on the left, gas $B$ on the right, the whole in complete isolation except for terrestrial gravity, the two gases in thermal contact at the dividing wall. The tubes are closed at the top; the volume and the geometry are fixed. This is ‘the open $U$’. There is no heat bath. for the sake of the argument, assume that the equilibria, in the terrestrial gravitational field, is isentropic.

The tubes are thermally connected only at the bottom. Wait for equilibrium to be established; then the temperatures will be equal there, but different at the top. Now connect the tops of the $U$ with a heat conducting wire, thus creating ‘the closed $U$’. We are going to neglect the heat loss in the wire as well as its heat capacity. The temperature will eventually equalize at the top, finding a new equilibrium at which the temperatures at the top are equal. This means that there has been a flow of heat and, because the change is spontaneous, involving no heat transfer from the environment, there has been a net increase of the total entropy. The process that has just taken place is therefore irreversible.

Next, disconnect the wire and let the system return to the original configuration. But this is impossible, for it would require a decrease in the entropy. Therefore the isentropic equilibrium does not exist.

Student Let us examine the process in a little more detail, starting with no thermal connection at the top, and different temperatures $T_1$, $T_2$ there. Let $S_0$ be the total entropy of the system. Now two things will happen in succession.

First, the thermal connection at the top is connected. This constitutes a change of the system by external interference. It leaves the system out of equilibrium. If the entropy of this new configuration can be defined, call it $S_1$.

Second, the system, left out of equilibrium will find a new equilibrium, with entropy $S_2$. Given the properties of each gas we can calculate both $S_2 - S_1$. but what is the value of $S_1$.

Maxwell. Because the system, after the end of the first stage, is out of equilibrium, the entropy that you call $S_1$ is not defined.

Student In that case I may make a suggestion. Is it not possible to assign the value $S_2$ to $S_1$? I may perhaps propose this as the definition of $S_1$. by this definition the change in entropy is due to the interference with the system (the establishment of the thermal connection) and the subsequent establishment of the new equilibrium would be adiabatic since there is no interference from the outside during the second stage.

Maxwell. I do not like that definition of $S_1$ but I admit that my argument has been dealt a severe blow.

Student Thank you professor.

Let us subject the usual account of what happens in an elementary experiment involving free expansion. See Section III.6. To reinforce the usual picture it is common to discuss
attempts to reverse the expansion, with or without the help of some of Maxwell’s demons. One suggestion has been to consider the fact that, unlikely though it is, if we wait long enough then all the particles will eventually find themselves inside the original, smaller volume, this without any interference and no change in entropy. Consequently, if we manage to close the gate at that very moment, thus returning the system to the original configuration, then that was the event that changed the entropy. It is a wonder that this conclusion was not announced long ago.

Let us not be so glib. When the wire is installed we get a new system with different boundary conditions, now $T_1 = T_2$. We did not have any use for the space entropy till now, but now we need it to satisfy the stronger boundary conditions.

If the state of equilibrium is isentropic it can be described by the Lagrangian

$$\mathcal{L} = \sum \rho_i (\dot{\Phi}_i - gz) - f_i - s_i T, \quad i = 1, 2. \quad f_i = \mathcal{R}_i \rho_i T \ln \frac{\rho_i}{T_{n_i}}.$$ 

We shall need to generalize our expression for the entropy density and we shall learn that the following expression allows to describe simple systems that, in the strict sense are not in equilibrium

$$s_i = \rho_i S_i + s_{ex,i}, \quad i = 1, 2.$$ 

The term $s_{ex,i}$ is new; it has been included for the following reason. The equations of motion are

$$\mathcal{R} \rho_{0,i} (\ln \frac{\rho_{0,i}}{T_{n_i}} - n_i) - s_i, \quad s_i = \rho_{0,i} S_i + s_{ex,i} = 0, \quad (1)$$

$$\dot{\Phi}_i - \vec{v}_i^2/2 - gz - \mathcal{R} T (\ln \frac{\rho_i}{T_{n_i}} + 1) - ST.$$ 

Eliminating the logarithm we obtain, in the case of a stationary configuration with $\vec{v}_1 = \vec{v}_2 = 0$,

$$\dot{\Phi}_i - gz - \mathcal{R} (n_i + 1) T - s_{ex,i} T / \rho_{0,i} = 0.$$ 

The $\dot{\Phi}_i$ are constants, Lagrange multipliers. It is clear that, without the new contribution to the entropy, the temperature cannot be uniform. Landau and Lifshitz arrange this by stating that the $z-$dependence of the gravitational term is taken up by the additional entropy term,

$$s_{ex,i} = -gz \rho_{0,i} / T_0 + \text{constant}.$$ 

This formula is found in Landau and Lifshitz, page ???. The above equations of motion are not stated explicitly there, but they are nothing else than standard, fundamental relations of thermodynamics and they are the relations that are subsumed.

So we learn that an apparent incompatibility between thermodynamics and the statistical theory of equilibria can be resolved by admitting the existence of the extra contribution to the entropy. It is independent of the density (it is proportional to the equilibrium density, fixed.)

So far we have assumed that the equilibrium configuration is isothermal, in order to emphasize that the need for this extra complication of a ‘space-entropy’ $s_{ex,i}$ arises in the traditional framework and that it appears in a highly respected textbook. If instead the equilibrium state is isentropic; then there is no need for this complication; not yet that is,
since we simply deduce the existence of a temperature gradient, different in the two arms of the U. Since the two branches are in thermal contact at the bottom, we would get

\[ T_1 - T_0 = -\frac{gh}{R_1(n_1 + 1)} = -\frac{gh}{C_{p,1}}, \]

\[ T_2 - T_0 = -\frac{gh}{R_2(n_2 + 1)} = -\frac{gh}{C_{p,2}}, \]

where \( h \) is the difference in altitude between the top and the bottom of the U. The appearance of a temperature gradient in a system that is at equilibrium is anathema to the prophets of statistical mechanics. Here one could resolve the issue peacefully by declaring that the final, stationary configuration just described is not a true equilibrium state. But that begs the question and it leaves nothing for thermodynamics to say about the system under investigation.

In this state of continuing conflict it is tempting to raise the spectrum of a violation of the second law of thermodynamics. To examine this possibility we must assume, for the sake of the argument, that the isolated atmosphere is isothermal. A version of the U was evoked by Maxwell. His argument involves installing a heat engine between the two tops of the U and utilizing the temperature difference to generate energy. But the heat bath represents a difficulty since it leads to heat flow into the U, complicating the analysis.

In the absence of a heat bath, and with complete isolation of the system, the simplified argument goes like this. At a certain moment, after equilibrium has been established, connect the tops of the U with a heat conducting wire, thus creating ‘the closed U’. We are going to neglect the heat loss in the wire as well as its heat capacity. “The temperature will eventually equalize at the top; this means that there has been a flow of heat and an increase of the total entropy. The process that has just taken place is therefore irreversible, so that, when the wire is eventually removed, the system cannot return to the original, isentropic configuration. Therefore the isentropic equilibrium does not exist.”

Let us not be so glib. When the wire is installed we get a new system with different boundary conditions, now \( T_1 = T_2 \). We did not have any use for the space entropy till now, but now we need it to satisfy the stronger boundary conditions.

Let the final temperature at the connected tops of the closed U be \( T_3 \); we expect it to be between \( T_1 \) and \( T_2 \); then

\[ g = C_{p,1}(T_0 - T_3) + s_{ex,1}/\rho_0,1(0) - s_{ex,1}/\rho_0,1(h) \]

\[ = C_{p,2}(T_0 - T_3) + s_{ex,2}/\rho_0,2(0) - s_{ex,2}/\rho_0,2(h). \]

Contributions from the space entropy are needed whenever the two gases have different heat capacities.

Let us try to determine the final, equilibrium temperature \( T_3 \). The internal energy of the initial system, before coupling, is

\[ U = U_1 + U_2 = \int_0^h dz(n_1\rho_1T + n_2\rho_2T). \]
The initial equilibrium densities can be calculated from Eq. (1), according to which, to a very good approximation,

\[ \frac{\rho_0(z)}{\rho_i(0)} = \frac{T_{n_i}(z)}{T_{n_i}(0)} \]

Since, ideally, no energy was supplied from the outside, the total energy must be unchanged.

The calculation is not complicated; even without calculation it is clear that there is a unique temperature \( T_3 \) between \( T_1 \) and \( T_2 \) for which the total internal energy of the closed \( U \) is equal that of the open one.

What about the entropy? We cannot answer this question, for in the case of the connected system, when a space entropy is needed, we have no way to normalize it. But intuitively it is clear that we can repeat the cycle indefinitely and that no physically significant quantity can change over a cycle. So we are forced to conclude that either process, connecting or disconnecting, is reversible. It is not adiabatic in the strict sense, since the entropy profiles change, but it is possible and perhaps convenient to think of the total entropy as being preserved.

And this is not absurd.
This should precede to U.

**IX.6. Thermodynamics for a system that is not isolated**  Page 211

The system is an ideal gas confined between two parallel plates, kept at uniform but unequal temperatures $T_1 > T_2$. To help fix a picture let the plates be horizontal and introduce a vertical coordinate $z$, although gravity will be left out of it for the time being. The system is assumed to be stationary, the velocity is zero and all the fields are time independent.

Fig.9.6.1. The slab. Two boundary plates are maintained at fixed, unequal, temperatures.

We wish to describe this system by the methods of local thermodynamics and begin by writing down the Lagrangian,

$$\mathcal{L}(T, \rho) = \rho(\dot{\Phi} - \vec{v}^2/2) - f - sT \quad (9.6.1)$$

The usual pair of equations of motion,

$$\frac{\partial}{\partial \rho}(f + sT) = 0, \quad \frac{\partial}{\partial T}(f + sT) = 0$$

give us, upon elimination of the entropy, the statement that

$$T \frac{\partial \mu}{\partial T} - \mu = \text{constant}, \quad \mu := \frac{\partial f}{\partial \rho}, \quad (9.6.2)$$

The chemical potential, which is the same as the specific enthalpy, is a linear function of the temperature, modulo a constant.

In the case of an ideal gas it is

$$T \frac{\partial \mu}{\partial T} - \mu = (n + 1)\mathcal{R}(T - T_0) = \text{constant}.$$  

This is not compatible with the boundary conditions that we have selected.
Seebeck discovered that, when the two plates are clamped at fixed, unequal temperatures, then a static voltage difference can be observed. There is an interaction with a spontaneously created electromagnetic field, with the electrostatic field strength constant. Conversely, if a constant electric field is applied across the slab, the effect is to add a potential to the energy,

\[ \mathcal{L}(T, \rho) = \rho(\dot{\Phi} - \dot{v}^2/2 - kz) - f - sT, \]

where \( k \) is a constant. In this case, instead of (9.2.2),

\[ T \frac{\partial \mu}{\partial T} - \mu = -kz \]

and for an ideal gas

\[ T \frac{\partial \mu}{\partial T} - \mu = (n + 1)R(T - T_0) = -kz \]

With a constant temperature gradient one can accommodate the required boundary conditions on the temperature.

Instead of an electrostatic field gravitation can be used to produce the same kind of effect, though the strength of the potential is inconveniently small.

**IX.7. The speed of sound across the slab**

In a first example of the use of thermodynamic methods in a non-adiabatic situation, stationary but not an equilibrium, state, we shall calculate the speed of propagation of a sound wave propagating vertically; that is, in the direction perpendicular to the boundary. Following the usual procedure we perturb the density, \( \rho = \rho_0 + d\rho \) and the temperature, \( T = T_0 + dT \) and find with the help of the continuity equation and equations (9.2.1), to first order in the perturbation, that

\[ \ddot{d}\rho = -(\rho\dot{v})' = \frac{d}{dz}\rho_0 \frac{d}{dz} \dot{\Phi} = \frac{d}{dz} \frac{dp}{d\rho} \bigg|_{ad} d\rho. \]

The adiabatic derivative is \( \gamma RT \), so finally

\[ \ddot{\rho} = \frac{d}{dz} \gamma RT \frac{d\rho}{dz}. \]

Sound speed increases in the direction of a positive temperature gradient.

So do we understand this system? We have treated it as an adiabatic system, or we can, if we include the dynamical electromagnetic field, together with an interaction term of the type \( \vec{E} \cdot \vec{k}\rho \), where \( \vec{k} \) is a constant vector in the direction of the temperature gradient. This makes sense if we think that the temperature gradient is caused by the field, but that does not really describe the situation. What we are doing is to apply heat baths to both plates; the electric field is then seen as a response of the system. That is exactly what is called the Seebeck effect. But if this interpretation is correct, then should we be able to use our
theory to predict the value of the potential difference between the plates? An unknown coupling strength is involved, but we may hope that it is universal. It is important to test these ideas, for if they should fail then we would have an important problem to confront.

Let us speculate: what alternative explanation is available, if the appeal to an external field is unsuccessful. Well, there is at least one other way to account for it. The system is not isolated, so our long held preference for a uniform entropy is not really justified here. It is not extravagant to suppose that, when heat is applied, and energy appears to pass through the slab, the system reacts by creating an entropy gradient. These are questions that are worth asking.

IX.7. The larger picture

This prediction concerning the propagation of sound in a medium undergoing heat transfer may be wrong, but is there an alternative theory? Traditional, non equilibrium thermodynamics is much concerned with calculating the amount of heat transmitted and with measuring the associated coefficients. But studies of the system itself, when subject to stationary heat transfer, are hard to find. And yet the problem is very similar to one that has received much attention, the effect of external forces including gravity and electromagnetism on extended systems, especially at equilibrium. Such systems are always regarded as simple extensions of equilibrium thermodynamics, with additional variables. And electromagnetic currents are not essentially different from heat currents.

An outstanding problem is that of defining entropy for systems that are out of equilibrium. A sensible procedure is to obtain, if necessary measure, the entropy of a system in local equilibrium. If in addition the free energy is known we define an adiabatic system by fixing the entropy. Let us be quite clear about what is meant by this.

From the beginning we have stressed what we think is a central point of Gibbsean thermodynamics. It is a variational principle where temperature and volume are varied with pressure and entropy kept fixed. Applying this principle to extended systems we have taken it to mean that the entropy is a given function of the mass density, in many cases a linear function, often with a constant coefficient. In the case of heterogeneous systems we have adopted, as a working hypothesis, the assumption that the entropy is a linear function of the several densities.

In this section we have tried to apply the same ideas to a system that is not isolated, but subject to outside interference. For guidance, we may look for analogies. In the case of steady electric or magnetic fields one introduces the notation of polarizability. The field is often taken as given, and there is a contribution to the energy density that is attributed to its presence, perhaps $\epsilon \rho \vec{D}^2$ or $\epsilon \rho \vec{D}^2 T$, where $\vec{D}$ is the electric induction. It is not unusual to include such contributions and to proceed exactly as one does for an isolated system.

But the analogy is not perfect; the imposed temperature difference is not an additional dynamical variable, but a limitation placed on the space of boundary conditions under consideration. In section III.5 it was pointed out that the pressure on the walls can never be chosen freely; most choices are incompatible with the variational equations. To insist on a particular set of boundary conditions one may have to change the free energy; for example, by including external forces. And here the analogy with our problem is close;
to accommodate a particular set of boundary conditions we need to make sure that the variational equations are compatible with them.

So much for the mathematics. From the physical point of view we feel that the stationary configuration is not quite an equilibrium. Apparently, heat is passed through the system and we expect the system to react. It is natural to think that the injection of heat may have an effect on the entropy, but we probably cannot say more than that. All we can do is to guess the general form of the entropy distribution, the subject to the condition that it be consistent with the boundary conditions. This forces us to give up the idea of a purely specific entropy assigned to each particle and the simplest solution is to assume an extra, spacial contribution, independent of the mass density.

It seems that this proposed extension of (extended) thermodynamics is within the compass of the program me of Prigogine (1965). We share Prigogine’s hope that the ideas of Gibbs concerning equilibria remain valid for stationary configurations, and indeed Gibbs’ work on equilibria does allow a very natural and direct extension. But we have gone a little step beyond Prigogine, without deviating from Gibbs, for we have given a recipe for the adiabatic dynamical system to which the stationery states belong. The prescription is this: Study the stationary system; choose the free energy density and fix the entropy; this defines an adiabatic system. Then adopt the variational equations associated with the Lagrangian as the equations of motion for this adiabatic system.

**What is heat flow?**

The most important of all historical changes in our attitude towards heat and energy is that energy is conserved and that heat is not; heat is not a material substance. So what is heat flow? Would it not make more sense to speak of energy flow? The suggestion made here would place the system in the comfortable environment of hamiltonian systems, with the hamiltonian density

\[ h = \rho \tilde{v}^2 / 2 + f + sT, \quad s = \rho S + s_{ex}. \]

Now

\[ \dot{h} = \dot{\rho} \tilde{v}^2 / 2 + \rho \tilde{v} \cdot \tilde{v} + \dot{\rho} \frac{\partial f}{\partial \rho} + T \frac{\partial f}{\partial T} + \dot{s}T + s \dot{T}. \]

The two terms that contain \( \dot{T} \) cancel on shell because the relation \( \frac{\partial f}{\partial T} + s = 0 \). With the equations of motion

\[ \ddot{v} = -\nabla (\tilde{v}^2 / 2 + \frac{\partial f}{\partial \rho} + ST), \quad \dot{\rho} = -\nabla \cdot (\rho \tilde{v}), \]

where the extra entropy does not appear, it becomes

\[ \dot{h} = -\nabla \cdot (\rho \tilde{v}) [\tilde{v}^2 / 2 + \frac{\partial f}{\partial \rho} + ST] - \rho \tilde{v} \cdot \nabla (\rho \tilde{v}^2 / 2 + \frac{\partial f}{\partial \rho} + \rho ST) \]

\[ = -\nabla \cdot [\rho \tilde{v} (\tilde{v}^2 / 2 + f + p + \rho ST)]. \]
We used $s = S \dot{\rho}$ and the canonical definition of the pressure in terms of $f$. This allows the identification of

$$\vec{J} = \rho(\vec{v}^2/2 + f + p + \rho ST) \vec{v}$$

as an energy current. The extra entropy makes no contribution to it.

Since $\vec{v} = 0$ at equilibrium, there is no energy transfer within the fluid. Since $\vec{v} = 0$ for the stationary configurations there is no energy transfer within the slab, under stationary conditions.

It must be admitted that, intuitively, a transfer of energy must be taking place, from the hot boundary to the cold one. But the only effect that this has on the fluid is to create the extra contribution to the entropy. This contribution was made during the approach to the stationary configuration; in the final, stationary state there is no further change. If entropy is being created the dynamical system does not know of it. The only thing that distinguishes this stationary state from an equilibrium state is the expression for the entropy.

Perhaps the effect of an applied electric or magnetic field can be considered to be analogous. That is, it would appear that the extra entropy plays the same role as dielectric polarization and magnetization. As far as I know it has always been considered reasonable to deal with systems in the presence of electromagnetic fields by the methods of thermodynamics.

Consequently, we feel that the heat flux defined by the heat equation has no real meaning; it serves only to account for the fact that, in the case that the heat reservoirs that ensure the boundary conditions are finite, energy is taken out of the hot reservoir and added to the cold one. Possibly, one is justified in referring to this process as one of heat conduction.

Further light on the question can be had, for example, by studying the transfer of heat or energy through a meniscus, from a liquid to its vapor. See Kjelstrup, Bedeau and ... (2008).
IX.4. Air and Argon

The densities for the pure gases at standard conditions are: Air .00012, Argon .0001784. The adiabatic parameters for pure Air: 6.32 E-11, Argon: 7.6 6 E-8; that is,

\[ S_N = 23.48R/mol, \quad S_O = 16.38R/mol. \]

**where do these values come from?**

This case is different since the two gases have different adiabatic index. By “Air” we mean an ideal gas with \( n = 5/2 \) and atomic weight 29. Eq.s (10.3.1-3) apply, but the data are different.

The fixed parameters are

\[ R_1 = \frac{R}{29}, \quad R_2 = \frac{R}{40}, \quad R = .8314 \times 10^8, \quad n_1 = 5/2, \quad n_2 = 3/2. \]

The data at ground level, \( z = 0 \),

\[ T = 293.159, \quad \rho_1(0) = 1.2 \times 10^{-3}, \quad \rho_2(0) = 1.116 \times 10^{-5}, \quad \frac{\rho_1}{\rho_2} = 107.527. \]

Should this be for “Normal conditions”, \( T = 293.15K \)?

This case is more difficult, chiefly because there are fixed parameters to be chosen. Observations seem to indicate that the ratio \( \rho_1/\rho_2 \) varies slowly, but there is no solution that makes \( \rho_1/\rho_2 \) independent of altitude. Because Air is very dominant we expect it to be only a little perturbed by the presence of Argon; that is, the specific entropy is likely to have a value close to what is observed in the absence of Argon. In other words, the variable \( x \) is likely to be close to 1 under normal conditions at ground level. Taking \( x = .99 \) we get from (9.3.3) the value \( y = 4.68249 \).

Eq.s (9.3.1-2) tell us that

\[ c := T \left( \frac{\ln x + 3.5}{29} - \frac{\ln y + 2.5}{40} \right) \]

must be uniform. Setting \( x = .99, y = 4.44 \) at sea level we get the value, \( c = 7.0462 \). Also at sea level

\[ \frac{k_{01}}{k_{02}} = \frac{\rho_1}{\rho_2} \frac{y}{e^T x} = .68249. \]

Having thus obtained good trial values of the parameters we calculate \( x, y \) and \( T \) by

\[ T^{-1} = \frac{1}{c} \left( \frac{3.5 + \ln x}{29} - \frac{2.5 + \ln y}{40} \right) = -e \frac{k_{01} x \ln x}{k_{02} y \ln y} \frac{40}{29} \]

and finally the altitude by

\[ g(z - z_0) = R_1 T (\ln x + 3.5) \]

268
obtain values from zero to +11 km. The results are in Fig. and in the table. The lapse rate is steady at 10 $K/km$.

<table>
<thead>
<tr>
<th>x</th>
<th>.99</th>
<th>.991</th>
<th>.992</th>
<th>.993</th>
<th>.994</th>
<th>.995</th>
</tr>
</thead>
<tbody>
<tr>
<td>y</td>
<td>3.72</td>
<td>3.285</td>
<td>2.931</td>
<td>2.628</td>
<td>2.350</td>
<td>2.094</td>
</tr>
<tr>
<td>T</td>
<td>300</td>
<td>266</td>
<td>241</td>
<td>222</td>
<td>205</td>
<td>189</td>
</tr>
<tr>
<td>$\rho_1/\rho_2$</td>
<td>100</td>
<td>100.7</td>
<td>102.4</td>
<td>105</td>
<td>109</td>
<td>113</td>
</tr>
<tr>
<td>z</td>
<td>0</td>
<td>3.4</td>
<td>5.9</td>
<td>7.9</td>
<td>9.6</td>
<td>11.2</td>
</tr>
</tbody>
</table>

The theory predicts a small reduction in the concentration of Argon at high altitudes.

Since the values of $x$ and $y$ are determined we can calculate the adiabatic parameters; at ground level

$$ k_{01} = \rho_1 \frac{(eT)^n}{x} = 8.485 \times 10^{-14}, \quad k_{02} = \rho_1 \frac{(eT)^n}{y} = 1.6735 \times 10^{-13} $$

Then we are free to fix these parameters independent of the elevation and use them to evaluate the individual densities. Calculate entropies. Apply the same method to the case that $n_1 = n_2$.

Fig.9.4.1 shows the temperature profile and the line $T = 300 - 10z$; the lapse rate is very close to uniform.

### The significance of a constant lapse rate

must be explained. Reference has been made to Fourier’s heat equation, namely

$$ \dot{T} \propto \vec{\nabla}T, $$

in Section III,?. If this venerable relation is to be respected, then any stationary atmosphere must have $\vec{\nabla}T = 0$. This property is respected by the polytropic atmosphere and that is indeed a principal reason why it is of interest, as emphasized by Emden in 1908. Here, as in the following example, this property is satisfied, to a very good approximation, but not exactly. That the linear relation between the temperature and the altitude is respected in the present example is explained by the small amount of Argon in our atmosphere.

The presence of water vapor in our atmosphere has a pronounced effect on the measured lapse rate; we shall try to calculate this effect.

### IX.5. Air and water. Introduction

This is the mixture that controls life on earth. We shall take up the study with respect for generations that have studied it before us and conscious of the special difficulties that characterize $H_2O$.

Water presents a problem in that there is no simple, analytic equation of state. The classical van der Waals equation was developed to account for the domain near the critical
point. In the case of water, to agree with the measured values of the critical temperature
and the critical pressure, the density predicted is off by nearly a factor of two, giving 10.95
mol/Lit instead of the measured value 17.87. Conversely, the density of water in normal
conditions is 998.2 g/Lit or 54 mol/Lit, which would imply that \( b\rho = 1.6 > 1 \). In the van
der Waals model this parameter varies from 0 to 1.

Data for water. The measured values are, molecular weight 18.015,

\[
T_{cr} = 647K, \quad p_{cr} = 220atm, \quad \rho_{cr} = 17.87mol/Lit
\]

Standard van der Waals parameters

\[
a = 5.536atm(Lit/mol)^2, \quad b = .03049Lit/mol
\]

Check

\[
p = \frac{.08314 \times 647\rho}{1 - .03049\rho} - 5.536\rho^2
\]

Value 220.45 at inflection point \( \rho = 11.069 \). File AirH20-7

12235

Our study will be directed at near-normal conditions. Much work has been done to
create an accurate equation of state for water, over a very wide range of temperatures, but
they lack the attractive feature of the van der Waals model in that the coexistence of liquid
and water is not built in. Instead, we propose to use a van der Waals model specifically
adapted to near normal conditions.

At \( T = 293\ K \) the data are as follows. Vapor pressure 2.3 kPa, densities

\[
\rho_{liq} = 998.2g/Lit = 55.4mol/Lit, \quad \rho_{vap} = 17.3g/m^3 = .00096mol/Lit, \quad (9.4.1)
\]

the ratio of densities is

\[
\frac{\rho_{vap}}{\rho_{liq}} = 1.73285 \times 10^{-5} = \frac{y^u}{y^v}. \quad (9.4.2)
\]

We shall construct a van der Waals model on these data.

The van der Waals formula can be written

\[
\frac{p}{p_{cr}} = 8\frac{T}{T_{cr}} \frac{y}{1-y} - 27y^2
\]

where \( T_{cr} \) and \( p_{cr} \) are free parameters. To use the common tangent procedure we write the expression for the free energy density in the form

\[
\frac{f}{p_{cr}} = \frac{8T}{T_{cr}} y \ln \frac{y}{1-y} - 27y^2 + ..., \quad (9.4.3)
\]

270
where \( y = b \rho \) and +... stands for a term that is linear in \( y \) and that does not affect our calculations of the equilibrium. With the common tangent method we find that this high ratio of coexistent densities (at \( T = 293K \)) implies that \( T_{cr} \) must have a value near 1178.55. The proposed model, intended to be applicable near normal conditions, is thus (in bars)

\[
\frac{p}{p_{cr}} = \frac{8T}{1178.55} \frac{y}{1 - y} - 27y^2,
\]

with effective van der Waals parameters \( a', b' \) to be determined.

Check. Plot \((8 \times 1178.55/1178.55) - 27y^2\). Inflection point at \( y = 1/3 \), value 1, in file AirH2O-4. Plot \((8 \times 293/1178.55) - 27y^2\). Inflection point at \( y = 1/3 \), value 1, in file AirH2O-4.

The two normalized densities and the associated pressure, calculated with the common tangent method using (9.4.4), are:

\[
y_{liq} = b' \rho_{liq} = .9199258777 = 55.4b' \text{ mol/Lit}, \quad y_{vap} = 1.59401 \times 10^{-5} = .00096b' \text{ mol/Lit}. \tag{9.4.5}
\]

Both data give the same value for \( p/p_{cr} \) (at \( T = 293K \))

\[
p/p_{cr}' = 3.16967 \times 10^{-5} p_{cr}'. \tag{9.4.6}
\]

and the same value for \( b' \),

\[
b' = .016605, \quad a' = 5.5382,
\]

The value of \( a' \) was obtained from \( 647(a'/b^2) = 1187.55(a/b^b) \). We drop the primes from now on.

For the latest calculations see AirH2O-8 and -4. Check. File AirH2O-5. Both densities give \( p = 3.16967 E-5 \). change \( p/p_{cr} \) to this value. the value 2.20425 is (almost explained by the factor 72 in my original calculations. verified minimum at 1.59403E5 and at .919926.

The measured value of the vapor pressure at normal conditions is 2.3388kPa; To agree with this we must change the value of \( p \); finally the van der Waals expression to be used near normal conditions is

\[
p = \frac{1}{10} \left( \frac{0.08314 T \rho}{1 - b \rho} - a \rho^2 \right) \tag{9.4.7}
\]

As could be expected, the “critical pressure is off by a factor of almost 2 from the experimental value of 220 atm. Recall that we are looking for a model to serve us at low temperatures.

The many significant figures in some of these numbers bespeaks the low compressibility of the liquid, \( xdp/dx \approx 6.8 \times 10^{-3} \); the compressibility is the inverse, the experimental value is \( 4.6 \times 10^{-10} / Pa \).
To complete the determination of the parameters of the model we confront the calculated densities (9.4.4) with the measured values (9.4.1) to get

\[ a = 5.532 \text{atm}(\text{Lit/mol})^2, \quad b = .0166\text{Lit/gmol}. \]

Our model is defined by these values; the critical parameters are

\[ T = 1187.55K, \quad p_{cr} = 743.4\text{atm} \]

Finally, the following formula was used for the pressure of the liquid-vapor equilibrium at near-normal conditions

\[ p = \frac{.08314 \times 1187.55\rho}{1 -.0166\rho} - 5.5382\rho^2 \]

Verified at critical; verified at normal File AirH2O-9.

The model of water determined we easily calculate, using the common tangent, the equilibrium configuration for a modest range of temperature.

<table>
<thead>
<tr>
<th>T</th>
<th>p (9.4.4)</th>
<th>p exp.</th>
<th>y''(9.4.4)</th>
<th>y'' exp.</th>
<th>y''</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.5040E-3</td>
<td>1.2281E-3</td>
<td>1.0243E-5</td>
<td>0.866E-5</td>
<td>.922908668</td>
</tr>
<tr>
<td>20</td>
<td>2.3389E-3</td>
<td>2.3388E-3</td>
<td>1.5940E-5</td>
<td>1.594E-5</td>
<td>.919925878</td>
</tr>
<tr>
<td>30</td>
<td>3.7790E-3</td>
<td>4.2455E-3</td>
<td>2.4056E-5</td>
<td>2.801E-5</td>
<td>.91692</td>
</tr>
<tr>
<td>50</td>
<td>8.4718E-3</td>
<td>1.2344E-2</td>
<td>5.0605E-5</td>
<td>7.372E-5</td>
<td>4.9108489</td>
</tr>
<tr>
<td>70</td>
<td>1.7280E-2</td>
<td>3.1176E-2</td>
<td>9.7250E-5</td>
<td>1.86E-4</td>
<td>.904682723</td>
</tr>
<tr>
<td>90</td>
<td>3.2519E-2</td>
<td>7.0117E-2</td>
<td>1.7304E-4</td>
<td>3.85E-4</td>
<td>.898422971</td>
</tr>
<tr>
<td>110</td>
<td>9.24309E-2</td>
<td>8.4277E-2</td>
<td>2.8904E-4</td>
<td>5.25E-4</td>
<td>.892034</td>
</tr>
</tbody>
</table>

Table. Pressure in atm, y = bρ dimensionless.

12366

**IX.6. Phase separation in a mixture of Air and Water**

Data, for “Air” I used Nitrogen, molecular weight 29,

\[ T_{cr} = 128K, \quad p_c = 34\text{atm}, \quad \rho_c = .044\text{mol/Lit} = .0012754\text{gr/cm}^3, \]

\[ a = 1.408, \quad b = .03913. \]

This gives

\[ p_c = \frac{1}{27} \frac{1.408}{.03913^2} = 34.29. \]

For \( H_2O \) we use ???

\[ T_2 = 1178.55K, \quad p_{cr} = 743.4\text{Atm}, \quad \rho_c = 26.4 \]
and (9.4.3-4). (The actual value is 17.87 for \( \rho_c \).)

\[ a = 5.5382, \quad b = 0.16605. \]

This gives, for water alone at normal conditions

\[ p_c = \frac{1}{27.016605^2} 5.5382 = 743.9. \]

We shall test the merit of regarding the atmosphere as a two-phase mixture of 2 fluids. The influence of gravity will be ignored but we shall nevertheless assume that the two phases separate.

We take the free energy density of this system to be

\[ f = f_1 + f_2 + \alpha \rho_1 \rho_2. \]

To discover the spinodal line we use the formula from Section VI.3 with a slightly different notation.

\[
\left( \frac{T/T_1}{x(1-x)^2} - \frac{27}{4} \right) \left( \frac{T/T_2}{y(1-y)^2} - \frac{27}{4} \right) = \beta := \frac{\alpha^2}{b_1 b_2 T_1 T_2 R^2}. \tag{9.6.1}
\]

Here \( T_1, T_2 \) are the two critical temperatures. When \( \beta = 0 \) there are only the spinodal lines of each separate fluid. For small, positive \( \beta \) there appears ovals, below 210\,K for \( \beta = 1 \), below 1149 \,K when \( \beta = 10 \). These oval quickly grow to the limits of the domain \( 0 < x, y < 1 \) for lower temperatures.

At normal conditions, \( T = 293 \), if air and \( H_2O \) are in comparable densities, the interaction affects the ratio of densities of the two forms of \( H_2O \), from 20 when \( \beta = 10 \) to 100 when \( \beta = 100 \). The effect is less pronounced if there is little air in the mixture and much less so if \( \rho_2/\rho_1 >> 1 \). Before proceeding to test this against experiment we must determine the condition of equilibrium.

The expression for the pressure is

\[
p = \frac{8}{27} \frac{a_1}{b_1^2} \left( \frac{x T/T_1}{1-x} - x^2 \right) + \frac{8}{27} \frac{a_2}{b_2^2} \left( \frac{y T/T_2}{1-y} - y^2 \right) + \frac{\alpha}{b_1 b_2} xy. \tag{9.6.2}
\]

Verified at both critical points.

At normal conditions, \( T = 293 \) the spinodals are at \((x,y) = (0.614, 0.011) \) and \((0.489, 0.990) \).

These are indicative of the location of coexistence; the liquid - gas densities will embrace the spinodals: \( \rho_2^b < .011, \quad .990 < \rho_2 < 1 \).

The pressure of Air at normal conditions is given by the formula

\[
\frac{8}{27} \frac{a_1}{b_1^2} \left( \frac{293}{128} \frac{x}{1-x} - \frac{27}{8} x^2 \right).
\]

We expect 1 atm when \( \rho_1 \) is about 1\,g/Lit. Instead the formula gives \( x = 0.0018 \) or \( \rho_1 = 1.35\,g/Lit. \)
The pressure of $H_2O$ at normal conditions is

$$\frac{8 a_2}{27 b_2^2} \left( \frac{293}{647} \frac{y}{1 - y} - \frac{27}{8} y^2 \right).$$

We expect this to be .0023 atm when $\rho_2 = .0138g/Lit$. Instead it is 1 atm at about 840 g/Lit or $y = .874$. This is partial failure of the van der Waals formula; we have not tried to tweak the formula to get a better fit but continue to describe the model, such as it is.

Finally the condition for equilibrium under normal conditions is that at $T = 293K$ and $p = 1$ atmosphere,

$$\mu_i^u = \mu_i^v, \quad i = 1, 2,$$

with

$$\frac{\mu_i}{\mathcal{R}T_i} = \frac{T}{T_i} \left( \ln \frac{x}{1 - x} + \frac{1}{1 - x} \right) - \frac{27}{4} x + \sqrt{\frac{b_1}{T_i}} \beta \rho_2 - \frac{T}{T_i} \ln(b_1T^{3/2})$$

and similarly for $\mu_2$.

12472

Between two mixtures, represented by two points in the density diagram, equilibrium is the condition that the temperature, the pressure and both chemical potentials be continuous at the meniscus. These conditions are expected to be satisfied on a pair of coexistence lines that embrace the two spinodal lines. To find points of coexistence we draw the isobar $p = 1$ atm, and choose a point on it

$$= a = 0007 + .0001n, \quad y = b = .0007 - .0001n,$$

where $n$ is a parameter that slides from -1 to +1. Then we plot these loci

$$p = 1, \quad \mu(x, y) = \mu(a, b), \quad \mu_2(x, y) = \mu_2(a, b).$$

They meet, of course, at the selected point. They also meet, or should meet, at the corresponding coexistent point in the density diagram and this can be arranged with a little tweaking of the parameter $n$. The first result obtained was

$$(x, y)^u = (.00046, .00090), \quad \bar{\rho}^u = (.438, .414)g/Lit,$$

a nearly equal concentration by mass in the gas, and

$$(x, y)^v = (.0258, .8404), \quad \bar{\rho}^v = (240, 386)g/Lit,$$

showing a large contribution of absorbed air in the liquid.

This was done with coupling strength $\alpha = -1.75$. Now what do the experiments say?

The most commonly used values of $k$ is $k = 1$; then the singularity appears at

$$\left( \frac{\mathcal{R}T}{x(1 - bx)} - 2a \right) \left( \frac{\mathcal{R}T}{y(1 - by)} - 2a \right) = \alpha^2.$$
The table gives some values of the critical temperature for a range of values of the interaction parameter. Quite unexpectedly, the critical density remains practically fixed at 
\[ \rho_1 = \rho_2 = 16.6\text{mol/Lit}, \]
these are the individual pressures and, as we have argued, the pressure *tout court*. It is quite close to the experimental value of \( \rho_c = 17.8\text{ mol/Lit} \), a significant improvement over the van der Waals formula (11mol/Lit).

\[
\begin{array}{cc}
\alpha & 800, 700, 601, 500, 450, 400, 300, 200, 100 \\
T_{cr} & 303, 401, 500, 596, 648, 697, 796, 895 993 \\
\end{array}
\]

The pressure is the same in both phases; the interaction is responsible for the separation and the separation makes the contribution of the interaction term vanish; the pressure is therefore the van der Waals pressure.

With \( \alpha = 469 \) we get the correct critical temperature and a critical density of 16.6 mol/Lit, which is a better than the van der Waals formula can do. But the van der Waals formula was made to fit the experiment and since it does apply to this situation we may look for better values of the parameters. Being close already makes this easy. With
\[ a = 5.41\text{Lit}^2\text{atm/mol}^2, \quad b = 2.85 \times 10^{-5}\text{m}^3/\text{mol}, \]
we move the predicted critical point to
\[ T_{cr} = 648\text{K}, \quad p = \rho_1 = \rho_2 = 17.5\text{mol/Lit}, \quad p = 221\text{atm}. \]
What we have done is to use the van der Waals free energy density but pressure a new criterion for criticality. And now critical density and critical temperature agree with the experimental findings. The pressure in the unmixed regions are accounted for as well, but the pressure in the region of overlap comes out to be about 7 times \( p_1 \). Perhaps the explanation for this is that, even in this region the degree of overlap is much less than complete.

Another suggested value of \( k \) is 1/2. In this case the singularity appears at
\[
\left( \frac{RT}{x(1-bx)} - 2a - \frac{\alpha}{4}y^5x^{-1.5} \right)\left( \frac{RT}{y(1-by)} - 2a - \frac{\alpha}{4}x^5y^{-1.5} \right) = (\alpha)^2(xy)^{-0.5},
\]
The densities are not quite independent of the strength of the interaction. With the same strategy we arrive at
\[ a = .6556, \quad b = .033, \quad \alpha = 5540 \]
to match the experimental values.

\[ T = 657.2, \quad p_1 = p_2 = 221\text{Atm}, \quad x = y = 17.5. \]
But what is especially interesting about the choice \( k = 1/2 \) is that the third pressure term vanishes. So it seems that, with this form of interaction, the interpretation is much simpler.
There is no true mixing going on; the interaction reduces \( \rho_1 \rho_2 \) to zero, the separation of the phases is complete.

Since the two components are thought to be effectively separably, the observed pressure is 16.6 mol/Lit in the first model and 19 mol/Lit in the second model, both values much better than the prediction of the original van der Waals model.

At temperatures below critical the vapor pressure may be found by the condition that two points \( \rho^u, \rho^v \) in the density plane have the same values of \( q_1, q_2, p \). Since the pressure is symmetric under interchange of the coordinates this will more easily come about if

\[
\rho^u_1, \rho^v_2 = \rho^v_1, \rho^u_2.
\]

Then the three conditions amount to just one,

\[
q_1(x, y) = q_2(y, x).
\]

With \( k = 1 \) this amounts to

\[
\mathcal{R}T(\ln \frac{x}{1 - bx} + \frac{1}{1 - bx}) - 2ax + \alpha y = \mathcal{R}T(\ln \frac{x}{1 - bx} + \frac{1}{1 - bx}) - 2ax + \alpha x.
\]

I tried this and the result is disappointing. I could not understand what happens at the critical point.

Google says that pure steam is invisible.

This attempt at describing clouds must be counted as a failure, so far. The alternative is a more traditional approach. I have not had the time to pursue this direction of investigation. The more interesting pursuit is the theory of atmosphere, with the effect of gravity included.

**The singular and the critical points**

Eq.s (10.6.4-5), for fixed values of \( T \) and the parameters, define a family of mappings, parameterized by the temperature, from density space to the space of chemical potentials. There is a region or regions where this mapping is one-one and other regions where it many-to-one. Any point where the image of the inverse map changes dimension is a “singular point”. A singularity of the mapping is a point where the Jacobian of the mapping vanishes:

\[
D_T(z) := \det \left( \frac{\partial \mu_i}{\partial \rho_j} \right) = \det \left( \frac{\partial^2 f}{\partial \rho_i \partial \rho_j} \right) = 0.
\]

It is easy to calculate it,

\[
\mu_{1,1} = \frac{\mathcal{R}T}{\rho_1} - \frac{\alpha}{4} \rho_1^{-3/2} \rho_2^{1/2}, \quad \mu_{1,2} = \frac{\alpha}{4} \rho_1^{-1/2} \rho_2^{-1/2},
\]

276
and

$$\rho_1 \rho_2 D_T = (RT - \frac{\alpha}{4} \sqrt{\rho_2 \rho_1}) (RT - \frac{\alpha}{4} \sqrt{\rho_1 \rho_2}) - \left(\frac{\alpha}{4}\right)^2$$

There is a highest value of $T$ for which this can vanish; it is at the point at which

$$A := \zeta + \zeta^{-1}, \quad \zeta := \sqrt{\frac{\rho_1}{\rho_2}}$$

is maximal; $\zeta = 1$, the point of equal molar densities, where

$$T_{cr} = \frac{\alpha}{4R}.$$ 

At a fixed sub-critical temperature there is a region in the density plane in which the chemical potentials

$$q_1 = RT (\ln k_1 + 1 + n_1) + \frac{\alpha}{2} \zeta^{-1}, \quad q_2 = RT (\ln k_2 + 1 + n_2) + \frac{\alpha}{2} \zeta$$

and the pressure,

$$p = R (\rho_1 + \rho_2) T$$

do not fix the densities. This is illustrated in Fig. X.5.1. The two radial lines, jointly, is the locus of singular points for a fixed value of the temperature and each of the other curves is the locus of a fixed value of the pressure. The two intersections are two points at which the two gradients of $f$ are parallel to each other. The equality of pressures tells us that the two tangents coincide.

At a low altitudes, when the temperature is above critical, the system will assume a unique density, varying with elevation. Going to higher altitudes there may come a point where $T = T_{cr}$. At still higher elevation two densities are permitted; the actual physical system will make a choice, but we do not know what the choice will be. Perhaps there will be regions with one density and regions with the other, in a kind of broken symmetry. Here, where we do not have enough information, we can only speculate. In the case of a mixture of air and steam, for example, the vapor may consist of tiny droplets. Then the influence of surface tension will become decisive and the droplets will grow, and eventually produce rain. All we can do here is to calculate the critical temperature, and the density profile of the atmosphere below a critical elevation.

**Low altitudes**

The equations of motion are

$$\dot{\Phi}_1 - \mu_1 gz = RT (\ln x + 1 + n_1) + \frac{\alpha}{2} \zeta^{-1},$$

$$\dot{\Phi}_2 - \mu_2 gz = RT (\ln y + 1 + n_2) + \frac{\alpha}{2} \zeta,$$

$$\rho_1 \ln x + \rho_2 \ln y = 0.$$ 

(10.6.3)
With the input of data at ground level, \( z = 0 \), we can fix all the parameters, then calculate the profile of the atmosphere below the critical point. As an illustration, consider a mixture of air and water (vapor).

\[
n_1 = n_2 = \frac{5}{2}, \quad T = 300K, \quad \rho_1 = 10^{-3}, \quad \rho_2 = 10^{-4} = 1, \quad p = 10^6.
\]

For \( \alpha \) we shall take a value that makes the critical temperature interesting,

\[
T_{cr} = 250K, \quad \alpha = 1000\mathcal{R}.
\]

This may seem high, but note that the pressure is independent of \( \alpha \). As to the adiabatic parameters we set \( x = 1 \) and with less confidence, \( y = 1 \), at ground level; then

\[
k_{01} = 5.3 \times 10^{-11}, \quad k_{02} = 5.3 \times 10^{-12}
\]

Now we get the values of the remaining parameters,

\[
\Phi_1 = \mathcal{R}300(5/2) + 500\mathcal{R}\sqrt{10} = 908\mathcal{R}, \quad \Phi_2 = \mathcal{R}300(\ln .5 + 5/2) + 500\sqrt{1/10}\mathcal{R} = 2331\mathcal{R}.
\]

At any altitude, the adiabatic parameters remain fixed and

\[
x/y = \frac{\rho_1}{\rho_2} = -\frac{\ln y}{\ln x},
\]

from which

The locus of points in the density plane occupied by the system at one altitude or another is a piecewise continuous line. Let us assume that it crosses the line \( \rho_1 = \rho_2 \) where \( T = T_0 \) and \( \rho_1 = \rho_2 = \rho_0 \), say. We choose the coordinate system so that this happens at the elevation \( z = 0 \). Then the constants are fixed at

\[
\dot{\Phi}_1 = \mathcal{R}T_0(\ln x_0 + 1 + n_1) + \alpha/2,
\]

\[
\dot{\Phi}_2 = \mathcal{R}T_0(\ln y_0 + 1 + n_2) + \alpha/2.
\]

The adiabatic condition gives us \( x_0y_0 = 1 \) and the equations of motion take the form

\[
-\mu_1gz = \mathcal{R}T \ln \frac{x}{x_0} + \frac{\alpha}{2}(\zeta^{-1} - 1),
\]

\[
-\mu_2gz = \mathcal{R}T \ln \frac{y}{y_0} + \frac{\alpha}{2}(\zeta - 1),
\]

We can now eliminate the temperature to obtain

\[
\left( \mu_1gz + \frac{\alpha}{2}(\zeta^{-1} - 1) \right) \ln \frac{y}{y_0} = \left( \mu_2gz + \frac{\alpha}{2}(\zeta - 1) \right) \ln \frac{x}{x_0}
\]

278
and with the adiabatic condition,

\[
\left( \mu_1 gz + \frac{\alpha}{2} (\zeta^{-1} - 1) \right) \rho_1 + \left( \mu_2 gz + \frac{\alpha}{2} (\zeta - 1) \right) \rho_2 = 0,
\]

Two conclusions can be made. First, that an interaction of the type considered implies a (probably minor) adjustment of the atmospheres considered. Second, that an appropriately strong interaction will lead to discontinuity in the concentration. It is plausible that the presence of gravity will lead to a separation such that the change in total density is negative at the separating surface.

\[
\left( \mu_1 gz + \frac{\alpha}{2} (\zeta^{-1} - 1) \ln \frac{y}{y_0} \right) = \left( \mu_2 gz + \frac{\alpha}{2} (\zeta - 1) \ln \frac{y}{x_0} \right)
\]

Fig.10.5.1. The region between the two straight lines (red) is where there are two solutions for the densities for the same values of \( p \) and \( T \). A very small increase in the temperature makes this region go away. The coordinates are the normalized densities \( x \) and \( y \).

X.5. **Air and \( H_2O \) Old**

**Air**

We shall treat Air as a van der Waals gas with adiabatic index \( n = 5/2, \gamma = 1.4 \), molecular weight 29. For air the precise values of the van der Waals parameters are not so important; we may use the values for pure Nitrogen,

\[
a_1 = 1.408 \text{atm}(L/mol)^2, \quad b_1 = 0.03913 \text{L/mol}.
\]

But given \( T_c \) and \( p_c \) and calculating as copied below, the value I get for \( a \) is 1/10 of this. Instead I base my calculations on the following experimental values

\[
T_c = 128K, \quad p_c = 34 \text{atm}
\]

This gives for Air,

\[
a_1 = .1408 \text{atm}(mol/m^3)^2, \quad b = 0.03913 \text{mol}/L = 3.913 \times 10^{-5} \text{mol}/m^3
\]

(compared to the experimental value \( \rho_c = .12 \text{mol}/L \)) and now it all fits:

\[
p_c = \frac{8.314T_c}{7.826 \times 10^{-5}} - \frac{14081}{3b^2} = 33.8 \text{ atm},
\]

likewise for Air. (I freely confuse bar with atmosphere) Note carefully the units
In an atmosphere of pure air (zero humidity) the entropy is independent of altitude. Under standard conditions,

\[ z = 0, \quad T = 273.16, \quad p = 10^5 \]

we have

\[ \rho_1 = 0.0012754 \text{g/cm}^3 = 0.044 \text{mol/L}, \quad b_1\rho_1 = 0.001716. \]

and

\[ S_1 = -R \ln\left(\frac{0.0012}{(1 - 0.001716)(273e)^{5/2}}\right) = 23.247R. \]

The ‘official’ value is \(?\). Do I need it?

When gravity is taken account the isentropic, dry atmosphere has

\[ T = 273.16 + 9z, \]

the altitude in kilometers, and

\[ \rho = T^{5/2}e^{-z/R1T}. \]

\(??\)

\(H_2O\)

We shall treat \(H_2O\) as a van der Waal’s gas with the pressure, in terms of molar densities,

\[ p = \frac{RT}{1 - b_2\rho} - a_2\rho^2, \quad R = 8.314 \text{J/mol}. \]

this will give the pressure in bars when the density is entered in \(\text{mol/m}^3\), \(b\) in \(\text{m}^6/\text{mol}\) and \(a\) in \(\text{bar} \cdot (\text{m}^6/\text{mol})^2\).

Van der Waals’ formula does not give a very good fit. With parameters from Wikipedia, \(a_2 = 0.5537Pa \cdot (\text{m}^3/\text{mol})^2\), \(b_2 = 3.049 \times 10^{-5} \text{m}^6/\text{mol}\) one has

\[ T_c = 647K, \quad \rho_c = 1/3b = 10.95 \times 10^3 \text{mol/m}^3. \]

But the last disagrees with the experimental value of 17.5\text{mol/Lit}.

This value of \(b_2\) is inferred directly from the experimental values of temperature and pressure,

\[ b_2 = \frac{RT_c}{8p_c} = \frac{8.3145 \times 647.2}{8 \times 221 \times 10^5} = 3.0436 \times 10^{-5} \text{m}^3/\text{mol}. \]

In a limited range of temperatures we can get a much better fit to the experiments by relating \(b_2\) to the experimental value of the critical density. We shall take \(b_2\) from the formula \(\rho_c = 1/3b\). In the same units we take

\[ a_2 = 0.2079, \quad b_2 = 1.865 \times 10^{-5}, \quad R = 5.094 \]

280
to get

\[ T_c = 647.2K, \quad \rho_c = 17.87, \]

and

\[ p_c = (5.094 \times 17873 \times 647.2)^{3/2} - .2079 \times (17.8973 \times 10^3)^3 = 219.9atm. \]

We have treated the gas constant as an adjustable parameter. For an ideal gas it has the value 8.314 and at very high temperatures our vapor behaves much like an ideal gas. But we are concerned solely with a much lower range of temperatures and with an equation of state that is consistent with the experimental data in a limited domain.

The main hydrodynamic equations are sufficient to determine the variation with altitude,

\[ \mathcal{R} \rho \left( \ln \frac{\rho}{(1 - b \rho) T^n} - n \right) + \rho S = 0 \]

\[ \dot{T} - g z - \mathcal{R} T \left( \ln \frac{\rho}{(1 - b \rho) T^n} + \frac{1}{1 - b \rho} - 2a \rho \right) - ST = 0. \]

Eliminating the logarithm we get the simple relation

\[ \dot{T} - g z = \mathcal{R} T (n + \frac{1}{1 - b \rho} - 2a). \]

This predicts a nearly constant temperature gradient. The only assumption is that the entropy density is proportional to the mass density.

**Humid Air**

We describe a stationary state without convection; this is the state that is taken as background for studies involving convection and sound propagation. The total Lagrangian is

\[ \mathcal{L} = \rho_1 (\dot{T} - g z) - f_1 - f_2 - s_1 T - s_2 T - f_{int}. \]

We expect that the time scale is such as to allow the mixture to reach an equilibrium consisting of two different mixtures, one a liquid with a minute amount of air dissolved in it and the other a mixture of air and water vapor. We use a superscript \( u \) for the vapor and the superscript \( v \) for the liquid. Equilibrium is determined by the following equations,

\[ T^u = T^v = T, \text{say} \quad p^u = p^v = p, \text{say} \quad \vec{q}^u = \vec{q}^v. \]

We use the notation

\[ \vec{q} = (q_1, q_2), \quad \vec{\rho} = (\rho_1, \rho_2). \]

All the equations are valid pointwise in \( \mathbb{R}^3 \). The densities are defined everywhere but each is zero in "the other" domain. For the interaction term we follow the example of van der Waals,

\[ f_{int} = \alpha \rho_1 \rho_2. \]
Coexistence can occur at only one elevation; we choose the coordinate system so that it happens at $z = 0$.

The critical temperature is the highest temperature at which the determinant of the matrix of coefficients

$$\frac{\partial^2 f}{\partial \rho_i \partial \rho_j}, \quad f = f_1 + f_2 + f_{\text{int}}$$

is zero. We have, in terms of molar densities

$$f_1 = R_1 \rho_1 T \ln \left( \frac{\rho_1}{T_n} \right), \quad f_2 = R_2 \rho_2 T \ln \left( \frac{\rho_2}{(1-b\rho_2)T_n} - a \rho_2^2 \right),$$

and thus

$$\frac{\partial f}{\partial \rho_1} = R_1 T (\ln \frac{\rho_1}{T_n} + 1) + \alpha \rho_2,$$

$$\frac{\partial f}{\partial \rho_2} = R_2 T (\ln \frac{\rho_2}{(1-b\rho_2)T_n} + \frac{1}{1-b\rho_2}) + \alpha \rho_1$$

and finally

$$\frac{\partial^2 f}{\partial \rho_1 \partial \rho_1} = \frac{\partial^2 f}{\partial \rho_1 \partial \rho_2} = \alpha,$$

$$\frac{\partial^2 f}{\partial \rho_2 \partial \rho_2} = R_2 T \left( \frac{1}{\rho_2} + \frac{1}{(1-b\rho_2)^2} \right) - 2a.$$

The determinant is thus

$$\frac{R_1 R_2 T^2}{\rho_1} \left( \frac{1}{\rho_2} + \frac{1}{(1-b\rho_2)^2} \right) - \alpha^2.$$

In terms of molar densities it is

$$\frac{T^2}{\rho_1} \left( \frac{1}{\rho_2} + \frac{1}{(1-b\rho_2)^2} \right) - \beta, \quad \beta = \frac{\alpha^2}{R^2}.$$

**Composition of the atmosphere**

We shall use molar densities. The Lagrangian density without the kinetic terms is

$$\mathcal{L} = \sum \left( \rho_i (\dot{\Phi}_i - f_i - s_i T) - s_i T \right) + \alpha \sqrt{\rho_1 \rho_2}$$

with

$$f_i + s_i T = R \rho_i \ln \left( \frac{\rho_i}{(1-b_i \rho_i)T_n k_i} \right) + g z \mu_i \rho_i, \quad i = 1, 2,$$

where

$$s_i = \rho_i S_i, \quad S_i = -R \ln k_i$$

and $S_1, S_2$ are assumed constant. The equations of motion are

$$\dot{\Phi}_i - g z \mu_i = R T \ln \frac{\rho_i}{(1-b_i \rho_i)T_n k_i} + \frac{R T}{1-b_i \rho_i} + \frac{\alpha (\rho_j \rho_i)^{1/2}}{2 \rho_i}, \quad i, j = 1, 2/2, 1.$$
\[
\sum R \rho_i \ln \frac{\rho_i}{(1 - b_i \rho_i) T n k_i} = n R \rho. 
\]

Eliminating the logarithms we obtain
\[
\sum (\dot{\Phi}_i - g z \mu_i) \rho_i = T R (n \rho + \sum \frac{\rho_i}{1 - b_i \rho_i}) + \alpha \sqrt{\rho_1 \rho_2}. 
\]

For added interest we shall suppose that the parameters are such that the conditions for separation are satisfied at some altitude and fix the coordinates by taking the critical point to occur at \( z = 0 \). At that point \( x = y = 1/3 \) and the temperature is one of several values with the same value of \( A := (t - 1)^2 (t - 5)^2 \).

the number of such values is 4 if \( A < 1.6 \) otherwise 2.

Stop discarding stuff here!
This subject is controversial. Not that there is any ongoing debate. * The debate died during the 19’th century, under the weighty authority of Boltzmann and Maxwell. So let us just say that some of us do not understand why a certain pronouncement has never been the subject of tests.

**Statement**

“In an isolated, homogeneous thermodynamic system, in equilibrium, the temperature is uniform, and this is true whether or not a static gravitational field is present.”

Most of the many proofs that have been offered to back up this statement are formulated within the context of kinetic theory. These proofs will not be reviewed in this text. I readily accept that they may be valid. They have no bearing on the problem that I propose to examine, which is this:

**Present goal**

“To describe an ideal thermodynamical system, formulated as a macroscopic Eulerian field theory of thermodynamical variables, densities, temperature, pressure and entropy, that interacts with gravitation and that has a static, isothermal equilibrium.”

This is what has been attempted in this book. The result cannot confirm or contradict the meaning of the ‘statement’ as it is understood in the context of kinetic theory. There is the possibility that it will indicate that kinetic theory and thermodynamics (in the sense that we are using the term) are not completely equivalent, but it cannot be a judgement of either.

It is frequently argued that any doubt that may be cast on the ‘statement’ is an attack on the second law of thermodynamics. Whether this is true or not is a much more difficult question and we shall not get involved with it at this point. The problem would become interesting, and perhaps vital, in the event that the ‘statement’ were found to be false, experimentally.

What we shall do here is to begin with the most naive, most complete and most popular approach to atmospheres, one that predicts a temperature gradient.

In the event of success we shall have the means to study practical, thermodynamic problems with a paradigm that is internally consistent; something that, at present we do not have. For example, how does sound propagate in the isothermal atmosphere? The standard approach studies a perturbation of a state of equilibrium, setting $\rho = \rho_0 + \delta \rho$, $T = T_0 + \delta T$, where $(\rho_0, T_0)$ is a solution of the equations of motion. What equations of motion? We would need to find equations of motion that allow for an isothermal equilibrium state. The mere statement that the equilibrium state is isothermal is of no use.

* Perhaps there is some coming on now. See Pacek and Shihan () and Levy (2013).
IX.7. The isothermal atmosphere.

A famous controversy concerns the temperature profile of an isolated atmosphere in a constant gravitational field. A pillar of statistics proclaims that, at equilibrium, the temperature of any extended system is uniform, and more, that this statement remains true in the presence of a gravitational field. One of the first to voice disagreement with this dictum was Loschmidt, who was crushed by the united authority of Boltzmann and Maxwell. A steady flow of papers have been published over a period of more than 100 years, all proving that there can be no temperature gradient. A few papers have managed to get past editors and referees with proofs of the contrary. Taking up the question again at this time seems almost redundant, and yet.....

It must be said that the belief in the isothermal atmosphere is, in many cases, just that, a belief or conviction, unsupported by any evidence. That said, what would qualify a scientist to issue an expert opinion?

What physics is involved?

1. Gravitation. What is absolutely clear, yet frequently overlooked, is that it is futile to try to make a decision without a deep knowledge of gravitation. That the controversy involves gravitation is in fact fortunate, for no force is better understood. At the deepest level we have General Relativity with its Equivalence Principle. It tells us that that gravitation is a force that resides in the space time metric and that the interaction is strongly restricted by invariance under general coordinate transformations. An intimate knowledge of General Relativity is probably not required, but one should know that, in non-relativistic physics the only component of the metric that is needed is the time-time component $g_{00}$ and that it takes the form

$$g_{00} = c^2 - 2G\phi.$$ 

Here $c$ is the velocity of light and $\phi$ is the Newtonian gravitational potential. In field theories, this component of the metric appears in conjunction with a time derivative, and that is the origin of the following rule:

To introduce the effect of gravitation in any dynamical framework, simply add the Newtonian potential to the energy density.

In some less developed contexts this prescription fails to be meaningful, or insufficiently precise, but then there is no alternative. I think that it may be agreed that, in any context in which it cannot be applied, we lack enough knowledge about gravitation to have a meaningful discussion about the influence of gravitation on an atmosphere.

2. Thermodynamics. This word is frequently taken to refer to the study of equilibria exclusively. But that is not enough. There are several cogent reason why a dynamical theory is needed. In the first place, any discussion of equilibria per se, without a description of the systems of which they are the equilibria, is likely to be inconclusive. The concept of equilibrium is, in my opinion, meaningful only in the context of a dynamical system. And again, without a dynamical theory we shall not know how to introduce the gravitational field or to determine its effects.
Any discussion that restricts the input of thermodynamics to statements about abstract equilibria is not likely to be useful. That leads us to:

3. Non-equilibrium thermodynamics. Under this banner there has been a great deal of activity in the last half-century. This point of view is probably not going to be of much help, for the following reason. The term non-equilibrium strongly suggests that any attempt to get away from the equilibrium is an exploration of the unknown. For example, it is widely held that there is not, until now, a reliable account of 4. entropy. But without an understanding of the role of entropy we are lost, just as we should be lost without an understanding of gravitation.

4. Adiabatic thermodynamics. Actually thermodynamics is advanced well beyond the study of equilibria. Already in 1825 Laplace formulated a successful theory of sound propagation, based in part on the postulate that this phenomenon is isentropic; that is, that the entropy per particle does not change when the density and the temperature are executing the motion that is sound. Furthermore, the calculation is done within a dynamical framework, involving the equation of continuity and the Bernoulli equation. Finally, this is an apt example, for it is very close to the issue at hand. So let us examine the calculation in a little more detail.

There is nothing controversial about the equation of continuity; nothing needs to be said about it. When Laplace postulates that sound propagation is isentropic he refers to the fact that the entropy of an ideal gas is related to the temperature and the density by the polytropic relation,

\[ \frac{\rho}{T^n} = \text{constant}, \]

where \( n \) is a constant that is characteristic of the gas. That is; this combination of density and temperature is a constant of the motion. The value of the constant is directly related to the entropy per particle; that is, to the specific entropy.

This dynamical calculation of the speed of sound, and many others, demonstrates that something is in fact known about entropy away from equilibrium. Furthermore, it strongly suggest that a reliable dynamical framework is available that may serve to investigate the effect of gravitation on an isolated atmosphere that consists of an ideal gas.

The theory of ideal gases has been in use for more than 150 years. Chances are very good that an agreement can be reached about how to proceed.

**IX.8. Reply to Maxwell**

We assume that

1. The system is completely isolated in a vessel with fixed volume.
2. There is a unique, stable, static configuration (no flow and all fields time independent); we shall refer to it as the equilibrium state.
3. The energy density includes the gravitational energy \( \rho \phi \), where \( \phi = gz \) is the gravitational potential.
4. The minimal entergy principle of Gibbs is applicable.

Consider a homogeneous fluid at rest, with a well defined but so far unspecified free energy density \( f \). In the presence of a static gravitational field \( \phi \) the Lagrangian density
is
\[ \mathcal{L} = \rho \dot{\Phi} - \rho \dot{\phi} - f - sT. \]

The equations of motion are:
\[
\frac{\partial \mathcal{L}}{\partial T} \bigg|_{\rho} = 0, \quad \frac{\partial \mathcal{L}}{\partial \rho} \bigg|_{T} = \text{constant}.
\]
The first is the adiabatic condition. Combining both we find
\[ \phi + \mu = \text{constant}, \]
where the chemical potential \( \mu \) is the adiabatic derivative of \( u = f + sT \) with respect to \( \rho \).

In the case of an ideal gas with adiabatic index \( n \) it is
\[ \phi + (n + 1)RT = \text{constant}, \]
which implies the standard lapse rate, when \( \phi = gz \),
\[
\frac{\partial T}{\partial z} = \frac{-gz}{(n+1)R}.
\]

Surprisingly, this result does not depend on any property of the entropy. It is frequently stated that a principle of maximal entropy implies an isothermal atmosphere; if that is true then it is in conflict with the principle of minimum energy.

We have found a version of the minimal energy principle that, so far, has been found to be valid. It states that the entropy density is maximal with respect to variations that leave the energy density \( e \) fixed. The calculation carried out in Section ... can be repeated with little change to show that \( S \) should be uniform.

We conclude that, if the axiom of maximum entropy is formulated so as to be consistent with the axiom of minimum energy then the specific entropy must be uniform.

After this initial investigation of the model has shown that the equilibrium state is not isothermal we shall consider reasonable modifications, in order to bring it into line with the ‘statement’.

**The temperature gradient of the model**

The equations are easily combined to show that
\[
\text{grad} \ T = \frac{-g}{R(n+1)}.
\]

This is the conclusion of all the text books that deal with the isentropic atmosphere.

The formula gives a value for the temperature gradient that is in fair agreement with observation in lower part of our atmosphere.

The fact that the value that is predicted by this naive model, when applied to our atmosphere, is in agreement with observation, does not impress atmospheric scientists.
It must be admitted that there are good reasons for that; the earth’s atmosphere is far from being isolated. Incoming radiation warms the surface and that in turns leads to the warming of the air by infrared radiation. And then there is convection. It would be unreasonable to maintain that the success of the prediction is anything but a coincidence ... and yet ...?

Let us stipulate that it is, in fact, mere chance! We have no issue with the standpoint of the atmospheric scientist. The point that is under discussion is different. We are trying to understand the isolated atmosphere, with the idea that this is a necessary prerequisite for understanding real ones.

Since we get an unacceptable result from a naive application of thermodynamics, we must modify one or more of our assumptions.

We still hope to find that an isothermal atmosphere is possible, and to find the thermodynamic model that incorporates it.

Properties of the model

The isentropic model has a number of features that recommend it. It is well to summarize these properties before we undertake to improve it.

- The model includes the principal equations that define hydrodynamics, as well as the principal equations of thermodynamics.
- The model has a symplectic structure, with the Poisson bracket

\[ \{A, B\} = -\int d^3x \left( \frac{\partial A}{\partial v_i} \frac{\partial B}{\partial x_i} \frac{\partial}{\partial \rho} A, B \right) \]

and equations of motion

\[ \dot{\rho} = \{\rho, H\}, \quad \dot{\vec{v}} = \{\vec{v}, H\}, \]

where

\[ H = \int d^3x \left( \rho(\vec{v}^2/2 + \phi) + f + sT \right). \]

- The model has a simple Lagrangian structure, with Lagrangian density

\[ L = \rho(\dot{\Phi} - \vec{v}^2/2 - \phi) - f - sT, \]

where \( \Phi \) is a velocity potential, \( \vec{v} = -\text{grad} \quad \Phi \). The full set of equations, (10.2.2-7) are the Euler-Lagrange equations.

- The total entropy is a constant of the motion.
- The interaction with gravitation is consistent with Newtonian gravity and, as will be seen later, with Einstein’s theory of gravitation, General Relativity.

These properties give the model a degree of internal coherence that one may be reluctant to give up, and we shall have to be very cautious about introducing changes.

We note that the hydrostatic equation is deduced from one of the Euler-Lagrange equation with the help of the assumptions that were made about the entropy. Variation of the density gives

\[ \dot{\Phi} - \vec{v}^2/2 - \phi - q - ST = \text{constant}, \quad (10.7.1) \]
where \( q = \partial f / \partial \rho \) is the chemical potential. To simplify the exposition we shall refer to this equation in lieu of Eq.\( (10.2.6). \)

### Possible improvements of the model

Eq.\( (10.2.1) \) defines the ideal gas, probably the most successful models in all of thermodynamics. Certainly, changes are conceivable, but as it seems that they would have to be major changes, we have not made any attempts in that direction.

Equation \( (10.2.2) \), or \( (10.2.2') \) probably needs little comment; it is one of the fundamental relations of thermodynamics, assumed to hold at each point of a gas at equilibrium. It is an example of what Callen calls the main assumption of extended thermodynamics. Eq.\( (10.2.2') \) is the Tetrode-Zachur formula for the entropy, a major result of kinetic theory. No improvement will be attempted.

Equation \( (10.2.3) \) warrants a little more discussion. If, as was assumed, the specific entropy is uniform, then the Euler-Lagrange equation \( (10.2.8) \) is equivalent to the hydrostatic equation \( (10.2.6) \). If, on the other hand the specific entropy is not uniform, then we obtain instead

\[
\rho \nabla \phi + \nabla p + T \rho \nabla S = 0.
\]

\( (10.2.9) \)

That is, a variable entropy gives rise to a force that tends to reduce the inhomogeneity. The existence of the effect is generally recognized; we do not need the Lagrangian formulation to reach this conclusion. It suggests that the variational equation Eq.\( (10.2.8) \) is more fundamental to thermodynamics than the hydrostatic condition \( (10.2.6) \). The Gibbsean variational principle states that the energy is extremal with respect to variations of density and temperature; Eq.s \( (10.2.2) \) and \( (10.2.8) \) are precisely the expressions of this principle. The static version Eq.\( (10.2.6) \) is valid only when the specific entropy density is uniform. But there is no need to insist on this point.

With or without the use of \( (10.2.8) \), we easily reach the conclusion that giving up the uniformity of the specific entropy does nothing to change the conclusion that we reached with respect to the gradient of the temperature; the value remains the same. (Besides, we need the uniformity of \( S \) to assure that the total entropy is conserved.)

Do it.

### The entropy

Perhaps the difficulty has to do with the assumptions that we made about the entropy. Those are standard assumptions that are made always, unless there is an energy source, as in an explosion. Yankusevic, an expert on explosions, relies on the isentropic atmosphere for all his calculations. Only at the end does he state that the final and true state of equilibrium is isothermal. It is true that the isentropic atmosphere is the better model of real atmospheres, but another reason that he works with it is that there is no alternative. There is no thermodynamic theory of an isothermal atmosphere that he can use.
So, what can be done with the entropy. Allowing the specific entropy to vary with position makes no difference. We get a more promising result if we allow the entropy density to have an ‘extra’ contribution that is not proportional to the density,

\[ s = \rho S + s_{\text{ex}}. \]  

(10.2.10)

The simplest possibility is that \( s_{\text{ex}} \) is independent of the density. In this case our two basic equations take the form; the adiabatic condition:

\[ \mathcal{R}(\ln \frac{\rho}{T_n} - n) + S + \frac{s_{\text{ex}}}{\rho} = 0, \]  

(10.2.11)

and Eq.(9.3.8)

\[ gz + RT(\ln \frac{\rho}{T_n} + 1) + ST = \text{constant}. \]  

(10.2.12)

Eliminating the logarithms as before we find

\[ gz + \mathcal{R}T(n + 1) = T\frac{s_{\text{ex}}}{\rho} + \text{constant}. \]  

(10.2.13)

Assuming that, at equilibrium, \( T \) is uniform

\[ s_{\text{ex}} = \frac{gz}{T_0} \rho_0 + \text{constant}. \]  

(10.2.14)

Here, as a result of Eq.(10.2.12),

\[ \rho_0 \propto T^n e^{-gz/\mathcal{R}T_0}, \]  

(10.2.15)

which is a standard result.

This appears to solve our problem!

Yes, but at what cost? Instead of the usual recipe for the introduction of the gravitational field we have had to postulate an additional contribution to the entropy as well. So the gravitational field interacts, not only with the mass or the energy as in newtonian gravitation and in General Relativity, but it has the additional effect of producing an entropy density, with a gradient that acts as an additional force on the gas. This seems a high price to pay for the desired result.

And there is another problem. By the equations of motion, \( \partial \mathcal{L}/\partial \rho = 0 \) on shell; thus

\[ \mathcal{L} = \mathcal{L} - \frac{\partial \mathcal{L}}{\partial \rho} = (\rho \frac{\partial}{\partial \rho} - 1)(f + s_{\text{ex}}T). \]

This quantity is the pressure on the wall, and normally it is equal to the thermodynamic pressure \( p \), but with the extra term added to the entropy we obtain

\[ \mathcal{L} = p - s_{\text{ex}}T = gz(\rho - \rho_0) + \text{constant}, \]
and at equilibrium the pressure on the walls is independent of the elevation. This is only the simplest example of many: postulating the extra contribution to the entropy upsets all previous investigations regarding the role of gravity in thermodynamics.

Other attempts?

1. Real gases are not ideal. True, real gases are different, but that does not affect the problem, which is this: what is the thermodynamics of a gas (real or no) in the presence of a gravitational field? Or, in the light of the discussion in the preceding section, what is the entropy of a real gas in a gravitational field?

2. The definition of equilibrium. We define equilibrium as the state (unique in the case of an ideal gas) in which there is no flow and all the fields are time independent. Possibly, you may say, no such state exists. The following statement, from a modern book on instability theory that we shall have occasion to quote later, is interesting: “A fluid at rest is the most simple basic state imaginable and should be realizable with near perfection...”. This statement comes from a treatise on Benard cells.

The theory of convective instabilities, including Reynolds’ treatment of Benard cells, as well as the standard approach to atmospheres, all agree that if in the usual polytropic atmosphere the absolute value of the temperature gradient is greater than \(-g/R(n+1)\) (heating from below), then it is stable to convection. There is no record of atmospheres, or laboratory experiments, in which it is near zero.

The fact that the specific entropy density is uniform is incorporated into all applications that we know of, except those that involve combustion. It guarantees that the total entropy is conserved. The only other way to ensure that the total entropy is a constant of the motion is to add an extra, time independent contribution, independent of the density.

X.8. The experiments of Roderich Graeff

The background of these experiments, carried out over a period of 15 years is interesting. With quite different goals for his experiments, Graeff needed an isothermal environment. In his laboratory there was a positive gradient, more than he could accept. When he isolated a space within the laboratory the gradient began to decrease, then turned negative! He was puzzled, this is against the second law as he understood the second law. Eventually he became obsessed with this and over many years he sought ways to improve the measurements. The very long relaxation times (months) in his earlier experiments were reduced (to 2 days) by using a gas under pressure. And the result were always the same.

Imagine an inner column (under pressure) surrounded by vacuum pads, twice. The temperature is monitored on the outside, between the inner and the outer vacuum pads, and innermost. The temperature gradient is positive on the outside, negative at the center, and near zero at the halfway point. He reorients the whole thing, upside down, on its side, always getting consistent results. A distant goal is to describe vorticity in the framework of General Relativity.

Graeff’s equipment is not very advanced technically. It would be good to have a high-tech confirmation of his

291
X. ROTATIONAL FLOW

Fetter and Walecka has provided us with an efficient and elegant action principle for hydrodynamics. It has been found to be adequate in the case when the velocity field is irrotational, when it can be expressed as

\[ \vec{v} = -\vec{\nabla} \Phi. \] (10.1.1)

But this is a strong limitation and it is time to lift it.

Traditional hydrodynamics has 4 independent variables, the density and the 3 components of the velocity. The action principle of Fetter and Walecka has only 2, so we need to introduce 2 more. But it will not do to seek a generalization of Eq.(10.1.1) for the scalar velocity potential is needed.

X. 1. The scalar velocity potential is essential

In the first place, the Euler-Lagrange equation

\[ \delta A/\delta \Phi = \dot{\rho} + \vec{\nabla} \cdot (\rho \vec{v}) = 0 \]

is the equation of continuity, the very essence of hydrodynamics.

As important is the tradition that incorporates gravitation into field theories, especially into hydrodynamics, by including the Newtonian potential into the Hamiltonian density. We regard hydrodynamics as a non-relativistic approximation to General Relativity, but is there any generally relativistic field theory that has the expected non-relativistic limit? Granted that it is suggested by the correspondence between hydrodynamics and particle mechanics, but our subject is field theories.*

Consider the generally relativistic field theory with Lagrangian density

\[ \mathcal{L} = \int d^4x \sqrt{-g} \left( \rho (\rho_{\mu\nu} \psi_{,\mu} \psi_{,\nu} - c^2) - W[\rho] \right). \] (10.1.1)

To explore the non-relativistic limit set

\[ g_{00} = c^2 - 2\phi, \quad g_{11} = g_{22} = g_{33} = -1, \] (10.1.2)

other components zero, expand in powers of \(1/c\) and take the limit \(c \to \infty\). To make this work out we need to set

\[ \psi = c^2 t + \Phi, \] (10.1.3)

then terms of order \(c^2\) cancel and we are left with the Fetter-Walecka Lagrangian density

\[ \mathcal{L}_{FW} = \rho (\dot{\Phi} - \vec{\nabla} v^2/2 - \phi) - W[\rho]. \] (10.1.4)

This is our only, or at any rate the best, justification for the expectation that Newtonian hydrodynamics is the non-relativistic limit of General Relativity. We have already seen, in

* Actually a relativistic theory of interacting particles does not exist.
Section III.11, that Eq.(10.3) leads to the correct transformation law for the field $\Phi$ under Galilei transformations.

We conclude that the required generalization of (10.1.1) must include additional fields with 2 degrees of freedom, with an action that reduces to (10.1.1) by projection. Two additional dynamical variables are needed, one additional pair of canonical variables, either an additional scalar field or else some gauge field with only two physical components.

The simple introduction of another scalar velocity potential would not lead to rotational flow, and gauge theories with just one propagating modes are few: the Majorana neutrino field and the antisymmetric 2-form field ($Y_{\mu\nu}$) of Ogievetskij and Polibarinov.

The “notoph” field has six components,

$$\begin{align*}
Y_{ij} &= \epsilon_{ijk}X^k, \\
Y_{0i} &= \eta_i, \\
i, j &= 1, 2, 3.
\end{align*}$$

The gauge group consists of the transformations

$$\delta Y = d \wedge \xi,$$

with an arbitrary one-form $\xi$; by this means the field $\vec{\eta}$ can be reduced to zero, leaving the field $\vec{X}$ that has been associated with fluid flow since antiquity. Variation of the Lagrangian with respect to $\eta$ gives the constraint $\vec{\nabla} \wedge \vec{X} = 0$ and leaves only one pair of canonically conjugate variables.

As with all non-relativistic vector fields the problem of a Lorentz covariant generalization is urgent. The idea that every 3-vector, non-relativistic fields should grow a fourth component has been popular and in particle mechanics one replaces

$$\begin{align*}
\dot{X}^i &\rightarrow \left( \frac{d}{d\tau} \vec{X}, \ X^0 = \sqrt{c^2 - \vec{X}^2}. \right)
\end{align*}$$

But the proper time $\tau$ has no place in a theory of fields and, besides, the vector field contains 3 pairs of presumptive canonically conjugate variables. Instead, the relativistic 2-form has exactly the required number of degrees of freedom.

The relativistic notoph Lagrangian includes the Maxwell Lagrangian and a coupling term

$$L_{OP} = dY^2 + \frac{1}{8\pi}F^2 + \gamma YF.$$

We must include an interaction with the fields $\rho$ and $\Phi$; the most natural way is to set the total Lagrangian matter density to be

$$L_{\text{matter}} = L_{FG} + \frac{\rho}{2}dY^2 + \frac{1}{8\pi}F^2 + \gamma YF + \frac{\kappa \rho}{\sqrt{-g}}d\psi \wedge dY.$$

The last term is included since it is gauge invariant, but the electromagnetic terms will be neglected in the present context.

Thus, written out in full, our present relativistic Lagrangian density is

$$L = \frac{\rho}{2}(g^{\mu\nu}\psi_{,\mu}\psi_{,\nu} - c^2) + \frac{\rho}{2}dY^2 + \kappa \rho \frac{c^2}{2}e^{\mu\nu}\lambda\rho Y_{\mu\nu,\lambda}\psi_{,\rho} - f - sT,$$

(10.1.7)
A full examination of this relativistic field theory is planned for the second volume of this book; here we shall limit our study to the non-relativistic version. See Ogievetski and Palubarinov (1964), Kalb and Ramona (), Lund and Regge (), Fronsdal, (2011).

X.2. Non-relativistic hydrodynamics. Couette flow

In the non-relativistic limit the proposed total Lagrangian density is simple,

\[ \mathcal{L} = \rho(\dot{\Phi} + \dot{\vec{X}}^2/2 + \kappa \rho \dot{\vec{X}} \cdot \vec{\nabla} \Phi - \vec{\nabla}^2/2 - \phi) - W[\rho], \]

with the thermodynamic extension

\[ \mathcal{L} = \rho(\dot{\Phi} + \dot{\vec{X}}^2/2 + \kappa \rho \dot{\vec{X}} \cdot \vec{\nabla} \Phi - \vec{\nabla}^2/2 - \phi) - f - sT. \]

The Euler-Lagrange equations include one that comes from variation of the gauge field \( \vec{\eta} \), namely

\[ \vec{\nabla} \wedge \rho \vec{m} = 0, \quad \vec{m} := \rho \vec{v}, \quad \vec{v} := \dot{\vec{X}} + \kappa \vec{\nabla} \Phi. \]  

(10.2.1)

Variation of \( \Phi \) gives the equation of continuity,

\[ \dot{\rho} + \vec{\nabla} \cdot \rho \vec{v}, \quad \vec{v} := \kappa \dot{\vec{X}} - \vec{\nabla} \Phi. \]  

(10.2.2)

The flow vector is thus \( \rho \vec{v} \). Variation of \( \vec{X} \) leads to

\[ \frac{d}{dt} \vec{m} = 0. \]  

(10.2.3)

Finally, variation of the density gives

\[ \dot{\Phi} + \dot{\vec{X}}^2/2 + \kappa \rho \dot{\vec{X}} \cdot \vec{\nabla} \Phi - \vec{\nabla}^2/2 - \phi = \mu. \]  

(10.2.4)

The significance of the parameter \( \kappa \) will become clear as we study the applications; for our first application of this theory we shall set it to zero.

Laminar Couette flow

Couette flow has been been studied for 200 years, with the main interest being the spontaneous onset of turbulence. The experiment has a homogeneous fluid contained in the space between two concentric cylinders, as in Fig.(10.2.1), both cylinders turning independently. The simplest type of flow velocity is horizontal, stationary and circular, in cylindrical coordinates,

\[ \omega(r)(-y, x, 0), \quad r := \sqrt{x^2 + y^2} \]  

(10.2.5)

The boundary conditions are “no-slip”, meaning that the velocity of the flow, at the cylindrical boundaries, are the same as the velocity of the walls. To simplify the analysis one thinks of the cylinders as being long, and ignore end effects.
In experiments, in which the rotation speeds of the two cylinders are increased slowly from zero, this type of flow is observed at low speeds. We begin by describing this regime.

Fig.10.2.1. Couette flow.

The Navier-Stokes equation

This equation is the basis for every traditional analysis of this simplest type of flow:

$$\frac{D}{Dt} \vec{u} = \frac{1}{\rho} \nabla p + \bar{\mu} \rho \Delta \vec{u}. \quad (10.2.6)$$

Here $\bar{\mu}$ is the viscosity of the fluid, in the simplest case a constant.

Stationary flow is possible only if the effect of viscosity is negligible, this requires that $\bar{\mu} = 0$ or else that $\Delta \vec{u} = 0$. \hfill (10.2.7)

The usual justification for this restriction is more involved: With the hypothesis of circular flow the density can only depend on the coordinate $r$ and the same is true of the pressure; hence the pressure term is a radial force and the projection of the last term along the direction of motion must also be zero; hence $\Delta \vec{u} = 0$.

With the flow stationary, as postulated (and observed), this condition allows the general solution

$$\vec{u} = \frac{a}{r^2} (-y, x, 0) + b(-y, x, 0), \quad a, b \text{ constant.}$$

The first is irrotational for $r > 0$,

$$\frac{a}{r^2} (-y, x, 0) = a \nabla \theta, \quad \arctan \frac{y}{x};$$

the second is the flow of a solid body.

The boundary conditions will be analyzed below.

This prediction of the Navier-Stokes equation is a brilliant success, being in very good agreement with experiments, at low speeds of rotation. the only difficulty is that there is no clear guide to constructing an expression for the energy density. It would be natural to expect that the ‘kinetic energy density’

$$\rho \vec{u}^2 / 2 \quad (10.2.8)$$

is an important part of it, giving rise to the centripetal acceleration; this turns out not to be the case.

A question of sign
Consider the simplest cases, when \( a = 0 \) and the flow is that of a solid body. We have

\[
\frac{D}{Dt} \vec{u} = \frac{d}{dt} \vec{u} + (\vec{u} \cdot \nabla) \vec{u}.
\]

When the flow is stationary the first term is zero, and when it is of the solid body type

\[
\frac{D}{Dt} \vec{u} = b^2(-y\partial_x + xd_y)(-y, x, 0) = -b^2(x, y, 0) = -\nabla(\vec{u}^2/2).
\]

That is, the acceleration is towards the center and \( \vec{u}^2/2 \) is the kinetic potential.

In the complimentary case of potential flow,

\[
\frac{D}{Dt} \vec{u} = a^2 \frac{r^2}{r^2}(-y\partial_x + x\partial_y)\left(-y, x, 0\right) = -a^2 \frac{r^4}{r^4}(x, y, 0) = -\nabla(-\vec{u}^2/2);
\]

it is inwards as well, hence correct, but now the kinetic potential is \(-\vec{u}^2/2\). The difference in sign between the two cases means that we cannot, in the general case, express the centripetal acceleration as the gradient of (10.2.8). The prospects for finding an energy density that is appropriate for use with the Navier-Stokes equation are therefore not encouraging.

The action principle comes to the rescue. The Hamiltonian density is

\[
h = \rho(\dot{\vec{X}}^2/2 + (\nabla \Phi)^2/2 + \phi) + f + sT.
\]

Instead of the expected square of the ‘total velocity’ we have the sum of two squared velocities. But the equation of motion, obtained by taking the gradient of (10.2.4), is

\[
\nabla \Phi + \nabla \left(\dot{\vec{X}}^2/2 - (\nabla \Phi)^2/2 - \nabla \phi\right) = \frac{1}{\rho} \nabla p.
\]

Both of these equations have the correct signs, the second equation agrees with the Navier-Stokes equation with the two different signs and the first gives the Hamiltonian with the same sign for the two terms. This comes about because one velocity is a time derivative while the other is a space derivative.

We conclude that the action principle is not in conflict with the traditional treatment of this type of flow, but it completes it by including the equation of continuity as well as an energy density; the Hamiltonian is a first integral of the motion.

**Viscosity**

No action principle can apply to a viscous fluid, but there is a natural way to modify the Euler-Lagrange equation. Instead of (10.2.3) we pose

\[
\frac{d}{dt} \vec{m} = \bar{\mu} \rho \Delta \vec{v}.
\]

Further discussion of viscosity is relegated to the second volume.
X.3. The energy-momentum tensor

The energy-momentum tensor is based on Cauchy’s stress tensor, but the basic role that it plays in relativistic field theories was explained by Emmy Noether. In any special relativistic field theory with Lagrangian density $\mathcal{L}$, it is the result of evaluating the integrals

$$\delta \int d^4x \mathcal{L} = \int d^4x \mathcal{G}\mathcal{L},$$

where $\mathcal{G}$ is a generator of infinitesimal translations, on shell. The calculation was done in Chapter III, but we shall repeat it here, in outline. If $\mathcal{L}$ is expressed entirely in terms of a family of fields $\alpha, \ldots$ and their first order derivatives, then the variation is

$$\int d^4x \mathcal{G}\mathcal{L} = \int d^4x \left( \frac{\partial \mathcal{L}}{\partial \alpha} G\alpha + \sum_{\mu} \frac{\partial \mathcal{L}}{\partial \alpha,\mu} \partial_\mu G\alpha \right).$$

An integration by parts of the second term, and use of the Euler-Lagrange equations, gives

$$\int d^4x \mathcal{G}\mathcal{L} = \int d^4x \partial_\mu \left( \sum_{\alpha} \sum_{\mu} \frac{\partial \mathcal{L}}{\partial \alpha,\mu} G\alpha \right).$$

Taking $G = \partial_\nu, \nu = 0, 1, 2, 3$, this becomes

$$\partial_\mu T^\mu_\nu = 0, \quad T^\mu_\nu = \sum_{\alpha = \Phi, \rho} \frac{\partial \mathcal{L}}{\partial \alpha,\mu} \alpha,\nu - \delta^\mu_\nu \mathcal{L},$$

In the special case of potential flow, the action of Fetter and Walecka gives the energy-momentum tensor with components

$$T^{0}_0 = \rho \dot{\Phi} - \mathcal{L} = h, \quad \text{energy density},$$
$$T^{i}_0 = -\dot{\Phi} \rho \Phi,\nu, \quad \text{energy flow density}$$
$$T^{i}_i = \rho \Phi,\nu, \quad \text{momentum density}$$

and stress tensor

$$T^i_j = -\Phi,\nu \rho \Phi,\mu - \delta^i_j \mathcal{L}.$$  

We can verify the conservation law (10.3.2). It splits into these two cases. The first one,

$$\partial_0 T^{0}_0 + \partial_j T^j_0 = 0$$

reduces to

$$\frac{d}{dt} h + \nabla \cdot (\rho \phi \vec{v}) = 0, \quad v_i := -\Phi,\nu,$$

or

$$\frac{\partial}{\partial t} h + \vec{\nabla} \cdot (h + p) \vec{v} = 0.$$  

297
when this is integrated over a woman Σ the second term reduces to a surface integral over the boundary $d\Sigma$, which vanishes by virtue of the boundary conditions if Σ is the extent of the vessel that contains the fluid. Also, if Σ is any domain that moves with the fluid, so that the flow on the boundary $d\Sigma$ is tangential, then this term makes no contribution. Hence, in both these cases, the total energy in Σ is a constant of the motion. This justifies referring to (10.3.3) as a statement of energy conservation. See Eq.(3.8.1). The other one, \[
\frac{\partial}{\partial t} T_0^0 + \partial_j T_j^i = 0
\]
becomes
\[
\frac{d}{dt}(\rho v_i) + \partial_j(\rho v_j v_i) = -\partial_i p, \quad i = 1, 2, 3,
\]
is often referred to as a statement of momentum conservation, but that is misleading. Using the equation of continuity we can rewrite it as follows
\[
\frac{d}{dt} v_i + (\vec{v} \cdot \vec{\nabla}) v_i = -\frac{1}{\rho} \partial_i p, \quad i = 1, 2, 3.
\]
It is true that the left side of this equation is the substantive time derivative of the velocity and that therefore the left side of (10.3.8) is the rate of change of the momentum, but it is not zero! Eq.(10.3.8) is the Navier - Stokes equation for this case; it expresses the non-conservation of momentum!

More generally, when the field $\vec{X}$ is included,
\[
T_0^0 = \rho \dot{\Phi} + \rho \dot{\vec{X}}^2 - \mathcal{L} = h,
\]
\[
T_0^i = -\dot{\Phi} \rho \Phi, i + \dot{\Phi} \kappa \rho \dot{\vec{X}}_j, \quad T_k^0 = \dot{\Phi}, k \rho + X_{i,k} m_i,
\]
and
\[
T_k^j = -\Phi, k \rho \Phi_j + \Phi, k \kappa \rho \dot{\vec{X}}_j - \delta^j_k \mathcal{L}.
\]
The energy conservation law (10.3.3) retains its form (with two extra terms in $h$), while the law of momentum conservation becomes
\[
\frac{d}{dt} T_k^0 + \partial_j T_k^j = \frac{\partial_0 (\Phi, k \rho)}{1} + \frac{\partial_0 (\rho X_{i,k} \dot{X}_i)}{2} + \frac{\partial_0 (\kappa \rho X_{i,k} \Phi_i)}{3} + \frac{-\partial_j (\rho \Phi_k \Phi_j)}{4} + \frac{\partial_j (\kappa \rho \Phi_k \dot{X}_j)}{5} + \frac{-\partial_k p}{6}.
\]
With the help of continuity
\[
1 + 4 + 5 = \partial_0 (\rho \Phi_k) + \partial_j (\rho \Phi_k v_j) = \rho \dot{\Phi}_k + \rho v_j \Phi_{kj} = \rho \dot{\Phi}_k + \rho (\vec{v} \cdot \vec{\nabla} \phi) / 2 + \kappa \rho \dot{X}_j \Phi_{kj}.
\]
and the field equation $\dot{m} = 0$,

\begin{align*}
2 + 3 &= \partial_0(X_{i,k}m_i) = m_i\dot{X}_{i,k} = \rho\dot{X}_{i,k} + \kappa\rho\dot{\Phi}_{j}X_{i,k}.
\end{align*}

\begin{align*}
5 + 6 &= \kappa\rho\dot{\Phi}_{j}X_{i,k} + \kappa\dot{\Phi}_{k}\rho\dot{X}_{j} - \partial_kp.
\end{align*}

Combining everything we get

\begin{align*}
\frac{d}{dt}T_0^k + \partial_jT_k^j = \rho\partial_k\left(\dot{\Phi} - (\vec{\nabla}\Phi)^2/2 + \dot{X}^2/2 + \kappa\dot{X} \cdot \vec{\nabla}\Phi\right) - \partial_kp,
\end{align*}

which is zero by virtue of the Bernoulli equation.

**X.4. Stability of laminar Couette flow according to Rayleigh**

The first attempt to understand the limits of stability of laminar Couette flow is due to Rayleigh (1904). The derivation of Rayleigh’s argument is repeated in detail in several textbooks (Chandrasekhar 1955, Kornschmieder 19 ) without any explanation of the fact that the results are contradicted by the experiments. Their more successful calculations are presented, not as refutations but as refinements of Rayleigh arguments.

Rayleigh’s argument is based on ‘angular momentum conservation’; he considers an element of the fluid, moving with the fluid. But angular momentum of a fluid element is conserved only if the torque is tangential to the boundary. To see this we repeat the calculation from (10.3.1), with 

\begin{align*}
G = \vec{x} \wedge \vec{\nabla}.
\end{align*}

For simplicity we limit ourselves to the simplest case, to the Fetter - Walecka theory with potential flow. Then (10.3.1) becomes

\begin{align*}
\int d^4 x(\vec{x} \wedge \vec{\nabla}) \mathcal{L} = \int d^4 x \left(\sum_{\mu} \frac{\partial}{\partial \mu} \frac{\mathcal{L}}{\partial \Phi_{\mu}} (\vec{x} \wedge \vec{\nabla}) \alpha\right).
\end{align*}

This reduces to

\begin{align*}
\rho D^t \vec{\ell} = -\tau,
\end{align*}

where $\rho\vec{\ell} = \rho\vec{x} \wedge \vec{v}$ is the angular momentum density and $\tau = \vec{x} \wedge \vec{\nabla}p$ is the torque density.

Integrated over a domain $\Sigma$ this results in

\begin{align*}
\frac{d}{dt} \int_{\Sigma} d^3 x \rho \vec{\ell} = \int_{d\Sigma} \rho\vec{\ell}(\vec{v} \cdot d\vec{\sigma}) + \int_{d\Sigma} p\vec{x} \wedge d\vec{\sigma}.
\end{align*}

Rayleigh’s stability criterion is based on conservation of angular momentum during a virtual, radial motion of an element of fluid. In Rayleigh’s context $\Sigma$ is bounded by two cylinders within the fluid, concentric with the rotating cylindrical walls, and the argument concerns the vertical component of the angular momentum. The surface element $d\vec{\sigma}$ is
radial and the second term on the right is zero. But the first term on the right is not zero
and the angular momentum conservation invoked by Rayleigh is not real.

X.5 An alternative criterion for stability of laminar Couette flow

We return to the Bernoulli equation, eq. (10.2.4),

\[
\mu - \dot{\Phi} = \frac{\dot{X}^2}{2} + \kappa \rho \dot{X} \cdot \nabla \Phi - \Phi^2/2 - \phi =: C. \tag{10.5.1}
\]

In the case of a stationary flow, when both vector fields are time independent, the function
\( C := \mu - \dot{\Phi} \) is a function of the density only.

Proposed rule to determine the limit of stability

It is known that some types of instability are accompanied by bubble formation. We
suggest that this may be related to local vacuation and thus to particular values of the
\( C(\rho) \). To test this hypothesis we proceed as follows.

Experiments start with both cylinders at rest, then they are rotated independently, with
angular speeds \( \omega_i, \omega_o \) that are increased slowly, until instability of the flow is observed. The
most interesting experimental results have been presented in the form of a partition of the
plane of of angular speeds into a stable and an unstable region. The line, of shape similar
to a hyperbola marks the onset of instability, the stable region lies below. See Fig.10.5.1.

By means of Eq.(10.5.1) we can plot the lines of constant \( C(\rho) \) - if this function is one-
valued, lines of constant density - in the plane with coordinates related to the velocities.
We shall carry out the calculation in two stages.

Stage 1

Laminar Couette flow is stationary, horizontal and circular. We have seen that the
Navier - Stokes equation allows only two types, irrotational flow and solid body flow. This
suggests that

\[
-\nabla \Phi = \frac{a}{r^2} (-y, x, 0), \quad \dot{X} = b(-y, x, 0). \tag{10.5.2}
\]

The first equation is unique but the second condition is not; it is an assumption that will
be imposed for simplicity at this stage. It is suggested by the fact that this additional
vector field has appeared in the literature in this form only, as a fixed, non-dynamic, solid
body flow (Hall and Vinen, 1964, Fetter 2009). Both fields are harmonic.

Our action principle also admits solutions of this form but unlike the traditional ap-
proach, that treat the case of incompressible fluids, it implies an inhomogeneous density.
The constraints are

\[
\nabla \cdot (\rho \vec{v}) = 0, \quad \vec{v} = \kappa \ddot{X} - \nabla \Phi = 0,
\]

and

\[
\nabla \wedge \vec{m} = 0, \quad \vec{m} = \rho (\ddot{X} + \kappa \nabla \Phi). \]

300
The first is consistent with (10.5.2), but the second constraint implies that
\[ \vec{m} = \frac{c}{r^2}(-y, x, 0), \quad c \text{ constant}, \]
and thus
\[ \rho = \frac{c}{\kappa a/r^2 - b}. \quad (10.5.3) \]
This seems like a not unreasonable density distribution, so we continue to investigate this special case.

In terms of \( a, b \) and \( r \),
\[ C(r) = b^2 r^2/2 + \kappa ab - a^2/2r^2, \quad r_i < r < r_o. \]

**Boundary conditions**

The walls of the two cylinders move with angular velocities
\[ \omega_i \hat{\theta} = \frac{\omega_i}{r}(-y, x, 0), \quad \omega_o \hat{\theta} = \frac{\omega_o}{r}(-y, x, 0), \quad \omega_i, \omega_o \text{ constant.} \]

Because the velocity of mass transport is \( \vec{v} := \kappa \vec{X} - \vec{\nabla} \Phi \), this is the velocity that must satisfy the no-slip boundary conditions Thus
\[ \frac{\omega_i}{r_i} = \frac{a}{r_i^2} + \kappa b, \quad \frac{\omega_o}{r_o} = \frac{a}{r_o^2} + \kappa b, \]
or, taking \( r_o = 1 \) as our unit of length,
\[ a = r_i \frac{\omega_i - \omega_o r_i}{1 - r_i^2}, \quad \kappa b = \frac{\omega_o - \omega_i r_i}{1 - r_i^2}, \quad r_i = .883. \]

Next,
\[ C(r) = \frac{b^2}{2r^2} + \kappa ab - a^2 r^2. \]
which allows us to express the function \( C(r) \) in terms of the angular velocities \( \omega_i \) and \( \omega_o \). Fig. 10.5.2 shows loci of constant values of this expression in the \( \omega_o, \omega_i \) plane, at the inner cylinder, \( r = r_i \). Fig (10.5.1) shows the lines of constant \( C(r_i) \) in the \( \vec{\omega} \) plane. The unit of length is \( r_o \) the abscissa is \( \omega_o \) and the ordinate is 1.55 \( \omega_i \). In this illustration the radius is \( r = r_i \). The red, green and grey curves shows the loci \( C/10^6 = -.2, - 1 \text{ and } + 1 \), respectively.

The value of \( \kappa \) was adjusted to make the red curve resemble the stability boundary curve measured by Andereck et al, reproduced in Fig 10.5.2; the best value is
\[ \kappa = -.445 \pm .001, \]
301
The slope of the curve in the first quadrant is independent of \( \kappa \); it agrees with the experiment to better than 10 percent and must be considered as an unqualified success of the model.

The slope of the curve in the fourth quadrant is extremely sensitive to the value of \( \kappa \); it may be interpreted as an experimental determination of this parameter, applicable to water.

The calculation was repeated at \( r_i < r < r_o \). In the fourth quadrant the locus \( C = -2E + 6 \) moves upwards; it follows that the instability is likely to manifest itself - when the cylinders are rotated in opposite directions, as the rotation speed of the inner cylinder is increased - at the inner boundary; this too is in agreement with observation. In the first quadrant the locus is essentially independent of the radius; thus when the cylinders are rotated in the same direction the instability should appear at either cylinder at the same speed.

Returning to Eq.(10.5.3) we find that the density is finite in the stable domain and that it increases without limit as the limit in the first quadrant is approached. This suggests that, when the cylinders are turning in the same direction, as the limit of stable, laminar, Couette flow is approached, the required high values of the density lead to a breakdown of the theory. Oddly, this limit coincides with the prediction of Rayleigh.

The fluid in many experiments, including that of Andereck et al, was water. The large variations of density in the present model are inconsistent with the very limited compressibility of that fluid. For this reason we shall study the limit of incompressible fluids.

Calculate \( \rho(r_i)/\rho(r_o) \).

Stage 2

The constraints tell us that there are constants \( a, b \) such that

\[
-\vec{\nabla} \Phi = \frac{a}{r^2}(-y, x, 0), \quad \vec{m} = \frac{b}{r^2}(-y, x, 0).
\]

The velocity of mass transport is

\[
\vec{v} = \kappa \frac{\vec{m}}{\rho} - (1 + \kappa^2) \vec{\nabla} \Phi = \left( \frac{\kappa b}{r^2 \rho} + (1 + \kappa^2) \frac{a}{r^2} \right) (-y, x, 0).
\]

The only constraint on this field is that it must be harmonic, to avoid the effect of viscosity; this implies that

\[
\rho = \frac{\rho_o}{1 - \alpha (r^2 - r_o^2)}.
\]

this has the same form as (10.5.3) but here the constants \( \alpha \) is arbitrary. In terms of these vector fields

\[
C = \frac{\vec{m}^2}{2\rho^2} - (\kappa^2 + 1) \vec{\nabla} \Phi^2 / 2
\]
and takes the value
\[ C = \frac{1}{2r^2} \left( \frac{b^2}{\rho^2} - (\kappa^2 + 1)a^2 \right), \]
with boundary conditions
\[ a = \frac{r_i^2 \rho_o \omega_o - r_i^2 \rho_i \omega_i}{(\rho_o - \rho_i)(\kappa^2 + 1)}, \quad b = \frac{r_i^2 \omega_i - r_o^2 \omega_o}{\kappa(\rho_o - \rho_i)}. \]

Since the fluid in the first intended application is water, which is nearly incompressible, we use a linear approximation for \( \rho(r) \) and set
\[ g = r_i/r_o = .883, \quad q = \rho_i/\rho_o \]
and choose the units so that \( r_o = \rho_o = 1 \).

As before, we calculate the loci of \( C \) in the \( \vec{\omega} \)-plane, at both boundaries, searching for values of \( \kappa \) and \( q \) that fit the experimental data.

At the inner boundary this is successful only if \( q > 1 \), which means that the density is higher there. We do not know of any measurements, but this situation seems very unlikely.

At the outer boundary the only solution also has \( q < 1 \) and now the density increases outward, as expected. In this case the instability appears first at the outer boundary. The pressure increases outwards.

The result is essentially the same for both radii, shown in Fig. 5.4 for \( C/10^6 = -.2 \) (red), -1 (green) and +1 (grey), for \( \kappa = .7788 \). Having in mind a nearly incompressible fluid we have set \( \rho(\to_i)/\rho(r_o) = 1.01 \). The choice that produces the best agreement with the measurements of Andereck et al. the sensitivity to the value of \( \kappa \) is extreme.

In a second attempt we set \( \rho(\to_i)/\rho(r_o) = .95 \). The resulting figure is essentially the same, but now the best value of \( \kappaappa = -.7897 \).

**Conclusions**

At first sight the results are spectacular, in as much as the experimental stability curve could be reproduced under two different assumptions, the second stage with no assumption other than the choice of \( \rho(\to_i)/\rho(r_o) \) and the value of the parameter \( \kappa \). But the extreme sensitivity to the value of \( \kappa \) is confusing, and the fact that the desired top of stability curve is obtained only for a very narrow range of values of this parameter is disturbing.
What follows should be printed, examined and culled for interesting points before being discarded.

Here we consider a mixture of two gases, each a van der Waals gas with parameters that have been chosen for a good fit to the properties of each pure gas. This strongly reduces the number of adjustable parameters.

Shifting from ordinary to molar densities adds linear terms (in the densities) to $f$ without affecting the pressure, and irrelevant constants to the chemical potentials. (For the same reason the term $T^n$ in the logarithms could be ignored in this analysis, but to preserve the familiar formulas we shall leave them in place.) The expression for the internal energy is

$$ f = f_1 + f_2 + \alpha (\rho_1 \rho_2)^k, \quad (6.2.1) $$

$$ f_1 = RT \rho_1 \ln \frac{\rho_1}{(1 - b_1 \rho_1) T^{n_1}} - a_1 \rho_1^2, \quad f_2 = RT \rho_2 \ln \frac{\rho_2}{(1 - b_2 \rho_2) T^{n_2}} - a_2 \rho_2^2, \quad (6.2.2) $$

This representation is similar to that used by Lemmon and Jacobsen. The difference is, first, that they do not use the van der Waals expressions for $f_1$ and $f_2$ and, second, that they combine $f_1$ and $f_2$ in a slightly different way. It is not known whether this is significant.

We shall compare more directly with Scott and Konynenburg who write the molar free energy as

$$ F_{S-K} = RT \ln \frac{\rho}{V-B} - \frac{A}{V} + RT \left( (1-r) \ln(1-r) + r \ln r \right). $$

Here $V = 1/\rho$ is the molar volume and $r = \rho_2/\rho$; $A$ is a second order, symmetric, homogeneous polynomial in the two densities and $B$ is second order polynomial in $r$, symmetric about $r = 1/2$. Terms linear in the densities are irrelevant for this study; the constant $V^{\otimes}$ represents the entropy of a reference state and can also be ignored. Thus

$$ F_{S-K} = RT \rho_1 \ln \frac{\rho_1}{1-B \rho} + RT \rho_2 \ln \frac{\rho_2}{1-B \rho} - A \rho^2. $$

When we take $k = 1$ the last term is exactly matched by the sum of 3 terms in Eq.(6.2.1),

$$ A \rho^2 = a_1 \rho_1^2 + a_2 \rho_2^2 - \alpha \rho_1 \rho_2. $$

To get the correct value of $f$ in the limit where only one of the two components is present it is necessary to take the appropriate experimental values of $a_1$ and $a_2$. The only other difference is that we are taking the excluded volumes from the observation of pure liquids while Scott and Konynenburg replace both $1 - b_1 \rho_1$ and $1 - b_2 \rho_2$ by the same expression $1 - B \rho$ where $B$ is an arbitrary, homogeneous, second order polynomial in the concentration $r$, but a constant in most of the cases that have been studied in detail. This is physically motivated in that it makes both components contribute to a total excluded volume. In our approach the only free parameter is $\alpha$, the same as $a_{12}$ in Scott and Konynenburg, while they have an additional parameter in $B$.

As a means to additional simplification of the analysis we shall write

$$ x = b_1 \rho_1, \quad y = b_2 \rho_2. $$
Dropping linear terms (linear in the densities) we get, when \( k = 1 \),

\[
\frac{f b_1}{\mathcal{R}} = T x \ln \frac{x}{1-x} - \frac{a_1}{R b_1} x^2 + \frac{b_1}{b_2} \left( T y \ln \frac{y}{1-y} - \frac{a_2}{R b_2} y^2 \right) + \frac{\alpha}{R b_2} x y.
\]

The gas/liquid critical temperatures are

\[
T_i = \frac{8}{27 R b_i}, \quad i = 1, 2.
\]

We introduce the reduced temperature

\[
T_r = T / T_1
\]

and the parameters

\[
b = b_1 / b_2, \quad c = T_2 / T_1 > 1, \quad \beta = \frac{27}{4} \frac{\alpha}{R b_2 T c_1}
\]

To get the final form

\[
\hat{f} = \frac{f b_1}{R T c_1} = T_r (x \ln \frac{x}{1-x} - \frac{27}{8} x^2 + b \left( T_r y \ln \frac{y}{1-y} - \frac{27}{8} y^2 \right) + \beta x y.
\]

The two parameter \( b \) and \( c \) are measures of the disparity between the two fluids. The variables are the the reduced temperature \( T_r \) and the two normalized densities \( x \) and \( y \), and the only adjustable parameter is the interaction strength \( \beta \). From this point on the hat on \( f \) will be omitted. Recall that certain linear terms have been ignored.

The chemical potentials are, up to irrelevant numerical factors and constant terms,

\[
\mu_x(x, y) = T_r \left( \ln \frac{x}{1-x} + \frac{1}{1-x} \right) - \frac{27}{4} x + \beta y,
\]

\[
\mu_y(x, y) = b T_r \left( \ln \frac{y}{1-y} + \frac{1}{1-y} \right) - b c \frac{27}{4} y + \beta x.
\]

The first derivatives of the free energy densities are

\[
\mu_i(x, y) = \mathcal{R}_i T \left( \ln \frac{\rho_i}{(1-b_i \rho_i)T^{n_i}} + \frac{1}{1-b_i \rho_i} \right) - 2 a_i \rho_i \rho_j + \beta \rho_j, \quad i, j = 1, 2 \text{ or } 2, 1.
\]

\[
f_{ii} = \frac{\mathcal{R}_i T}{\rho_i (1-b_i \rho_i)}, \quad f_{12} = \beta = \alpha k.
\]

The second derivatives

\[
f_{xx} = \frac{T_r}{x(1-x)^2} - \frac{27}{4}, \quad f_{yy} = b \frac{T_r}{y(1-y)^2} - b c \frac{27}{4}, \quad f_{xy} = \beta,
\]

305
and the pressure,
\[
\frac{pb_1}{RTc_1} =: p_r = T_r \left( \frac{x}{1-x} + b \frac{y}{1-y} - \frac{27}{8} (x^2 + bcy^2) \right) + \beta xy.
\]

The reduced temperature takes the value \( T_r = 1 \) at the critical point of the first fluid and the value \( T_r = c > 1 \) at the critical point of the second liquid.

Here we record all the functions in complete generality, for reference.

\[
f = f_1 + f_2 + f_{\text{int}}, \quad f_{\text{int}} = \alpha (\rho_1 \rho_2)^k,
\]

\[
f_1 = R_1 T \rho_1 \ln \frac{\rho_1}{(1 - b_1 \rho_1)T^{n_1}} - a_1 \rho_1, \quad f_2 = R_2 T \rho_2 \ln \frac{\rho_2}{(1 - b_2 \rho_2)T^{n_2}} - a_2 \rho_2^2,
\]  

\[
\mu_i(x, y) = R_i T \left( \ln \frac{\rho_i}{(1 - b_i \rho_i)T^{n_i}} + \frac{1}{1 - b_i \rho_i} \right) - 2a_i \rho_i + \beta \rho_j, \quad i, j = 1, 2 \text{ or } 2, 1.
\]

\[
f_{ii} = \frac{R_i T}{\rho_i (1 - b_i \rho_i)} - 2a_i, \quad f_{12} = \beta = \alpha k.
\]

### VI.3. Mixture of similar fluids

The condition for coexistence of two mixtures, with densities \((\rho_1, \rho_2)^u\) and \((\rho_1, \rho_2)^v\) is that both chemical potentials, as well as the pressure, take the same value at both,

\[
\mu_1^u = q_1^v, \mu_2^u = q_2^v, p^u = p^v.
\]

Two van der Waals fluids are similar if the parameters \(b\) and \(c\) are both equal to 1. In this case the free energy, as well as the pressure, is symmetric with respect to the exchange of the two densities, and there are ‘symmetric’ solutions of the form \((\rho_1, \rho_2)^u = (\rho_2, \rho_1)^v\). For such solutions we have

\[
\mu_1(x, y) = \mu_2(y, x) \quad (6.3.1)
\]

The locus of such points is shown in Fig.s 6.3.1-3 for several values of the temperature and for several values of the strength \(\beta\) of the interaction. Coexistent mixtures are found by plotting loci of constant pressure, the green lines.

It should be noted that not all coexistent pairs of mixtures are symmetric, even if the van der Waals parameters are equal.

Below we shall rediscover these mixtures. Note that Fig.s 6.3.1-4 include both high and low temperatures. The green (nearly straight) lines are isobars.
Fig. 6.3.1. The locus defined by Eq.(6.3.1) for the case $T = .99$, $\beta = .1$.

Fig. 6.3.2. The locus defined by Eq.(6.3.11) for the case $T = 1.01$, $\beta = .5$.

Fig. 6.3. The locus defined by Eq.(6.3.1) for the case $T = .9$, $\beta = -.1$.

Fig. 6.3.4. Sim19d. The locus defined by Eq.(6.3.1) for the case $T = 1.5$, $\beta = 5$, with the pressure locus for $p = 1$.

**High temperatures, $T_r > 1$**

The most interesting aspect of mixtures, and the one most investigated, is the existence of “critical points”. Among these are singularities of the free energy density, the function

$$f : \mathbb{R}^2 \rightarrow \mathbb{R}, \ (\rho_1, \rho_2) \mapsto f(\rho_1, \rho_2).$$
By definition, a singularity of \( f \) is a point in \( \mathbb{R}^2 \) where the matrix of second order partial derivatives of \( f \) with respect to the densities is not invertible. Using Eq.(6.2.3) and the subsequent equations we find that this condition takes the form:

\[
\left( \frac{T}{x(1-x)^2} - \frac{27}{4} \right) \left( \frac{T}{y(1-y)^2} - c \frac{27}{4} \right) = \beta^2/b.
\]

But the free energy is more than a function of the densities; it is a family \( \{f^T\} \) of functions on \( \mathbb{R}^2 \), indexed by the temperature. A critical point of the free energy is a value \( T_c \) of \( T \) and a point \( C \in \mathbb{R}^2 \) such that, in a neighborhood of \( T_c \otimes C \) the image of the mapping \( p, T \mapsto x, y \) consists of one point when \( T < T_c \) and of three points when \( T > T_c \), or vice versa. For a more general account of the theory see Arnold, ... van der Waals,... See Gibbs (1878) page 169.

In Fig.6.3.5 we show the locus of points where the last equation holds, the set of points in \( \mathbb{R}^2 \), the density plane, where \( f^T \) is singular, for \( \beta = \pm 0.5 \) and \( T_r = 1.05 \). When \( T_c \) is increased the small, closed curve becomes smaller, to disappear when \( T \) exceeds a value 1.0745. This is a critical point of the mixture, a point of a unique temperature and a unique pair of densities. In addition, as we shall explain in the next section, the points where the line \( y = kx \) is tangent to the figure are also considered to be critical, by the experimenter, but they are not singular points.

A list of critical points is given at the end of this section.

The better to understand the nature of these coexistent mixtures we plot the free energy as a function of the two densities in a 3-dimensional plot, Fig.6.3.6. Here \( T_r = 1.5 \) and \( \beta = 5 \). What seems likely by inspection is verified by numerical calculation: the function \( f(x, y) \) has two local minima at

\[
x = .4844, \quad y = .0907 \quad \text{and} \quad x = .0907, \quad y = .4844.
\]
where $\mu_1 = \mu_2 = .08$. Fig.6.3.7 shows the profile of the free energy for a fixed value of $x + y (=5751)$, which in this case is close to the pressure locus $p = 1.55$, to display the two minima. We suspect that they are coexistent mixtures and to verify we first plot the locus of singular points for these values of $T_r$, $\beta$, in Fig.6.3.8. There appears a closed line of singular points that shrinks to a point, $x = .4848, y = .0904$, when $T_r$ is increased to 1.74. With this, singular value of $T_r$ we plot the loci of loci of $\mu_1$ and $\mu_2$ through the singular point, where they have a common tangent, through this point, as well as the locus of constant pressure through this point. See Fig. 6.3.10.

Returning to $T_r = 1.5$ (below the singular point) we plot the loci of $\mu_1$ and $\mu_2$ (both $= 0$) through this point, as well as the locus of constant pressure through this point. We find that the three curves have a second common intersection and tangent at the reflected point $x = .0904, y = .4848$, as shown in Fig.6.3.9. The two $\mu_1$ loci have a third intersection at $\rho_1 = \rho_2 = .26$, but the pressure at this point is lower. We tentatively conclude that, starting at this point, with a homogeneous 50:50 mixture, increasing the pressure will cause the mixture to separate, aided by gravity and, given enough time, into two quite different mixtures.
Fig. 6.3.6. Profile. The surface $z = f(x, y)$ for $T_r = 1.5, \beta = \pm 5$.

Fig. 6.3.7. Section 1. The intersection of the surface in Fig. AM with the pressure locus $p = .959$.

Fig. 6.3.8. Sim 20.1. The locus of singular points for the case $T = 1.5, \beta = 5$. The critical temperature is at $T = 1.74$. 

310
Fig. 6.3.10. Sim20.3. The diverging (red) lines are loci of $\mu_1, \mu_2$ through the singular point. The middle line (green) is the isobar through the same point.

Fig. 6.3.10. Sim20.2. The loci $\mu_1 = 0, \mu_2 = 0$ and the pressure locus $p = .959$ for $T_r = 1.5, \beta = \pm 5$. Here $T_r$ is below the singular temperature.
the rest of this Chapter needs work. Skip to page 154.

Fig.6.3.11. Sim20.4. The locus of singular points for the case \( T = 1.001, \beta = 5 \).

Fig.6.3.12. Sim20.5. The locus of singular points for the case \( T = .999, \beta = 5 \).

The critical points described so far have the earmarks of immiscibility; they are not associated with condensation. This structure of two minima is a phenomenon that depends on the value chosen for \( \beta \); in the next table we give the smallest value of this parameter that results in immiscibility, for each value of the temperature.

\[
\begin{align*}
T &= 1.5, \quad \beta = 3.5 \quad (x + y \approx .8) \\
T &= 1.4, \quad \beta = 2.8 \quad (x + y \approx .66) \\
T &= 1.3, \quad \beta = 2 \quad (x + y \approx .64) \\
T &= 1.2, \quad \beta = 1.5 \quad (x + y \approx .70)
\end{align*}
\]
\[ T = 1.1, \ \beta = .8 \ (x + y \approx .74) \]
\[ T = 1.05, \ \beta = .5 \ (x + y \approx .70) \]
\[ T = 1.02, \ \beta = .2 \ (x + y \approx .67) \]
\[ T = 1, \ \beta = 0 \ (x + y \approx .70) \]
\[ T = .9, \ \beta = -.6 \ (x + y \approx .70) \]
\[ T = .8, \ \beta = -1.2 \ (x + y \approx .70) \]
\[ T = .7, \ \beta = -2 \ (x + y \approx .70) \]

The value indicated for the total molar density \( x + y \) results in the highest bumps. The values given for \( \beta \) are approximate, upper limits for immiscibility.

**Low temperatures.** \( T_r < 1 \)

The location of singularities was very useful for our understanding of immiscibility for \( T_r > 1 \), but of no apparent use in connection with saturation, which happens for \( T_r < 1 \). It is generally understood, a consequence of Raoult’s theorem on the additivity of vacuum pressures, that the boiling point of an immiscible mixture is lower than that of either constituent.

The last table shows that immiscibility can occur for \( T_r < 1 \) if \( \beta > 0 \). We shall now examine what happens as the temperature is lowered for a fixed value of \( \beta \).

What follows is in a very preliminary state. the main conclusion is that a critical point due to immiscibility is very different from condensation.
Fig. 6.3.13. Oct17.1. Loci of $\mu_1$ (purple, vertical), $\mu_2$ (red, horizontal) and the pressure (green, meandering), for the case $T_r = .98$, $p_r = .233$, $\beta = .01$.

Fig. 6.3.14. Loci of $\mu_1$, $\mu_2$ and the pressure, for the case $\beta = .01$, $T_r = .94$ and $p_r = .196$.

Fig. 6.3.15. The free energy along a line that includes the two unequal mixtures.

Fig. 6.3.13 shows loci of the chemical potentials, for interaction strength $\beta = -1.4544$, and isobars, either or both adjusted to produce triple intersection. Because of symmetry - which is mildly unrealistic, this model has 3 coexistent phases, which indicates a potentiality of systems that violate Gibbs’ phase rule. The temperature is just below critical, $T_r = .98$. * In this domain the pressure locus twists around the nearly straight lines of

* The highest temperature for which condensation could be established by the computer was $T_r = .999$, with $\mu_1 = m\mu_2 = 1.445$. 

314
potential loci, crossing them 3 times. As we turn on the interaction we can follow the deformation of this phenomenon. Fig.6.3.14 shows the situation for $\beta = .01, T_r = .94$.

Three intersections indicate 3 stable phases, two are gas/liquids and one is a 50/50 liquid mixture.

The blue line is anchored at the upper left intersection, at $x = x_0 = .17903, y_0 = .50401$; its equation is $y = y_0 - k(x - x_0)$; it is shown with $k = 1$ and it passes through the other liquid point at the lower right. We plot a section of the function $f(x, y)$ along this line and find the characteristic double minima at $(x_0, y_0)$, value -.195573. See Fig.6.3.15.Oct18.2.

Next we aim our blue line at the liquid/liquid point, with $k = .01$. Again $F$ has a double minimum, one at $(x_0, y_0)$ and the other at the liquid/liquid point. The value of $f$ is not the same here. This can be remedied by adding a linear term $1.49(x + y)$ to $f$; this has no effect on the phenomena that we are studying.

This makes $\mu_1 = \mu_2$, corrected for this linear contribution to $f$, equal to zero.

Finally, following a strategy that should allow the discovery of all phases, we pivot the blue line to search for other structure. The only new minimum that appears is found with $k = 80$ at $x = y = .1822$, where $f$ takes the value -.19511, slightly higher than the other minima. It seems to be a metastable (almost stable), very dense liquid, a 50:50 mixture. I believe that a more careful calculation will show that the value is actually the same; note that this point is an intersection in Fig.18.1 and that it has the same pressure.

![Diagram](image)

Fig.6.3.16. Oct18.3. Loci of $\mu_1, \mu_2$ and the pressure, for the case $\beta = .01, T_r = .5$.

We next repeat this analysis for the case of a much stronger interaction, setting $\beta = .08, T_r = .94$. The result is in Fig.s Oct19.1 and Oct19.2. The liquid/liquid mixture has disappeared and the liquid/gas mixtures will disappear after a further small drop in the temperature. Condensation is now limited to a much smaller temperature interval.
Fig. 6.3.17. Oct19.1. Loci of $\mu_1, \mu_2$ and the pressure, for the case $\beta = .08, T_r = .94$. ???

Fig. 6.3.18. Here $\beta = .08, T_r = .94$. The function $f$ along the line $y = .543 - (x - .225)$. 

316
Fig.6.3.19. Loci of $mu_1$, $mu_2$ and the pressure, for the case $\beta = 5, T_r = .99$. Figure 6.3.20. Oct19.4. Here $\beta = 5, T_r = .99$. The function $f$ along the line $y = .5217 - 5(x - .007125)$.

Finally, for the value $\beta = 5$, signifying a strong interaction, we find a symmetric pair of liquid phases and a 50:50 gaseous mixture.

The table that follows gives the critical temperature and pressure for a range of values of $\beta$.

\[
\begin{align*}
\alpha &= -1, & T_c &= 1.14867, & c &= \left(\frac{1}{3}, \frac{1}{3}\right), & p_c &= .2876. \\
& & T_c &= .8522, & c &= \left(\frac{1}{3}, \frac{1}{3}\right), & p_c &= -.0089. \\
\alpha &= -.9, & T_c &= 1.13385, & c &= \left(\frac{1}{3}, \frac{1}{3}\right), & p_c &= .28385. \\
& & T_c &= .8670, & c &= \left(\frac{1}{3}, \frac{1}{3}\right), & p_c &= .017. \\
\alpha &= -.8, & T_c &= 1.1190, & c &= \left(\frac{1}{3}, \frac{1}{3}\right), & p_c &= .2801. \\
& & T_c &= .8818, & c &= \left(\frac{1}{3}, \frac{1}{3}\right), & p_c &= .0429. \\
\alpha &= -.7, & T_c &= 1.1042, & c &= \left(\frac{1}{3}, \frac{1}{3}\right), & p_c &= .2764. \\
& & T_c &= .8967, & c &= \left(\frac{1}{3}, \frac{1}{3}\right), & p_c &= .0689.
\end{align*}
\]
\[ \alpha = -0.6, \ T_c = 1.08935, \ c = \left(\frac{1}{3}, \frac{1}{3}\right), \ p_c = 0.2727. \]

\[ T_c = 0.9115, \ c = \left(\frac{1}{3}, \frac{1}{3}\right), \ p_c = 0.0948. \]

\[ \alpha = -0.5, \ T_c = 1.07455, \ c = \left(\frac{1}{3}, \frac{1}{3}\right), \ p_c = 0.2690. \]

\[ T_c = 0.9263, \ c = \left(\frac{1}{3}, \frac{1}{3}\right), \ p_c = 0.1207. \]

\[ \alpha = -0.4, \ T_c = 1.0597, \ c = \left(\frac{1}{3}, \frac{1}{3}\right), \ p_c = 0.2653. \]

\[ T_c = 0.9411, \ c = \left(\frac{1}{3}, \frac{1}{3}\right), \ p_c = 0.1467. \]

\[ \alpha = -0.3, \ T_c = 1.0449, \ c = \left(\frac{1}{3}, \frac{1}{3}\right), \ p_c = 0.2616. \]

\[ T_c = 0.9560, \ c = \left(\frac{1}{3}, \frac{1}{3}\right), \ p_c = 0.1727. \]

\[ \alpha = -0.2, \ T_c = 1.0301, \ c = \left(\frac{1}{3}, \frac{1}{3}\right), \ p_c = 0.2579. \]

\[ T_c = 0.9708, \ c = \left(\frac{1}{3}, \frac{1}{3}\right), \ p_c = 0.1987. \]

\[ \alpha = -0.1, \ T_c = 1.01528, \ c = \left(\frac{1}{3}, \frac{1}{3}\right), \ p_c = 0.2542. \]

\[ T_c = 0.9856, \ c = \left(\frac{1}{3}, \frac{1}{3}\right), \ p_c = 0.2245. \]

\[ \alpha = 0, \ T_c = 1, \ c = \left(\frac{1}{3}, \frac{1}{3}\right), \ p_c = 0.25. \]

\[ \alpha = 0.1, \ T_c = 0.9856, \ c = \left(\frac{1}{3}, \frac{1}{3}\right), \ p_c = 0.2467. \]

\[ T_c = 1.01528, \ c = \left(\frac{1}{3}, \frac{1}{3}\right), \ p_c = 0.2764. \]

\[ \alpha = 0.2, \ T_c = 0.97128, \ c = \left(\frac{1}{3}, \frac{1}{3}\right), \ p_c = 0.2430. \]

\[ T_c = 1.0301, \ c = \left(\frac{1}{3}, \frac{1}{3}\right), \ p_c = 0.3023. \]

\[ \alpha = 0.3, \ T_c = 0.9560, \ c = \left(\frac{1}{3}, \frac{1}{3}\right), \ p_c = 0.2393. \]

\[ \alpha = 0.3, \ T_c = 1.0449, \ c = \left(\frac{1}{3}, \frac{1}{3}\right), \ p_c = 0.3282. \]
\[ \alpha = .4, \ T_c = .94117, \ c = (\frac{1}{3}, \frac{1}{3}), \ p_c = .2356. \]

\[ 1.0597, \ c = (\frac{1}{3}, \frac{1}{3}), \ p_c = .3540. \]

\[ \alpha = .5, \ T_c = .92635, \ c = (\frac{1}{3}, \frac{1}{3}), \ p_c = .2319. \]

\[ T_c = 1.07455, \ c = (\frac{1}{3}, \frac{1}{3}), \ p_c = .3801. \]

\[ \alpha = .6, \ T_c = .9115, \ c = (\frac{1}{3}, \frac{1}{3}), \ p_c = .2282. \]

\[ T_c = 1.08935, \ c = (\frac{1}{3}, \frac{1}{3}), \ p_c = .4060. \]

\[ \alpha = .7, \ T_c = .8967, \ c = (\frac{1}{3}, \frac{1}{3}), \ p_c = .2244. \]

\[ T_c = 1.1042, \ c = (\frac{1}{3}, \frac{1}{3}), \ p_c = .4320. \]

\[ \alpha = .8, \ T_c = .8818, \ c = (\frac{1}{3}, \frac{1}{3}), \ p_c = .2207. \]

\[ T_c = 1,1190, \ c = (\frac{1}{3}, \frac{1}{3}), \ p_c = .4579. \]

\[ \alpha = .9, \ T_c = .86707, \ c = (\frac{1}{3}, \frac{1}{3}), \ p_c = .21707. \]

\[ T_c = .86707, \ c = (\frac{1}{3}, \frac{1}{3}), \ p_c = .48385. \]

\[ \alpha = 1, \ T_c = .8522, \ c = (\frac{1}{3}, \frac{1}{3}), \ p_c = .2133. \]

\[ T_c = .8522, \ c = (\frac{1}{3}, \frac{1}{3}), \ p_c = .5098. \]

We have a good idea of the structure of these critical points, but the overall picture is much more complicated.

Fig.10.5.1. The limit of stability.

319
XII. RELATIVITY

The impetus for developing an action principle for hydrodynamics and thermodynamics was to prepare for a study of astrophysics, the structure of stars and galaxies. The relation of these fields of science to each other is less than evident. However, already in 1870 the physicist Homer Lane published a paper with the following title:

“On the Theoretical Temperature of the Sun, under the Hypothesis of a gaseous Mass maintaining its Volume by its internal Heat and depending on the laws of gases as known to terrestrial Experiment” (Lane 1870)

Half a century later Eddington marveled at the success of a theory that treated the interior of the Sun as if it consists of an ideal gas. And even today the best that can be done to describe the interior structure of stars is to apply the experience that has been gained by terrestrial experiments.

We are going to consider the hydrodynamics of self gravitating fluids by means of Einstein's equations for the metric, in the context of the General theory of Relativity. Stars and galaxies tend to rotate, in some it may be said that rotation is their dominant characteristic; this has been the principal difficulty for some time. It is a problem that the preceding chapter has already prepared us for, but more preparation is needed: we can approach General Relativity only after promoting our theory to a relativistic, Lagrangian field, theory in the sense of the Special Theory of Relativity.

XII.2. Introduction to General Relativity

This sketch of an introduction to General Relativity divides naturally into several parts:

1. A very short summary of the first stage of General Relativity. The elevation of the Lorentzian metric of Special Relativity to a dynamical field with matter as its source, and the idea of geodesic motion. Section XII.2.

2. The development of a dynamical action principle for the metric. Section XII.3.
   a. The gravitational field in empty space.
   b. The identification of the source of the metric field with the energy-momentum tensor of a matter field model.
   c. Interaction with the electromagnetic field.
   d. Tolman’s phenomenology.
A very short summary of the first stage of General Relativity

Special relativity was created in 1905. It arose from the demand that the laws of mechanics have the same invariance group as Maxwell’s theory of electromagnetism, the Poincaré group or the inhomogeneous Lorentz group. It became necessary to formulate physical laws in a language that makes Lorentz invariance manifest, in order that the attention could be directed to physics without the need to worry about consistency with the new principles at each stage. This had the effect of introducing the Lorentzian metric into all the equations of fundamental physics. For example, Maxwell’s field equations now take the form

\[ g^{\mu\nu} \partial_\mu F_{\nu\lambda} = J_\lambda. \]  (12.2.1)

The prominence of the metric led Einstein to seek a larger role for it, and this resulted in the idea of geodesic motion. The next great leap forward was the realization that Newton’s equations for the motion of a particle in a gravitational field could be interpreted as geodesic motion in the special metric

\[ ds^2 = (1 - \frac{2\phi}{c^2})(c dt)^2 - d\vec{x}^2, \]  (12.2.2)

where \( \phi \) is the newtonian gravitational potential. The distance between two points in space time is

\[ \int_a^b ds = \int_a^b \sqrt{g_{\mu\nu} dx^\mu dx^\nu} \]

and the equation that minimizes the value of this expression is

\[ \ddot{x}^\mu - \Gamma^{\mu}_{\nu\lambda} \dot{x}^\nu \dot{x}^\lambda = 0, \]  (12.2.3)

where the dots stand for derivatives with respect to \( s \) and \( \Gamma \) is the metric connection,

\[ \Gamma^{\mu}_{\nu\lambda} = \frac{1}{2} g^{\mu\rho} (g_{\nu,\lambda} + g_{\lambda,\nu} - g_{\lambda,\rho}). \]  (12.2.4)

The proliferation of indices is frightening, but most of the coefficients of \( \Gamma \) are zero and a little work leads to the revelation that Eq. (12.2.3) is precisely the Newtonian equations of motion.

XII.3. The development of a dynamical action principle for the metric

a. The recognition of geodesic motion was not just an interpretation of Newton’s equations of motion; it was a major discovery with important experimental consequences. But the theory needed further development. In Newtonian theory the potential was determined by solving the Poisson equation with the mass distribution as a source,

\[ \Delta \phi = -4\pi G \rho, \]  (12.3.1)

with \( G \) a universal constant. It relates the field \( \phi \) to the source, the matter distribution. The search for a suitable generalization would take 10 years of labor by Einstein, Hilbert, Poincaré and others.
The answer is as follows. A covariant derivative is defined with the help of the metric connection (12.2.4),
\[ D_\mu := \partial_\mu - \Gamma_\mu, \]
The Gaussian curvature tensor is
\[ [D_\mu, D_\nu] = R_{\mu\nu} = R_{\mu\nu}^a L_b^a, \]
where the \( L_b^a \) are matrices, the generators of ‘local Lorentz transformations’. Alternatively, if \( A \) is any co-vector field,
\[ [D_\mu, D_\nu] A_\rho = (R_{\mu\nu})^\lambda_\rho A_\lambda. \]
Two contractions leads to the curvature scalar \( R = g^{\mu\rho} (R_{\mu\nu})_\rho^\nu \) and this scalar field, by virtue of being the only candidate with required characteristics, is the Lagrangian density for the metric field.

Variations of the action
\[ A_{\text{metric}} = \int d^4x \sqrt{-g} R \quad (12.3.2) \]
with respect to the metric,
\[ \delta A_{\text{metric}} = \int d^4x \sqrt{-g} \delta g^{\mu\nu} G_{\mu\nu} = 0. \quad (12.3.3) \]
gives a unique field equation
\[ G_{\mu\nu} = 0. \quad (12.3.4) \]
When the variation \( \delta g^{\mu\nu} \) in Eq. (12.2.3) is specialized to the type of variation that results from a change of coordinates,
\[ \delta g^{\mu\nu} = D_\mu \xi_\nu + D_\nu \xi_\mu, \]
one finds by means of an integration by parts the identity
\[ G^{\mu\nu};_\nu = 0. \quad (12.3.5) \]
This is the famous Bianchi identity; it is indeed satisfied identically, for it merely expresses the invariance of the action under coordinate transformations. The simplest way to write this equation is
\[ \frac{\partial}{\partial x^\mu} \sqrt{-g} G^{\mu\nu} + \sqrt{-g} G^{\lambda\rho} \Gamma^\nu_{\lambda\rho} = 0. \]
Eq. (12.3.4) is Einsteins field equation for the metric field in vacuum; that is, the field equation for ‘empty space’ ... space-time devoid of matter.

A special solution to equation (12.3.4), stationary and spherically symmetric, was found very soon by Schwarzschild (1917); it has an interesting topological structure and led to the concept of Black Holes. But our interest is in space with matter, as a star or a galaxy, not empty space.
b. In the presence of matter the metric field equation is expected to take the form

\[ G_{\mu\nu} = T_{\mu\nu}. \]  

(12.3.6)

Instead of zero, characteristic of vacuum, it has something on the right hand side that represents matter, the source of the gravitational metric field. An integrability condition arises from the fact that the left side satisfies the Bianchi identity, consistency demands that the source tensor \( T \) must satisfy the same condition, the Bianchi constraint,

\[ T^{\mu\nu;\nu} = 0. \]  

(12.3.7)

The key to satisfying this condition is that the Bianchi identity is derived from invariance under coordinate transformations. A whole class of models that satisfy this last condition is found by taking the matter tensor to be the energy momentum tensor of a coordinate invariant, Lagrangian field theory, with action

\[ A_{\text{matter}} = \int d^x \sqrt{-g} \mathcal{L}, \]

and energy momentum tensor

\[ T_{\mu\nu} = 2 \frac{\delta}{\delta g^{\mu\nu}} \mathcal{L} - \mathcal{L} g_{\mu\nu}. \]

The constraint is not satisfied identically, but on shell, by virtue of the matter field equations. It is a gift to us, offered by any relativistic field theory.

c. This was indeed the method by which the first consistent field theories with a matter-metric interaction were constructed, first of all the so called Maxwell-Einstein theory that unites electromagnetism and General Relativity. The Lagrangian density is

\[ - \frac{1}{4} g^{\mu\nu} g^{\lambda\rho} F_{\mu\lambda} F_{\nu\rho}, \]

and the energy momentum tensor (verify this)

\[ T_{\mu\nu} = g^{\lambda\rho} F_{\mu\lambda} F_{\nu\rho} - g_{\mu\nu} \mathcal{L}. \]

But this theory does not involve the theory of fluids or other types of matter. Similar field theoretic models are plentiful, but they do not describe extended distributions of matter. No relativistic field theory of fluids has been available.

d. Lacking a dynamical matter model suitable for stellar structure, Tolman, in 1934, proposed a phenomenological expression for the matter tensor,

\[ T_{\mu\nu} = (\rho + p) U_{\mu} U_{\nu} - \rho g_{\mu\nu}. \]  

(12.3.8)
Here $\rho$ is a scalar density field possibly associated with the distribution of mass, $p$ is an isotropic pressure density and $U$ is a four vector field. Tolman interpreted the space components in terms of matter flow and imposed the normalization

$$g^{\mu\nu}U_\mu U_\nu = 1.$$  \hspace{1cm} (12.4.2)

This condition was inspired by the model of non interacting particles. The model does not have a conserved current, the condition of continuity of classical hydrodynamics is abandoned. Nevertheless, faute de mieux, Tolman’s suggestion has been used in almost all investigations of stellar structure, from Eddington and Chandrasekhar forward.

The most obvious objection to Tolman’s formula is that it fails to incorporate an equation of continuity, a defect that is significant in a theory that aspires to be a generalization of hydrodynamics.

Even more important is the fact that Tolman’s matter tensor is not directly related to a matter model and it has no dynamical content. There are no matter equations of motion that could be used to verify the Bianchi identities. Instead, the suggestion is to regard the condition (12.3.4),

$$T^{\mu\nu};_\nu = 0$$

as a substitute for dynamics. Thus matter has no intrinsic properties; instead it is subject to the consistency conditions that allow it to appear as a source for the gravitational field. In this sense it is like the Navier Stokes equation that simply defines the the acceleration of particles in the fluid in terms of unspecified force fields.

An analogy will help put the right accent on this, and is of great interest by its own rights. Maxwell-Dirac electrodynamics couples to field theories, mainly by introducing an interaction term of the form $eA_\mu J^\mu$ in the Lagrangian. Maxwell’s equations now take the form

$$\partial_\mu F^{\mu\nu} = eJ^\nu.$$  

The left side is evidently divergence less, so the right hand side must be divergenceless as well; that is, conserved. And this condition, $J^{\mu\nu};_\nu = 0$, must be satisfied by virtue of the Dirac field equations for the matter field.

It will be objected that, though this is true in Maxwell-Dirac theory, and though it is true that it is a requisite for perturbation theory, it is not satisfied in the theory of electromagnetic fluids. Indeed that is so, and as we have said, Minkowski’s treatment of electrodynamics leaves a lot to be desired.

Finally, Tolman’s formula for the energy momentum tensor is based on the idea of a single, timelike 4-vector velocity field. It cannot accommodate rotating matter, which is fatal since most heavenly bodies are rotating.

**XII.1. Variational principles in Special Relativity**

“To include rotating bodies in General Relativity, we must upgrade every 3-vector field to a relativistic 4-vector field.” This simplistic rule has been dominant since Einstein used it in his relativistic theory of particles, where the prescription was completely successful, as
it led to relativistic concepts of mass, energy and momentum, combined to a 4-dimensionsal energy-momentum vector

\[(cp^1, cp^2, cp^3, p^0 = E), \quad E^2 - c^2p^2 = c^4m^2,\]

where the constant \(c\) is the velocity of of light. Unfortunately the same idea was applied to the velocity fields of liquids.

Verify this! First, already in 1908, Minkowski used it in the context of electromagnetism. As Minkowski was aware, and as all modern textbooks tell us, the electromagnetic interactions of a fluid at rest give rise to contributions \(\epsilon \vec{E}^2 - \mu \vec{B}^2 / c^2\) to the energy density. To find the appropriate generalization to the case that there is motion in the fluid he first performs a Lorentz transformation to a reference frame that is moving with constant velocity \(\vec{v}\); then he promotes \(\vec{v}\) to a four-vector with components

\[ (v^\mu) = (\vec{v}, v^0). \]

To this we must already object, but there is more to come. Having thus gotten the four-vector velocity into his formalism Minkowski simply assumes that the expression that he has obtained is valid as it stands, for arbitrary motions of the liquid. This is what passes as electromagnetism of fluids to this day. Perhaps we should try to do better, in some future chapter of this book.

Of more immediate interest to us is that the approach taken by Minkowski to electrodynamics was adopted without change by Tolman in 1934. We shall have much to say about that.

It is evident that we cannot adopt this approach; the velocity potential can be promoted to a relativistic scalar field, and the gradient to a 4-vextor velocity field, but the velocity field \(\dot{\vec{X}}\) is another matter. An objection from the back row: Is it not true that one often promotes this vector field to a 4-vector by replacing the time derivative by the proper time derivative? This proper time is the time as recorded by a “co-moving” clock. It is a concept that is useful to help explain the relative nature of time in the special theory of relativity, and it may be appropriate in the case of the motion of particles, but proper time has no place in a theory of fields, which is what hydrodynamics is.

We shall accept that, in the relativistic context, the scalar velocity potential becomes a scalar field in the 4-dimensional sense, and that \(\dot{\Phi}, \vec{\nabla} \Phi\) combine to make a four-vector. The relativisticalization of the Fetter-Walecka Lagrangian is easy to construct (Fronsdal 2007).

### XII.2. Special Relativistic potential theory

The first guess is successful; just consider the Lorentz invariant action

\[
\int d^3x \, dt \left( \frac{\rho^2}{2} (g_{\mu\nu} \dot{\psi}_\mu \dot{\psi}_\nu - c^2) - W[\rho] \right). \quad (12.1.1)
\]
The metric tensor is Lorentzian, diagonal with components \((-1, -1, -1, c^2)\). The tensor \((g^{\mu\nu})\) is the inverse matrix. The fields \(\rho\) and \(\psi\) are four-dimensional scalar fields. In flat space, with the Lorentzian metric it is

\[
2 \int d^3x dt \left( \frac{\rho}{c^2} \dot{\psi}^2 - (\nabla \psi)^2 - c^2 \right) - W[\rho].
\]

To take the non-relativistic limit it is tempting to drop the first term. The trouble is that, in spite of the factor \(1/c^2\), the variation of both terms under an infinitesimal Lorentz transformation,

\[
\delta \dot{\psi} = c \vec{u} \cdot \nabla \psi, \quad \delta \vec{\psi} = \vec{u} \dot{\psi},
\]

are comparable; of course, for they cancel in this Lorentz invariant combination. To arrive at a non-relativistic theory that is invariant to first order in \(u/c\) we need to retain this contribution to the variation under Lorentz transformations. This was done by expanding

\[
\psi = tc^2 + \Phi, \quad \frac{1}{c^2} \dot{\psi}^2 = c^2 + 2\dot{\Phi} + ...
\]

where the elided terms are of order \(1/c^2\). These can be safely dropped, for the necessary contribution to the Lorentz transformation is provided by the variation of the linear term,

\[
\delta \Phi = \vec{u} \cdot \nabla \Phi.
\]

the result is the Fetter-Walecka action; it is invariant under Galilei transformations, as we have seen in Section III.11. This is the simplest way to be convinced that the non-relativistic theory is invariant under Galilei transformations.

The action of the Galilei group on the vector field \(\dot{X}\) will be explained at the end of this chapter.

The non-relativistic theory as a gauge theory

I have promised to solve the problem of constructing a theory with the correct number of degrees of freedom for hydrodynamics. this pledge is essentially satisfied, at least in the absence of viscosity, by the fact that, according to the field equation

\[
\nabla \cdot (\rho \dot{X} + \kappa \rho \nabla \Phi) = 0,
\]

\(\dot{X}\) is a free field. But some clarification is needed.

It will be shown in the next section that the theory is the non-relativistic limit of a relativistic gauge theory that is familiar in another context and that has been carefully analyzed. From the narrow, non-relativistic standpoint we must complete the theory by imposing constraints.

The main constraint is

\[
\nabla \wedge (\rho \dot{X} + \kappa \rho \nabla \Phi) = 0.
\]
It is difficult to justify this within the present context; it is only in the fully developed relativistic theory (next section) that its interpretation in terms of gauge fixing can be confirmed. But (12.2.3) has a major effect on the non-relativistic theory and that can be discussed here.

At first sight, (12.2.3) seems to bring our efforts to naught. In the special case that the density is uniform, as in the case of an incompressible fluid and some solids, it says that the curl of our velocity is zero! But this is too hasty, for there are at least two ways to escape this conclusion.

In the first place, the incompressible fluid is an idealization. Returning to the case of stationary, cylindrical Couette flow, with

\[ \dot{X} = b(-y, x, 0), \quad \nabla \Phi = a(-y, x, 0), \quad a, b \text{ constant}, \]

the general solution of (12.2.3) is

\[ \rho = \frac{C}{br^2 + \kappa a}, \quad C \text{ constant}. \]

this result is one reason why we want to retain the \( \kappa \) term in the Lagrangian.

It will be shown that this constraint does not fix the gauge completely, there is an additional constraint.

In the second place a coupling to the magnetic field of the type

\[ \vec{B} = 0, 0, B, \quad B \text{constant} \]

introduces another parameter into the solution,

\[ \rho = \frac{\gamma Br^2 + C}{br^2 + \kappa a}, \quad C \text{ constant}. \]

Here \( \gamma \) is a coupling constant. This solution is sufficiently general to account for the experiments.

A second constraint (next section) is

\[ \nabla \cdot \vec{X} := c^{(2)} \Theta, \quad \Delta \Theta = 0. \]

The field \( \Theta \) plays a role in connection with Galilei invariance. all this will become more clear in the relativistic context.

**XII.3. The relativistic, antisymmetric tensor field**

A dramatic effect of relativization is that the fields become propagating. In particular, propagation of the fields into empty space may be unavoidable, therefore it is prudent to keep the number of propagating modes at a minimum. And that leads us to the antisymmetric tensor gauge field and its well known properties. This field has at most one
scalar, propagating mode. It was introduced by Ogievetskij, and Polubarinov (1964). In another context it is known as the $B$-field, or the Kalb-Ramond field.

The 3-vector field $\vec{X}$ is the space part of the 4-vector with components

$$d\tilde{Y}^\mu = \frac{1}{2} \varepsilon^{\mu\nu\lambda\sigma} Y_{\nu\lambda,\sigma} = (\dot{\vec{X}}, \vec{\nabla} \cdot \vec{X}).$$

Let $Y = (Y_{\mu\nu})$ be an antisymmetric tensor field (a 2-form) and consider the Lagrangian density

$$dY^2 = \frac{c^2}{2} g^{\mu\mu'} g^{\nu\nu'} g^{\lambda\lambda'} Y_{\mu\nu,\lambda} \sum_{\text{cyclic}} Y_{\mu'\nu',\lambda'}.$$  \hfill (12.3.1)

Greek indices run over 1,2,3,0, latin indices over 1,2,3. The (inverse) metric tensor is the Lorentzian, diagonal with $g_{11} = g_{22} = g_{33} = 1, g_{00} = -1/c^2$. It is invariant under the gauge transformation $\delta Y = d\xi$. In a 3-dimensional notation,

$$X^i = \frac{1}{2} \varepsilon^{ijk} Y_{jk}, \quad \eta_i = Y_{0i},$$

The equation $\eta_i = \partial_0 \xi_i - \partial_i \xi_0$ can always be solved for the vector field $\vec{\xi}$; there is a family of gauges in which the field $\vec{\eta}$ vanishes. In addition, the vector field $\vec{X}$ can be reduced to a gradient field. This spinless field is the only propagating mode.

In flat space, with Cartesian coordinates, in terms of $\vec{X}$ and $\vec{\eta}$,

$$dY^2 = \frac{1}{2} \left( \dot{\vec{X}} + \vec{\nabla} \wedge \vec{\eta} \right)^2 - \frac{c^2}{2} (\vec{\nabla} \cdot \vec{X})^2.$$  \hfill (12.3.2)

The free field equations associated with this expression for the Lagrangian density are

$$\frac{d}{dt} \left( \dot{\vec{X}} + \vec{\nabla} \wedge \vec{\eta} \right) - c^2 \vec{\nabla} \cdot (\vec{\nabla} \cdot \vec{X}) = 0, \quad \vec{\nabla} \wedge (\dot{\vec{X}} + \vec{\nabla} \wedge \vec{\eta}) = 0.$$  \hfill (12.3.3)

The only mode that propagates in vacuum mode is a scalar mode. But we can add sources,

$$\frac{d}{dt} \left( \dot{\vec{X}} + \vec{\nabla} \wedge \vec{\eta} \right) - c^2 \vec{\nabla} \cdot (\vec{\nabla} \cdot \vec{X}) = \vec{K}, \quad \vec{\nabla} \wedge (\dot{\vec{X}} + \vec{\nabla} \wedge \vec{\eta}) = \vec{K}',$$  \hfill (3)

so that, in their presence, the field $\dot{\vec{X}}$ need not be be irrotational.

A stationary solution for the geometry of cylindrical Couette flow is $\vec{X} = bt(-y, x, 0)$, $\vec{\nabla} \wedge \vec{X} = 2b(0, 0, 1)$ and $\vec{\nabla} \cdot \vec{X} = 0$; it is a solution of these field equations in a gauge where $\vec{\eta} = 0$, with $\vec{K} = 0$, but with $\vec{K}' = 2b(0, 0, 1)$. It is known (Barnett 1915) that a magnetic field is produced by a rotating cylinder made of iron and it is believed that the effect is general with an effective magnetization proportional to the magnetic moment. In the hope of accounting for this effect, without a microscopic model, we may add a gauge invariant interaction term, the exterior product

$$\gamma YF = \frac{\gamma}{4} \tilde{Y}^{\mu\nu} F_{\mu\nu} = \gamma (\vec{X} \cdot \vec{E} + c^{-1} \vec{\eta} \cdot \vec{B}).$$  \hfill (12.3.5)
where $\tilde{Y}$ is the dual,
\[
\tilde{Y}^{\lambda \rho} = \frac{1}{2} \epsilon^{\mu \nu \lambda \rho} Y_{\mu \nu},
\]

$F$ is the electromagnetic field strength, $F_{ij} = (\nabla \wedge A)_{ij} = c^{-1} B_{ij}, F_{0i} = E_i$ and $\gamma$ is a constant parameter with dimension $g/\text{sec} \cdot \text{cm}^3$. This ties in nicely with speculations that have been voiced by several workers, of an intimate connection between solid body motion and electromagnetism. The electric field may be related to measurements of Tolman (1910) and Wilson and Wilson (see Cullwick 1959, Rosser 1971).

The propagating, scalar mode is a new form of matter that interacts with gravity and with the electromagnetic field strength, being endowed with electric and magnetic polarizability, it would be a contribution to Dark Matter.

The term $\rho \dot{\vec{X}} \cdot \nabla \tilde{\Phi}$ can be made invariant under Lorentz transformations by expanding it to
\[
\rho \frac{c^2}{2} \epsilon^{\mu \nu \lambda \rho} Y_{\mu \nu, \lambda} \psi_{,\rho}.
\]

Here $\psi$ is a Lorentz scalar; if $\rho$ is uniform it is a boundary term.

Introduce the dual as above, then
\[
\frac{c^2}{2} \epsilon^{\mu \nu \lambda \rho} Y_{\mu \nu, \lambda} \psi_{,\rho} = \tilde{Y}_{0i,0} \psi_{,i} + \tilde{Y}_{0i} \psi_{,0} - \tilde{Y}_{ij} \psi_{,j},
\]
and
\[
\frac{c^2}{2} \epsilon^{\mu \nu \lambda \rho} Y_{\mu \nu, \lambda} \psi_{,\rho} = \dot{\vec{X}} \cdot \nabla \psi - (\nabla \cdot \vec{\eta}) \psi + (\nabla \wedge \vec{\eta}) \cdot \nabla \psi.
\]

The first term on the right is the one that appears in the non relativistic theory, the term that we are trying to promote to the relativistic context. In the second term $\psi$ appears in the role of a Lagrange multiplier and imposes the additional constraint
\[
\nabla \cdot \vec{X} = 0.
\]

Now we consider the total Lagrangian density
\[
\mathcal{L} = \frac{\rho}{2} (g^{\mu \nu} \psi_{,\mu} \psi_{,\nu} - c^2) + \rho dY^2 + \kappa \rho \frac{c^2}{2} \epsilon^{\mu \nu \lambda \rho} Y_{\mu \nu, \lambda} \psi_{,\rho} + \frac{\gamma}{4} \rho \tilde{Y}^{\mu \nu} F_{\mu \nu} - f - sT
\]
and the action $A(q, a) = \int d^3x dt \mathcal{L}$. The first term is the Lorentz invariant contribution that appears in the non relativistic approximation as $\rho (\dot{\Phi} - \nabla \tilde{\Phi}^2/2)$.

The variation of the action with respect to $\psi$ is $-\delta \psi$ times
\[
\frac{d}{dt} \left( \rho \left( \frac{\dot{\psi}}{c^2} - \kappa \nabla \cdot \vec{X} \right) \right) + \nabla \cdot \left( \rho (\kappa \dot{\vec{X}} - \nabla \tilde{\Phi} + \kappa \nabla \wedge \vec{\eta}) \right) = \frac{d}{dt} J^0 + \nabla \cdot \vec{J}.
\]
In the non relativistic limit $\dot{\psi}/c^2$ is unity. The boundary conditions require that the current $\vec{J}$ be normal to the boundary. The last equation reduces to the equation of continuity. In a physical gauge

$$\dot{\rho} + \vec{\nabla} \cdot \left( \rho (\kappa \vec{X} - \vec{\nabla} \Phi) \right) = 0.$$

This confirms that the conserved flow is

$$\rho (\kappa \vec{X} - \vec{\nabla} \Phi).$$

The variation of the action with respect to the field $\vec{X}$ is

$$\int d^3x dt \delta \vec{X} \cdot \left( \frac{d}{dt}(\rho(\dot{\vec{X}} + \kappa \vec{\nabla} \psi + \vec{\nabla} \wedge \vec{\eta})) + \vec{\nabla}(\rho(\kappa - c^2 \vec{\nabla} \cdot \vec{X})) - \gamma \vec{E} \right).$$

Setting this to zero gives the field equation

$$\frac{d}{dt}(\rho(\dot{\vec{X}} + \kappa \vec{\nabla} \Phi + \vec{\nabla} \wedge \vec{\eta})) + \vec{\nabla}(\rho(\kappa - c^2 \vec{\nabla} \cdot \vec{X})) = \gamma \vec{E}.$$

If we want the stationary, solid-body rotating motion of the non relativistic theory to be a solution of the relativistic theory, then we need to postulate an electric field that ensures the mutual cancelation of the last two terms; that is, $\gamma \vec{E} = \kappa \vec{\nabla} \rho$. An electric field is expected on the basis of an experiment by Tolman (1910). It may also have something to do with the anomalous Seebeck effect. But at this time we are far from understanding all the ramifications of this interaction with the electromagnetic field. That an unexpected role may be played by the electric field in connection with vortex motion, or that an electromagnetic analogy may be glimpsed here, was suggested by Feynman in connection with liquid helium (Feynman 1954 page 273).

The variation of the action with respect to the field $\vec{\eta}$ is

$$\int d^3x dt \delta \vec{\eta} \cdot \left( \vec{\nabla} \wedge (\rho(\dot{\vec{X}} + \kappa \vec{\nabla} \Phi + \vec{\nabla} \wedge \vec{\eta})) - \frac{\gamma}{c} \vec{B} \right).$$

Setting this to zero gives the field equation

$$\vec{\nabla} \wedge (\rho(\dot{\vec{X}} + \kappa \vec{\nabla} \Phi + \vec{\nabla} \wedge \vec{\eta})) = \frac{\gamma}{c} \vec{B}.$$

But this is implied by the other field equations. The variation $\delta \vec{\eta}$ is part of a certain gauge transformation $\delta Y = (\delta \vec{X}, \delta \vec{\eta})$; gauge invariance tells us that for such variations the sum of (12.1.8) and (12.1.10) is identically zero. But the former is zero for any variation, by the field equation (12.2.9), so (12.2.10) must be zero also. We mention this because (12.2.10-11) are simpler than (12.2.8-9). Eq. (12.2.12) is a constraint that comes from variation of the field $\eta$. In the non relativistic context the gauge is fixed and this field is absent; but the constraint must be taken into account. It is this constraint, somewhat mysterious in the non-relativistic context, that reduces the number of degrees of freedom from 3 to 1.

The two equations (12.2.11) and (12.2.13 are mutually consistent by Maxwell’s second equation, $dF = 0$ or $\vec{B} = c \vec{\nabla} \wedge \vec{E}$, provided that $\gamma$ is constant (as is required by the gauge invariance of (12.2.3)) from now on.
Maxwell’s equations

To improve our understanding of the role that is played by the vector potential we shall leave out the scalar velocity potential.

If we were to insist on maintaining the naive solution with \( \rho \) and \( b \) constant, then Eq.(12.1.11) would give us a uniform magnetic field,

\[
\nabla \wedge (\rho \dot{X}) = 2\rho b(0,0,1) = \frac{\gamma}{c} \mathbf{B}
\]

and by Eq.(12.1.9), \( \vec{E} = 0 \). But this contradicts Maxwell’s equation,

\[
\dot{\vec{E}} - c \nabla \wedge \vec{B} = -\gamma \dot{\vec{X}}.
\]

So \( \rho \) and \( b \) cannot both be constant.

In general, the equation (12.2.14) is replaced by

\[
\nabla \wedge (\rho \dot{X}) = \frac{1}{R} \rho \partial_R (R^2 b)(0,0,1) = \frac{\gamma}{c} \mathbf{B}
\]

and Maxwell’s equation

\[
\dot{\vec{E}} - c \nabla \wedge \vec{B} = -\gamma \dot{\vec{X}}
\]

becomes

\[
\nabla \wedge \frac{1}{R} \rho \partial_R (R^2 b)(00,1) = -\frac{\gamma^2 b}{c^2} (-y, x, 0)
\]

or

\[
\frac{1}{r} \partial_R \frac{1}{R} \partial_R (\rho b R^2) = -\frac{\gamma^2}{c^2} b.
\]

Near the center we expect \( b \) to be nearly constant; this is verified then

\[
\rho = \frac{k}{R^2} - \frac{\gamma^2 R^2}{c^2} \frac{R}{4}, \quad k \text{ constant.}
\]

which may be reasonable, but not impossible close to the center. Very far from the source we expect that \( \rho \) becomes constant. This constant, the density of the vacuum, is analogous to the electromagnetic polarizations \( \epsilon_0 \) and \( \mu_0 \) that are absent from the formulas because they have been absorbed into the fields. The solution is then

\[
b(R) = \frac{b(0)}{R^2} \exp\left[-\frac{\gamma^2}{\rho_0 c^2} \frac{R^2}{2}\right].
\]

So the system has found a way to avoid generating velocities greater than the speed of light at a large distance from the center.

Several directions are open to investigation. In the first place it is known that the mixing (not an interaction) of the antisymmetric field with electromagnetism makes the photon massive and removes the infrared divergence from QED. This takes us far from thermodynamics and will be taken up elsewhere.
But the implications for General Relativity are interesting and very much within the range of thermodynamics.

**The energy-momentum tensor**

The terms in the Lagrangian density that contain the metric are

\[
dY^2 = \frac{c^2}{4} g^{\mu\nu} g^{\lambda\lambda'} g_{\mu\nu,\lambda} (Y_{\mu'\nu',\lambda'} + Y_{\nu'\lambda',\mu'}) + \frac{1}{8} g_{\lambda'\mu',\nu'} g^{\mu\nu} F_{\mu\nu} F_{\mu\nu}
\]

In flat space, in the physical gauge, on shell,

\[
\dot{X}^3 = b(-y, x, 0)
\]

and the only non zero components of \(dY\) are

\[
\dot{Y}_{23} = -by, \quad \dot{Y}_{31} = bx
\]

\[
dY^2 = \frac{c^2}{2} (\dot{Y}_{23}^2 + \dot{Y}_{31}^2) = \frac{c^2}{2} g^{00} g^{33} (g^{11}\dot{Y}_{31}^2 + g^{22}\dot{Y}_{23}^2)
\]

and

\[
\frac{1}{8} g^{\mu\nu} g^{\nu\nu'} F_{\mu\nu} F_{\mu\nu} = B_{12}^2 = g^{33} (g^{11}\dot{B}_{31}^2 + g^{22}\dot{B}_{23}^2).
\]

Other terms not only vanish; they are all second order in vanishing components of the metric. We can therefore evaluate the energy momentum tensor using these on shell values. The non zero components are

\[
T_{11} = \rho c^2 g^{00} g^{33}\dot{Y}_{31}^2 + g^{33} B_{32}^2 - pg_{11},
\]

\[
T_{22} = \rho c^2 g^{00} g^{33}\dot{Y}_{23}^2 + g^{33} B_{23}^2 - pg_{22},
\]

\[
T_{33} = \rho c^2 g^{00} (g^{11}\dot{Y}_{31}^2 + g^{22}\dot{Y}_{23}^2) + (g^{11} B_{31}^2 + g^{22} B_{23}^2) - pg_{33}.
\]

On shell,

\[
T_{11} = \rho b^2 x^2 + (2\rho bc/\gamma)^2 x^2 - p,
\]

\[
T_{22} = \rho b^2 y^2 + (2\rho bc/\gamma)^2 y^2 - p,
\]

\[
T_{33} = \rho b^2 (x^2 + y^2) + (2\rho bc/\gamma)^2 (x^2 + y^2) - p
\]

The on shell pressure is

\[
p = \mathcal{L} - 2 B_{12}^2 = \frac{\rho}{2} b^2 (x^2 + y^2) - (2\rho bc/\gamma)^2 (x^2 + y^2).
\]

The field equation from variation of \(\rho\) is

\[
\frac{1}{2} b^2 (x^2 + y^2) = \mu,
\]

332
where \( \mu \) is the chemical potential. Differentiating we get the hydrostatic equation

\[
\rho \sqrt{\frac{1}{2}} b^2 (x^2 + y^2) = \nabla p
\]

Relativistic invariance implies momentum conservation in the form \( \partial_i T_{ij} = 0 \). It remains to verify that it holds as a consequence of the field equations.

**Solutions of Einstein’s equations**

In the linear approximation, in the gauge in which

\[
\partial_i g_{ij} = 0
\]

it reduces to Poisson’s equation for the components,

\[
\Delta g_{\mu\nu} = 8\pi G T_{\mu\nu}.
\]

This implies that the stress tensor satisfies

\[
\partial_i T_{ij} = 0,
\]

which seems unlikely. But consider the field equations.

The most important are these

1. The Euler-Lagrange equation

\[
\frac{\delta}{\delta \rho} L = 0.
\]

The Lagrangian has the form

\[
L = \rho K + V,
\]

with \( K \) and \( V \) independent of the density; hence

\[
K = q,
\]

the chemical potential. The gradient is the hydrostatic condition,

\[
\rho \partial_\mu K = \partial_\mu p.
\]

Consider the variation of the action that is generated by a coordinate transformation on all the fields from which it is constructed; variation is a sum,

\[
\delta A = \int d^4 x \left( \delta g_{\mu\nu} T^{\mu\nu} + \sqrt{-g} \sum \delta \psi \frac{\delta L}{\delta \psi} \right).
\]

If the action is invariant, then this variation is zero. On shell, the second term is zero, so on shell, the first term is zero as well

\[
\delta \int d^4 x \delta g_{\mu\nu} \sqrt{-g} T^{\mu\nu} = 0.
\]
In the case of a coordinate transformation,
\[ \delta g_{\mu\nu} = \xi_{\mu;\nu} + \xi_{\nu;\mu}, \]
This equation becomes
\[ \int d^4 x \xi_\mu (\sqrt{-g} T^{\mu\nu})_{;\nu} = 0 \]
and, since \( \xi \) is arbitrary it follow that \( \sqrt{-g} T^{\mu\nu}_{;\nu} = 0. \)
It can be verified directly, but all the field equations have to be used.
In the case at hand, the equation derived from variation of \( \vec{X} \) is just a statement that, if the fields are time independent, then the electric field is zero.
We must translate this solution to the Mannheim coordinates. In these coordinates the non zero coefficients are
\[ Y_{12} = -Y_{21} = X^3 = btr, \quad \psi = c^2 t + at\phi. \]
The terms in the Lagrangian density that contain the metric are
\[ dY^2 = \frac{c^2}{4} g^{\mu\mu'} g^{\nu\nu'} g^{\lambda\lambda'} Y_{\mu\nu,\lambda}(Y_{\mu'\nu',\lambda'} + Y_{\nu'\lambda',\mu'} + Y_{\lambda'\mu',\nu'}) \]
\[ = \frac{c^2}{4} g^{\mu\mu'} g^{\nu\nu'} g^{00} Y_{\mu\nu,0} Y^{\mu'\nu',0} = \frac{c^2}{2} (g^{11} g^{22} - g^{12} g^{12}) g^{00} \]
(this on the assumption that \( g^{i0} = 0 \)). Next, the Maxwell field, a two form.

The variations of the physical components are zero, but the transformation takes us out of the physical gauge. But here we can adopt a remedy that is popular in electrodynamics; we tweak the action by the Lorentz group by making a simultaneous choice of gauge; under this new transformation rule the effect of a Lorentz transformation is nil; the trivial transformation. The answer is that the Galilei group does not act on the field \( \vec{X} \). Strictly, this is true only when \( \vec{\nabla} \cdot \vec{X} = 0. \)
XII.2. Introduction to General Relativity

This sketch of an introduction to General Relativity divides naturally into several parts:

1. A very short summary of the first stage of General Relativity. The elevation of the Lorentzian metric of Special Relativity to a dynamical field with matter as its source, and the idea of geodesic motion. Section XII.2.

2. The development of a dynamical action principle for the metric. Section XII.3.
   a. The gravitational field in empty space.
   b. The identification of the source of the metric field with the energy-momentum tensor of a matter field model.
   c. Interaction with the electromagnetic field.
   d. Tolman’s phenomenology.
A very short summary of the first stage of General Relativity

Special relativity was created in 1905. It arose from the demand that the laws of mechanics have the same invariance group as Maxwell’s theory of electromagnetism, the Poincaré group or the inhomogeneous Lorentz group. It became necessary to formulate physical laws in a language that makes Lorentz invariance manifest, in order that the attention could be directed to physics without the need to worry about consistency with the new principles at each stage. This had the effect of introducing the Lorentzian metric into all the equations of fundamental physics. For example, Maxwell’s field equations now take the form

$$g^{\mu\nu}\partial_{\mu}F_{\nu\lambda} = J_{\lambda}. \quad (12.2.1)$$

The prominence of the metric led Einstein to seek a larger role for it, and this resulted in the idea of geodesic motion. The next great leap forward was the realization that Newton’s equations for the motion of a particle in a gravitational field could be interpreted as geodesic motion in the special metric

$$ds^2 = (1 - \frac{2\phi}{c^2})(cdt)^2 - d\vec{x}^2, \quad (12.2.2)$$

where $\phi$ is the newtonian gravitational potential. The distance between two points in space time is

$$\int_{a}^{b} ds = \int_{a}^{b} \sqrt{g_{\mu\nu}dx^\mu dx^\nu}$$

and the equation that minimizes the value of this expression is

$$\ddot{x}^\mu - \Gamma_{\nu\lambda}^\mu \dot{x}^\nu \dot{x}^\lambda = 0, \quad (12.2.3)$$

where the dots stand for derivatives with respect to $s$ and $\Gamma$ is the metric connection,

$$\Gamma_{\nu\lambda}^\mu = \frac{1}{2}g^{\mu\rho}(g_{\nu\rho,\lambda} + g_{\rho\lambda,\nu} - g_{\rho\lambda,\rho}). \quad (12.2.4)$$

The proliferation of indices is frightening, but most of the coefficients of $\Gamma$ are zero and a little work leads to the revelation that Eq. (12.2.3) is precisely the Newtonian equations of motion.

XII.3. The development of a dynamical action principle for the metric

a. The recognition of geodesic motion was not just an interpretation of Newton’s equations of motion; it was a major discovery with important experimental consequences. But the theory needed further development. In Newtonian theory the potential was determined by solving the Poisson equation with the mass distribution as a source,

$$\Delta \phi = -4\pi G \rho, \quad (12.3.1)$$

with $G$ a universal constant. It relates the field $\phi$ to the source, the matter distribution. The search for a suitable generalization would take 10 years of labor by Einstein, Hilbert, Poincaré and others.
The answer is as follows. A covariant derivative is defined with the help of the metric connection (12.2.4),

\[ D_\mu := \partial_\mu - \Gamma_\mu, \]

The Gaussian curvature tensor is

\[ [D_\mu, D_\nu] = R_{\mu\nu} = R_{\mu\nu}^{\alpha}L_\alpha^b, \]

where the \( L_\alpha^b \) are matrices, the generators of ‘local Lorentz transformations’. Alternatively, if \( A \) is any co-vector field,

\[ [D_\mu, D_\nu]A_\rho = (R_{\mu\nu})^\lambda_\rho A_\lambda. \]

Two contractions leads to the curvature scalar \( R = g^{\mu\rho}(R_{\mu\nu})^\nu_{\rho} \) and this scalar field, by virtue of being the only candidate with required characteristics, is the Lagrangian density for the metric field.

Variations of the action

\[ A_{\text{metric}} = \int d^4x \sqrt{-g}R \]

with respect to the metric,

\[ \delta A_{\text{metric}} = \int d^4x \sqrt{-g} \delta g^\mu\nu G_{\mu\nu} = 0. \]

This is the famous Bianchi identity; it is indeed satisfied identically, for it merely expresses the invariance of the action under coordinate transformations. The simplest way to write this equation is

\[ \partial_{\partial x^\mu} \sqrt{-g}G^{\mu\nu} + \sqrt{-g}G^{\mu\rho}\Gamma_{\lambda\rho}^\nu = 0. \]

Eq. (12.3.4) is Einstein’s field equation for the metric field in vacuum; that is, the field equation for ‘empty space’ ... space-time devoid of matter.

A special solution to equation (12.3.4), stationary and spherically symmetric, was found very soon by Schwarzschild (1917); it has an interesting topological structure and led to the concept of Black Holes. But our interest is in space with matter, as a star or a galaxy, not empty space.
b. In the presence of matter the metric field equation is expected to take the form

\[ G_{\mu\nu} = T_{\mu\nu}. \]  \hspace{1cm} (12.3.6)

Instead of zero, characteristic of vacuum, it has something on the right hand side that represents matter, the source of the gravitational metric field. An integrability condition arises from the fact that the left side satisfies the Bianchi identity, consistency demands that the source tensor \( T \) must satisfy the same condition, the Bianchi constraint,

\[ T^{\mu\nu;\nu} = 0. \]  \hspace{1cm} (12.3.7)

The key to satisfying this condition is that the Bianchi identity is derived from invariance under coordinate transformations. A whole class of models that satisfy this last condition is found by taking the matter tensor to be the energy momentum tensor of a coordinate invariant, Lagrangian field theory, with action

\[ A_{\text{matter}} = \int d^4x \sqrt{-g} \mathcal{L}, \]

and energy momentum tensor

\[ T_{\mu\nu} = 2\frac{\delta}{\delta g^{\mu\nu}} \mathcal{L} - \mathcal{L} g_{\mu\nu}. \]

The constraint is not satisfied identically, but on shell, by virtue of the matter field equations. It is a gift to us, offered by any relativistic field theory.

c. This was indeed the method by which the first consistent field theories with a matter-metric interaction were constructed, first of all the so called Maxwell-Einstein theory that unites electromagnetism and General Relativity. The Lagrangian density is

\[ -\frac{1}{4} g^{\mu\nu} g^{\lambda\rho} F_{\mu\lambda} F_{\nu\rho}, \]

and the energy momentum tensor (verify this)

\[ T_{\mu\nu} = g^{\lambda\rho} F_{\mu\lambda} F_{\nu\rho} - g_{\mu\nu} \mathcal{L}. \]

But this theory does not involve the theory of fluids or other types of matter. Similar field theoretic models are plentiful, but they do not describe extended distributions of matter. No relativistic field theory of fluids has been available.

d. Lacking a dynamical matter model suitable for stellar structure, Tolman, in 1934, proposed a phenomenological expression for the matter tensor,

\[ T_{\mu\nu} = (\rho + p) U_\mu U_\nu - pg_{\mu\nu}. \]  \hspace{1cm} (12.3.8)
Here $\rho$ is a scalar density field possibly associated with the distribution of mass, $p$ is an isotropic pressure density and $U$ is a four vector field. Tolman interpreted the space components in terms of matter flow and imposed the normalization

$$g^{\mu\nu}U_\mu U_\nu = 1. \quad (12.4.2)$$

This condition was inspired by the model of non interacting particles. The model does not have a conserved current, the condition of continuity of classical hydrodynamics is abandoned. Nevertheless, *faute de mieux*, Tolman’s suggestion has been used in almost all investigations of stellar structure, from Eddington and Chandrasekhar forward.

The most obvious objection to Tolman’s formula is that it fails to incorporate an equation of continuity, a defect that is significant in a theory that aspires to be a generalization of hydrodynamics.

Even more important is the fact that Tolman’s matter tensor is not directly related to a matter model and it has no dynamical content. There are no matter equations of motion that could be used to verify the Bianchi identities. Instead, the suggestion is to regard the condition (12.3.4),

$$T^{\mu\nu}_{\ ;\nu} = 0$$

as a substitute for dynamics. Thus matter has no intrinsic properties; instead it is subject to the consistency conditions that allow it to appear as a source for the gravitational field. In this sense it is like the Navier Stokes equation that simply defines the the acceleration of particles in the fluid in terms of unspecified force fields.

An analogy will help put the right accent on this, and is of great interest by its own rights. Maxwell-Dirac electrodynamics couples to field theories, mainly by introducing an interaction term of the form $eA_\mu J^\mu$ in the Lagrangian. Maxwell’s equations now take the form

$$\partial_\mu F^{\mu\nu} = eJ^\nu.$$

The left side is evidently divergence less, so the right hand side must be divergenceless as well; that is, conserved. And this condition, $J^{\mu,,\mu} = 0$, must be satisfied by virtue of the Dirac field equations for the matter field.

It will be objected that, though this is true in Maxwell-Dirac theory, and though it is true that it is a requisite for perturbation theory, it is not satisfied in the theory of electromagnetic fluids. Indeed that is so, and as we have said, Minkowski’s treatment of electrodynamics leaves a lot to be desired.

Finally, Tolman’s formula for the energy momentum tensor is based on the idea of a single, timelike 4-vector velocity field. It cannot accommodate rotating matter, which is fatal since most heavenly bodies are rotating.
XII.5. Rotating heavenly bodies

Our study of cylindrical Couette flow suggests an approach to the study of rotating heavenly bodies. Here I shall use the Lagrangian with the $\vec{X}$ field included, as it stands, without extra terms that may be needed for relativity, in the context of Newtonian gravity. The velocity should therefore be small compared to the velocity of light.

**Solid-body flow**

We examine the case of uniform, solid-body rotation about a fixed axis. The stationary, solid-body solution is $\vec{v} = \omega(-y, x, 0)$, $\omega = \text{constant}$. To satisfy the equation of continuity, the density, the pressure and the temperature depend on $r = \sqrt{x^2 + y^2}$ and $z$ only. Then the only remaining matter equation is

$$\frac{\omega^2}{2} r^2 - \phi = C V T, \quad (1)$$

where $R$ is the distance from the center, and $T$ is the absolute temperature modulo an additive constant. The gradient of this equation is the universally used hydrostatic equation. It coincides with the Navier Stokes equation in the case of vanishing viscosity (the Euler equation).

Besides Eq. (1), and the equation of state, the only other equation of newtonian gravity is Poisson’s equation

$$\Delta \phi = -4\pi G \rho.$$ 

**The earth**

The rotation of the earth is very nearly of the solid-body type. The gradient of $C V T$ is the pressure; it is normal to the surface; therefore the formula for the surface takes the form

$$\frac{\omega^2}{2} r^2 - \phi = \text{constant}.$$ 

Since the rotation is relatively slow it is a good approximation to approximate the potential,

$$\phi \approx -\frac{MG}{R}. \quad (2)$$

In this approximation the formula for the surface takes the form

$$\frac{\omega^2}{2} r^2 + \frac{MG}{R} \approx \text{constant}. \quad (3)$$

As the first term increases from the poles to the equator, $R$ must increase also; the distance from the center is greater at the equator (the equatorial bulge). Since the variation of $R$ from an average $R_0$ is small we can further approximate this as

$$z^2 + r^2 \left(1 - \frac{2}{\omega^2} \frac{R_0^3}{MG}\right) = \text{constant}.$$
This is the shape of the earth as given in the text books. It is an oblate spheroid, flattened at the poles. The problem is to determine an appropriate equation of state.

Turning back to Eq.(1), with no approximations, the first term is

\[ \frac{\omega^2}{2} R^2 \frac{2}{3} (1 - P_2), \]

where \( P_2(\cos \theta) \) is the Legendre polynomial. Since

\[ \Delta R^2 P_2(\cos \theta) = 0, \]

Poisson’s equation for the Newtonian potential takes the form

\[ \Delta \phi = 2 \omega^2 - \Delta C_V T = 4\pi G \rho. \]

The equation of state is an algebraic relation between \( C_V T \) and \( \rho \). Therefore, these functions have the following property. If \( C_V T(R, \theta) \) is constant on the manifolds defined by

\[ f(R, \theta) = \text{constant}, \]

then \( \rho \) is constant on the same manifolds. To this problem the only known solution is that both functions depend on \( R \) only, which is in contradiction with Eq.(2).

**Incompressible density**

Suppose first that the density is constant, then

\[ C_V T = -c R^2, \quad c = \text{constant}, \]

\[ \phi = R^2 \left( \frac{\omega^2}{2} \sin^2 \theta + c \right) = R^2 \left( \frac{\omega^2}{3} + c - \frac{\omega^2}{3} P_2 \right) + \text{constant}, \]  

(4)

\[ \Delta \phi = 2 \omega^2 + 6c = -4\pi G \rho. \]  

(5)

Equivalently, with \( d = c + \omega^2/3 \) a positive constant,

\[ C_V T = (\frac{\omega^2}{3} - d) R^2, \]  

(6)

\[ \phi = R^2 (d - \frac{\omega^3}{3} P_2) + \text{constant}, \]  

(7)

\[ \Delta \phi = 6d = -4\pi G \rho. \]  

(8)

To choose the boundary we first note that no atmosphere has been postulated; nevertheless there is some justification for assuming that pressure, and thus also the temperature and the density, must be constant along the boundary. The velocity is always tangential and this requires only that the boundary is invariant under polar rotations. But the newtonian

341
potential beyond the boundary must be that of empty space, and it must be continuous at the surface.

We conclude, therefore, that the surface is a sphere, with radius $R_0$. In that case the constant in (7) must be chosen so that

$$\phi = (R^2 - 3R_0^2)d - \frac{\omega^2}{3} R^2 P_2.$$  

The Legendre polynomial decreases from the poles towards the equator; the potential and its radial derivative increase and the inward force of gravity decreases, in agreement with observations on Earth. On the surface the internal Newtonian potential takes the value

$$\phi = -R_0^2(2d + \frac{\omega^2}{3} P_2),$$

To ensure continuity at the surface and zero density on the outside we may take the potential beyond the boundary to be

$$\phi = -R_0^3 \frac{2d}{R} - \frac{\omega^2}{3} R_0^5 \frac{P_2}{R^3}, \quad \Delta \phi = 0.$$  

(9) The total mass from Eq.(8) is

$$M = 2d GR_0^3,$$

and the outside metric can be expressed as

$$\phi = -\frac{MG}{R} - \frac{\omega^2}{3} R_0^5 \frac{P_2}{R^3}.$$  

(10) For the earth, a good approximation may be Eq.(2) with a small correction in the direction of Eq.(10).
XI. General velocity fields

The material in this chapter is covered, in more polished form, by the papers


and several unfinished manuscripts

“The effect of galactic rotations on gravitational lensing and the interpretation in terms Dark Matter,”

“Rotating matter in General relativity”, in collaboration with T.J. Wilcox.

“Applications to electrodynamics”, in collaboration with D.Chester.

Perhaps this is the place to make an important announcement. The motivation for searching for an action principle, in a context where it has been sought in vain for 150 years, is not just an aesthetic one, though that would have been sufficient. Actual benefits that accrue from an action principle are far more important. As may easily be observed, a branch of physics theory that does not yet have an action principle is essentially descriptive, with little or no predictive power. A poignant example is electromagnetism in materials, another is astrophysics. See this in contrast with the almost unlimited power of prediction of quantum electrodynamics, where the results of observations are predicted with up to a dozen significant figures. This astounding success of action principles arise from a structure that does not allow much freedom in choosing the interaction. In particular, the kinetic part of the Lagrangian density is essentially fixed, and the interaction turns out to be the simplest one possible. In contemporary hydrodynamics it is not uncommon to introduce equations in which the interaction is represented by polynomials involving both scalar fields and the velocity vector fields. Later it will be seen why this is incompatible with an action principle.

XI.1. Introduction

Many branches of theoretical physics have found their most powerful formulation as action principles. An action principle was known for Eulerian hydrodynamics, but it is limited to potential flows and its use is restricted. The alternative ‘Lagrangian’ version of hydrodynamics also has an action principle formulation, but it does not incorporate the equation of continuity. This chapter presents a general action principle for hydrodynamics, with an extension to thermodynamics, that includes the equation of continuity and that - the main novelty - encompasses general velocity fields.

Here it would be appropriate to tell the story of discovery, where strange clues were understood after much search and finally led to the solution - a solution at any rate. More profound understanding came later and is still coming. Some of this deeper understanding has, nevertheless, been included here since it may help to motivate the reader to go on with a story that would otherwise appear to be both strange and naive.

Degrees of freedom

343
To formulate an action principle one begins by choosing the dynamical variables. The principal variable is a velocity field but, in order that Euler-Lagrange equations give a differential equation for the velocity, the velocity has to be represented as a derivative of a more basic variable. In the case of potential flows it is a space derivative, \(-\vec{\nabla}\Phi\), the alternative is a time derivative, \(d\vec{X}/dt\). The latter is basic in studies of turbulence.

The study of hydrodynamics begins by counting the number of degrees of freedom, the density and the flow velocity together makes four of them. The restriction to potential flow has only two, the density and the velocity potential make one canonical pair.

Minkowski (1908) and Tolman (1934) promoted the 3-vector velocity field to a relativistic 4-vector field. Tolman’s 4-velocity is normalized to reduce the number of degrees of freedom to 3 (plus the density), but neither Minkowski nor Tolman introduced a canonical structure and no equation of continuity appears, either in Relativistic Astrophysics or in the theory of electromagnetism in continuous materials.

Schutz (1967) attempted to construct an action principle for relativistic thermodynamics in which the principal variable would be a 4-velocity. To construct an action principle it was necessary that this 4-vector field be a derivative of something more basic. The gradient of a scalar field gives only one degree of freedom, so Schutz added other 4-vector fields derived from additional tensor fields. This theory has not known further development.

The theory proposed here has 3 velocity degrees of freedom, as expected. The density is a fourth independent variable and the four together make 2 canonical pairs. Because we are aiming at a relativistic theory another way to count degrees of freedom is more to the point. The relativistic generalization of the model developed here will be presented later except for a very brief sketch. But it is relevant to point out that the 4 degrees of freedom that appear in traditional non relativistic hydrodynamics are faithfully reproduced. The inclusion of a scalar velocity potential as one of the dynamical variables is inevitable in view of the need to generate the equation of continuity, a scalar equation, as one of the Euler-Lagrange equations of motion. This field is the canonical conjugate of the density. The additional velocity field introduced here is related to a relativistic 2-form of the type introduced by Ogievetsky and Palubarinov by fixing the gauge; it is well known that it has one propagating mode; hence one canonical pair of independent variables.

**Two kinds of flow**

In the case of potential flows of a homogeneous fluid the velocity field is the gradient of a scalar potential. The Eulerian point of view is natural and convenient; the density and the scalar potential form a canonically conjugate pair of dynamical variables and variation of the scalar velocity potential yields the equation of continuity. In general, the variational approach requires a vector potential as well, such as appears in the alternative, Lagrangian formulation, the velocity is represented as the time derivative \(\dot{\vec{X}}\) of a vector field (a vector potential). The density does not have a conjugate momentum and there is no equation of continuity.

It is a well known and remarkable fact that some phenomena in fluid mechanics are characterized by two kinds of flow. The vortices that are seen in the wakes of ships are created locally; the angular momentum decreases as the inverse square of the distance from the center; this is characteristic of potential flow. In experiments involving fluids confined between a pair of concentric, rotating cylinders (Couette flow) it is observed that motion
generated by steady rotation of the enveloping vessel tends to create a flow pattern that is close to that of a solid body, accompanied by local vortices that are described in terms of potential flow.

Here the Navier-Stokes equation comes through with the successful prediction that, in the presence of viscosity, precisely these two kinds of stationary flow are possible.

In their study of flow patterns in superconducting Helium, Landau (1954) and Feynman (1954) describe the small vortices in terms of potential flow (‘phonons’), while the alternative, competing flow is referred to as ‘motion of the system as a whole’; or solid-body flow (‘rotons’). This point of view is still dominant in the more recent literature, see for example the review by Fetter (2009). No independent field theoretical degree of freedom was associated with the second kind of flow, in this context. But in some important studies of vortex lines the flow vector $\vec{X}$ is a prominent, dynamical field. In an approach initiated by Onsager and pursued in two remarkable papers, by Rasetti and Regge (1975) and by Lund and Regge (1976), they introduce a separate velocity field, associated with the motion of vortex lines. These papers are physically and mathematically related to the present paper.

The Navier-Stokes equation has maintained a dominant position in hydrodynamics for more than 100 years. It has known numerous successes and no real failures, but see Brenner (2013) and especially the review by Martin (2010). It suffers, nevertheless, from an ambiguous relationship with the energy concept. This is understandable, since it was designed to describe processes in which energy is dissipated, but it implies a lack of completeness for which most workers have felt a need to compensate. It is therefore usually supplemented by an ‘energy equation’. But the choice of an expression for this ‘energy’ is seldom canonical and cannot be fully justified. Dissatisfaction with this approach is occasionally expressed in the literature, as in this example (Khalatnikov (1965). After listing a “complete system of hydrodynamic equations” (equations 2-5) he presents one more, “the energy conservation law $\partial E/\partial t + \text{div} Q = 0$”, and then he says: “It is necessary to choose the unknown terms in Eq.s (2-5) in such a way that this last equation be automatically satisfied.”

The variational principle for hydrodynamics that is presented here combines potential flows and ‘solid-body’ flows, just as Navier-Stokes does, but two independent vector fields are needed, one derived from a scalar potential, the other from a vector potential.

The introduction of a pair of velocity fields is by no means new. Please see the quoted review by Martin (2010) as well as earlier reviews quoted therein.

**Development of an action principle for rotational motion**

Up to this point our attention has been focused, deliberately, on the special case when the flow velocities are gradients, the vorticity or curl being zero,

$$\vec{v} = -\vec{\nabla} \Phi, \quad \Rightarrow \quad \vec{\nabla} \wedge \vec{v} = 0.$$

Although it is restrictive, this limitation was accepted because we want to formulate thermodynamics, as far as possible, as a Lagrangian field theory. Many problems in thermodynamics and hydrodynamics involve no flow and in many others the flow is irrotational. The theory of potential flows therefore has many applications. Some of the most vital
problems of hydrodynamics are, nevertheless, concerned with turbulence. A relativistic
Lagrangian is also needed for General Relativity and here too the restriction to potential
flows is hard to bear. To discover how to achieve greater generality we shall now turn
our attention to some simpler systems where the restriction to flows of the gradient type
cannot be maintained.

The rest of this section is a digression and can be skipped. The main point that is made
is to emphasize the need for better measurements of the temperature.

Incompressible limit of the ideal gas

In this chapter we shall be dealing mostly with liquids. Since it is advantageous to keep
the discussion of hydrodynamic flows as simple as possible, we shall sometimes replace the
ideal gas with index \( n \) by the limit defined by letting \( n \) go to zero. We therefore record at
this place the applicable formulas. The free energy density and the pressure, in the limit
when \( n = 0 \), are

\[
 f = \mathcal{R} T \ln \rho, \quad p = \mathcal{R} \rho T.
\]

Apparently, the temperature is just a parameter, though not necessarily uniform. The for-
mula for the pressure is useless and has to be replaced, in hydrodynamics, by an expression
in terms of the density. The adiabatic condition becomes

\[
\mathcal{R} \ln \rho + S = 0,
\]

so that if the density is to be non-uniform the specific entropy has to be non uniform as
well. Note that this relation does not fix the temperature. The adiabatic derivative,

\[
\frac{dp}{d\rho} = \kappa = \mathcal{R} T
\]

is the square of the velocity of sound. That equation too becomes meaningless and is
replaced by \( \partial p(\rho)/\partial \rho \). However, this may be too hasty.

For an ideal gas

\[
T = (\rho/k)^{1/n}, \quad \ln k = n - \frac{S}{\mathcal{R}}.
\]

It may be of interest to examine the limit with more care. If we set

\[
S = S_0 + nS_1, \quad \mathcal{R} \ln \rho = -S_0 + n\left(\frac{B}{\mathcal{R}} + 1\right), \quad S_0 = \text{constant},
\]

then we find that, in the limit \( n \to 0 \),

\[
\mathcal{R} \ln T = S_1 + B, \quad \mathcal{R} \ln \rho = -S_0, \quad (11.1.1)
\]

and

\[
\mathcal{R} \ln \frac{p}{\mathcal{R}} = S_1 + B - S_0 \quad (11.1.2)
\]
or
\[ p = \frac{R e^{B/R} e^{(S_1 - S_0)/R}}{R} \].

The pressure may have its origin in minute variations of the density (first factor), in minute variations of the entropy (second factor), both escaping direct observation. Of course, it is not proposed that every incompressible liquid is the limit of an ideal gas. It is just that this limit is available and thus allows us to include at least one type of incompressible liquid in the discussion. Unfortunately, we have no information about the functions $B$ and $S_1$. The conclusion is that, in the incompressible limit, the pressure is determined by the other variables through the equations of motion, but this information does not close the loop by feeding back into the equation. This is exactly how the pressure is dealt with in standard treatment and it is responsible for the fact that the predictive power is very limited. Any real test of the theory must be done with compressible fluids.

The only thing that can be said about the incompressible limit of an ideal gas is that the density is determined by the entropy. This is exactly what we find in Landau and Lifshitz, Fluid Mechanics, page 45. However, what is done on the next page is more difficult to understand. There, the incompressible fluid is suddenly replaced by an ideal fluid. It would be better to deal with an ideal fluid throughout, in the approximation of small values of $n$, to see if the final quantity that is calculated there depends on the derivatives $B$ and $S_1$.

Measurements of the density become both difficult and irrelevant for some liquids. To verify the model one has to measure the temperature, though that too is difficult, to measure and to interpret, even on a stationary state.

In the approximation that takes the liquid to be incompressible, pressure and density become independent variables and the mathematical model becomes under determined. We are reduced to asking whether a particular flow profile can be explained in terms of a reasonable pressure profile, or conversely. We can investigate the pressure in a situation where the flow is steady, but we cannot be sure that such a flow exist. The complete theory is thermodynamics with an equation of state.

**XI.2. Couette flow, gradient velocity**

This is the simplest example, and therefore best suited to serve as a first introduction to vorticity.

Consider a situation that is effectively 2-dimensional because of translational symmetry; for example, when nothing depends on a vertical coordinate $z$ and the flow is confined to the horizontal $x,y$ plane. Couette flow is the case of a pair of concentric cylinders that can be rotated around a common axis. With both cylinders at rest we postulate a state in which the space bounded by the two cylinders is filled with a fluid at rest with all variables time independent, and uniform. The effect of gravity will be neglected. The cylinders are long enough that end effects can be neglected as well.

Plane Couette flow, flows confined between moving planes, is easier to analyze but less instructive; it is relegated to Section 6 of this chapter.

Fig.11.2.1. Cylindrical Couette flow.

We begin to rotate the inner cylinder. For this to have any effect on the fluid we need to postulate a degree of adherence of the liquid to the surface of the inner cylinder. The
layer of the fluid closest to the cylinder is dragged along, in a process that transfers energy to the liquid. It is hoped that, with care, the acceleration is a quasi stationary sequence of changes. If a stationary state, or one that can be considered as approximately stationary over moderate time periods, is eventually reached, in which \( \vec{v} \) and the other fields are all approximately time independent, then it would perhaps be reasonable to assume that energy is no longer being transferred. Whether this is true or not can only be determined by a deep study of heat transfer, or by experiment. Sufficient for our analysis is the assumption that, in an approximately stationary state, the frictional force between the cylinder and the nearest layer of fluid is rendered ineffective and that the relative velocity is constant, perhaps zero. This is summed up by the no-slip boundary condition

\[
\vec{v}|_{r=r_0} = \vec{v}|_{\text{inner boundary}} = \omega_0(-y, x).
\]

The angular velocity is a constant in time, equal to that of the cylinder, or less. But in the latter case (if it is less) it is likely that a steady flow of energy (‘heat’), originating from friction at the boundary layer and/or from the inner cylinder is transmitted through the fluid and dissipated through the outer cylinder. (One may call this an example of ‘heat transfer’, but this is not much more than giving a name to what we do not understand.)

The no-skip boundary condition has been widely applied, and because we wish to compare our approach to the traditional one it serves our purpose to do the same. At a later stage of development we may wish to make use of a much more detailed description of boundary layers, as may be found, for example, in REF

The rotational axis is the \( z \) axis and the velocity is represented as a 2-vector in the \( x, y \) plane, later as a 3-vectors. The coordinates are inertial and Cartesian. No boundary conditions are imposed on the velocity at the outer wall, so far.

We propose to treat this idealized stationary state as an adiabatic system; failure to succeed will constitute important information and a formidable challenge. We begin with the familiar Lagrangian density

\[
\mathcal{L} = \rho(\dot{\Phi} - \vec{v}^2/2) - f - sT. \tag{11.2.1}
\]

**Horizontal flow**

The problem is essentially 2-dimensional and \( r \) is the 2-dimensional, polar radius. When all the variables are time independent the Euler-Lagrange equations reduce to

\[
\text{div}(\rho\vec{v}) = 0, \quad \dot{\Phi} - \vec{v}^2/2 = \mu, \tag{11.2.2}
\]

where \( m \) is the chemical potential and \( \dot{\Phi} \) is a constant. In the case of an ideal gas,

\[
\dot{\Phi} - \vec{v}^2/2 = (n + 1)RT. \tag{11.2.3}
\]

If we assume that \( s = \rho S \), with \( S \) uniform as usual, then this last equation can be transformed to the more familiar Bernoulli equation,

\[
\rho\ddot{v} + \rho \nabla(\vec{v}^2/2) + \nabla p = 0. \tag{11.2.4}
\]
Because we are going to deal with systems that may be dissipative, the assumption about the entropy is just a working assumption, subject to revision. For this reason we prefer to use Eq.(11.2.3); it is independent of any assumption about the entropy. It follows that the most interesting observations are those that record the temperature.

We assume that the flow lines are circles, \( r^2 = x^2 + y^2 = \text{constant} \),

\[ \vec{v} = \omega(r)(-y, x). \]

This is a field with vanishing curl only if

\[ \omega(r) = ar^{-2}, \quad a = \text{constant}, \]

and even then it is not, in the strict sense, a gradient. Although

\[ \vec{v} = a\vec{\nabla}\theta, \quad \theta := \arctan \frac{y}{x}, \]

the scalar \( \theta \) is not one-valued, though the vector field is. By allowing the velocity potential \( \Phi \) to be multivalued,

\[ \vec{v} = a\frac{(-y, x)}{r^2} = -\vec{\nabla}\Phi, \quad \Phi = a\theta, \quad a = \text{constant}, \]

we are able to extend our approach to include special rotations, with \( \vec{\nabla} \wedge \vec{v} \neq 0 \) at the origin only (though ill defined at that one point). In the present case the origin is outside the vessel and the curl is zero at all points of the fluid.

This is the only possible stationary, horizontal, circulating, potential flow. The angular velocity is greater at smaller radius; it is therefore likely that it is driven by rotating the inner cylinder and that it settles according to the no slip condition. There is no opportunity to adjust the outer boundary conditions; either the fluid slips there or else the angular speed of the outer cylinder must be adjusted in accordance with \( \omega(r)r^2 = a \). We assume that this is done.

The divergence of \( \vec{v} \) (for any choice of \( \omega(r) \)) is zero, so the equation of continuity reduces to \( \vec{v} \cdot \vec{\nabla}\rho = 0 \), requiring \( \rho \) to depend on \( r \) and \( z \) only. From now on it is taken for granted that \( \rho \) is a function of \( r \) and \( z \).

This type of stationary motion has been observed, but the principal goal of most experiments has been to measure the onset of turbulence as, with increasing rotational speeds, the laminar flow breaks down. Our interest shall be focused, in the first place, on the laminar flow at low angular speeds.

The principal equation of motion, Eq. (11.2.3) reduces, in the case that the velocity takes the form (11.2.5), to

\[ \frac{a^2}{2r^2} + (n + 1)RT = C = \text{constant}. \]  

* In contrast with the foregoing, this equation is independent of any assumption about the entropy.
It appears that this temperature lapse has not been measured. The experiment would be difficult to interpret because of the suspected heat flow caused by the friction, within the liquid and between the liquid and the wall. As a matter of fact all theoretical interpretation of this experiment is incomplete for the same reason.

In the limiting case of an incompressible liquid it gives

\[
\frac{a^2}{2r^2} = C - \mathcal{R}T, \quad \mathcal{R}T = e^{(S_1+B)/\mathcal{R}}.
\]  

(11.2.7)

This is consistent with the interpretation of the fluid as a collection of classical particles, and in full agreement with the Navier Stokes equation, except that the latter simply balances the pressure gradient against the centripetal force and a contribution associated with the viscosity, usually without relating it to an equation of state or to the temperature, and very rarely connecting it to entropy. ** The kinetic energy acts as an effective potential and gives rise to a repulsive, radial force, balanced by the negative of the potential gradient, Eq.(11.2.4). We shall have more to say about this interpretation later.

** It is common, in the case of liquids, to treat them as incompressible. In this case, as Eq.(11.2.9) shows, it is justified to treat the pressure gradient as unknown, to be determined by the need to get reasonable solutions to the equations. But of course this puts severe limits on the predictive power of the theory.
Fig. 11.2.1. The gradient flow that results from rotating the inner cylinder. The curved lines show the positions of particles initially lined up radially. The inner cylinder is the driver of the motion and it is turning anti-clockwise.

XI.3. Solid-body flow

Consider next the complimentary experiment in which there is friction at the outer cylinder only, making it the driver of the motion. The problem is the same, except for different boundary conditions,

\[ \vec{v}|_{r=r_1} = \vec{v}|_{\text{outer boundary}} = \omega_1(-y, x). \]

Our initial study of potential motion revealed only one solution, and here its application is anti-intuitive since it has the angular velocity increasing towards the center, away from the driving wall. For the general problem, in which the two cylinders move independently, we have two independent boundary conditions but only a one dimensional space of potential motions. Clearly we have come to a situation where we cannot limit our attention to gradient velocity fields. Still, we are not yet ready to concede that this is the limit of the Lagrangian approach to thermodynamics.

It has been reported that the motion of a liquid, even a rarified gas, driven by the rotation of the outer cylinder, tends towards the motion of a solid body. As the speed is increased, various instabilities set in, but our first concern is to understand the laminar motion observed at low speeds.

The motion of a rigid body is characterized by the velocity field

\[ \vec{v} = b(-y, x, 0), \quad b \text{ constant}, \]

and this is not a gradient. If we assume this flow in the context of the equations of motion derived for potential flow; that is, if we simply use the above velocity field in the field equations, then we obtain similar results; in particular, instead of (11.2.7),

\[ \frac{b^2}{2} r^2 = C - RT, \quad RT = e^{(S_1+B)/R}. \] (11.3.1)
Here the left side has the wrong sign, the ‘fictitious force’ is attractive. Note that to get
this unphysical result we applied the potential theory beyond its domain of validity. It is
a problem that shall frustrate all efforts, until the only possible solution pops into view.

It is evident that we have to escape from under the restriction to gradient velocities. To
gather further clues to help us proceed it is natural to ask how the Navier Stokes equation
handles this situation.

**Navier Stokes**

The standard treatment of non-potential flows is based on the continuity equation and
the Navier-Stokes equation,

\[
\dot{\rho} + \text{div}(\rho \vec{v}) = 0,
\]

\[
\rho \left( \vec{v} + (\vec{v} \cdot \vec{\nabla})\vec{v} \right) = -\vec{\nabla}p - \mu \Delta \vec{v}.
\]  

(11.3.2)

This allows for flows of both kinds, potential flow and solid body flow. The new elements
are three. First, the nature of the velocity field is not constrained to be a gradient. In
the second place the term \( \rho \vec{\nabla} v^2/2 \) in (11.2.3) has been replaced by the term \( \rho (\vec{v} \cdot \vec{\nabla})\vec{v} \) in
(11.3.2). Finally, there is a new term, the viscosity term \( \mu \Delta \vec{v} \).

If the coefficient \( \mu \) vanishes, of the second equation only the radial component remains.
It is an ordinary differential equation for the functions \( \omega, \rho \) and \( p \) and the system is un-
derdetermined. If \( \mu \neq 0 \), the tangential component imposes the additional requirement that

\[ \Delta \vec{v} = 0. \] 

(11.3.2)

We shall see that this leads to unique solutions for reasonable boundary conditions, either
or both cylinders driving. The fact that uniqueness is obtained only when the viscosity is
taken into account is more than a little odd, in our opinion, since there is no lower limit
on the value of the coefficient \( \mu \). But this is the standard treatment. Given the form

\[ \vec{v} = \omega(r)(-y, x, 0). \]

of the velocity, but with \( \omega(r) \) now arbitrary since the velocity field is not required to be a
gradient, within the class of flows that we are considering the general solution of Eq.(11.3.2)
is

\[ \vec{v} = \omega(r)(-y, x, 0), \quad \omega(r) = \frac{a}{r^2} + b, \]

(11.3.3)

\( a \) and \( b \) constants.

The boundary conditions at \( r = r_0, r_1 \) give us

\[ \omega(r_0) = ar_0^{-2} + b = \omega_0, \quad \omega(r_1) = ar_1^{-2} + b = \omega_1, \]

When the \( a \) term dominates we have the highest angular velocity at the inner surface; this
is as expected when the inner cylinder is driving. If the \( b \) term dominates we have nearly
constant angular velocity, as expected for a solid body. When the outer cylinder is driving
we expect that the angular velocity will be larger at the outer boundary. If both cylinders
are rotating in opposite directions, and both are driving, then $\omega(r)$ will have a change of sign. Explicitly,

$$a = \frac{\omega_0 - \omega_1}{r_0^{-2} - r_1^{-2}},$$

and

$$b = \frac{1}{r_1^2 r_2^2} \frac{r_1^2 \omega_1 - r_0^2 \omega_0}{r_0^{-2} - r_1^{-2}}.$$

The result is that Navier Stokes, with non zero viscosity, has just one extra solution besides the gradient, allowing it to satisfy no slip boundary conditions for all values of the angular velocities of the two cylinders. It is significant that this new solution, with $\vec{v} \propto (-y, x, 0)$, is the same as the static state observed from a rotating reference frame; its existence is required by the relativistic equivalence theorem. However, reformulating the theory in terms of comoving (rotating) coordinates will not enhance our understanding, more likely the opposite is true.

An important difference between Navier Stokes and the theory attempted in the preceding subsection is the following. As we said, the term $\vec{\nabla} v^2/2$ in Eq. (11.2.3) is replaced by the term $\vec{v} \cdot \vec{\nabla} \vec{v}$ in (11.3.1). One verifies that, when the velocity field is a gradient, both expressions are equal, but in the case of solid body rotation there is a change of sign,

$$\vec{\nabla} \vec{v}^2/2 = b^2 \vec{r} \text{ but } \vec{v} \cdot \vec{\nabla} \vec{v} = -b^2 \vec{r}.$$

The force produced by the first expression is attractive, while the Navier Stokes force is repulsive, as it must be. (A rapidly rotating rigid body breaks apart, it does not collapse towards the center!) Evidently, we must understand what lies behind this difficulty.

Persisting in our search for a variational principle we shall seize on this little paradox of a wrong sign. This will lead to a solution of our problem. At that stage interest in the process of discovery fades and the reader may prefer to skip it.

The centrifugal force

In particle physics the dynamical variable is the position of the particle.

The ‘fictitious’ centrifugal force in particle physics can be seen as coming from an effective ‘kinematic’ potential. The force is $\omega^2 \vec{r}$ directed outwards, and this is $-\vec{\nabla}[-\omega^2 r^2/2]$, so the effective potential is the negative of the kinetic energy. The unexpected sign comes from the fact that the the origin of this potential is in the term $m \vec{x}^2/2$ in the Lagrangian; this term appears with the same sign in the hamiltonian. Confusing? Let us say it in another way, the term in question appears with the positive sign in the Lagrangian and with the positive sign in the hamiltonian; but its contribution to the equation of motion is opposite in sign from a normal potential. We have seen that our potential model when used outside its domain of validity, gives the wrong sign in the equation of motion.
Fluid mechanics can be understood as a field theory, and there are two versions, sometimes claimed to be equivalent, a Eulerian formulation and an alternative ‘Lagrangian’ formulation, see Section I.7. The principal distinction is the following.

In the Eulerian formulation of fluid mechanics the dynamical variables are the scalar density field and a velocity vector field. This theory becomes a Lagrangian field theory, in the sense of being based on a dynamical action principle, only in the case that the velocity field is the gradient of a “velocity potential”. Thus formulated, this theory cannot describe solid body rotation because the term $\rho \vec{v}^2/2$ appears with the positive sign in the Lagrangian and therefore with the negative sign in the Hamiltonian. Let us be clear about this: the velocity associated with rotational motion in the $x, y$ plane is $\omega(-y, x, 0)$ and it is not a gradient, but there is a further obstacle. If we introduce a term $-\omega^2/2$ in the Lagrangian we get the right sign in the Hamiltonian but the wrong sign in the equations of motion (or vice versa).

The ‘Lagrangian’ version of fluid mechanics handles the centrifugal force very well, just as particle physics does, but it appears in the kinetic part of the Lagrangian. This way one gets the right sign for solid-body motion, but the wrong sign for the potential flow. This is because the dynamical variables are not $\rho$ and $\vec{v}$ but $\rho$ and a vector field usually denoted $\vec{x}$, satisfying $\dot{\vec{x}} = \vec{v}$. To avoid confusion we shall call it $\vec{X}$. * The books explain that this vector field denotes the position of a particle in the fluid; one chooses an initial value and calls on the equations of motion to predict the future path of the theory. This

* Actually, to describe both types of flow correctly one needs two vector fields, as explained below.
explanation tends to obscure the fact that this version of the theory is also a field theory, with field variables $\rho$ and $\vec{X}$, and 

$$\vec{v} := \dot{\vec{X}}.$$ 

The velocity is the time derivative of the basic field variable and the term $\rho \vec{v}^2/2$ is now in the kinetic part of the Lagrangian.

The Navier Stokes equation is based directly on particle mechanics. The main equation does not involve the gradient of a hamiltonian and no hamiltonian exists. The dynamical field is the velocity but the gradient of no kinetic potential enters the calculations. Instead the substantive derivative appears,

$$\frac{D\vec{v}}{Dt} = \frac{\partial \vec{v}}{\partial t} + (\vec{v} \cdot \vec{\nabla}) \vec{v}.$$ 

Let us look once more at the example of rotary motion. The gradient theory describes a motion of the type $\vec{v} = (a/r^2)(-y, x, 0)$, and in this case

$$(\vec{v} \cdot \vec{\nabla})\vec{v} = \vec{\nabla} \vec{v}^2/2.$$ 

But in the case of solid body motion, when $\vec{v} = b(-x, y, 0)$ ($a$ and $b$ are constants), we find that

$$(\vec{v} \cdot \vec{\nabla})v = -\vec{\nabla} \vec{v}^2/2.$$ 

The Navier Stokes equation is based on particle mechanics and both kinds of motion are treated correctly, but there is no hamiltonian; this is because the dynamical variable is the velocity. To get beyond this stage, to set up a Lagrangian theory of non potential flow, it is necessary to introduce the field $\vec{X}$, as in the ‘Lagrangian’ version of fluid mechanics.

XI.4. Lagrangian foundations for the Navier Stokes equation

In their studies of vortices in superfluid Helium, Landau and Lifshitz (1955) and Feynman (1955) state that the motion within isolated vorticies is irrotational, except for the singularity at the center. This justifies the introduction of a velocity potential, in terms of which the formulation of a quantization condition for vorticity is natural. In the more recent literature, with a wider field of applications, the Fetter-Walecka Lagrangian is used explicitly (Fetter 2010). The role of the solid-body component of the flow is not neglected, in fact it is quite essential, but it is regarded as a constraint, as having an effect only on the boundary conditions. It is as if the non-potential component of the flow is fixed; no independent degree of freedom was attributed to it. This approach is moderately successful, but the existence of an independent degree of freedom cannot be denied. Our proposal, the final aim of which is to imbed the Navier-Stokes equation into an action principle, takes this circumstance as a cue.

With the Lagrangian density that we have used for potential flow as a starting point, we begin by adding a new term,

$$\mathcal{L} = \rho \left( \Phi - \frac{\rho}{2} (\vec{\nabla} \Phi)^2 + \frac{1}{2} \dot{\vec{X}}^2 \right) - f - sT.$$ 

355
This is the proposed solution to our search for a variational principle. In simple terms, it is the obvious way out of an impasse. We have two formulations of hydrodynamics; one is limited to gradient flows, the other does not account for the equation of continuity, so we need both!

The hamiltonian density is then

\[ H = \frac{\rho}{2} (\nabla \Phi)^2 + \frac{\rho}{2} \dot{X}^2 + f + sT. \]  \hspace{1cm} (11.4.1)

This is correct for certain non potential flows, most notably for solid body rotation, when

\[ \dot{X} = b(-y, x, 0). \]

The new vector field is expected to make a contribution to the conserved flow, so another term is needed; thus

\[ L = \rho \left( \dot{\Phi} + \frac{1}{2} \dot{X}^2 + \kappa \dot{X} \cdot \nabla \Phi - \frac{1}{2} (\nabla \Phi)^2 \right) - f - sT, \]  \hspace{1cm} (11.4.2)

where \( \kappa \) is a constant whose value must remain unspecified until its role is understood.

Let us list all the Euler - Lagrange equations associated with (11.4.2).

1. Variation of \( T \): the adiabatic relation, as before.
2. Variation of \( \Phi \): the continuity equation, now

\[ \dot{\rho} + \nabla \cdot (\rho \vec{v}) = 0. \]  \hspace{1cm} (11.4.3)

The flow velocity is

\[ \vec{v} := \kappa \dot{X} - \nabla \Phi. \]  \hspace{1cm} (11.4.4)

3. Variation of the vector field:

\[ \frac{\partial}{\partial t} (\rho \vec{m}) = 0, \]  \hspace{1cm} (11.4.5)

where the ‘momentum’ is

\[ \rho \vec{m} := \rho (\dot{X} + \kappa \nabla \Phi). \]

We shall have much to say about this equation; at first sight the absence of a source term seems odd.

4. Variation of the density:

\[ \dot{\Phi} - \frac{1}{2} (\nabla \Phi)^2 + \frac{1}{2} \dot{X}^2 + \kappa \dot{X} \cdot \nabla \Phi - \frac{\partial f}{\partial \rho} - ST = 0. \]  \hspace{1cm} (11.4.6)

The hamiltonian is still as given in Eq.(11.4.1). Note that two independent vector fields, \( \dot{X} \) and \( \nabla \Phi \), are needed to get the correct signs for both squared velocity terms; opposite in (11.4.6), both positive in the hamiltonian. The term \( \dot{X} \cdot \nabla \Phi \) does not contribute to the hamiltonian, but it is crucial for the equation of continuity.

356
Numbers 2 and 3 are solved by taking $\rho$ to depend on $r$ only, $\Phi$ constant, and

$$\Phi = t\dot{\Phi} + a\theta, \quad \vec{\nabla}\Phi = \frac{a}{r^2}(-y, x, 0), \quad \vec{X} = bt(-y, x, 0). \quad (11.4.7)$$

when these solutions are inserted into (11.4.6) we get, for an ideal gas

$$\frac{a^2}{2r^2} - \frac{b^2}{2}r^2 + \kappa ab = C - (n + 1)RT. \quad (11.4.8)$$

The term $\vec{X} \cdot \vec{\nabla}\Phi$ is constant in this case.

**Taking stock**

With the Lagrangian density (11.4.2) a significant forward step in our program has been achieved. We now know that the idea of a viable Lagrangian formulation of thermodynamics is not absolutely limited to potential flows. This leaves many things yet to be done, for example, the complete interpretation of the two vector fields that make up the total flow, and the integration with electromagnetism. Most of all, we need to apply the new, tentative insight to a range of phenomena; all that we know at present is that our new Lagrangian density is suitable for cylindrical Couette flow. Before ending this chapter we shall examine a closely related phenomenon, the flow along plane, moving walls or linear Couette flow. See Section 6.

The specific model for cylindrical Couette flow has some features that warn of difficulties that may arise. So far, the field $\vec{X}$ appears through its time derivative only, but for various reasons we must expect space derivatives to appear as well. From at least one perspective such fields are disquieting. One of the most tempting interpretations of the field $X$ relates it to the electromagnetic vector potential; this is because of the existence of various effects (including the Barnett effect) that signal a direct link between magnetization and rotation. But the solution (11.4.7) gives a specific value for the ‘magnetic’ field $\vec{\nabla} \wedge \dot{\vec{X}}$ that appears to be quite strong. We know that the steady rotation of the earth is accompanied by a magnetic field that is strongly erratic in direction and magnitude. For this reason, while we are intrigued by the possibility of an interpretation of the vector field that is strongly tied to electromagnetism, we may be doubtful of a direct relationship.

A more serious objection, one that we shall take as a principal guide to the completion of the theory, is that it has too many degrees of freedom to serve as a formulation of simple hydrodynamics.

We shall continue this discussion in Section ?.

**XI.5. Comparing two approaches**

**Viscosity**

An important feature of reality that is encompassed by the Navier Stokes equation is viscosity. In the Lagrangian approach one concedes from the start that viscosity is absent from the adiabatic equations of motion. But applications of the theory do not end there.

357
It will be recalled that a major trend in thermodynamics, advanced under the banner of non-equilibrium thermodynamics, actually consists of formulating a set of conservation laws: conservation of mass (the continuity equation), the conservation of momentum (the Navier-Stokes equation) and the conservation of energy. Then some of these equations are replaced by ‘non-conservation equations’, the most important example being the Navier-Stokes equation, a deformation of the momentum equation,

$$\rho \left( \ddot{\vec{v}} + (\ddot{\vec{v}} \cdot \vec{\nabla}) \vec{v} \right) = -\vec{\nabla}p - \mu \Delta \vec{v}. \quad (11.5.1)$$

The vector field $\rho \vec{v}$ side is interpreted as the momentum; it is not conserved but the change is determined by the forces, including both the pressure and the effect of viscosity. The equations describe a system that is subject to external forces and they affect the momentum, beyond the acceleration that is due to the pressure.

With the formulation of adiabatic dynamics as an action principle we are well situated to adopt the same procedure. Recall that variation of the action with respect to the field $\vec{X}$ gives

$$\frac{d}{dt} \rho (\dot{\vec{X}} + \kappa \vec{\nabla} \Phi) = 0. \quad (11.5.2)$$

We shall interpret this equation as the conservation of the ‘momentum’

$$\vec{m} = \rho (\dot{\vec{X}} + \kappa \vec{\nabla} \Phi).$$

In the presence of dissipation caused by external forces we follow the vaunted strategy, replacing the equation by

$$\frac{d}{dt} \rho (\dot{\vec{X}} + \kappa \vec{\nabla} \Phi) = \mu \Delta (\dot{\vec{X}} - \frac{1}{\kappa} \vec{\nabla} \Phi). \quad (11.5.3)$$

To compare this with the Navier-Stokes equation we identify the flow velocity

$$\vec{v} := \kappa \dot{\vec{X}} - \vec{\nabla} \Phi$$

with the velocity of Navier-Stokes. To obtain an equation for this velocity we must use Eq.(11.5.3) or

$$\ddot{\vec{X}} = \frac{\nu}{\kappa} \Delta \vec{v} - \kappa \vec{\nabla} \Phi - \dot{\rho} \left( \dot{\vec{X}} + \kappa \vec{\nabla} \Phi \right).$$

together with the Euler-Lagrange equation that comes from variation of the density. Taking the gradient of that equation we obtain

$$-\frac{d}{dt} \vec{\nabla} \Phi = \vec{\nabla} \left( - \frac{1}{2} (\vec{\nabla} \Phi)^2 + \frac{1}{2} \dot{\vec{X}}^2 + \kappa \dot{\vec{X}} \cdot \vec{\nabla} \Phi - \frac{\partial f}{\partial \rho} - ST \right)$$

Combining this with (11.5.3) we get,

$$\rho \left( \ddot{\vec{v}} + (\ddot{\vec{v}}^2 + 1) \left[ (\vec{\nabla} \Phi)^2 / 2 - \dot{\vec{X}}^2 / 2 - \dot{\vec{X}} \cdot \vec{\nabla} \Phi \right] \right) = -\vec{\nabla}p - \mu \Delta \vec{v}. \quad (11.5.4)$$
This is in substantial agreement with Navier-Stokes in the case of cylindrical Couette flow, as we have seen, provided that the parameter $\kappa$ is not too large.

**Predicting the flows**

A major success of the application of the Navier Stokes equation to laminar, cylindrical Couette flow is the prediction, on the basis of the tangential component (11.3.2) - $\mu \Delta \vec{v} = 0$, of just two kinds of flow, potential flow and solid-body flow. Intuitively, the latter is a little unexpected; this flow is attained, or nearly attained, when the outer cylinder is driving and the inner cylinder is slipping. The Euler-Lagrange equations associated with the Lagrangian density (11.4.2) place no restrictions on the factor $b$ in the solution $\vec{X} = b(-y, x, 0)$. But after introducing the viscosity we find that in this respect qs well, the action principle handles the problem exactly as Navier-Stokes does.

**The density profile**

Here we shall make the very questionable assumption that, at equilibrium, the temperature is uniform. A very different approach to calculating the density will follow in Section ??

When the angular velocity $b$ varies with $r$, the term $\vec{X} \cdot \vec{\nabla} \Phi$ in the Lagrangian density is no longer a constant. If $b \propto r^{-\epsilon}$ we obtain, for stationary configurations,

$$\frac{1}{2} \dot{\vec{X}}^2 + \dot{\vec{X}} \cdot \vec{\nabla} \Phi - \frac{1}{2} (\vec{\nabla} \Phi)^2 = \frac{a^2}{2r^2} - \frac{b_1^2}{2}r^{2(1-\epsilon)} + ab_1 r^{-\epsilon} = C - (n + 1)RT. \quad (11.5.4)$$

This is in substantial agreement with Navier Stokes in the limit of small $\epsilon$. And it offers an extra free parameter for a small amount of fudging.

Fig. 11.5.1 shows a sample temperature profile. The small dip for small radius is produced by the $ab$ term on the left hand side of (11.5.12). A similar feature has been observed (REF).

![Temperature profile](image)

Fig.12.7.3. A temperature profile for cylindrical Couette flow, plotted against the horizontal radius. The position of the walls is not indicated.
The expression \((n + 1)RT\) on the right hand side is not valid at very low temperatures, but in the case of an ideal gas, with uniform entropy, it is proportional to a power of the density and it is perhaps reasonable to expect it to go to zero with the density. In that case one may expect the onset of turbulence to occur for a fixed value of the parameter

\[
\frac{a^2}{2r^2} - \frac{b^2}{2} r^{(1-\beta)} + ab_1 r^\beta = C_0. \tag{11.5.5}
\]

In the \(a, b\) plane this is a hyperbola open to the positive \(b\) axis. This too is in qualitative accord with experiments.

The energy

The principal reason for bringing out an alternative to the approach that relies of the Navier Stokes equation is of course the improved position of the energy concept. The equations of motion do not differ greatly from the equations used in the traditional method but, instead of an hoc formula for “energy” that is required to be conserved as an additional postulate, we have a first integral of the equations of motion. We note that some authors require that the “energy equation” hold in consequence of the other conservation equations, thus expressing a point of view similar to ours. Khalatnikov 1956.) In the presence of viscosity the rate of energy dissipation can be obtained from the equations of motion,

\[
\frac{d}{dt} \tilde{\mathcal{H}} = \tilde{\nabla} \cdot \mu \Delta \tilde{\mathbf{v}}.
\]

The usefulness of a variational formulation can only be demonstrated by application. From a practical point of view the advantages may be limited. The theory is presented, not because the traditional point of view is found wanting, but because, if an action principle is available then making use of it presents advantages.

XI.6. The constraint

There was no hint, in the first 5 Sections of this chapter, of how the number of dynamical degrees of freedom is reduced to just 4, and a full explanation will be deferred to the next Chapter. This is because the concepts that are involved are more familiar, and simpler, in the relativistic context. The relativistic theory is a 4-dimensional gauge theory; there appears, besides the 3-component field \(\tilde{\mathbf{X}}\) another vector field \(\tilde{\mathbf{\eta}}\) that can be transformed to zero by a gauge transformation. In the non relativistic theory that is the present subject this field does not appear, but the field equation that results from its variation must be taken into account. This is the constraint

\[
\tilde{\nabla} \wedge (\rho \tilde{\mathbf{X}} + \kappa \rho \tilde{\nabla} \Phi) = 0.
\]

With a gauge fixing condition \(\tilde{\nabla} \cdot \tilde{\mathbf{X}} = 0\) it has the effect of reducing the total number of independent variables to 4, as in ordinary hydrodynamics. See Section . Here we just want to mention an apparent difficulty. In the limiting case of an incompressible fluid,
when the density is uniform, the constraint implies that the curl of $\dot{X} = 0$. This would, of course, invalidate the entire theory. But this apparent difficulty will find a natural resolution below.

There is no obvious difficulty when the density is non-uniform, since in general the constraint is

$$(\nabla \rho) \wedge \dot{X} + \kappa \rho \nabla \wedge \dot{X} + \kappa \nabla \rho \wedge \nabla \Phi = 0.$$ 

To approach the limit of uniform density, in the context of Couette flow, suppose that

$$\rho = \rho_0 + cr^2/2, \quad c > 0, \text{ constant.}$$

This is consistent with some analyses that give $\rho \propto \exp(cr^2/2)$. The constraint becomes

$$c \nabla \dot{X} + (\rho_0 + cr^2/2) \nabla \wedge \dot{X} + c \kappa \dot{r} \wedge \nabla \Phi = 0.$$ 

Now let $c$ tend to zero keeping $c\kappa = \alpha$ fixed, then

$$\rho_0 \nabla \wedge \dot{X} = -\alpha \dot{r} \wedge \nabla \Phi = -\alpha\alpha(0,0,1),$$

the last for the case that $\vec{v} = (a/r^2)(-y,x,0)$. All this is of course very appropriate for a solid body. In the Lagrangian the term with $\kappa$ may cause concern, except that $\dot{X} \cdot \nabla \Phi$ tends to a constant. In the equation of continuity $\nabla \cdot \rho \dot{X}$ tends to zero.
XI.7. Stability of Couette flow

The main interest in Couette flow, from the very beginning, has been the question of instabilities of the laminar flow that is observed when the speed of rotation is increased. One approach to stability is perturbation theory. The unperturbed motion is of the form of ‘solid-body’ rotation, with fixed angular velocity (Fetter 2009) or a combination of this with potential flow (Andereck et al 1986). Usually, the perturbation is assumed to affect only the potential field; this field is the only dynamical variable. This system is characterized by a Fetter-Walecka Lagrangian and it was treated as such in the review by Fetter already quoted. From our present perspective, a complete treatment should include a variation of both vector fields. The success of the application of the Navier-Stokes equation to the stability of flow in an incompressible fluid does not extend to thermodynamical systems defined by an equation of state. This may be related to the fact that the interaction between kinetics and heat is carried by the potential component of the flow. We propose that a more general approach to stability problems may give some new insight.

Let us emphasize that two velocity fields already appear in traditional treatments of Couette flow, though one of them is frozen at the fixed, unperturbed value or else not mentioned at all. Our suggestion is to treat both fields as independent field variables.

Here is a very preliminary attempt to extend our model to an investigation of instabilities. The expression \((n + 1)RT\) on the right hand side of (XII.5.4) is not valid at very low temperatures, but in the case of an ideal gas, with uniform entropy, it is proportional to a power of the density and it is perhaps reasonable to expect it to go to zero with the density. In that case one may expect the onset of turbulence to be associated with a vacuum bubble, when the density and thus also the quantity

\[
\frac{\dot{X}^2}{2} + \kappa \dot{X} \cdot \vec{\nabla} \Phi - \vec{\nabla} \Phi^2/2 = \frac{1}{2(\kappa^2 + 1)} (\dot{m}^2 - \vec{v}^2 + 2\kappa \dot{m} \cdot \vec{v}) = \mu [\rho] + \text{constant. (11.7.1)}
\]

reaches a particular value. Here \(\dot{m} = \dot{X} + \kappa \vec{\nabla} \Phi, \vec{v} = \kappa \dot{X} - \vec{\nabla} \Phi\).

In the \(a, b\) plane this resembles a hyperbola open to the positive \(b\) axis. This too is in qualitative accord with experiments. See Fig.s 11.7.1-2.
Fig.11.7.1. This is the locus, in the plane with coordinates $\omega_o/\omega_i = \text{angular velocity of outer/resp. inner cylinder}$, of equation (12.7.1) for a fixed value of $C_0$. The best value for $\kappa$ is $-1/3$. 
Fig. 11.7.2. The experimental envelope of stability as per Andereck et al. The ratio between inner and outer cylinder radii is .83.

Stability of Couette flow was studied long ago by Rayleigh. His criterion for stability was not successful, nevertheless it has been presented in several text books, including Chandrasekhar (1961). Rayleigh’s argument was intuitive and, we think, faulty. Rather than discussing Rayleigh’s reasoning we shall approach the problem via the variational principle.
Propagation of sound

With another degree of freedom we expect a second type of sound. It will be convenient to express the equations of motion in terms of the fields $\rho, \vec{v}$ and $\vec{m}$,

$$\vec{v} = \kappa \dot{\vec{X}} - \vec{\nabla} \Phi, \quad \vec{m} = \dot{\vec{X}} + \kappa \vec{\nabla} \Phi.$$ 

The propagation is in the $x$-direction and all the vectors are in the same direction, which allows us to dispense with the arrows. Thus

$$\dot{\vec{X}} = \frac{\kappa v + m}{\kappa^2 + 1}, \quad \vec{\nabla} \Phi = \frac{\kappa m - v}{\kappa^2 + 1}.$$ 

The equations needed are

$$\dot{\rho} + \frac{\partial}{\partial x}(\rho v) = 0,$$

$$\frac{\partial}{\partial t}(\rho m) = 0,$$

$$\dot{\Phi} + \frac{1}{\kappa^2 + 1} (m^2/2 + \kappa m v - v^2/2) = \mu.$$ 

In a linear approximation (weak signal), replace $\rho, m, v$ by $\rho + \delta \rho, m + \delta m, v + \delta v$. The unperturbed flow velocity $\vec{v}$ is taken to vanish. Thus

$$\delta \dot{\rho} + \rho \delta v' = 0,$$

$$\rho \delta \dot{m} + m \delta \dot{\rho} = 0,$$

$$\delta \dot{\Phi} + \frac{1}{\kappa^2 + 1} (m \delta m + \kappa m \delta v) = \frac{\partial p}{\partial \rho} \delta \rho.$$ 

For a harmonic disturbance, in which all the fields are proportional to $\exp(i\omega t + ikx)$,

$$\omega \delta \rho + k \rho \delta v = 0 \quad \rho \delta m + m \delta \rho = 0,$$

and

$$i\omega \delta \Phi + \frac{1}{\kappa^2 + 1} (m \delta m + \kappa m \delta v) = \frac{\partial p}{\partial \rho} \delta \rho.$$ 

Next $\delta \Phi = (1/ik)(\kappa \delta m - \delta v)/(\kappa^2 + 1)$,

$$\frac{\omega}{k} (\kappa \delta m - \delta v) + (m \delta m + \kappa m \delta v) = (\kappa^2 + 1) \frac{\partial p}{\partial \rho} \delta \rho$$

and

$$\frac{\omega}{k} (-\kappa m + \frac{\omega}{k}) - (m^2 + \kappa m \frac{\omega}{k}) = (\kappa^2 + 1) \frac{\partial p}{\partial \rho} \delta \rho =: (\kappa^2 + 1)c^2.$$ 

Finally

$$(\frac{\omega}{k} - \kappa m)^2 = (\kappa^2 + 1)(c^2 + m^2),$$

365
where $c$ is the speed of ordinary sound, associated with the case $\vec{m} = 0$.

To get a sense of this suppose $c^2 = 10^5 m^2/sec^2$ and that the speed of second sound is 20m/sec. The speed of first sound is $\sqrt{\kappa^2 + 1}c$. Then $\kappa, m$ have to be related by

$$(\kappa^2 + 1)^{1/2}(10^5 + m^2)^{1/2} - \kappa m = 400.$$ 

For some low values of $\kappa$ we find

$\kappa = .1, \quad m = -206 \text{ or } 285,$

$\kappa = .2, \quad m = -170 \text{ or } 330.$

What is characteristic of the second type of sound is that the momentum flow $\rho \vec{m}$ is not participating. If contact with a wall affects the momentum then this explains why this kind of sound is not excited mechanically with a stiff membrane. With ordinary sound the momentum velocity is not affected but the density is.

If the normal speed increases by a factor 2 the lower speed increases by a factor of about 1.3.

Perhaps this may serve to advance our understanding of the interpretation of the variable $\vec{m}$ and the parameter $\kappa$.

Let us use these values to show the displacement vectors. Also let $C$ vary with temperature and predict the variation of $m^2$.  

366
XI.8. Couette flows between plane walls

Here again is the Navier Stokes equation,

\[ \rho \left( \ddot{\mathbf{v}} + (\mathbf{v} \cdot \nabla)\mathbf{v} \right) = -\nabla p - \mu \Delta \mathbf{v}. \]  \hspace{1cm} (11.8.1)

Consider the similar problem of flow in the space bounded by plane walls parallel to the \( x, z \)-plane, \( y = y_0 \) and \( y = y_1 \). We limit our attention to stationary flows parallel to the \( x \) axis,

\[ \mathbf{v} = (v, 0, 0), \]

with the function \( v \) depending only on \( y \).

What the Navier Stokes equation has to say is this. Projected on the direction of the flow, the velocity and the pressure are homogeneous (constant), and the equation reduces to

\[ \Delta v_x = 0. \]

This has the general solution

\[ \mathbf{v} = (a + by)(1, 0, 0), \quad a, b \quad \text{constant}. \]  \hspace{1cm} (11.8.2)

Again, the Navier Stokes equation allows only two kinds of flow, but the characters of these two flows are not as in the cylindrical case; here the potential flow is ‘solid-body’ type and the other one does not have either attribute.

We are studying stationary flows, with \( \dot{\mathbf{v}} = 0 \); since the velocity is constant along the direction of motion,

\[ \frac{D\mathbf{v}}{Dt} := \ddot{\mathbf{v}} + (\dot{\mathbf{v}} \cdot \nabla)\mathbf{v} = 0. \]  \hspace{1cm} (11.8.3)

Consequently, all that remains is the equation

\[ 0 = -\nabla p - \mu \Delta \mathbf{v}, \]  \hspace{1cm} (11.8.4)

projected on the \( y \)-axis, the pressure gradient is balanced against the viscosity. Although the kinetic energy - if it is relevant to invoke energy in the context of the Navier Stokes equation - varies with the position, there is no force associated with this variation. It is true that the kinetic energy is uniform in the special case that the flow is potential, when \( b = 0 \). But the absence of a kinetic force (even when \( b \neq 0 \)) tells us that the other type of flow is of a very different character, since a non zero gradient of the kinetic energy in any flow is expected to generate a flow generates a force. Perhaps this is behind some imprecise remarks found in the literature, to the effect that, in the context of the Navier Stokes equation, the relation between linear flow and cylindrical flow is not understood.

What is the meaning of (11.8.4)? One may, for example, assume that the pressure is that of an ideal gas,

\[ p = R \rho T, \]

but since the temperature is very rarely measured, perhaps the polytropic relation will be used instead,

\[ p \propto \rho^\gamma. \]
Unfortunately the pressure also is rarely measured. As far as the viscosity term is concerned
the situation is worse, for usually, if any measurements are made, the purpose is to measure
the viscosity. Consequently, it is very rare that an analysis is made in the interest of
verifying a theory and all that can be said is that known experimental results do not
contradict the Navier Stokes equation. Indeed, how could they?

It seems strange that few experiments on Couette flow are made with the idea of studying
the laminar flow; but in fact the aim is usually to determine the conditions under which it
breaks down, to be replaced by more complicated flows including turbulence. Our purpose
is more modest, since we aim to understand laminar flow only, but more ambitious since
we are looking for an application of a general theory with definite precepts including as
far as possible a Lagrangian variational principle. The most urgent question is always the
simplest: can we understand the observed laminar flow in the limiting case in which the
role of viscosity is negligible?

Our theory, in the present state of development, includes an equation of continuity that,
when the flow has the form (11.8.2),
\[
\vec{v} = \kappa \dot{\vec{X}} - \nabla \Phi = (a + by)(1, 0, 0),
\]
(11.8.5)
demands that the density depend on the coordinate \(y\) only. Solutions for the vector and
scalar fields include the following
\[
-\nabla \Phi = a(1, 0, 0), \quad \vec{X} = bt(y, 0, 0).
\]
The field equation is satisfied,
\[
\partial_t (\rho \dot{\vec{X}} + \kappa \nabla \Phi) = 0,
\]
and finally there is the equation that comes from variation of the density,
\[
\frac{a^2}{2} - \kappa aby - \frac{b^2y^2}{2} = C - (n + 1)RT.
\]
(11.8.6)
This contrasts with the Navier Stokes equation (11.8.4). The fluid is contained between
moving walls located at two values of the coordinate \(y\). If this interval includes the point
plane with coordinate \(y = -a/b\), then the temperature has a minimum, see Fig. (11.8.2).

The order of magnitude of the variation of temperature is that of \(v^2\). If the velocity
is 1 m/sec this will imply a temperature variation of approximately \(1/C_p\), a very small
variation indeed. So it is unlikely that this temperature variation has been observed.

It is nevertheless significant that, in remarkable contrast with the Navier Stokes ap-
proach, our approach leads to a definite, quantitative prediction without the intervention
of viscosity, presumably valid in the limit when the viscosity can be neglected. Admittedly,
this prediction rests on the assumption that the flow profile is as in (11.8.2). This restric-
tion cannot yet be derived within the new approach but it is not illogical to attribute it to
viscosity.

There is no conflict between Eq.s (11.8.4) (Navier Stokes) and (11.8.6); the latter applies
under the assumption that the viscosity is negligible in this particular situation.
Fig. 11.8.1. The velocity profile. The two walls are moving in opposite directions. Improve this.

Fig. 11.8.2. An example of the density profile. The two walls are moving in opposite direction with the same speed.
The following subsection does not lead anywhere, so far.

**Pressure gradient**

This section is not developed far enough to reach any conclusion.

- Let us modify the preceding system by making the boundary plates horizontal and use gravity to stabilize the system; this makes it possible to remove the upper wall. It is customary to treat the upper boundary as “free”; and what does this mean?

Without an upper wall the idea of “no-slip” does not apply; there is some interaction with the overlying atmosphere, but it is of a different type and certainly it is much less important. We are inclined to think that no boundary conditions should be imposed there, other than the usual conditions of continuity of pressure, temperature and chemical potential across the boundary. It is usual, however, to require the transverse derivative of the velocity to be zero.

The easiest way to get a pressure gradient is to incline the lower boundary against the vertical.

As earlier we suppose that the density is incompressible and that $\mu$ is uniform. And as before we are trying to determine stationary configurations of the fluid.

Assume that the liquid is incompressible, so that the density is constant in space and time. Also assume that the velocity is uniform in the direction of the flow, so

$$v_y = 0, \quad \partial_x v_x = 0.$$ 

The Navier Stokes equation has 2 components. The component in the direction of the flow is

$$\partial_x p + \mu \Delta v_x = 0.$$ 

A pressure gradient is imposed by the boundary conditions; this equation tells us that the boundary that assign different pressures at two values of $x$ are possible only if the viscosity is not zero. We insist that the velocity be independent of $x$; that is, constant in the direction of the flow. Then

$$p(x, y) = p_0(y) + xp_1(y), \quad p_1(y) + \mu \partial_y^2 v_x(y) = 0.$$ 

There remains only the Navier Stokes equation projected on the vertical direction,

$$0 = \partial_y p + g = 0.$$ 

The pressure is thus

$$p(x, y) = p_0(y) - gy - (\mu \partial_y^2 v_x) x,$$

It is usual to assume that

$$v_x(y) = a + by + cy^2, \quad v_y = 0.$$ 

The non slip boundary condition requires that the constant $a = 0$.

The standard treatment of this problem (see for example Yih 1963) seems to imply that this type of flow is impossible. Intuitively it is in fact difficult to see how to realize
it, and certainly some external force would be required to sustain it indefinitely, but the mathematical setup does not contain any condition to rule it out. Part of the difficulty is that, with the assumption that the density is incompressible, we have no independent information about the pressure. The pressure is determined by the requirement that the equations have solutions; the theory has no predictive power other than foreseeing the pressure distribution for hypothetical flows. There is no independent conclusions concerning what kinds of flows can be realized for any particular fluid.

Let us suppose that the flow described above is possible. The kinetic part of the Lagrangian is

\[ \vec{v}^2/2 + 2\vec{v} \cdot \vec{\nabla} \Phi + (\vec{\nabla} \Phi)^2. \]

There is no contribution to balance the \( x \) dependence of the pressure; so the most reasonable choice of \( \vec{\nabla} \Phi \) is a constant. Since this theory cannot accommodate a pressure gradient the most sensible course is to take a hint from the Navier Stokes equation. In fact, what is needed is an extra term in the Lagrangian density:

\[ -\vec{x} \cdot \mu \Delta \vec{v}. \]

The viscosity is regarded as an “external” force that balances the pressure gradient.

So we learn that the presence of viscosity is not always inconsistent with a Lagrangian formulation.

The physics of this situation seems to be as follows. The force that sustains the pressure gradient is the adhesion of the bottom layer of the liquid to the bottom. The upper layers are not immediately affected, until \( \vec{\nabla} \vec{v} \) becomes appreciable, at which point a force of magnitude \( (1/\rho) \vec{\nabla} \rho \) is felt by the liquid in the bulk. This force, essentially external, now attacks locally and it can be derived from the potential \( -\vec{x} \cdot \mu \Delta \vec{v} \). Since \( \vec{\nabla} \vec{v} \) is constant, it is a uniform force acting like a gravitational potential, preserving energy in the sense that the total hamiltonian, including the new potential, is preserved.

Xl.9. Superfluid Helium. Part B Under development

The adiabatic propagator

Variables \( \rho, \dot{X}, v \). Zero order variables constants, with \( v = 0 \).

Equation of continuity:

\[ \dot{\rho} + (\rho v)' = 0. \]  \hspace{1cm} (1)

Dissipation equation

\[ (d/dt)(\rho w) = \bar{\mu} \rho \Delta v, \quad w = (1 + \kappa^2)\dot{X} - \kappa v \]

\[ \rho \delta \dot{w} + w \delta \dot{\rho} = \bar{\mu} \rho \delta v. \]

\[ \rho \left( (1 + \kappa^2)\delta \dot{X} - \kappa \delta \dot{v} \right) + (1 + \kappa^2)\dot{X} \delta \dot{\rho} = \bar{\mu} \rho \Delta \delta v. \]

\[ (1 + \kappa^2)\delta \dot{X} = \kappa \delta \dot{v} + (1 + \kappa^2)\dot{X} \delta v' + \bar{\mu} \Delta \delta v. \]  \hspace{1cm} (2)

Bernoulli equation

\[ \dot{\Phi} + \frac{1 + \kappa^2}{2} \delta \dot{X}^2 = \mu, \quad \Phi' = \kappa \dot{X} - v. \]
\[
\delta \dot{\Phi} + (1 + \kappa^2) \dot{X} \delta \dot{X} = \delta \mu.
\]
\[
\delta \dot{\Phi}' + (1 + \kappa^2) \dot{X} \delta \dot{X}' = \delta \mu'.
\]
\[
\kappa \delta \ddot{X} - \dot{v} + (1 + \kappa^2) \dot{X} \delta \dot{X}' = \delta \mu'.
\]
\[
\kappa \delta \ddot{X} + (1 + \kappa^2) \dot{X} \delta \dot{X}' = \delta \dot{v} + \delta \mu'.
\] (3)

Continue
\[
\kappa \delta \ddot{X}' + (1 + \kappa^2) \dot{X} \delta \dot{X}'' = \delta \dot{v}' + c_1^2 \delta \rho'' / \rho.
\] (3)

Using (1),
\[
\omega^2 \left( \kappa \delta \ddot{X}' + (1 + \kappa^2) \dot{X} \delta \dot{X}'' \right) = \delta \dot{v}' (\omega^2 - c_1^2 k^2).
\] (3)

Eq. (2)
\[
(1 + \kappa^2) \delta \ddot{X}' = \kappa \delta \dot{v}' + (1 + \kappa^2) \dot{X} \delta \dot{v}'' + \bar{\mu} \Delta \delta v'.
\] (2)

\[
(1 + \kappa^2) \delta \ddot{X} = \left( \kappa + (1 + \kappa^2) \dot{X} - \frac{\bar{\mu}}{i \omega} \Delta \right) \delta \dot{v}'.
\] (2)

Using (2) and (3)
\[
\omega^2 - c_1^2 k^2 = \frac{\omega^2}{1 + \kappa^2} \left( \kappa + (1 + \kappa^2) \dot{X} - \frac{\bar{\mu}}{i \omega} \Delta \right) \left( \kappa + (1 + \kappa^2) \dot{X} + \frac{\bar{\mu}}{i \omega} \Delta \right)
\]
\[
\omega^2 - c_1^2 k^2 = \frac{\omega^2}{1 + \kappa^2} \left( \kappa + (1 + \kappa^2) \dot{X} - \frac{\bar{\mu}}{i \omega} \Delta \right) \left( \kappa + (1 + \kappa^2) \dot{X} + \frac{\bar{\mu}}{i \omega} \Delta \right)
\]

With \( \sqrt{1 + \kappa^2} \dot{X} =: \dot{X} \) and \( \hat{\kappa} := \kappa / \sqrt{1 + \kappa^2} \)
\[
\omega^2 - c_1^2 k^2 = \left( \hat{\kappa} \omega + \dot{X} k \right) \left( \hat{\kappa} \omega + \dot{X} k + i \bar{\mu} k^2 \right)
\]

If \( z = \omega / k \), the speed, then
\[
z^2 - c_1^2 = \left( \hat{\kappa} z + \dot{X} \right) \left( \hat{\kappa} z + \dot{X} + i \bar{\mu} k \right)
\]

We are now prepared to resume the study of the interesting dynamic properties of He II. We have constructed a model, intended to dramatize rather than emulate the properties of Helium below the \( \lambda \) point, as a mixture of two fluids, a normal fluid with a fixed specific entropy and a superfluid with zero entropy. Here we shall study the interesting behavior of the fluid when it is set into motion.

Specifically, we consider, as in Section XIII. ??, cylindrical Couette flow. The most dramatic aspect is as follows. When the outer cylinder is rotated at a steady speed, the fluid exhibits a pronounced reluctance to follow. At low speeds, instead of adapting to the
rotation of the outer cylinder by a nearly solid-body flow, small, isolated vertical whirls appear. In papers that appeared in the mid-fifties, Landau and Lifshitz, and Feynman, tried to account for this behavior by considering the balance of energy of the two kinds of motion, showing that, given the angular momentum imparted to the fluid, small whirls were energetically favored; that is, more so than is the case for normal fluid.

Clearly, in this case viscosity plays an important role, but before considering viscosity we must decide what are the dynamical variables of mixtures; at least, of the particular mixture at hand. The simplest possibility is that there is only one density but two velocities, potential flow for the superfluid and solid-body flow for the normal fluid. This would agree with ideas originally favored by Landau. And, if only because it is the most economical option, let us examine it, momentarily setting aside the two-fluid theory. The principal difficulty would seem to be that, above the \( \lambda \) point, where the superfluid is absent, the variation of the superfluid density would reduce to a constraint, the equation of continuity, generated by the coupling term \( \rho_2 \kappa \dot{X} \cdot \nabla \Phi \). The flow velocity would be proportional to \( \rho_2 \), hence zero, and there would be no conservation law for the normal density. It seems more natural to retain both potential flows and the two associated conserved flows.

Accordingly, we start from the Lagrangian examined in Section XIII and ask how to introduce the new vector potential(s). Above the \( \lambda \) point, and below this point as well, the normal component seems to merit its name, so it is natural to expand the normal part of the Lagrangian,

\[
L_1 = \rho_1 \left( \dot{\Phi}_1 - (\nabla \Phi_1)^2 / 2 + \dot{\Phi}_1^2 / 2 + \kappa_1 \dot{X} \cdot \nabla \Phi_1 \right) - f_1 - s_1 T.
\]

Once more invoking economy, there seems to be no need to distinguish two different vector potentials. Assuming, until further development, that the vector potential applies to both densities we arrive at the following total Lagrangian density,

\[
L = \sum \rho_i \left( \dot{\Phi}_i - (\nabla \Phi_i)^2 / 2 + \dot{\Phi}_i^2 / 2 + \kappa_i \dot{X} \cdot \nabla \Phi_i \right) - f - sT.
\]

Here, as usual, \( s = \rho_1 S_1 + \rho_2 S_2 \) (with \( S_2 = 0 \)).

The conserved flows are \( \rho_1 \vec{v}_1 \) and \( \rho_2 \vec{v}_2 \) with

\[
\vec{v}_i = \kappa_1 \dot{X} - \nabla \Phi, \quad i = 1, 2.
\]

The momentum is

\[
\vec{m} = \rho (\dot{X} + \sum \kappa_i \rho_i \nabla \Phi_i).
\]

The total dynamical viscosity is sometimes a linear function of the densities, more often not. In the present case it is natural to suppose that it is proportional to \( \rho_1 \). In that case viscosity will have no direct effect on the flow of the superfluid. The momentum equation, when viscosity is included, is

\[
\dot{\vec{m}} = \mu \vec{v}_1,
\]

with the dynamoical viscosity \( \mu \) possibly a linear function of \( \vec{v}_1 \).
In the case of a flow of the cylindrical Couette type, the effect of viscosity is to restrict the flow to a combination of potential and solid-body types. Consider a simple, stationary configuration where there is one local vertex at the origin,

\[ \Phi_1 = 0, \quad \Phi_2 = a\theta, \quad -X = bt(-y, x, 0) \]

Suppose that there is no loss of energy at the boundary, and no transfer of angular momentum from the boundary cylinder to the fluid. The total angular momentum is

\[ L_z = \int d^3x (\rho_1 br^2 + \rho_2 a) = \pi L_0 (\rho_1 \frac{br^4}{4} + \rho_2 ar) \bigg|_{r_0}. \]

The total energy is

\[ E = \frac{\pi L}{2} (\rho_1 \frac{b^2 r^4}{8} - \rho_2 \frac{a^2}{r}) \bigg|_{r_0}. \]

This will have a minimum value for the smallest possible value of

The rest of this section should be ignored until it is significantly improved.

• Now let us give the bottom plate a constant inclination of angle \( \beta \), descending in the \( x \) direction. Contrary to usual practice we shall maintain the orientation of the axes, \( x \) axis horizontal and \( y \) axis vertical. We assume that the pressure gradient is perpendicular to the bottom plate, and that it is balanced against the gravitational force.

\[ p = p_0 - g \cos \beta (x \sin \beta + y \cos \beta); \]

so that

\[ p + \phi = p_0 + g \sin \theta (x \cos \beta - y \sin \beta). \]

The gradient of this is the part of the gravitational force that is uncompensated by the pressure on the plate. Now it is no longer possible to ignore the contribution of the velocity terms in

\[ \dot{\Phi} + \frac{\dot{A}^2}{2} + \vec{A} \cdot \vec{\nabla} \Phi - (\vec{\nabla} \Phi)^2/2 = \phi + p = p_0 + g \sin \theta (x \cos \beta - y \sin \beta). \quad (11.4.8) \]

We have no guide to choosing the correction \( \delta p \), the last term.

Again we want \( u_x \) to be uniform, so

\[ \Phi = ct + ax + f(y). \]

We try linear expressions for \( \dot{A} \):

\[ \dot{A}_x = a + bx + cy, \quad \dot{A}_y = dx + ey, \]

so that the left side becomes

\[ c + (a + bx + cy)^2/2 + (dx + ey)^2/2 + a(a + bx + cy) + f'(dx + ey) - (a^2 + f'(y)^2)/2. \]

The next subsection needs to be revised or eliminated.
Galilei invariance

A Galilei transformation is an infinitesimal Lorentz transformation in the limit when terms of order $c^{-2}$ are neglected. Thus for any tensor field $A$,

$$\delta A_{0,jk\ldots} = \vec{u}_k A_{ijk\ldots}.$$ 

In the absence of external fields, Eq. (11.7.8) imply that the time derivative of

$$\int d^3x \left( \rho (\dot{\vec{X}} + \vec{\nabla} \Phi + \vec{\nabla} \wedge \vec{\eta}) \right)$$

is equal to a surface integral; therefore this quantity is conserved and may be identified with the total momentum.

One verifies that the vector

$$\dot{\vec{X}} + \vec{\nabla} \cdot \vec{X} \vec{\nabla} \Phi + \vec{\nabla} \wedge \vec{\eta}$$

is invariant under Galilei transformations. The vector

$$\dot{\vec{X}} + \vec{\nabla} \Phi + \vec{\nabla} \wedge \vec{\eta}$$

is invariant under Galilei transformations if $\vec{\nabla} \cdot \vec{X} - 1$ is of order $c^{-2}$ and thus to be neglected.

Viscosity is interpreted as a breakdown of momentum conservation that preserves Galilei invariance and may be taken into account by a modification of (11.7.8). If we neglect the last two terms it takes the form

$$\frac{d}{dt} \left( \rho (\dot{\vec{X}} + \vec{\nabla} \Phi + \vec{\nabla} \wedge \vec{\eta}) \right) = \mu \nabla \left( \dot{\vec{X}} + \vec{\nabla} \Phi + \vec{\nabla} \wedge \vec{\eta} \right).$$

the following subsection is preserved only because of calculations involving radiation.

The hamiltonian density is the Legendre transform of $\mathcal{L}$:

$$\mathcal{H} = \rho \left( \dot{\Phi} + E^2 + \vec{H}^2 + \frac{1}{2} (\vec{\nabla} \Phi)^2 \right) + f + sT.$$ (11.7.4)

The Euler-Lagrange equations still include the adiabatic condition and the equation of continuity,

$$\dot{\rho} + \vec{\nabla} \cdot (\rho \vec{v}) = 0, \quad \rho \vec{v} := \rho \vec{E} - \rho \vec{\nabla} \Phi,$$ (11.6.5)

but Eq. (11.4.5) turns into

$$\frac{\partial}{\partial t} \left( \rho \dot{\vec{E}} + \rho \vec{\nabla} \Phi \right) - \vec{\nabla} \wedge (\rho \dot{\mu} \vec{H}) = 0.$$ (11.7.6)

What is most remarkable about this is that, by adding the seemingly inconsequential “gauge fixing” term $\dot{\vec{X}} \cdot \vec{\nabla} \Phi$, without affecting the expression for the hamiltonian, the
interpretation is at once radically changed by the identification of the electric field with the velocity.

Of course, this identification is absurd ... or is it? The situation will be lifted if we find that it is indeed absurd; that alone would justify making such an outrageous suggestion.

With the fields (11.4.7) and \( a = 0 \) we get

\[
\vec{H} = 2b \hat{\mu} t(0, 0, 1).
\]

The appearance of a “magnetic” field parallel to the axis of rotation is expected, but the time dependence is an embarrassment; it gives rise to a \( t^2 \) term in the hamiltonian:

\[
\dot{H} = 4b^2 \hat{\mu} t.
\]

the Pointing vector is

\[
\vec{E} \wedge \hat{\mu} \vec{H} = 2bb\hat{\mu}t(x, y, 0),
\]

and the inward radiated energy accounts for the increase in the energy density:

\[
\int \dot{H} dv = \int \vec{E} \wedge \hat{\mu} \vec{H} \cdot d\sigma,
\]

where the surface integral goes over the cylinder side.

This picture is not absurd, but the prediction of a strong magnetic field is simply wrong.

**XI.10. Generalized Couette flow; cells**

A more general ansatz for the velocity potential is

\[
\Phi = a\theta + A(x + iy) = 3\left( \ln z + A(z) \right),
\]

with \( A \) complex analytic. Since this function is harmonic, the velocity is divergence less.

Taking \( A = z^4 \) with imaginary part \( 3(x^3 - xy^3) \) we get flow lines of the form

\[
\chi(x, y) := \Re\Phi = a \ln r + (x^4 + y^4 - 6x^2y^2) = \text{constant},
\]

as shown in Fig.11.8.1 for the case that \( a = 1 \).

Fig.11.8.1. The red lines are the flow lines, \( \ln r + x^4 - 6x^2y^2 - 6x^2y^2 + y^4 = -5, -3, -2, -1.3, -0.9, -0.75, -0.65 \) and \(-0.597 \) (this last one purple). Since \( \text{div } \vec{v} = 0 \) is zero they are loci of constant density \( \vec{v} \cdot \nabla \rho = 0 \). The other lines are the loci (anti clockwise) \( \Phi = 1 \) (blue), 2, 3, 4, 5 (black) and 6 (purple). They show a modest deviation from the relation \( v^2 \propto 1/r^2 \).

For a range of values of the constant these lines very nearly fill a square with corners at \((\pm 0.5, \pm 0.5)\). (The vertical side crosses the axis at \( x = .514 \).) This can be improved by
adding higher powers. In Fig. 11.8.2 we have used \( A(z) = \text{Re}(\ln z + z^4 + .24z^8) \). The variation of the horizontal coordinate along the vertical side is now reduced to .004.

![Diagram](image)

Fig.11.8.2. An improvement of the previous figure, with the term .24 \( z^8 \) added to the function \( A \) in order to straighten the sides of the square. This one is nearly perfect.

A Benard pattern (See the next section.) can be produced by packing the squares. In this example \( \Phi \) and \( \chi \) are conformal conjugate, but that is not the only way.

In Fig.11.8.3, our best approximation to an equilateral triangle.

The next figure shows another cell, with \( A = z^8 \). We expect that the sides of the octagon can be straightened out by adding higher powers.
When, as in the examples, the velocity is divergence-less (since $\Phi$ is harmonic), the equation of continuity demands that, if the viscosity is neglected, the density can be expressed in terms of the harmonic conjugate function $\chi$. In the case shown in the first figure the centrifugal potential is one half of

$$v^2 = \frac{a^2}{r^2} - \frac{2a}{r^2}(x^4 + y^4 - 6x^2y^2) + r^6.$$  

The equations of motion, if the equation of state is uniform and there are no external forces, require that the density be expressed algebraically in terms of $v^2$, while the equation of continuity is solved most simply by having it expressed in terms of the conformal conjugate field $\chi$. It is perhaps encouraging that the first two terms of the expansion of the function $a^2e^{-2\chi/a}$ agrees with those of $v^2$.

The impression is that there may well be a class of conservative models with cell structure. But let us not forget that each model requires a particular equation of state.

More study needed; what is the contribution of viscosity?
Fig. 11.8.4. Approximation to a hexagonal cell.

Finally, doubly periodic patterns can be produced with the help of elliptic functions. At this time I do not have the expertise, or the computer, to deal with that case.
More generally the flow lines are

\[ \zeta(a, \vec{x}) := \mathcal{R}(a \ln z + z^k) = c \]

As a function of position it coincides with \( \Phi \). The vortex velocity for stationary flow is

\[ \vec{X} + \kappa \nabla \zeta. \]

If \( k = 0 \) it is

\[ \left( \frac{\kappa a}{r^2} + b \right)(-y, x, 0), \]

In that case the constraint demands the density

\[ \rho \propto r^2 \left( \frac{\kappa a}{r^2} + b \right) \]

If that is not possible the system may look for a value of \( k \) that gives a better density. Since \( k \) is an integer the creation of whirls will be quantized.

The table gives the maximal size of closed flow boxes for some values of \( a = 10^l \) and \( k \). The size is given in the same units as \( z, x, \) and \( y \).

<table>
<thead>
<tr>
<th>TABLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k/\ell )</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>6</td>
</tr>
<tr>
<td>7</td>
</tr>
<tr>
<td>8</td>
</tr>
<tr>
<td>.1</td>
</tr>
<tr>
<td>16</td>
</tr>
<tr>
<td>24</td>
</tr>
<tr>
<td>32</td>
</tr>
</tbody>
</table>

Calculation in “fandrho”.

I did the kinetic energy for I did two whirls and a central square in whirls.1.
XI.11. Convection and viscosity. Benard’s experiments

This chapter needs work.

The geometric flow patterns of the previous section can be packed to make a two dimensional periodic pattern. Such patterns appeared in experiments initiated by Benard and analyzed by Reynolds. Later it was recognized that the phenomenon appears spontaneously within the sphere of everyday experience, as in cooking and in wet paint, and that it may be a component of the behavior of clouds in the atmosphere.

Imagine a uniform gas confined by 2 large, horizontal plates, maintained at separate, constant temperatures. A large aspect ratio is necessary to reduce the effect of the horizontal boundary; therefore the distance between the plates is often small, about 1 mm, while the horizontal dimensions are at least 10 cm. It is found that with a positive temperature gradient, warmer on top, the gas is stable.

With a negative temperature gradient, warmer below, it is not stable. This was known by the end of the 19'th century; it was discussed at length by Emden, writing in 1907, and it is standard lore in meteorology. But Benard conducted controlled experiments, on a laboratory scale, and what he found was this. A positive or very small, negative temperature difference did not lead to convection. Apparently, under these conditions there is a stable, static configuration. But beyond a certain threshold, when the temperature gradient is sufficiently negative, he discovered the ‘Benard cells’. The volume between the plates developed cells of closed currents of a certain characteristic size and polygonal shape. The threshold of temperatures for the onset of currents could be determined and it was calculated by Reynolds. To facilitate the observation it is advantageous to use a liquid with a fairly high viscosity. The analysis depends critically on the viscosity and on the influence of gravity. In this connection a thermodynamic theory was developed that may throw some light on the isothermal atmosphere. For this reason we shall try to get acquainted with the concept of viscosity and the calculations that have been done to understand this type of experiment.

This system is not isolated. Heat is supplied from below to compensate for the heat loss from the upper side. Gravity is evidently important, since there is a distinct role played by the vertical direction and the difference between up and down. It is easy to criticise the analysis on the basis that the system is not in equilibrium and that thermodynamics, in the narrow sense, does not apply. But the accepted treatment is successful.

The analysis of Benard’s experiments was reviewed by Chandrasekhar, and in more recent times by Koschmieder (1993). It is based on the Navier-Stokes equation with the effect of gravitation included,

\[ \rho \frac{D\vec{v}}{Dt} + \text{grad} p + \vec{g} \rho + \mu \Delta \vec{v} = 0, \quad \mu = \rho \nu. \]

The new term, \( \mu \Delta \vec{v} \) is the effect of viscosity, a kind of sticky quality of the fluid, parameterized by the constant \( \mu \). Honey is a viscous fluid, water less so, but even air has a measurable index of viscosity, \( \mu = .0024 \text{ sec/cm}^2 \). The effect of gravity is represented by the potential \( \phi = gz \).
Like the Bernoulli equation, the Navier-Stokes equation admits rotational as well as irrotational solutions, solutions with curl \( \vec{v} \) zero or non zero. The Navier-Stokes equation is used to study situations where the curl is not zero. The otherwise very complete study by Chandrasekhar does not ask if irrotational solutions exist or not, and none are found.

This may due to the fact that the Navier-Stokes equation, when used together with the equation of continuity, implies dissipation; it is not a conservative system. In the Benard experiment there is a transport of energy, from the lower plate that is being kept at a constant temperature, through the fluid, to the upper fluid where it is dispersed into the surroundings. The fluid system is stationary, but not in equilibrium and it is not expected to be conservative. The conjunction of dissipation and viscosity is responsible for some of the most interesting phenomena of hydrodynamics, but let us focus our attention on the Bernard problem.

Instead of immersing ourselves in the very complicated classical analysis, let us begin by asking if it is certain that the system is not conservative. From our standpoint it would be useful to know if some aspects of the problem admit a formulation in terms of an action principle. It is conceivable that the Benard cells, in special cases, contain discrete vortex lines and that the velocity field is irrotational locally, on the complement of the vortex lines.

Consider the Lagrangian density

\[ \mathcal{L} = \rho (\dot{\Phi} - \vec{v}^2/2 - \nu \nabla \cdot \vec{v} - \phi) - f - sT. \]

The term \(-\nu \rho \Delta \Phi\) is new; \(\nu\) is a constant. Variation of \(\Phi\) and \(\vec{v}\) with \(\delta \vec{v} + \nabla \delta \Phi = 0\) gives the Euler Lagrange equation

\[ \dot{\rho} + \text{div} (\rho \vec{v} - \nu \text{grad} \rho) = 0. \] (11.9.1)

It is a modified continuity equation that identifies the mass current as

\[ \vec{J} = \rho (\vec{v} - \nu \nabla \rho). \] (11.9.2)

This is unconventional but not unreasonable. To conserve the total mass we must impose a boundary condition on the vector field \(\vec{J}\), making it (rather than \(\vec{v}\)) tangential at the boundary.

Variation of \(\rho\) gives

\[ \dot{\Phi} - \vec{v}^2/2 - \nu \Delta \Phi - gz = \frac{\partial}{\partial \rho} (f + sT) + \text{constant} \] (11.9.3)

and taking the gradient we obtain a version of the Bernoulli equation with an extra term

\[ \rho \frac{D \vec{v}}{Dt} + \text{grad} p + \vec{g} \rho + \mu \Delta \vec{v} = 0, \quad \mu = \rho \nu. \]

This is the Navier-Stokes equation that has always been used to analyze this problem. For a derivation see Chandrasekhar ( ).

382
However, though this equation is a valid inference from the action principle, it is obtainable only under the assumption that $\vec{v}$ is irrotational, when $\Delta \vec{v}_i = \partial_i \text{div} \, v$.

The conventional treatment postulates the Navier-Stokes equation and the equation of continuity. It does not rely on a variational principle and the role of the equation of continuity is therefore somewhat different; there is no need to modify the mass current.

To turn the problem into an conservative and adiabatic one we had only to modify the expression for the flow. We aim to find out if this conservative theory can account for certain types of cellular flow.

The classical calculation assumes that the fluid is incompressible; it does not apply to an ideal gas. In fact is not applicable to any specific gas, for the equation of state is not given as an input to the calculation. Instead the pressure is adjusted so as to ensure that the equations have a solution of the type that is desired. We are interested in a fluid that is nearly ideal, ideal except for the viscosity, it presents a different problem.

**IX.11. Adiabatic analysis** Needs checking

The essence of what distinguishes this Section from all that has been done in this book is the inclusion of viscosity. It appears as a correction to the equations of motion for the velocity field and it is intended to apply in the general situation where the curl of the velocity is not zero. Here, nevertheless, we continue to derive the velocity from a velocity potential, using the Lagrangian of the preceding section and the associated equations of motion. This procedure differs in may ways from that of Chandrasekhar. (a) The restriction of vorticity, to the manifold of singularities of a velocity potential. This constitutes a deliberate limitation of our study, with the aim of finding out whether conservative cellular flows is an important special case. (b) The inclusion of the second term in the expression (9.6.2) for the current, which allows for the possible existence of conservative systems with viscosity. (c) The a priori choice of a thermodynamical equation of state, a natural thing to do if one is interested in a particular fluid. (d) Taking the non linear, centrifugal term $\rho \vec{v}^2/2$ into account. (e) Since the process is assumed to be adiabatic, there is no need for any additional information, such as conductivity.

I need to know the observed flows.

We begin with a study of rotational motion in 2 dimensions. A whirl, or vortex at $x = y = 0$ (Cartesian coordinates) is accounted for by taking

$$\Phi = a \theta = a \Im \ln(x + iy),$$

with $a$ constant. Note that $a$ has to be constant in order that the velocity be one valued. This has the consequence that the function $\Phi(x, y)$ is harmonic, the imaginary part of a complex analytic function (singular at the origin). In cartesian and in polar coordinates,

$$\vec{v} = -\frac{y}{r^2} \partial_x + \frac{x}{r^2} \partial_y = r^{-2} \partial_\theta.$$

Note that the $r$-dependent factor is unique; this is because we require that the velocity field be one valued. The streamlines are the loci $r = \text{constant},$ or $\ln r = \text{constant},$ since
\[
\ln r = \Re(\ln(x + iy)) \text{ is the conformal conjugate of } \Phi. \text{ Since } \Phi \text{ is harmonic, the divergence of } \vec{v} \text{ is zero, and the continuity equation demands that}
\]
\[
\vec{v} \cdot \vec{\nabla} \rho - \nu \Delta \rho = 0.
\]

The absence of viscosity (\(\nu = 0\)) thus implies that the gradient of the density is perpendicular to the velocity; that is, the density is a function of \(r\) alone. Conversely, if the density is a function of \(r\), not harmonic, then the viscosity must be zero.

For simplicity we here take \(\nu = 0\) and now the density is any function of \(r\) alone.

The squared velocity is \(\vec{v}^2 = a^2 r^{-2}\) contributes the centrifugal term in the equation of motion,
\[
\dot{\Phi} - \vec{v}^2/2 - \phi = \frac{\partial}{\partial \rho} (f + sT).
\]

An external force is represented by the potential \(\phi\). Taking the gradient we obtain, if the specific entropy is uniform,
\[
\rho \dot{\vec{v}} - a^2 \rho \frac{\vec{r}}{r^4} + \rho \vec{\nabla} \phi = -\vec{\nabla} p.
\]

If the pressure is zero, as in the case of vanishing density or single particle motion, we get a stationary state by choosing an external force that compensates the centrifugal potential, \(\phi = -a^2/2r^2\). In the absence of an external force we need a pressure gradient \(\vec{\nabla} p = a^2 \rho \vec{r}/r^4\).

In the case of an ideal gas variation of the Lagrangian with respect to the density gives
\[
\dot{\Phi} - \vec{v}^2/2 - \phi - R(n + 1)T = 0.
\]

For a stationary configuration \(\dot{\Phi}\) is a constant. In the absence of rotation the external force gives rise to a decrease of the temperature with the radius, related via Einstein’s equivalence principle to the atmospheric temperature lapse that is disavowed by many thermodynamicists and by atmospheric scientists. With rotation but no external force we obtain
\[
T = T_0 - \frac{a^2}{2R(n + 1)r^2}.
\]

If the density is uniform the density and the pressure are proportional to \(T^n\) and \(T^{n+1}\), respectively.

This type of distribution may perhaps be produced in a cylinder with a spinning knitting needle at the center, the circular motion of the liquid being produced by adherence to the needle, the adherence to the wall of the cylinder assumed to be negligible. The decrease of the velocity with distance from the center is reasonable when viscosity is neglected. With increasing viscosity the other layers will be dragged along until, at the limit of very large viscosity the liquid rotates as a solid body, with \(v \propto r\).

Show this?
What happens when the driving force is adherence to a rotating outer wall, the adherence to the needle being negligible (or in the absence of a needle) will be discussed at the end of this section.

Experiments designed to confirm or deny this behavior of an ideal gas have, to my knowledge, not been carried out. Experimenters are interested in the instabilities that set in at high values of the speed of rotation and high viscosity.

These solutions do not resemble Benard cells, but we can do better.

XI.12. Criticism of the classical analysis

The classical analysis is not conservative; this is entirely reasonable, since the system is not isolated. Having only the Navier Stokes equation and the equation of state at his disposal Chandrasekhar needs an additional equation. The Fourier heat equation comes to mind, but that is not used. Instead the following argument is advanced.

The theory does not have a conserved energy functional. In particular, the functional

\[ \int d^3x \left( u + \rho \overrightarrow{v}^2 / 2 \right) \]

is not conserved by the equations of motion. But energy is conserved nevertheless, and the balance is brought about by “conduction”. This is hazardous, for in as much as there is no conserved energy functional the above functional has no claim to being representative of energy. The lack of conservation of this functional in an element of volume is calculated. Since ‘energy’ is, after all, conserved, the apparent loss is interpreted as heat conduction. This results in a relation between the gradient of \( T \) and the conductivity \( \kappa \) of the fluid.

It is risky to question the correctness of a spectacularly successful analysis, by an acknowledged master of the subject. But it would not be fair to the reader of this book to pretend that I understand this work of Chandrasekhar; perhaps he, the reader, understands it.

I will go a bit further, at my peril. The concept of heat as a substance that flows went out almost 200 years ago. Is there such a thing? In a state of equilibrium, when the temperature differential is such that no convection appears, the fluid is entirely passive; nothing happens. Energy is lost from the upper boundary and re-supplied from the underside. To say that there is an energy flow is just to express an idea of continuity; it is difficult to accept that energy disappears at one point to re-appear at a finite distance. In the bulk of the fluid the “flow” does not seem to have any effect, or does it? The most likely possibility is that it affects the local entropy. Without asking to understand the process by which this happens, we can perhaps assume that, to each stationary configuration there corresponds a value of the entropy, and that local changes in the fluid can be regarded as adiabatic. That is, so long as the boundary temperatures remain fixed, the system is subject to adiabatic analysis. If that is so, we can perhaps achieve agreement with experiment by adjusting the parameter \( \beta \), the strength of the entropy density \( s_{ex} \).

We would thus relate this parameter, not to the gravitational constant, but to the imposed temperature difference.

The energy is not conserved. Therefore energy is siphoned off; more precisely it is passed through the fluid, in the form of heat conduction.
XI.13. The role of viscosity

This is old and probably should be ignored.

This is not an introduction to the theory of viscosity. Simply, we wish to describe how the calculation of the last two sections may be affected when a small amount of viscosity is allowed.

Observations of the system described in Section IV.5., evidently in the presence of the gravitational field, has revealed that, when the temperature exceeds a certain value, the equilibrium state of no motion is unstable. The theory of viscous fluids state that this must be so if the temperature difference $\Delta T$ satisfies the condition

$$\Delta T > \frac{g}{\nu},$$

where $g$ is the gravitational acceleration and $\nu > 0$ is a measure of the viscosity. In the limit $g \to 0$ this is true for all positive $\Delta T$ and also for negative $\Delta T$, by symmetry. In the (unphysical) case in which $\nu = 0$ every equilibrium state will be unstable. We are in a situation of a spontaneously broken symmetry.

Now since, in the absence of gravity the instability is symmetric with respect to up vs down, we should expect the same to be true when $g > 0$. And if $\nu$ is small enough then this implies that we might observe instabilities for a range values of $\Delta T$. This brings up the question of the value of $\Delta T$ at the center of this range. Do we have the right to say that it must necessarily be at 0?

Now let us return to the entropy calculation in Section IV.5. It must be admitted that the physical interpretation of this extra entropy is uncertain. Perhaps the following interpretation may have some merit. Let us suppose that the equilibrium state is unstable. Let us imagine introducing a small viscosity to make it stable at some temperature gradient. That may not work because perhaps we do not know where the range of $\Delta T$ that favors stability is located. We have assumed that it is centered at $T = 0$ and we found that it may be so but only if there is some extra entropy. Without that extra entropy the center will be at the range that corresponds to the a isentropic atmosphere and the isothermal atmosphere will be unstable to convection.

In some experiments, where convection is a disturbing element, the problem has been solved by filling the vessel with a penetrable foam. Now here is a real, physically clear example of interference with the system, most likely one that imposes an unnatural distribution of entropy. So we propose that the entropy that was postulated in order to save the standard approach does not in fact exist, unless we create it by introducing a kind of foam to prevent convection. And the isothermal atmosphere exists only when such a foam is introduced. Without foam it is the isentropic atmosphere that is stable.

To validate this point of view I propose the following experiment. In the slab geometry introduce a fairly large temperature difference, the higher temperature on top. Then the role of gravity should become unimportant and the spontaneous convection should be symmetric with respect to the inversion of up-down. This would prove nothing, except that we seem to have the right way to look at things. Remember that the present understanding of stability invokes gravity.

If this analysis is correct, then there is no longer any need to defend our calculation of the entropy distribution in an isothermal column against the charge that it is unnatural.
Relativity should be discussed in the foreword to VOLUME TWO, but a full treatment should come much later. Find outline.

XII. RELATIVITY

16517

The impetus for developing an action principle for hydrodynamics and thermodynamics was to prepare for a study of astrophysics, the structure of stars and galaxies. The relation of these fields of science to each other is less than evident. However, already in 1870 the physicist Homer Lane published a paper with the following title:

“On the Theoretical Temperature of the Sun, under the Hypothesis of a gaseous Mass maintaining its Volume by its internal Heat and depending on the laws of gases as known to terrestrial Experiment” (Lane 1870)

Half a century later Eddington marveled at the success of a theory that treated the interior of the Sun as if it consists of an ideal gas. And even today the best that can be done to describe the interior structure of stars is to apply the experience that has been gained by terrestrial experiments.

But we shall not attempt to guess the form of the free energy of the thermodynamic fluid that constitutes the stars; instead we are going to consider the hydrodynamics of self gravitating fluids by means of Einstein’s equations for the metric, in the context of the General theory of Relativity. Stars and galaxies tend to rotate, in some it may be said that rotation is their dominant characteristic; this has been the principal difficulty for some time. It is a problem that the preceding chapter has already prepared us for, but more preparation is needed: we can approach General Relativity only after promoting our theory to a relativistic, Lagrangian field, theory in the sense of the Special Theory of Relativity.

Here a long introduction to Special Relativity would be appropriate, but that would be redundant since there is a very extensive literature on that subject; so we shall ask the reader to consult another textbook, if necessary.

XII.1. Variational principles in Special Relativity

“To include rotating bodies in General Relativity, we must upgrade every 3-vector field to a relativistic 4-vector field.” This simplistic view has been dominant since Einstein used it in his relativistic theory of particles, where the prescription was completely successful, as it led to relativistic concepts of mass, energy and momentum, combined to a 4-dimensionsal energy-momentum vector

\[(c p^1, cp^2, cp^3, p^0 = E), \quad E^2 - c^2 p^2 = c^4 m^2,\]

where the constant \(c\) is the velocity of light. Unfortunately the same idea was applied to the velocity fields of liquids.
Verify this! First, already in 1908, Minkowski used it in the context of electromagnetism. As Minkowski was aware, and as all modern textbooks tell us, the electromagnetic interactions of a fluid at rest give rise to contributions $\epsilon \vec{E}^2 - \mu \vec{B}^2/c^2$ to the energy density. To find the appropriate generalization to the case that there is motion in the fluid he first performs a Lorentz transformation to a reference frame that is moving with constant velocity $\vec{v}$; then he promotes $\vec{v}$ to a four-vector with components

$$(v^\mu) = (\vec{v}, v^0).$$

To this we must already object, but there is more to come. Having thus gotten the four-vector velocity into his formalism Minkowski simply assumes that the expression that he has obtained is valid as it stands, for arbitrary motions of the liquid. This is what passes as electromagnetism of fluids to this day. Perhaps we should try to do better, in some future chapter of this book.

Of more immediate interest to us is that the approach taken by Minkowski to electrodynamics was adopted without change by Tolman in 1934. We shall have much to say about that.

It is evident that we cannot adopt this approach; the velocity potential can be promoted to a relativistic scalar field, and the gradient to a 4-vector velocity field, but the velocity field $\dot{\vec{X}}$ is another matter. An objection from the back row: Is it not true that one often promotes this vector field to a 4-vector by replacing the time derivative by the proper time derivative? This proper time is the time as recorded by a “comoving” clock. It is a concept that is useful to help explain the relative nature of time in the special theory of relativity, and it may be appropriate in the case of the motion of particles, but proper time has no place in a theory of fields, which is what hydrodynamics is.

We shall accept that, in the relativistic context, the scalar velocity potential becomes a scalar field in the 4-dimensional sense, and that $\Phi, \vec{\nabla}\Phi$ combine to make a four-vector. The relativistibization of the Fetter-Walecka Lagrangian is easy to construct (Fronsdal 2007).

### XII.2. Special Relativistic potential theory

The first guess is successful; just consider the Lorentz invariant action

$$\int d^3x dt \left( \frac{\rho}{2} \left( g^{\mu\nu} \psi_{,\mu} \psi_{,\nu} - c^2 \right) - W[\rho] \right). \quad (12.1.1)$$

The metric tensor is Lorentzian, diagonal with components $(-1, -1, -1, c^2)$. The tensor $(g^{\mu\nu})$ is the inverse matrix. The fields $\rho$ and $\psi$ are four-dimensional scalar fields.

Expanding in inverse powers of $c^2$ this relativistic action reduces precisely to that of Fetter and Walecka. In flat space, with the Lorentzian metric it is

$$2 \int d^3x dt \left( \frac{\rho}{2 c^2} \psi^2 - (\vec{\nabla}\psi)^2 - c^2 \right) - W[\rho].$$
To take the non-relativistic limit it is tempting to drop the first term. The trouble is that, in spite of the factor $1/c^2$, the variation of both terms under an infinitesimal Lorentz transformation,

$$
\delta \psi = c\bar{u} \cdot \vec{\nabla} \psi, \quad \delta \bar{\psi} = \bar{u} \bar{\psi},
$$

are comparable; of course, for they cancel in this Lorentz invariant combination. To arrive at a non-relativistic theory that is invariant to first order in $\bar{u}/c$ we need to retain this contribution to the variation under Lorentz transformations. This was done by expanding

$$
\psi = tc^2 + \Phi, \quad \frac{1}{c^2} \dot{\psi}^2 = c^2 + 2\Phi + ... 
$$

where the elided terms are of order $1/c^2$. These can be safely dropped, for the necessary contribution to the Lorentz transformation is provided by the variation of the linear term,

$$
\delta \Phi = \bar{u} \cdot \vec{\nabla} \Phi.
$$

the result is the Fetter-Walecka action; it is invariant under Galilei transformations, as we have seen in Section III.11. This is the simplest way to be convinced that the non-relativistic theory is invariant under Galilei transformations.

The action of the Galilei group on the vector field $\dot{X}$ will be explained at the end of this chapter.

The non-relativistic theory as a gauge theory

I have promised to solve the problem of constructing a theory with the correct number of degrees of freedom for hydrodynamics. This pledge is essentially satisfied, at least in the absence of viscosity, by the fact that, according to the field equation

$$
\vec{\nabla} \cdot (\rho \dot{X} + \kappa \rho \bar{\nabla} \Phi) = 0, \quad (12.2.2)
$$

$X$ is a free field. But some clarification is needed.

It will be shown in the next section that the theory is the non-relativistic limit of a relativistic gauge theory that is familiar in another context and that has been carefully analyzed. From the narrow, non-relativistic standpoint we must complete the theory by imposing constraints.

The main constraint is

$$
\vec{\nabla} \wedge (\rho \dot{X} + \kappa \rho \bar{\nabla} \Phi) = 0. \quad (12.2.3)
$$

It is difficult to justify this within the present context; it is only in the fully developed relativistic theory (next section) that its interpretation in terms of gauge fixing can be confirmed. But (12.2.3) has a major effect on the non-relativistic theory and that can be discussed here.

At first sight, (12.2.3) seems to bring our efforts to naught. In the special case that the density is uniform, as in the case of an incompressible fluid and some solids, it says that the curl of our velocity is zero! But this is too hasty, for there are at least two ways to escape this conclusion.
In the first place, the incompressible fluid is an idealization. Returning to the case of stationary, cylindrical Couette flow, with

\[ \dot{X} = b(-y, x, 0), \quad \nabla \Phi = a(-y, x, 0), \quad a, b \text{ constant}, \]

the general solution of (12.2.3) is

\[ \rho = \frac{C}{br^2 + \kappa a}, \quad C \text{ constant}. \]

this result is one reason why we want to retain the \( \kappa \) term in the Lagrangian.

It will be shown that this constraint does not fix the gauge completely, there is an additional constraint,

In the second place a coupling to the magnetic field of the type

\[ \vec{B} = 0, 0, B, \quad B \text{constant} \]

introduces another parameter into the solution,

\[ \rho = \frac{\gamma Br^2 + C}{br^2 + \kappa a}, \quad C \text{ constant}. \]

Here \( \gamma \) is a coupling constant. This solution is sufficiently general to account for the experiments.

A second constraint (next section) is

\[ \nabla \cdot \vec{X} := c(-2)\Theta, \quad \Delta \Theta = 0. \]

The field \( \Theta \) plays a role in connection with Galilei invariance. all this will become more clear in the relativistic context.

XII.3. The relativistic, antisymmetric tensor field

A dramatic effect of relativization is that the fields become propagating. In particular, propagation of the fields into empty space may be unavoidable, therefore it is prudent to keep the number of propagating modes at a minimum. And that leads us to the antisymmetric tensor gauge field and its well known properties. This field has at most one scalar, propagating mode. It was introduced by Ogievetskij, and Polubarinov (1964). In another context it is known as the \( B \)-field, or the Kalb-Ramond field.

The 3-vector field \( \dot{X} \) is the space part of the 4-vector with components

\[ d\dot{Y}^\mu = \frac{1}{2}e^{\mu\nu\lambda\sigma}Y_{\nu\lambda,\sigma} = (\dot{X}, \nabla \cdot \vec{X}). \]

Let \( Y = (Y_{\mu\nu}) \) be an antisymmetric tensor field (a 2-form) and consider the Lagrangian density

\[ dY^2 = \frac{c^2}{2}g^{\mu\nu}g^{\nu\nu'}g^{\lambda\lambda'}Y_{\mu\nu,\lambda} \sum_{\text{cyclic}} Y_{\mu'\nu',\lambda'}. \]
Greek indices run over 1,2,3,0, latin indices over 1,2,3. The (inverse) metric tensor is the Lorentzian, diagonal with \( g^{11} = g^{22} = g^{33} = 1, g^{00} = -1/c^2 \). It is invariant under the gauge transformation \( \delta Y = d\xi \). In a 3-dimensional notation,

\[
X^i = \frac{1}{2} \epsilon^{ijk} Y_{jk}, \quad \eta_i = Y_{0i},
\]

The equation \( \eta_i = \partial_0 \xi_i - \partial_i \xi_0 \) can always be solved for the vector field \( \vec{\xi} \); there is a family of gauges in which the field \( \vec{\eta} \) vanishes. In addition, the vector field \( \vec{X} \) can be reduced to a gradient field. This spinless field is the only propagating mode.

In flat space, with Cartesian coordinates, in terms of \( \vec{X} \) and \( \vec{\eta} \),

\[
dY^2 = \frac{1}{2} \left( \dot{\vec{X}} + \vec{\nabla} \cdot \vec{\eta} \right)^2 - \frac{c^2}{2} (\vec{\nabla} \cdot \vec{X})^2. \tag{12.3.2}
\]

The free field equations associated with this expression for the Lagrangian density are

\[
\frac{d}{dt} \left( \dot{\vec{X}} + \vec{\nabla} \cdot \vec{\eta} \right) - c^2 \vec{\nabla} (\vec{\nabla} \cdot \vec{X}) = 0, \quad \vec{\nabla} \times (\dot{\vec{X}} + \vec{\nabla} \times \vec{\eta}) = 0. \tag{12.3.3}
\]

The only mode that propagates in vacuum mode is a scalar mode. But we can add sources,

\[
\frac{d}{dt} \left( \dot{\vec{X}} + \vec{\nabla} \cdot \vec{\eta} \right) - c^2 \vec{\nabla} (\vec{\nabla} \cdot \vec{X}) = \vec{K}, \quad \vec{\nabla} \times (\dot{\vec{X}} + \vec{\nabla} \times \vec{\eta}) = \vec{K}', \tag{3}
\]

so that, in their presence, the field \( \dot{\vec{X}} \) need not be be irrotational.

A stationary solution for the geometry of cylindrical Couette flow is \( \vec{X} = bt(-y, x, 0) \), \( \vec{\nabla} \times \vec{X} = 2b(0, 0, 1) \) and \( \vec{\nabla} \cdot \vec{X} = 0 \); it is a solution of these field equations in a gauge where \( \vec{\eta} = 0 \), with \( \vec{K} = 0 \), but with \( \vec{K}' = 2b(0, 0, 1) \). It is known (Barnett 1915) that a magnetic field is produced by a rotating cylinder made of iron and it is believed that the effect is general with an effective magnetization proportional to the magnetic moment. In the hope of accounting for this effect, without a microscopic model, we may add a gauge invariant interaction term, the exterior product

\[
\gamma YF = \frac{\gamma}{4} \tilde{Y}^{\mu\nu} F_{\mu\nu} = \gamma (\vec{X} \cdot \vec{E} + c^{-1} \vec{\eta} \cdot \vec{B}), \tag{12.3.5}
\]

where \( \tilde{Y} \) is the dual,

\[
\tilde{Y}^{\lambda\rho} = \frac{1}{2} \epsilon^{\mu\nu\lambda\rho} Y_{\mu\nu},
\]

\( F \) is the electromagnetic field strength, \( F_{ij} = (\vec{\nabla} \times A)_{ij} = c^{-1} B_{ij}, F_{0i} = E_i \) and \( \gamma \) is a constant parameter with dimension \( g/sec cm^3 \). This ties in nicely with speculations that have been voiced by several workers, of an intimate connection between solid body motion and electromagnetism. The electric field may be related to measurements of Tolman (1910) and Wilson and Wilson (see Cullwick 1959, Rosser 1971).
The propagating, scalar mode is a new form of matter that interacts with gravity and with the electromagnetic field strength, being endowed with electric and magnetic polarizability, it would be a contribution to Dark Matter.

The term \( \rho \ddot{X} \cdot \nabla \Phi \) can be made invariant under Lorentz transformations by expanding it to

\[
\rho \frac{c^2}{2} \epsilon^{\mu \nu \lambda \rho} Y_{\mu \nu, \lambda} \psi_{,\rho}.
\]

Here \( \psi \) is a Lorentz scalar; if \( \rho \) is uniform it is a boundary term.

Introduce the dual as above, then

\[
\frac{c^2}{2} \epsilon^{\mu \nu \lambda \rho} Y_{\mu \nu, \lambda} \psi_{,\rho} = \dot{X} \cdot \nabla \psi - (\nabla \cdot X) \dot{\psi} + (\nabla \wedge \nabla) \cdot \nabla \psi.
\]

The first term on the right is the one that appears in the non relativistic theory, the term that we are trying to promote to the relativistic context. In the second term \( \dot{\psi} \) appears in the role of a Lagrange multiplier and imposes the additional constraint

\[
\nabla \cdot X = 0.
\]

Now we consider the total Lagrangian density

\[
\mathcal{L} = \frac{\rho}{2} (g^{\mu \nu} \psi_{,\mu} \psi_{,\nu} - c^2) + \rho dY^2 + \kappa \rho \frac{c^2}{2} \epsilon^{\mu \nu \lambda \rho} Y_{\mu \nu, \lambda} \psi_{,\rho} + \frac{\gamma}{4} \rho Y^{\mu \nu} F_{\mu \nu} - \rho f - sT
\]

and the action \( A(\langle q \rangle, a) = \int d^3x dt \mathcal{L} \). The first term is the Lorentz invariant contribution that appears in the non relativistic approximation as \( \rho (\dot{\Phi} - \nabla \phi^2 / 2) \).

The variation of the action with respect to \( \psi \) is \( -\delta \psi \) times

\[
\frac{d}{dt} \left( \rho \left( \frac{\dot{\psi}}{c^2} - \kappa \nabla \cdot X \right) \right) + \nabla \cdot \left( \rho (\kappa \dot{X} - \nabla \Phi + \kappa \nabla \wedge \nabla) \right) =: \frac{d}{dt} J^0 + \nabla \cdot \tilde{J}.
\]

In the non relativistic limit \( \dot{\psi} / c^2 \) is unity. The boundary conditions require that the current \( \tilde{J} \) be normal to the boundary. the last equation reduces to the equation of continuity. In a physical gauge

\[
\dot{\rho} + \nabla \cdot \left( \rho (\kappa \dot{X} - \nabla \Phi) \right) = 0.
\]

This confirms that the conserved flow is

\[
\rho (\kappa \dot{X} - \nabla \Phi).
\]
The variation of the action with respect to the field $\vec{X}$ is

$$
\int d^3x dt \, \delta \vec{X} \cdot \left( \frac{d}{dt} \left( \rho (\dot{\vec{X}} + \kappa \vec{\nabla} \Phi + \vec{\nabla} \wedge \vec{\eta}) \right) + \vec{\nabla} (\rho (\kappa - c^2 \vec{\nabla} \cdot \vec{X})) - \gamma \vec{E} \right).
$$

(12.3.10)

Setting this to zero gives the field equation

$$
\frac{d}{dt} \left( \rho (\dot{\vec{X}} + \kappa \vec{\nabla} \Phi + \vec{\nabla} \wedge \vec{\eta}) \right) + \vec{\nabla} (\rho (\kappa - c^2 \vec{\nabla} \cdot \vec{X})) = \gamma \vec{E}.
$$

(12.3.11)

If we want the stationary, solid-body rotating motion of the non relativistic theory to be a solution of the relativistic theory, then we need to postulate an electric field that ensures the mutual cancelation of the last two terms; that is, $\gamma \vec{E} = \kappa \vec{\nabla} \rho$. An electric field is expected on the basis of an experiment by Tolman (1910). It may also have something to do with the anomalous Seebeck effect. But at this time we are far from understanding all the ramifications of this interaction with the electromagnetic field. That an unexpected role may be played by the electric field in connection with vortex motion, or that an electromagnetic analogy may be glimpsed here, was suggested by Feynman in connection with liquid helium (Feynman 1954 page 273).

The variation of the action with respect to the field $\vec{\eta}$ is

$$
\int d^3x dt \, \delta \vec{\eta} \cdot \left( \vec{\nabla} \wedge (\rho (\dot{\vec{X}} + \kappa \vec{\nabla} \Phi + \vec{\nabla} \wedge \vec{\eta}) - \frac{\gamma}{c} \vec{B} \right).
$$

(12.3.12)

Setting this to zero gives the field equation

$$
\vec{\nabla} \wedge (\rho (\dot{\vec{X}} + \kappa \vec{\nabla} \Phi + \vec{\nabla} \wedge \vec{\eta}) = \frac{\gamma}{c} \vec{B}
$$

(12.3.13)

But this is implied by the other field equations. The variation $\delta \vec{Y}$ is part of a certain gauge transformation $\delta \vec{Y} = (\delta \vec{X}, \delta \vec{\eta})$; gauge invariance tells us that for such variations the sum of (12.1.8) and (12.1.10) is identically zero. But the former is zero for any variation, by the field equation (12.2.9), so (12.2.10) must be zero also. We mention this because (12.2.10-11) are simpler than (12.2.8-9). Eq. (12.2.12) is a constraint that comes from variation of the field $\eta$. In the non relativistic context the gauge is fixed and this field is absent; but the constraint must be taken into account. It is this constraint, somewhat mysterious in the non-relativistic context, that reduces the number of degrees of freedom from 3 to 1.

The two equations (12.2.11) and (12.2.13 are mutually consistent by Maxwell’s second equation, $dF = 0$ or $\vec{B} = c \vec{\nabla} \wedge \vec{E}$, provided that $\gamma$ is constant (as is required by the gauge invariance of (12.2.3)) from now on.

**XII.4. Non relativistic limit and Galilei transformations**

A concept of a non-relativistic limit of a relativistic field theory can be envisaged if each of the dynamical variables can be represented as a power series in $1/c$, beginning with a term of order zero; that is, $(1/c)^0$, or higher, $(1/c)^1, (1/c)^2, \ldots$. In the case of the model
considered we must assume that this is the case for the variables \( \rho, Y, \psi \). We neglect the coupling to the electromagnetic field for the moment. The non-relativistic limit of the Lagrangian exists if every term is of positive or zero order. Dropping all terms of positive order we may ask about the physical meaning of the remainder, including transformation properties.

Taking the basic variables to be \( \rho, Y \) and \( \psi \) we find that there is one term that is visibly of order \( c^2 \), in the kinetic term (12.2.2). To overcome this obstruction we must postulate a boundary condition
\[
\nabla \cdot \vec{X} = c^{-2} \Theta + o(c^{-3}),
\]
with \( \Theta \) of order 0. If we represent \( \vec{X} \) as \( \vec{X} = \nabla \wedge \vec{\alpha} + c^{-2} \nabla \beta \), then this implies that the field \( \vec{X} \), in the non relativistic limit, has no propagating mode, which was expected.

Is this sure?
The \( \kappa \) term introduces another term of order \( c^2 \) as is seen in Eq.(12.3.7) since \( \dot{\psi} = c^2 + \dot{\Phi} \),
\[
-(\nabla \cdot \vec{X}) \dot{\psi} = -\Theta + o(1/c^2).
\]

We conclude that the existence of a non-relativistic limit of the Lagrangian depends on the validity of (12.4.1).

We can now ask about the Galilei invariance of the bi-vector theory. The subgroup of ‘proper’ Galilei transformations derives from Lorentz transformations of the form
\[
\delta \vec{x} = t \vec{u} \gamma, \quad \delta t = (\vec{u} \cdot \vec{x} / c^2) \gamma, \quad \gamma = \frac{1}{\sqrt{1 - (u/c)^2}}.
\]

Infinitesimal Galilei transformations are related to first order Lorentz transformations. It is enough to retain terms linear in \( \vec{u} \), replacing \( \gamma \) by unity. Infinitesimal Galilei transformations are defined as the ‘contraction’ that consists of taking the limit \( c \to \infty \). But it would be imprudent to take that limit already at this stage, as we shall see. So the transformations to be considered are first order or infinitesimal Lorentz transformations,
\[
\delta \vec{x} = t \vec{u}, \quad \delta t = \vec{u} \cdot \vec{x} / c^2.
\]

In what we shall call a physical gauge the field \( \vec{\eta} \) vanishes. The Lorentz group acts on the antisymmetric field in the manner that is indicated by the indices, in particular
\[
\delta Y_{ij} = t \vec{u} \cdot \vec{\nabla} Y_{ij} + tu_i Y_{0j} + tu_j Y_{i0}, \quad \delta Y_{0j} = t \vec{u} \cdot \vec{\nabla} Y_{0j} + u_i Y_{ij} / c^2.
\]

The two terms that are linear in \( t \) vanish in a physical gauge, so each component \( Y_{ij} \) and each component of \( \vec{X} \) transforms as a scalar field under under Galilei transformations. The last term is another matter, its presence shows that the transformed field is not in the physical gauge, since \( \delta Y_{0j} \neq 0 \). So we have to make a gauge transformation
\[
\delta Y_{ij} = \partial_i \xi_j - \partial_j \xi_i, \quad \delta Y_{0j} = \partial_0 \xi_j - \partial_j \xi_0,
\]
such that
\[
\partial_0 \xi_j - \partial_j \xi_0 = -u_i Y_{ij} / c^2.
\]

394
The very existence of a non relativistic limit implies that the basic variables can be represented as power series in $1/c$. So even if this implies a change in $Y_{ij}$, that will be a change of order $1/c^2$ and we can be fairly confident that this is enough that this change can be ignored. We shall see below that great caution is necessary and it is worth while to point out that if $\vec{\nabla} \cdot \vec{X}$ is of order $1/c^2$ then the change $\delta Y_{ij}$ will be of order $1/c^4$. To see this take the curl of the last equation to get

$$\partial_0 \vec{\nabla} \wedge \xi = \vec{u}(\vec{\nabla} \cdot \vec{X})/c^2.$$ 

If, as we suppose, $\vec{\nabla} \cdot \vec{X}$ is of order $1/c^2$ then this makes $\xi$ of order $1/c^4$. We conclude that Galilei transformations affect the field $\vec{X}$ only the way that it affects scalar fields, by the argument shift $\delta \vec{x} = \vec{u}t$.

Dropping terms of order $1/c^2$ we find that the transformation properties of the field are

$$\delta \dot{\Phi} = t\vec{u} \cdot \vec{\nabla} \Phi + \vec{u} \cdot \vec{\nabla} \Phi, \quad \delta \vec{\nabla} \Phi = t\vec{u} \cdot \vec{\nabla}(\vec{\nabla} \Phi) + \vec{u}$$

and, with

$$\Theta := c^2 \vec{\nabla} \cdot \vec{X},$$

$$\delta \dot{\vec{X}} = (t\vec{u} \cdot \vec{\nabla})\dot{\vec{X}} + (\vec{u} \cdot \vec{\nabla})\dot{\vec{X}}, \quad \delta \Theta = t\vec{u} \cdot \vec{\nabla} \Theta + \vec{u} \cdot \dot{\vec{X}},$$

while $\Phi$, the components of $\vec{X}$ and those of its spatial derivatives transform as scalar fields with the generator $t\vec{u} \cdot \vec{\nabla}$.

The reason why we are proceeding cautiously is that there are terms in the Lagrangian of apparent order $c^2$, see (12.3.2),

$$\rho \left( - \frac{c^2}{2} (\vec{\nabla} \cdot \vec{X})^2 \right)$$

and (12.3.7)

$$\rho \kappa \left( - (\vec{\nabla} \cdot \vec{X}) \hat{\psi} \right), \quad \hat{\psi} = c^2 + \Phi.$$ (12.4.3)

Therefore, in order for the non-relativistic limit to exist it is required that $\vec{\nabla} \cdot \vec{X}$ be of order at least 2 in $1/c$.

The first of the two dangerous terms is ignorable and the other reduces Mod higher order terms to

$$-\rho \kappa \Theta.$$ 

To sum up, for the existence of the non-relativistic limit it is necessary and sufficient that $\vec{\nabla} \cdot \vec{X}$ be of order $\geq 2$ in $1/c$, and the only correction needed in the non-relativistic Lagrangian discussed earlier is the addition of $-\rho \kappa \Theta$, the field $\Theta$ defined as

$$\Theta := \lim_{c \to \infty} c^2 \vec{\nabla} \cdot \vec{X}.$$ 

This restores the incariance under Galilei transformations that was lost with the introduction of the $\kappa$ tedm in the Lagrangian.
Unfortunately this quantity $\Theta$ cannot be calculated within the non-relativistic theory. The relativistic equation of continuity, obtained by variation of $\psi$, yields

$$\dot{\rho} \nabla \cdot \vec{X} = \dot{\rho} + \nabla \cdot (\rho(\kappa \dot{\vec{X}} - \nabla \Phi)) = 0.$$ 

The non-relativistic conservation law must be valid up to corrections of order $1/c^2$. These corrections are encoded in the value of the field $\Theta$ and this introduces a degree of arbitrariness into the theory. The field $\Theta$ is an independent field although its variation under Galilei transformations is related to that of $\vec{X}$, making

$$\Theta + \dot{\vec{X}} \cdot \nabla \Phi$$

invariant. Invariance under Galilei transformations is thus formal; the choice $\Theta = 0$ characterizes a preferred Galilei frame of reference. This is an unsatisfactory result of including the $\kappa$ term. We shall retain it nevertheless, for it has turned out to be useful.

The total, non-relativistic Lagrangian density is thus

$$\rho \left( \dot{\Phi}(1 - \kappa) - \Theta(1 + \kappa) + \frac{\vec{X}^2}{2} + \kappa \dot{\vec{X}} \cdot \nabla \Phi - (\nabla \Phi)^2/2 \right) - f - sT.$$ 

The rest of the section to be reviewed.
Maxwell’s equations

To improve our understanding of the role that is played by the vector potential we shall leave out the scalar velocity potential.

If we were to insist on maintaining the naive solution with $\rho$ and $b$ constant, then Eq.(12.1.11) would give us a uniform magnetic field,

$$\vec{\nabla} \wedge (\rho \dot{\vec{X}}) = 2\rho b (0,0,1) = \frac{\gamma}{c} \vec{B}$$

and by Eq.(12.1.9), $\vec{E} = 0$. But this contradicts Maxwell’s equation,

$$\dot{\vec{E}} - c \vec{\nabla} \wedge \vec{B} = -\gamma \dot{\vec{X}}.$$ 

So $\rho$ and $b$ cannot both be constant.

In general, the equation (12.2.14) is replaced by

$$\vec{\nabla} \wedge (\rho \dot{\vec{X}}) = \frac{1}{R} \rho \partial_R (R^2 b)(0,0,1) = \frac{\gamma}{c} \vec{B}$$

and Maxwell’s equation

$$\dot{\vec{E}} - c \vec{\nabla} \wedge \vec{B} = -\gamma \dot{\vec{X}}$$

becomes

$$\vec{\nabla} \wedge \frac{1}{R} \rho \partial_R (R^2 b)(00,1) = -\frac{\gamma^2 b}{c^2} (-y, x, 0)$$

or

$$\frac{1}{r} \partial_R \frac{1}{R} \partial_R (\rho b R^2) = -\frac{\gamma^2}{c^2} b.$$ 

Near the center we expect $b$ to be nearly constant; this is verified then

$$\rho = \frac{k}{R^2} - \frac{\gamma^2 R^2}{c^2 4}, \quad k \text{ constant.}$$

which may be reasonable, but not impossible close to the center. Very far from the source we expect that $\rho$ becomes constant. This constant, the density of the vacuum, is analogous to the electromagnetic polarizations $\epsilon_0$ and $\mu_0$ that are absent from the formulas because they have been absorbed into the fields. The solution is then

$$b(R) = \frac{b(0)}{R^2} \exp[-\frac{\gamma^2}{\rho_0 c^2} \frac{R^2}{2}].$$

So the system has found a way to avoid generating velocities greater than the speed of light at a large distance from the center.

Several directions are open to investigation. In the first place it is known that the mixing (not an interaction) of the antisymmetric field with electromagnetism makes the photon massive and removes the infrared divergence from QED. This takes us far from thermodynamics and will be taken up elsewhere.
But the implications for General Relativity are interesting and very much within the range of thermodynamics.

The energy-momentum tensor

The terms in the Lagrangian density that contain the metric are

\[ dY^2 = \frac{c^2}{4} g^\mu\nu' g^\lambda\nu' (Y_{\mu\nu',\lambda'} Y_{\mu\nu',\lambda'} + Y_{\lambda'\mu',\nu'} + \frac{1}{8} Y_{\lambda'\mu',\nu'}) + g^\mu\nu' g^\mu\nu' F_{\mu\nu} F_{\mu\nu} \]

In flat space, in the physical gauge, on shell,

\[ \dot{X}^3 = b(-y, x, 0) \]

and the only non zero components of \( dY \) are

\[ \dot{Y}_{23} = -by, \quad \dot{Y}_{31} = bx \]

\[ dY^2 = \frac{c^2}{2} (\dot{Y}_{23}^2 + \dot{Y}_{31}^2) = \frac{c^2}{2} g^{00} g^{33} (g^{11} \dot{Y}_{31}^2 + g^{22} \dot{Y}_{23}^2) \]

and

\[ \frac{1}{8} g^{\mu\nu'} g^{\mu\nu'} F_{\mu\nu} F_{\mu\nu} = B_{12}^2 = g^{33} (g^{11} \dot{B}_{31}^2 + g^{22} B_{23}^2). \]

Other terms not only vanish; they are all second order in vanishing components of the metric. We can therefore evaluate the energy momentum tensor using these on shell values. The non zero components are

\[ T_{11} = \rho c^2 g^{00} g^{33} \dot{Y}_{31}^2 + g^{33} B_{32}^2 - p g_{11}, \]

\[ T_{22} = \rho c^2 g^{00} g^{33} \dot{Y}_{23}^2 + g^{33} B_{23}^2 - p g_{22}, \]

\[ T_{33} = \rho c^2 g^{00} (g^{11} \dot{Y}_{31}^2 + g^{22} \dot{Y}_{23}^2) + (g^{11} \dot{B}_{31}^2 + g^{22} B_{23}^2) - p g_{33}. \]

On shell,

\[ T_{11} = \rho b^2 x^2 + (2\rho bc/\gamma)^2 x^2 - p, \]

\[ T_{22} = \rho b^2 y^2 + (2\rho bc/\gamma)^2 y^2 - p, \]

\[ T_{33} = \rho b^2 (x^2 + y^2) + (2\rho bc/\gamma)^2 (x^2 + y^2) - p \]

The on shell pressure is

\[ p = \mathcal{L} - 2 B_{12}^2 = \frac{\rho}{2} b^2 (x^2 + y^2) - (2\rho bc/\gamma)^2 (x^2 + y^2). \]

The field equation from variation of \( \rho \) is

\[ \frac{1}{2} b^2 (x^2 + y^2) = \mu, \]
where \( \mu \) is the chemical potential. Differentiating we get the hydrostatic equation

\[
\rho \nabla \frac{1}{2} b^2 (x^2 + y^2) = \nabla p
\]

Relativistic invariance implies momentum conservation in the form \( \partial_i T_{ij} = 0 \). It remains to verify that it holds as a consequence of the field equations.

**Solutions of Einstein’s equations**

In the linear approximation, in the gauge in which

\[
\partial_i g_{ij} = 0
\]

it reduces to Poisson’s equation for the components,

\[
\Delta g_{\mu\nu} = 8\pi G T_{\mu\nu}.
\]

This implies that the stress tensor satisfies

\[
\partial_i T_{ij} = 0,
\]

which seems unlikely. But consider the field equations.

The most important are these

1. The Euler-Lagrange equation

\[
\frac{\delta}{\delta \rho} L = 0.
\]

The Lagrangian has the form

\[
L = \rho K + V,
\]

with \( K \) and \( V \) independent of the density; hence

\[
K = q,
\]

the chemical potential. The gradient is the hydrostatic condition,

\[
\rho \partial_\mu K = \partial_\mu p.
\]

Consider the variation of the action that is generated by a coordinate transformation on all the fields from which it is constructed; variation is a sum,

\[
\delta A = \int d^4x \left( \delta g_{\mu\nu} T^{\mu\nu} + \sqrt{-g} \sum \delta \psi \frac{\delta L}{\delta \psi} \right).
\]

If the action is invariant, then this variation is zero. On shell, the second term is zero, so on shell, the first term is zero as well

\[
\delta \int d^4x \delta g_{\mu\nu} \sqrt{-g} T^{\mu\nu} = 0.
\]
In the case of a coordinate transformation,

\[ \delta g_{\mu\nu} = \xi_{\mu;\nu} + \xi_{\nu;\mu}, \]

This equation becomes

\[ \int d^4x \xi_\mu (\sqrt{-g}T^{\mu\nu})_{;\nu} = 0 \]

and, since \( \xi \) is arbitrary it follow that \( \sqrt{-g}T^{\mu\nu}_{;\nu} = 0 \).

It can be verified directly, but all the field equations have to be used.

In the case at hand, the equation derived from variation of \( \vec{X} \) is just a statement that, if the fields are time independent, then the electric field is zero.

We must translate this solution to the Mannheim coordinates. In these coordinates the non zero coefficients are

\[ Y_{12} = -Y_{21} = X^3 = \text{btr}, \quad \psi = c^2 t + at\phi. \]

The terms in the Lagrangian density that contain the metric are

\[ dY^2 = \frac{c^2}{4} g^{\mu\mu'} g^{\nu\nu'} g^{\lambda\lambda'} Y_{\mu\nu,\lambda}(Y_{\mu'\nu',\lambda'} + Y_{\nu'\lambda',\mu'} + Y_{\lambda'\mu',\nu'}) \]

\[ = \frac{c^2}{4} g^{\mu\mu'} g^{\nu\nu'} g^{00} Y_{\mu\nu,0} Y^{\nu',0} = \frac{c^2}{2} (g^{11} g^{22} - g^{12} g^{12}) g^{00} \]

(this on the assumption that \( g^{i0} = 0 \)). Next, the Maxwell field, a two form.

The variations of the physical components are zero, but the transformation takes us out of the physical gauge. But here we can adopt a remedy that is popular in electrodynamics; we tweak the action by the Lorentz group by making a simultaneous choice of gauge; under this new transformation rule the effect of a Lorentz transformation is nil; the trivial transformation. The answer is that the Galilei group does not act on the field \( \dot{X} \). Strictly, this is true only when \( \vec{\nabla} \cdot \dot{X} = 0 \).
XII.2. Introduction to General Relativity

This sketch of an introduction to General Relativity divides naturally into several parts:

1. A very short summary of the first stage of General Relativity. The elevation of the Lorentzian metric of Special Relativity to a dynamical field with matter as its source, and the idea of geodesic motion. Section XII.2.

2. The development of a dynamical action principle for the metric. Section XII.3.
   a. The gravitational field in empty space.
   b. The identification of the source of the metric field with the energy-momentum tensor of a matter field model.
   c. Interaction with the electromagnetic field.
   d. Tolman’s phenomenology.
A very short summary of the first stage of General Relativity

Special relativity was created in 1905. It arose from the demand that the laws of mechanics have the same invariance group as Maxwell’s theory of electromagnetism, the Poincaré group or the inhomogeneous Lorentz group. It became necessary to formulate physical laws in a language that makes Lorentz invariance manifest, in order that the attention could be directed to physics without the need to worry about consistency with the new principles at each stage. This had the effect of introducing the Lorentzian metric into all the equations of fundamental physics. For example, Maxwell’s field equations now take the form

$$g^{\mu\nu}\partial_\mu F_{\nu\lambda} = J_\lambda.$$ (12.2.1)

The prominence of the metric led Einstein to seek a larger role for it, and this resulted in the idea of geodesic motion. The next great leap forward was the realization that Newton’s equations for the motion of a particle in a gravitational field could be interpreted as geodesic motion in the special metric

$$ds^2 = (1 - \frac{2\phi}{c^2})(cdt)^2 - d\vec{x}^2,$$ (12.2.2)

where $\phi$ is the newtonian gravitational potential. The distance between two points in space time is

$$\int_a^b ds = \int_a^b \sqrt{g_{\mu\nu}dx^\mu dx^\nu}$$

and the equation that minimizes the value of this expression is

$$\dddot{x}^\mu - \Gamma^\mu_{\nu\lambda} \ddot{x}^\nu \dot{x}^\lambda = 0,$$ (12.2.3)

where the dots stand for derivatives with respect to $s$ and $\Gamma$ is the metric connection,

$$\Gamma^\mu_{\nu\lambda} = \frac{1}{2}g^{\mu\rho}(g_{\nu\rho,\lambda} + g_{\rho\lambda,\nu} - g_{\rho\lambda,\rho}).$$ (12.2.4)

The proliferation of indices is frightening, but most of the coefficients of $\Gamma$ are zero and a little work leads to the revelation that Eq. (12.2.3) is precisely the Newtonian equations of motion.

XII.3. The development of a dynamical action principle for the metric

a. The recognition of geodesic motion was not just an interpretation of Newton’s equations of motion; it was a major discovery with important experimental consequences. But the theory needed further development. In Newtonian theory the potential was determined by solving the Poisson equation with the mass distribution as a source,

$$\Delta \phi = -4\pi G \rho,$$ (12.3.1)

with $G$ a universal constant. It relates the field $\phi$ to the source, the matter distribution. The search for a suitable generalization would take 10 years of labor by Einstein, Hilbert, Poincaré and others.
The answer is as follows. A covariant derivative is defined with the help of the metric connection (12.2.4),

\[ D_\mu := \partial_\mu - \Gamma_\mu, \]

The Gaussian curvature tensor is

\[ [D_\mu, D_\nu] = R_{\mu\nu} = R_{\mu\nu a} b L^a, \]

where the \( L^a \) are matrices, the generators of ‘local Lorentz transformations’. Alternatively, if \( A \) is any co-vector field,

\[ [D_\mu, D_\nu] A_\rho = (R_{\mu\nu})^\lambda_\rho A_\lambda. \]

Two contractions leads to the curvature scalar \( R = g^{\rho\mu}(R_{\mu\nu})^\nu_\rho \) and this scalar field, by virtue of being the only candidate with required characteristics, is the Lagrangian density for the metric field.

Variations of the action

\[ A_{\text{metric}} = \int d^4x \sqrt{-g} R \] (12.3.2)

with respect to the metric,

\[ \delta A_{\text{metric}} = \int d^4x \sqrt{-g} \delta g^{\mu\nu} G_{\mu\nu} = 0. \] (12.3.3)

gives a unique field equation

\[ G_{\mu\nu} = 0. \] (12.3.4)

When the variation \( \delta g^{\mu\nu} \) in Eq. (12.2.3) is specialized to the type of variation that results from a change of coordinates,

\[ \delta g^{\mu\nu} = D_\mu \xi_\nu + D_\nu \xi_\mu, \]

one finds by means of an integration by parts the identity

\[ G^{\mu\nu}_{\cdot\nu} = 0. \] (12.3.5)

This is the famous Bianchi identity; it is indeed satisfied identically, for it merely expresses the invariance of the action under coordinate transformations. The simplest way to write this equation is

\[ \frac{\partial}{\partial x^\mu} \sqrt{-g} G^{\mu\nu} + \sqrt{-g} G^{\lambda\rho} \Gamma^\nu_{\lambda\rho} = 0. \]

Eq. (12.3.4) is Einstein’s field equation for the metric field in vacuum; that is, the field equation for ‘empty space’ ... space-time devoid of matter.

A special solution to equation (12.3.4), stationary and spherically symmetric, was found very soon by Schwarzschild (1917); it has an interesting topological structure and led to the concept of Black Holes. But our interest is in space with matter, as a star or a galaxy, not empty space.
b. In the presence of matter the metric field equation is expected to take the form
\[ G_{\mu\nu} = T_{\mu\nu}. \] (12.3.6)

Instead of zero, characteristic of vacuum, it has something on the right hand side that represents matter, the source of the gravitational metric field. An integrability condition arises from the fact that the left side satisfies the Bianchi identity, consistency demands that the source tensor \( T \) must satisfy the same condition, the Bianchi constraint,
\[ T^{\mu\nu;\nu} = 0. \] (12.3.7)

The key to satisfying this condition is that the Bianchi identity is derived from invariance under coordinate transformations. A whole class of models that satisfy this last condition is found by taking the matter tensor to be the energy momentum tensor of a coordinate invariant, Lagrangian field theory, with action
\[ A_{\text{matter}} = \int d^4x \sqrt{-g} \mathcal{L}, \]

and energy momentum tensor
\[ T_{\mu\nu} = 2 \frac{\delta}{\delta g^{\mu\nu}} \mathcal{L} - \mathcal{L} g_{\mu\nu}. \]

The constraint is not satisfied identically, but on shell, by virtue of the matter field equations. It is a gift to us, offered by any relativistic field theory.

c. This was indeed the method by which the first consistent field theories with a matter-metric interaction were constructed, first of all the so called Maxwell-Einstein theory that unites electromagnetism and General Relativity. The Lagrangian density is
\[ \frac{-1}{4} g^{\mu\nu} g^{\lambda\rho} F_{\mu\lambda} F_{\nu\rho}, \]

and the energy momentum tensor (verify this)
\[ T_{\mu\nu} = g^{\lambda\rho} F_{\mu\lambda} F_{\nu\rho} - g_{\mu\nu} \mathcal{L}. \]

But this theory does not involve the theory of fluids or other types of matter. Similar field theoretic models are plentiful, but they do not describe extended distributions of matter. No relativistic field theory of fluids has been available.

d. Lacking a dynamical matter model suitable for stellar structure, Tolman, in 1934, proposed a phenomenological expression for the matter tensor,
\[ T_{\mu\nu} = (\rho + p) U_{\mu} U_{\nu} - pg_{\mu\nu}. \] (12.3.8)
Here $\rho$ is a scalar density field possibly associated with the distribution of mass, $p$ is an isotropic pressure density and $U$ is a four vector field. Tolman interpreted the space components in terms of matter flow and imposed the normalization

$$g^{\mu\nu}U_\mu U_\nu = 1.$$  \hfill (12.4.2)

This condition was inspired by the model of non interacting particles. The model does not have a conserved current, the condition of continuity of classical hydrodynamics is abandoned. Nevertheless, *faute de mieux*, Tolman’s suggestion has been used in almost all investigations of stellar structure, from Eddington and Chandrasekhar forward.

The most obvious objection to Tolman’s formula is that it fails to incorporate an equation of continuity, a defect that is significant in a theory that aspires to be a generalization of hydrodynamics.

Even more important is the fact that Tolman’s matter tensor is not directly related to a matter model and it has no dynamical content. There are no matter equations of motion that could be used to verify the Bianchi identities. Instead, the suggestion is to regard the condition (12.3.4),

$$T^{\mu\nu;\nu} = 0$$

as a substitute for dynamics. Thus matter has no intrinsic properties; instead it is subject to the consistency conditions that allow it to appear as a source for the gravitational field. In this sense it is like the Navier Stokes equation that simply defines the acceleration of particles in the fluid in terms of unspecified force fields.

An analogy will help put the right accent on this, and is of great interest by its own rights.. Maxwell-Dirac electrodynamics couples to field theories, mainly by introducing an interaction term of the form $eA_\mu J^\mu$ in the Lagrangian. Maxwell’s equations now take the form

$$\partial_\mu F^{\mu\nu} = eJ_\nu.$$  

The left side is evidently divergence less, so the right hand side must be divergenceless as well; that is, conserved. And this condition, $J^\mu;_\mu = 0$, must be satisfied by virtue of the Dirac field equations for the matter field.

It will be objected that, though this is true in Maxwell-Dirac theory, and though it is true that it is a requisite for perturbation theory, it is not satisfied in the theory of electromagnetic fluids. Indeed that is so, and as we have said, Minkowski’s treatment of electrodynamics leaves a lot to be desired.

Finally, Tolman’s formula for the energy momentum tensor is based on the idea of a single, timelike 4-vector velocity field. It cannot accommodate rotating matter, which is fatal since most heavenly bodies are rotating.
XII.5. Rotating heavenly bodies

Our study of cylindrical Couette flow suggests an approach to the study of rotating heavenly bodies. Here I shall use the Lagrangian with the $\vec{X}$ field included, as it stands, without extra terms that may be needed for relativity, in the context of Newtonian gravity. The velocity should therefore be small compared to the velocity of light.

### Solid-body flow

We examine the case of uniform, solid-body rotation about a fixed axis. The stationary, solid-body solution is $\vec{v} = \omega(-y, x, 0)$, $\omega = \text{constant}$. To satisfy the equation of continuity, the density, the pressure and the temperature depend on $r = \sqrt{x^2 + y^2}$ and $z$ only. Then the only remaining matter equation is

$$\frac{\omega^2}{2} r^2 - \phi = C V T, \quad (1)$$

where $R$ is the distance from the center, and $T$ is the absolute temperature modulo an additive constant. The gradient of this equation is the universally used hydrostatic equation. It coincides with the Navier Stokes equation in the case of vanishing viscosity (the Euler equation).

Besides Eq.(1), and the equation of state, the only other equation of newtonian gravity is Poisson’s equation

$$\Delta \phi = -4\pi G \rho. \quad (2)$$

### The earth

The rotation of the earth is very nearly of the solid-body type. The gradient of $C V T$ is the pressure; it is normal to the surface; therefore the formula for the surface takes the form

$$\frac{\omega^2}{2} r^2 - \phi = \text{constant.} \quad (2)$$

Since the rotation is relatively slow it is a good approximation to approximate the potential,

$$\phi \approx -\frac{MG}{R}. \quad (2)$$

In this approximation the formula for the surface takes the form

$$\frac{\omega^2}{2} r^2 + \frac{MG}{R} \approx \text{constant.} \quad (3)$$

As the first term increases from the poles to the equator, $R$ must increase also; the distance from the center is greater at the equator (the equatorial bulge). Since the variation of $R$ from an average $R_0$ is small we can further approximate this as

$$z^2 + r^2(1 - 2 \frac{R_0^3}{\omega^2 MG}) = \text{constant.}$$
This is the shape of the earth as given in the textbooks. It is an oblate spheroid, flattened at the poles. The problem is to determine an appropriate equation of state.

Turning back to Eq.(1), with no approximations, the first term is
\[
\frac{\omega^2}{2} R^2 \frac{2}{3} (1 - P_2),
\]
where \(P_2(\cos \theta)\) is the Legendre polynomial. Since
\[
\Delta R^2 P_2(\cos \theta) = 0,
\]
Poisson’s equation for the Newtonian potential takes the form
\[
\Delta \phi = 2 \omega^2 - \Delta C_V T = 4 \pi G \rho.
\]
The equation of state is an algebraic relation between \(C_V T\) and \(\rho\). Therefore, these functions have the following property. If \(C_V T(R, \theta)\) is constant on the manifolds defined by
\[
f(R, \theta) = \text{constant},
\]
then \(\rho\) is constant on the same manifolds. To this problem the only known solution is that both functions depend on \(R\) only, which is in contradiction with Eq.(2).

**Incompressible density**

Suppose first that the density is constant, then
\[
C_V T = -c R^2, \quad c = \text{constant},
\]
\[
\phi = R^2 \left( \frac{\omega^2}{2} \sin^2 \theta + c \right) = R^2 \left( \frac{\omega^2}{3} + c - \frac{\omega^2}{3} P_2 \right) + \text{constant}, \quad (4)
\]
\[
\Delta \phi = 2 \omega^2 + 6c = -4 \pi G \rho. \quad (5)
\]
Equivalently, with \(d = c + \omega^2/3\) a positive constant,
\[
C_V T = \left( \frac{\omega^2}{3} - d \right) R^2, \quad (6)
\]
\[
\phi = R^2 \left( d - \frac{\omega^3}{3} P_2 \right) + \text{constant}, \quad (7)
\]
\[
\Delta \phi = 6d = -4 \pi G \rho. \quad (8)
\]
To choose the boundary we first note that no atmosphere has been postulated; nevertheless there is some justification for assuming that pressure, and thus also the temperature and the density, must be constant along the boundary. The velocity is always tangential and this requires only that the boundary is invariant under polar rotations. But the newtonian
potential beyond the boundary must be that of empty space, and it must be continuous at the surface.

We conclude, therefore, that the surface is a sphere, with radius $R_0$. In that case the constant in (7) must be chosen so that

$$\phi = (R^2 - 3R_0^2)d - \frac{\omega^2}{3} R^2 P_2.$$  

The Legendre polynomial decreases from the poles towards the equator; the potential and its radial derivative increase and the inward force of gravity decreases, in agreement with observations on Earth. On the surface the internal Newtonian potential takes the value

$$\phi = -R_0^2(2d + \frac{\omega^2}{3} P_2),$$

To ensure continuity at the surface and zero density on the outside we may take the potential beyond the boundary to be

$$\phi = -R_0^2 \frac{2d}{R} - \frac{\omega^2}{3} R_0^5 \frac{P_2}{R^3}, \quad \Delta\phi = 0. \quad (9)$$

The total mass from Eq.(8) is

$$M = \frac{2d}{G} R_0^3,$$

and the outside metric can be expressed as

$$\phi = -\frac{MG}{R} - \frac{\omega^2}{3} R_0^5 \frac{P_2}{R^3}. \quad (10)$$

For the earth, a good approximation may be Eq.(2) with a small correction in the direction of Eq.(10).
Suppose instead that
\[ C_v T = -c R^a, \quad a = \frac{-2}{n-1}. \]
The density is proportional to \( T^n \) and for \( R \leq R_0 \)
\[ \phi = R^2 \frac{\omega^2}{2} \sin^2 \theta + c R^a = (R^2 - 3R_0^2) \frac{\omega^2}{3} + c R^a - \frac{\omega^2}{3} P_2, \quad (10) \]
\[ \Delta \phi = 2 \omega^2 + ca(a+1)R^{a-2} = -4\pi G \rho. \quad (11) \]
while on the outside,
\[ \phi = -\frac{2R_0^3 \omega^2}{R^3} + \frac{cR_0^{a+1}}{R} - \frac{\omega^2}{3} R_0^5 P_2, \quad (12) \]

For a fluid with a fixed equation of state and a fixed value of the specific entropy density, the manifolds of constant density and pressure, including the surface, are always spherical. But this is not likely to happen since it implies a singularity at the center. To avoid the singularity the fluid must become compressible as the center is approached.

If we accept the singularity at the center, then we may take \( n = 3 \), a value that has been much used in models for stellar structures. In this case the temperature falls off as \( 1/R \) and the density as \( 1/R^3 \), and there is no need to postulate a boundary.

**Another approach**

When we assume, as we did, that the nature of the flow is known, then we are led to an impasse, for the equations can be accommodated to a fixed equation of state only in the case of a spherical body. Another approach is more fruitful.

Suppose that we have determined the gravitational potential on the outside, that it has cylindrical symmetry, and that it falls off at great distances,
\[ \phi = -\frac{GM}{R} + \frac{\lambda_1}{R^3} P_2(\cos \theta) + \frac{\lambda_2}{R^5} P_4(\cos \theta) + \ldots \quad \text{outside.} \]

Next, we would impose continuity at the boundary. If the surface is spherical, \( R = R_0 \), then by continuity the regular potential for \( R \leq R_0 \) is
\[ \phi = f_0(R) + f_1(R) P_2(\cos \theta) + f_2(R) P_4(\cos \theta) + \ldots \quad \text{inside,} \]
where
\[ f_0(R_0) = -\frac{GM}{R_0}, \quad f_1(R_0) = \frac{\lambda_1}{R_0^3}, \quad f_2(R_0) = \frac{\lambda_2}{R_0^5}, \ldots \]
Next, inside,
\[ \Delta \phi = \Delta f_0 + (\Delta f_1 - \frac{6f_1}{R^2}) P_2(\cos \theta) + (\Delta f_2 - \frac{20f_2}{R^2}) P_4(\cos \theta) + \ldots = -4\pi G \rho \]
If convergence is granted we can use this result plus our equation of state, any relation between the density and the temperature, to calculate \( C_V T(R, \cos \theta) \). Finally, we can use Eq.(1) to determine the velocity field.

However, the appearance of the unknown and almost arbitrary functions \( f_i(R) \) means that no significant result can be obtained for the velocity field. As an illustration let us take

\[
f_0(R) = (R^2 - 3R_0^2) \frac{GM}{R_0^3}, \quad f_1(R) = \frac{\lambda_1 R^2}{R^5}, \quad f_2(R) = \frac{\lambda_2 R^4}{R_0^9}, \ldots .
\]

Then

\[
\Delta \phi = \frac{6GM}{R_0^3} = -4\pi \rho.
\]

This brings us back to the special case of an incompressible gas; \( C_V T \) can be anything and the kinetic energy remains undetermined. So we reach an impasse, even in the case that we make the radical assumption that the surface is spherical.

Conclusion. The usual account of the shape of the earth is not known to be compatible with a fixed equation of state. This would appear to be a minor problem in as much as the interior of the earth is far from uniform. In applications to certain stars, and especially to galaxies, the idea of a fixed equation of state is more natural; and none has been found that is compatible with the equations of motion.

This analysis was based on the non relativistic Euler equation. It overlooks the role of magnetic fields, known to be very important in galaxies.

For a better approach, using the new action principle for general flows see the two recent papers.

**Applying the general theory**

We have left out the potential flow, and therefore we could do nothing about the constraint \( \nabla \times (\rho \vec{m}) = 0 \) So we need some potential flow as well, but that has the effect of introducing a singularity in the kinetic potential,

\[
\dot{X}^2 / 2 + \kappa \dot{X} \cdot \nabla \Phi - \nabla \Phi^2 / 2.
\]

This is well know and we follow standard theory in assuming that

\[
\dot{X} = (b + \frac{af}{r^2})(-y, x, 0), \quad (f(0) + \kappa)^2 = \kappa^2 + 1.
\]

with \( f(r) \) approaching unity as \( r \) tends to zero. A common choice is \( f(r)/f(0) = \exp(-\alpha r^2) \). If \( \alpha \) is large, positive, this has an effect only close to the axis.

This makes

\[
\vec{m} = (b + f \frac{af}{r^2} - \kappa \frac{a}{r^2})(-y, x, 0).
\]

If \( \kappa = 1 \) then this field in non singular.
To satisfy the constraint is to take

$$\rho = c(br^2 + a(f - \kappa)), \quad c \text{ constant}$$

and here to neglect $f$ is a very small error. In fact, there is little risk in overlooking the problem altogether. we just have to remember that some of our expressions need a little improvement to be used very close to the axis.

The main equation of motion now takes the form

$$\frac{b^2 r^2}{2} - \frac{a^2}{2r^2} + \phi = \mu + \text{constant}.$$
XIII.1. A very short review

Pure electromagnetism; that is, the study of electromagnetic fields without anything else intervening, is a free, relativistic field theory based on a 4-vector field that shall be denoted $A$. The Lagrangian density of this field theory is

$$\mathcal{L}_{em} = \frac{-\epsilon_0}{8\pi} F^2,$$

where $F$ is the antisymmetric tensor field

$$F_{\mu\nu} := \partial_\mu A_\nu - \partial_\nu A_\mu, \quad F^2 := F^{\mu\nu} F_{\mu\nu}. \quad (13.1.1)$$

The factor $\epsilon_0$ is a constant. The ‘electric field’ and the ‘magnetic flux’ are

$$\vec{E} := \dot{A} - \vec{\nabla} A_0, \quad \vec{B} = \vec{\nabla} \times A. \quad (13.1.2)$$

We are interested in electromagnetic fields that coexist with matter fields. In order to maintain the action principle we must suppose that matter is described by an action principle of its own, with a Lagrangian $\mathcal{L}_{\text{matter}}$. The total Lagrangian density for the system will be

$$\mathcal{L} = \mathcal{L}_{em} + \mathcal{L}_{\text{matter}} + \mathcal{L}_{\text{int}}. \quad (13.1.3)$$

There are two quite different cases to be considered.

1. In the case that the matter density is zero almost everywhere, as when matter is concentrated on several isolated point particles, the simplest possible interaction is

$$\mathcal{L}_{\text{int}} = A^\mu J_\mu,$$

where the current $J$ is a vector field, the source of the electromagnetic field.

Variation of $A$ now gives the Euler Lagrange equations

$$F^{\mu\nu,\nu} = 4\pi J^\mu.$$

The left side of this equation satisfies the identity

$$(F^{\mu\nu,\nu})_\mu = 0;$$

therefore it is essential that the right hand side satisfy the constraint

$$J^{\mu,\mu} = 0.$$

This is a constraint on the matter sector that must be verified by virtue of the matter field equation. The most important example is the theory of Dirac electrons and Maxwell electrodynamics that forms the basis for Quantum ElectroDynamics.
2. In the case of a continuous matter distribution the same approach to interactions can be taken, in principle, but it requires a knowledge of the current on a microscopic scale that is not available. We shall describe the usual macroscopic approach, as explained e.g. in Jackson (1962). The microscopic current is replaced by a macroscopic average, for which we shall use the same symbol. In addition, the presence of the field is assumed to “polarize” the medium, creating an electric polarization that tends to reduce the applied electric field and a magnetic polarization that tends to reduce the applied magnetic flux.

This general idea can be applied to solids and to liquids, but here we shall limit our attention to liquids. In that case, because of the absence of shear in stationary liquids, it may be supposed that the polarization is aligned with the field (possibly against the field). The net fields can then be described as a ‘displacement field’ $\vec{D}$ and a ‘magnetic field’ $\vec{H}$

$$\vec{D} = \epsilon \vec{E}, \quad \vec{H} = \mu \vec{B}. \quad \text{(13.1.4)}$$

These relations is purely phenomenological, justified as a linear approximation. And yet, standard electromagnetic theory treats them as axioms and makes the additional assumption that the coefficients $\epsilon$ and $\mu$ are affine functions of density $\rho$, more precisely

$$\epsilon = \epsilon_0 + \hat{\epsilon} \rho, \quad \mu = \mu_0 + \hat{\mu} \rho, \quad \text{(13.1.5)}$$

where $\epsilon_0, \mu_0$ are the values in vacuum, constants satisfying $\epsilon_0 \mu_0 = c^2$ ($c$ the velocity of light), or $\epsilon_0 \mu_0 = 1$, depending on the system of units that is used. The coefficients $\hat{\epsilon}$ and $\hat{\mu}$ are also constants. These relations are known as ‘constitutional relations’, considered as compliments to the equation of state of the liquid. The independent fields are $\vec{E}$ and $\vec{B}$ or, more precisely, the 4 components of the 4-vector field $A$.

The equations for this electromagnetic potential are obtained as the result of a detailed, microscopic analysis and can be summarized as follows. The independent dynamical variables are the components of the 4-vector field $A$, to which the vector fields $\vec{E}$ and $\vec{B}$ are related by Eq.(13.1.2) and the vector fields $\vec{D}$ and $\vec{H}$ by Eq.(13.4). The analysis leads to the field equations

$$\dot{\vec{D}} = \vec{\nabla} \wedge \vec{H} + \vec{J}, \quad \vec{\nabla} \cdot \vec{D} = 4\pi J_0. \quad \text{(13.1.6)}$$

This is in the gauge $A_0 = 0$ that is commonly used and that we shall use as well. As equations for the electromagnetic field they make sense once the current is specified. Integrality of (13.1.6) requires that it be conserved.

At this point the classical analysis of the electromagnetic fields is viewed as complete, and the attention turns to developing a complimentary set of equations for the material variables. But we consider the following circumstance to be of the first importance. It is a simple fact that the above equations can be summarized as an action principle, similar to the one with which we began this section. The action is based on the Lagrangian density

$$\mathcal{L}_{em} = \frac{1}{4\pi} (\vec{E} \cdot \vec{D} - \vec{B} \cdot \vec{H}) + J^\mu A_\mu. \quad \text{(13.1.7)}$$

Eq.s (13.1.6) are the Euler Lagrange equations obtained by variations of $\vec{A}$ and $A_0$.
XIII.2. Matter equations

At this point in the classical analysis the attention turns to the matter field equations. These equations are essentially hydrodynamic: the equation of continuity,

\[ \dot{\rho} + \nabla \cdot (\rho \vec{v}) = 0, \]

and a version of the Navier Stokes equation. According to Jackson, in the case of a liquid that is electrically neutral, conducting and non-permeable ($\hat{\mu} = 0$), this equation takes the form

\[ \rho (\dot{\vec{v}} + (\vec{v} \cdot \nabla) \vec{v}) = -\nabla p + \vec{f} + \frac{1}{c} (\vec{J} \wedge \vec{B}). \] (13.2.1)

The approach is not really field theoretical, but based on particle dynamics. On the left hand side is the substantive time derivative. The pressure term is normal for the case of adiabatic dynamics. The term $\vec{f}$ represents an external force such as gravity. It may include a viscous force as well. The last term presents a problem. The appearance of a term involving the electromagnetic field was expected; instead there appears the current, not yet related to the fields. In fact, so far, the current is unspecified.

So far, there is no expression for the current, so that the system defined by the Euler Lagrange equations derived from Eq.(7), supplemented by Eq.(8), is under-determined. Who follows the further development, as offered by Jackson, may find the going difficult. First, Ohm’s law is invoked,

\[ \vec{J} = \sigma \vec{E}. \]

This is disorienting, for this law is similar to Fourier’s heat equation and has to do with dissipation. The problem is, of course, that Jackson does not separate adiabatic developments from more general changes; indeed the concept “adiabatic” is not available in the context, since the dynamical equations are not seen as derived from a Lagrangian variational principle. But the sequel is even more disquieting, for this equation is immediately replaced by

\[ \vec{J} = \sigma \left( \vec{E} + \frac{\vec{v}}{c} \wedge \vec{B} \right), \]

with the following ‘justification’: If the first equation holds in the laboratory system of coordinates, and with the assumption that the charge density $J_0$ is zero in that system, then by a Lorentz transformation one finds that the second equation is valid in a system moving with uniform velocity $\vec{v}$ with respect to it. But $\vec{v}$ is not uniform; it is the velocity field of the liquid.

The first discussion of electrodynamics in a moving frame is due to Minkowski(1908). He pointed out that the constitutive relations (5) take a different form in another coordinate system. This point was resurrected by Ridgely (1990) who used an argument parallel to that of Jackson, and like both previous authors, identified the relative coordinate velocity with the fluid velocity field. This procedure gives results that are sensible in the case of uniform or nearly uniform velocity fields, but one may ask: is it not possible to do better than this?
XIII.3. Lagrangian formulation, potential flow

Let us rein in our ambition for a moment and limit ourselves to the case of gradient type velocity fields. Consider the Lagrangian density

\[ L_{em} + L_{matter} = \frac{1}{4\pi} (\vec{E} \cdot \vec{D} - \vec{B} \cdot \vec{H}) + J^\mu A_\mu + \rho (\Phi - (\nabla \Phi)^2/2) - f - sT. \]  

(13.3.1)

It is incomplete in only one respect: it lacks an expression for the current. (We are assuming that (13.1.4-5) hold.) If we wish to retain the equation for the electromagnetic fields, then the current must be expressed entirely in terms of matter fields. If we assume, as Jackson does, that the charge density is zero, then the most natural possibility is that

\[ \vec{J} = e\rho(\vec{A} - \nabla \Phi), \quad J_0 = e\rho \]  

(13.3.2)

where \( e\rho \) is a scalar field; we shall suppose that \( e \) is a constant. Variation of \( \Phi \) gives the conservation law (in the gauge \( A_0 = 0 \))

\[ \dot{\rho} + \nabla \cdot \rho(\vec{A} - \nabla \Phi) = 0. \]  

(13.3.3)

There is only one conserved current; if we wish to preserve the conservation of mass, then we must interpret the vector density

\[ \vec{v} := e\vec{A} - \nabla \Phi \]  

(13.3.4)

as the flow velocity. With this interpretation the equations of motion that follow from Eq.(3.1) are exactly the equations used in the physics of non neutral plasmas, with one proviso: that the gradient field \( -\nabla \Phi \) be replaced by a general vector field.

Remark. The context does not allow us to choose \( \vec{J} \) and \( J_0 \) independently. The case chosen by Jackson for a first introduction to the subject, in which the charge density is zero while the current is not, is out of range of a study that remains focused to adiabatic dynamics. It is realized in the limit of infinite conductivity.

Among the Euler Lagrange equations the one that deserves the most attention is the one obtained by variation of \( \rho \):

\[ \dot{\Phi} + \frac{1}{4\pi} (\vec{E} \cdot \vec{D} - \vec{B} \cdot \vec{H}) - \frac{1}{2} (\nabla \Phi)^2 - e\vec{A} \cdot (e\vec{A} - \vec{A} \Phi) - CV T. \]

The gradient of this equation has a close resemblance to the Navier Stokes equation. If the latter is restricted to potential flow, then in the absence of the electromagnetic fields it is identical to it. The inclusion of electromagnetism is also conventional, especially the combination \( e\vec{A} - \nabla \Phi \) and the magnetic term. The electric term stands where we should have liked to see the square of the non potential part of the current.

The temptation is this very strong to seek an intimate connection between \( \vec{E} \cdot \vec{D} \) and the square of the velocity. Sustained attempts to validate this idea have, however failed. The simplest way to discredit the idea was discovered in our investigation of Couette flow:
If we identify the solid-body current with the electric field we are embarrassed by a quite unphysical magnetic contribution. The weakness of the magnetic field of the earth is quite sufficient to discredit the idea.

We are back to the principal question discussed on these pages: how to get away from the limitation to irrotational motion.

This does not work. Skip to Section 4.

Consider the following total Lagrangian,

\[ \mathcal{L}_{\text{em}} + \mathcal{L}_{\text{matter}} = \frac{1}{4\pi} (\vec{E} \cdot \vec{D} - \vec{B} \cdot \vec{H}) + J^\mu A_\mu + \rho \left( \dot{\Phi} + \frac{\dot{\vec{X}}^2}{2} + \vec{X} \cdot \vec{\nabla} \Phi - \frac{(\vec{\nabla} \Phi)^2}{2} \right) - f - sT. \]

where \( A, \vec{X}, \rho, \Phi \) and \( T \) are independent field variables. It describes two systems, with no mutual interactions: classical electrodynamics with an unspecified current and unspecified susceptibilities and a fluid with velocity \( \vec{v} = \dot{\vec{X}} - \vec{\nabla} \Phi \).

If we relate the two systems by identifying the susceptibilities as in Eq.(5),

\[ \vec{D} = \epsilon \vec{E}, \quad \vec{H} = \mu \vec{B}, \]

then we have plausible bias for describing the electromagnetic and hydrodynamic properties of a fluid. If we require that the current be that of a dynamic matter system, conserved by virtue of the matter field equations, then we must take

\[ \vec{J} = e \rho (\dot{\vec{X}} - \vec{\nabla} \Phi), \]

with \( e \) constant.

Variation of the density, the only variable that is common to both subsystems, then we obtain

\[ \frac{1}{4\pi} (\epsilon \vec{E}^2 - \mu \vec{B}^2) + \dot{\Phi} + \frac{\dot{\vec{X}}^2}{2} + \vec{X} \cdot \vec{\nabla} \Phi - \frac{(\vec{\nabla} \Phi)^2}{2} = C_V T. \]

Taking the garden we get the Navier Stokes equation with an additional magnetic force

\[ \vec{\nabla} \left( \frac{\epsilon}{4\pi} \vec{B}^2 \right). \]

This is known as the magnetic viscosity term, which is misleading in as much as it is adiabatic.

Recall that we hope, eventually, to construct a Lagrangian field theory that can be used in relativistic applications. It is inevitable therefore that spatial derivatives of the field \( \vec{X} \) must be introduced. As this will greatly complicate the theory, and what is more, will force us to recognize a new form of radiation, we should welcome a more economical alternative. At this point an alternative does seem to offer itself.
Suppose that to the Lagrangian density we add terms of the type $\vec{X} \cdot \vec{E}$, so as to produce a modified Lagrangian in which only the sum of these two fields appears, namely

$$L_{em} + L_{matter} = \frac{\rho}{2}(\dot{X} + \sqrt{\frac{\epsilon}{2\pi}}\vec{E})^2 - \frac{\rho}{2}\vec{B} \cdot \vec{H} + J^\mu A_\mu$$

$$+ \rho \left( \dot{\Phi} + (\dot{\vec{X}} + \sqrt{\frac{\epsilon}{2\pi}}\vec{E}) \cdot \vec{\nabla} \Phi - (\vec{\nabla} \Phi)^2 / 2 \right) - f - sT.$$ 

Let us consider the applications, at first, in two extreme cases.

1. In a fluid in which both susceptibilities are zero we fall back on our Lagrangian formulation of Navier Stokes theory. When the displacement field and the magnetic fields are weak we find in the linear approximation that they are governed by the following equations

2. In the opposite extreme, when the velocity is zero, the action reduces to that of the traditional electromagnetics of fluids at rest. When the mechanical flow is slow we find in the linear approximation
See Wikipedia articles Pierre Louis Maupertuis French Geodesic Mission
Pressure gradient

This section is not developed far enough to reach any conclusion.
• Let us modify the preceding system by making the boundary plates horizontal and use gravity to stabilize the system; this makes it possible to remove the upper wall. It is customary to treat the upper boundary as “free”; and what does this mean?

Without an upper wall the idea of “no-slip” does not apply; there is some interaction with the overlying atmosphere, but it is of a different type and certainly it is much less important. We are inclined to think that no boundary conditions should be imposed there, other than the usual conditions of continuity of pressure, temperature and chemical potential across the boundary. It is usual, however, to require the transverse derivative of the velocity to be zero.

The easiest way to get a pressure gradient is to incline the lower boundary against the vertical.

As earlier we suppose that the density is incompressible and that $\mu$ is uniform. And as before we are trying to determine stationary configurations of the fluid.

Assume that the liquid is incompressible, so that the density is constant in space and time. Also assume that the velocity is uniform in the direction of the flow, so

$$v_y = 0, \quad \partial_x v_x = 0.$$ 

The Navier Stokes equation has 2 components. The component in the direction of the flow is

$$\partial_x p + \mu \Delta v_x = 0.$$ 

A pressure gradient is imposed by the boundary conditions; this equation tells us that the boundary that assign different pressures at two values of $x$ are possible only if the viscosity is not zero. We insist that the velocity be independent of $x$; that is, constant in the direction of the flow. Then

$$p(x, y) = p_0(y) + xp_1(y), \quad p_1(y) + \mu \partial_y^2 v_x(y) = 0.$$ 

There remains only the Navier Stokes equation projected on the vertical direction,

$$0 = \partial_y p + g = 0.$$ 

The pressure is thus

$$p(x, y) = p_0 - gy - (\mu \partial_y^2 v_x)x,$$

It is usual to assume that

$$v_x(y) = a + by + cy^2, \quad v_y = 0.$$ 

The non slip boundary condition requires that the constant $a = 0$.

The standard treatment of this problem (see for example Yih 1963) seems to imply that this type of flow is impossible. Intuitively it is in fact difficult to see how to realize
it, and certainly some external force would be required to sustain it indefinitely, but the mathematical setup does not contain any condition to rule it out. Part of the difficulty is that, with the assumption that the density is incompressible, we have no independent information about the pressure. The pressure is determined by the requirement that the equations have solutions; the theory has no predictive power other than foreseeing the pressure distribution for hypothetical flows. There is no independent conclusions concerning what kinds of flows can be realized for any particular fluid.

Let us suppose that the flow described above is possible. The kinetic part of the Lagrangian is

\[ \frac{\bar{v}^2}{2} + 2\bar{v} \cdot \vec{\nabla} \Phi + (\vec{\nabla} \Phi)^2. \]

There is no contribution to balance the \( x \) dependence of the pressure; so the most reasonable choice of \( \vec{\nabla} \Phi \) is a constant. Since this theory cannot accommodate a pressure gradient the most sensible course is to take a hint from the Navier Stokes equation. In fact, what is needed is an extra term in the Lagrangian density:

\[ -\vec{x} \cdot \mu \Delta \bar{v}. \]

The viscosity is regarded as an “external” force that balances the pressure gradient.

So we learn that the presence of viscosity is not inconsistent with a Lagrangian formulation.

The physics of this situation seems to be as follows. The force that sustains the pressure gradient is the adhesion of the bottom layer of the liquid to the bottom. The upper layers are not immediately affected, until \( \vec{\nabla} \bar{v} \) becomes appreciable, at which point a force of magnitude \((1/\rho)(\vec{\nabla}p)\) is felt by the liquid in the bulk. This force, essentially an external, now attacks locally and it can be derived from the potential \(-\vec{x} \cdot \mu \Delta \bar{v}\). Since \( \vec{\nabla} \bar{v} \) is constant, it is a uniform force acting like a gravitational potential, preserving energy in the sense that the total hamiltonian, including the new potential, is preserved.

The rest is not interesting. Replace by a remark.

- Now let the us give the bottom plate a constant inclination of angle \( \beta \), descending in the \( x \) direction. Contrary to usual practice we shall maintain the orientation of the axes, \( x \) axis horizontal and \( y \) axis vertical. We assume that the pressure gradient is perpendicular to the bottom plate, and that it is balanced against the gravitational force.

\[ p = p_0 - g \cos \beta (x \sin \beta + y \cos \beta), \]

so that

\[ p + \phi = p_0 + g \sin \theta (x \cos \beta - y \sin \beta). \]

The gradient of this is the part of the gravitational force that is uncompensated by the pressure on the plate. Now it is no longer possible to ignore the contribution of the velocity terms in

\[ \Phi + \frac{\dot{A}^2}{2} + \dot{A} \cdot \vec{\nabla} \Phi - (\vec{\nabla} \Phi)^2 / 2 = \phi + p = p_0 + g \sin \theta (x \cos \beta - y \sin \beta). \quad (11.4.8) \]

We have no guide to choosing the correction \( \delta p \), the last term.
Again we want $u_x$ to be uniform, so

$$\Phi = ct + ax + f(y).$$

We try linear expressions for $\dot{A}$:

$$\dot{A}_x = a + bx + cy, \quad \dot{A}_y = dx + ey,$$

so that the left side becomes

$$c + (a + bx + cy)^2/2 + (dx + ey)^2/2 + a(a + bx + cy) + f'(dx + ey) - (a^2 + f'^2)/2.$$

This appears to be a copy.

**XI.7. Couette flows between plane walls** Needs checking.

Here again is the Navier Stokes equation,

$$\rho\left(\ddot{v} + (\ddot{v} \cdot \vec{\nabla})\dot{v}\right) = -\vec{\nabla}p - \mu \Delta \ddot{v}. \quad (11.7.1)$$

Consider the similar problem of flow in the space bounded by plane walls parallel to the $x, z$-plane, $y = y_0$ and $y = y_1$. We limit our attention to stationary flows parallel to the $x$ axis,

$$\ddot{v} = (v, 0, 0),$$

with the function $v$ depending only on $y$.

What the Navier Stokes equation has to say is this. Projected on the direction of the flow, the velocity and the pressure are homogeneous (constant), and the equation reduces to

$$\Delta v_x = 0.$$ 

and this has the general solution

$$\ddot{v} = (a + by)(1, 0, 0), \quad a, b \text{ constant.} \quad (11.7.2)$$

We are studying stationary flows, with $\ddot{v} = 0$; since the velocity is constant along the direction of motion,

$$\frac{D\ddot{v}}{Dt} := \ddot{v} + (\ddot{v} \cdot \vec{\nabla})\ddot{v} = 0. \quad (1.7.3)$$

Consequently, all that remains is the equation

$$0 = -\vec{\nabla}p - \mu \Delta \ddot{v}; \quad (11.7.4)$$

projected on the $y$-axis, the pressure gradient is balanced against the viscosity. Although the kinetic energy - if it is relevant to invoke energy in the context of the Navier Stokes equation - varies with the position, there is no force associated with this variation. It is true that the kinetic energy is uniform in the special case that the flow is potential, when
$b = 0$. That tells us that the other type of flow is of a very different character, since a non-zero gradient of the kinetic energy in any potential flow generates a force.

What is the meaning of (11.7.4)? One may, for example, assume that the pressure is that of an ideal gas,

$$p = \mathcal{R} \rho T,$$

but since the temperature is very rarely measured, perhaps the polytropic relation will be used instead,

$$p \propto \rho^\gamma.$$

Unfortunately the pressure also is rarely measured. As far as the viscosity term is concerned the situation is worse, for usually, if any measurements are made, the purpose is to measure the viscosity. Consequently, it is very rare that an analysis is made in the interest of verifying a theory and all that can be said is that known experimental results do not contradict the Navier Stokes equation. Indeed, how could they?

It seems strange that few experiments on Couette flow are made with the idea of studying the laminar flow; but in fact the aim is usually to determine the conditions under which it breaks down, to be replaced by more complicated flows including turbulence. Our purpose is more modest, since we aim to understand laminar flow only, but more ambitious since we are looking for an application of a general theory with definite precepts including as far as possible a Lagrangian variational principle. The most urgent question is always the simplest: can we understand the observed laminar flow in the limiting case in which the role of viscosity is negligible?

Our theory, in the present state of development, includes an equation of continuity that, when the flow has the form (11.6.2),

$$\vec{v} = \vec{A} - \vec{\nabla}\Phi = (a + by)(1, 0, 0), \quad (11.7.5)$$

(see Fig.(11.7.1)), demands that the density depend on the coordinate $y$ only. The vector and scalar fields are

$$-\vec{\nabla}\Phi = a(1, 0, 0), \quad \vec{X} = bt(y, 0, 0).$$

The field equation is satisfied,

$$\partial_t(\rho \vec{X} + \vec{\nabla}\Phi) = 0,$$

and finally there is the equation that comes from variation of the density,

$$\frac{a^2}{2} - aby - \frac{b^2y^2}{2} = C - (n + 1)\mathcal{R}T. \quad (11.7.6)$$

or

$$(n + 1)\mathcal{R}T = (by + a)^2 + \text{constant}$$

If $a$ and $b$ have opposite signs the temperature has a minimum. The position of the minimum relatively to the walls depends on where one places the walls, see Fig. (11.7.2).

The order of magnitude of the variation of temperature is that of $v^2$. If the velocity is 1 m/sec this will imply a temperature variation of approximately $1/C_p$, a very small
variation indeed. So there is probably no hope of deciding between the two theories by measurements.

It is nevertheless significant that, in remarkable contrast with the Navier Stokes approach, our approach leads to a definite, quantitative prediction without the intervention of viscosity. Admittedly, this prediction rests on the assumption that the flow profile is as in (11.7.2). This cannot be derived within the new approach but it is not illogical to attribute it to viscosity.

There is no conflict between Eq.s (11.7.4) (Navier Stokes) and (11.7.6); the latter applies under the assumption that the viscosity is negligible in this particular situation.

Fig.11.6.1. The velocity profile. The two walls are moving in opposite directions with the same speed. Revise this figure.

Fig.11.7.2. An example of the density profile. The two walls are moving in the same direction.
Pressure gradient

This section is not developed far enough to reach any conclusion.

- Let us modify the preceding system by making the boundary plates horizontal and use gravity to stabilize the system; this makes it possible to remove the upper wall. It is customary to treat the upper boundary as “free”; and what does this mean?

Without an upper wall the idea of “no-slip” does not apply; there is some interaction with the overlying atmosphere, but it is of a different type and certainly it is much less important. We are inclined to think that no boundary conditions should be imposed there, other than the usual conditions of continuity of pressure, temperature and chemical potential across the boundary. It is usual, however, to require the transverse derivative of the velocity to be zero.

The easiest way to get a pressure gradient is to incline the lower boundary against the vertical.

As earlier we suppose that the density is incompressible and that $\mu$ is uniform. And as before we are trying to determine stationary configurations of the fluid.

Assume that the liquid is incompressible, so that the density is constant in space and time. Also assume that the velocity is uniform in the direction of the flow, so

$$v_y = 0, \quad \partial_x v_x = 0.$$  

The Navier Stokes equation has 2 components. The component in the direction of the flow is

$$\partial_x p + \mu \Delta v_x = 0.$$  

A pressure gradient is imposed by the boundary conditions; this equation tells us that the boundary that assign different pressures at two values of $x$ are possible only if the viscosity is not zero. We insist that the velocity be independent of $x$; that is, constant in the direction of the flow. Then

$$p(x, y) = p_0(y) + xp_1(y), \quad p_1(y) + \mu \partial_y^2 v_x(y) = 0.$$  

There remains only the Navier Stokes equation projected on the vertical direction,

$$0 = \partial_y p + g = 0.$$  

The pressure is thus

$$p(x, y) = p_0 - gy - (\mu \partial_y^2 v_x) x.$$  

It is usual to assume that

$$v_x(y) = a + by + cy^2, \quad v_y = 0.$$  

The non slip boundary condition requires that the constant $a = 0$.

The standard treatment of this problem (see for example Yih 1963) seems to imply that this type of flow is impossible. Intuitively it is in fact difficult to see how to realize
it, and certainly some external force would be required to sustain it indefinitely, but the mathematical setup does not contain any condition to rule it out. Part of the difficulty is that, with the assumption that the density is incompressible, we have no independent information about the pressure. The pressure is determined by the requirement that the equations have solutions; the theory has no predictive power other than foreseeing the pressure distribution for hypothetical flows. There is no independent conclusions concerning what kinds of flows can be realized for any particular fluid.

Let us suppose that the flow described above is possible. The kinetic part of the Lagrangian is

\[ \bar{v}^2 / 2 + 2 \bar{v} \cdot \nabla \Phi + (\nabla \Phi)^2. \]

There is no contribution to balance the \( x \) dependence of the pressure; so the most reasonable choice of \( \nabla \Phi \) is a constant. Since this theory cannot accommodate a pressure gradient the most sensible course is to take a hint from the Navier-Stokes equation. In fact, what is needed is an extra term in the Lagrangian density:

\[ -\bar{x} \cdot \mu \Delta \bar{v}. \]

The viscosity is regarded as an “external” force that balances the pressure gradient.

So we learn that the presence of viscosity is not inconsistent with a Lagrangian formulation.

The physics of this situation seems to be as follows. The force that sustains the pressure gradient is the adhesion of the bottom layer of the liquid to the bottom. The upper layers are not immediately affected, until \( \nabla \bar{v} \) becomes appreciable, at which point a force of magnitude \((1/\rho)\nabla p\) is felt by the liquid in the bulk. This force, essentially an external, now attacks locally and it can be derived from the potential \(-\bar{x} \cdot \mu \Delta \bar{v}\). Since \( \nabla \bar{v} \) is constant, it is a uniform force acting like a gravitational potential, preserving energy in the sense that the total Hamiltonian, including the new potential, is preserved.

The rest is not interesting. Replace by a remark.

Now let the us give the bottom plate a constant inclination of angle \( \beta \), descending in the \( x \) direction. Contrary to usual practice we shall maintain the orientation of the axes, \( x \) axis horizontal and \( y \) axis vertical. We assume that the pressure gradient is perpendicular to the bottom plate, and that it is balanced against the gravitational force.

\[ p = p_0 - g \cos \beta (x \sin \beta + y \cos \beta), \]

so that

\[ p + \phi = p_0 + g \sin \theta (x \cos \beta - y \sin \beta). \]

The gradient of this is the part of the gravitational force that is uncompensated by the pressure on the plate. Now it is no longer possible to ignore the contribution of the velocity terms in

\[ \dot{\Phi} + \dot{\bar{A}}^2 / 2 + \dot{\bar{A}} \cdot \nabla \Phi - (\nabla \Phi)^2 / 2 = \phi + p = p_0 + g \sin \theta (x \cos \beta - y \sin \beta). \quad (11.4.8) \]

We have no guide to choosing the correction \( \delta p \), the last term.
Again we want \( u_x \) to be uniform, so

\[
\Phi = ct + ax + f(y).
\]

We try linear expressions for \( \dot{A} \):

\[
\dot{A}_x = a + bx + cy, \quad \dot{A}_y = dx + ey,
\]

so that the left side becomes

\[
c + \frac{(a + bx + cy)^2}{2} + \frac{(dx + ey)^2}{2} + a(a + bx + cy) + f'(dx + ey) - \frac{(a^2 + f'^2)}{2}.
\]
Boltzmann’s equation

1. Introduction.

We have come to a stage of the development of our program where it is essential to break out of the chains that have confined us to the special case of potential flow. We have seen, in the especially simple case of Couette flow, that non-potential flows are a fact of life. We have had some success in generalizing the axiom $\vec{v} = -\vec{\nabla}\Phi$, but we need to know what is the conventional approach to the problem, namely, the Navier Stokes equation and the underlying Boltzmann transport equation.

In spite of its title, this chapter is not an introduction to statistical mechanics. Instead, it is a study of the Boltzmann equation in its historical role in the development of the theory of non potential flows.

The Boltzmann equation deals with a phase space distribution function $f$, a function on the symplectic space $\mathbb{R}^6$ endowed with global coordinates $\vec{x}, \vec{p}$ and the usual Poisson bracket and of the time $t$. Boltzmann’s equation is

$$\dot{f} + \vec{\nabla}_x \cdot (\vec{p}f) + \vec{\nabla}_v \cdot (\vec{F}f) = \text{“collision terms”}.$$  

The right hand side is an expression that involves the scattering cross section. We shall confine ourselves to the “collisionless Boltzmann equation”

$$\dot{f} + \vec{\nabla}_x \cdot (\vec{v}f) + \vec{\nabla}_v \cdot (\vec{F}f) = 0,$$

also known among plasma physicists as the Vlasov equation.

The original Boltzmann equation is regarded as a statement of very general validity. Collisions are neglected by definition in the treatment of an ideal gas, and in a first approximation in the case of fluids of low density. It is worth pointing out that the collisionless Boltzmann equation is a strong simplification and at best an approximation to the genuine Boltzmann equation.

This equation is of the nature of a conservation law in six dimension, if complemented by the appropriate boundary conditions. It is used in this form in plasma physics, but to relate it to hydrodynamics and thermodynamics one must average over the velocities. The traditional approach sets up a hierarchy of “moments”. But before taking moments let us note that the equation can be formulated, when the external force is a gradient, as a hamiltonian equation of motion.

XI.2. Hamiltonian formulation

The natural symplectic structure on $\mathbb{R}^6$ is defined on pairs of functions,

$$\{A, B\}(\xi) = \sum_{i=1,2,3} \left( \frac{\partial A}{\partial x_i} \frac{\partial B}{\partial p_i} - A, B \right),$$

where $\xi_1, ..., \xi_6$ stand for the six natural coordinates. The only dynamical variable is the function $f$ and the observables are functionals of $f$. We shall confine ourselves to local functionals $\int d^6\xi \, Q(f)$, where $Q$ is a polynomial with coefficients in $\mathcal{C}_\infty(\mathbb{R}^6)$. 

427
The Poisson bracket on the infinite dimensional space of $\mathcal{C}_\infty$ functionals was defined by Morrison,
\[
\{\{A, B\}\} = \int d^6\xi \{\frac{\partial A}{\partial f}, \frac{\partial B}{\partial f}\} f.
\]

With this definition Boltzmann’s collision less equation is
\[
\dot{f} = \{\{H, f\}\},
\]
where the hamiltonian functional is
\[
H = \int d^6h(\xi), \quad h(\xi) = (\vec{p}^2/2 + \phi)f
\]
and external force is $\vec{F} = -\vec{\nabla}\phi$.  


REFERENCES


Bernoulli, D., Argentorat, 1738-220


Carnot, S., quoted by Emden (1907).


CHUEH, P.I. and PRAUSNITZ, J.M., ”Vapor-Liquid Equilibria at High Pressures: Calculation of Critical Temperatures, Volumes, and Pressures of Nonpolar Mixtures”, University of California, Berkeley, California


Dalton, page 73

Donnelly, R.J., Herman, R. and Prigogine, I., Non-equilibrium thermodynamics, variational techniques and stability, Proceedings of Symposium held at the Univ. of Chicago, 1965.


Dulong and Petit


Emden, Gaskugeln, Teubner 1907.


Fetter, A. L., “

Fetter, A.L. and Walecka, J.D., Theoretical Mechanics of Particles and Continua,
Fronsdal, C., Reissner-Nordstrom and charged polytropes,
Online First 09/11/2010 (ArXiv 0904.0427).
Fronsdal, C. and Wilcox, T. J., “An equation of state for dark matter”,
UCLA preprint 2011. To be submitted for publication.
Glavatskiy, K., “Multicomponent interfacial transport as described by the square
Graeff, R.W., Viewing the controversy Loschmidt-Boltzmann/Maxwell through
macroscopic measurements of the temperature gradients in vertical columns of water,
Helmholtz, H. “Die Thermodynamik chemischer Vorgänge”. In Wissenschaftliche
Abhandlungen; Barth, Germany, Volume II, 958-978 (1883).
Joule, J.P., Remarks on the heat and constitution of elastic fluids,
Phil.Mag. IV 211 (1857).
Karplus, R. and Neuman, M., Non-linear Interactions between Electromagnetic Fields,
Kaufman page 23.
Khalatnikov, I. M., *an Introduction to the theory of superfluidity*, Benjamin New York
1965.
Cambridge U. Press 1911.
Landau and Lifschitz
Lane, H.J., “On the Theoretical Temperature of the Sun, under the Hypothesis of a gaseous
Mass maintaining its Volume by its internal Heat, and depending on the laws of gases
as known to terrestrial Experiment”, Amer.J.Sci.Arts, Series 2, 4, 57- (1870).
Lemmon, E.W., Jacobsen, R.T., Penoncello, S.G. and Friend, D.G., “thermodynamic
Lieb, E.H. and Yngvason, J., “ The entropy concept for non-equilibrium states”,
arXiv 1305.3912.


Navier


Poisson, S.D., Théorie mathématique de la chaleur, 1835.


See page 15 about interactions vs collisions.


Ramsey, A.S., “Thermodynamics and Statistical Mechanics at Negative Absolute
Randall and Lewis (Pitzer and Brewer)
Reif,
Ritter, A., A series of papers in Wiedemann Annalen, now Annalen der Physik.
For a list see Chandrasekhar (1938). The volumes 5-20 in Wiedemann
Annalen appear as the volumes 241-256 in Annalen der Physik.
especially from page 199 onwards.
Savery, th., see the article on Savery in Wikipedia.
Schultz, B.F. Jr., Perfect fluids in General Relativity: Velocity potentials and a variational
Schwarzschild, K., Ueber das Gleichgewicht der Sonnenatmosphäre,
Göttinger Nachrichten, 41-53 (1906).
Stokes
Taub, A.H., General relativistic variational principle for perfect fluids,
Tisza, L., ”Thermodynamics in a state of flux. A search for new foundations”,
Proceedings of an International Symposium held at the University of Pittsburgh,
PA, in 1969, page 110.
Thomson, W., “On an absolute Thermometric Scale, Phil. Mag. 33, 313 (1848).
Thomson (Lord Kelvin) interpretation of early experiments.
Thomson, W., Lord Kelvin, On Homer Lane’s problem of a spherical gaseous nebula,
Nature 75 232-235 (1907).
Thomson, W., Lord Kelvin, On the convective equilibrium of temperature in the atmosphere, Manchester Phil.Soc. 2, 170-176 (1862).
Tolman, R.C., The electromotive force produced in solutions by centrifugal action,
Truesdell, C. *The tragicomical history of thermodynamics 1822-1854*,
Springer-Verlag, N.Y. 1980.
Trupp, A., *Physics Essays*, 12, No. 4, 1999
R S Turner, R.S., “The Ohm-Seebeck dispute, Hermann von Helmholtz, and the origins
Uhlenbeck page 48
Uhlenbeck,
Van der Waals, J.D., “Die continuitat des Gasforninge und flussige Zustandes”,
J.A. Barth, Leipzig 1899.


Wissner-Gross, A.D. and Free, C.E., “Causal Entropic Forces”,


White page 26

Gas-Gas Equilibria * J. DE SWAAN ARoNst AND G. A. M. DIEPEN Department of General and Inorganic Chemistry, Technical University, Delft, The Netherlands


Lecture Notes in Physics Volume 549 2000 Physics of Rotating Fluids Selected Topics of the 11th International Couette-Taylor Workshop Held at Bremen, Germany, 20?23 July 1999 Editors:

Christoph Egbers, Gerd Pfister

ISBN: 978-3-540-67514-3 (Print) 978-3-540-45549-3 (Online)

Generalized Variational Principle for Dissipative Hydrodynamics: Shear Viscosity from Angular Momentum Relaxation in the Hydrodynamical Description of Continuum Mechanics German A. Maximov N. N. Andreyev Acoustical Institute Russia 1. Introduction A system of hydrodynamic equations for a viscous, heat conducting fluid is usually derived on the basis of the mass, the momentum and the energy conservation laws (Landau & Lifshitz, 1986). Certain assumptions about the form of the viscous stress tensor and the energy density flow vector are made to derive such a system of equations for the dissipative viscous, heat conductive fluid. The system of equations based on the mass, the momentum and the energy conservation laws describes adequately a large set of hydrodynamical phenomena. However, there are some aspects which suggest that this system is only an approximation.

Consistent approximations and boundary conditions for ice-sheet dynamics from a principle of least action John K. DUKOWICZ, Stephen F. PRICE, William H. LIPSCOMB Climate, Ocean and Sea-Ice Modeling (COSIM) Project, Group T-3, MS B216, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA Email: duke@lanl.gov ABSTRACT. The formulation of a physical problem in terms of a variational (or action) principle conveys significant advantages for the analytical formulation and numerical solution of that problem. One such problem is ice-sheet dynamics as described by non-Newtonian Stokes flow, for which the variational principle can be interpreted as stating that a measure of heat dissipation, due to internal deformation and boundary friction, plus
the rate of loss of total potential energy is minimized under the constraint of incompressible flow. By carrying out low-aspect-ratio approximations to the Stokes flow problem within this variational principle, we obtain approximate dynamical equations and boundary conditions that are internally consistent and preserve the analytical structure of the full Stokes system. This also allows us to define an action principle for the popular first-order or is distinct from the action principle for the Stokes problem yet preserves its most important properties and elucidates various details about this approximation. Further approximations within this new action functional yield the standard zero-order shallow-ice and shallow-shelf approximations, with their own action principles and boundary conditions. We emphasize the specification of boundary conditions, which are problematic to derive and implement consistently in approximate models but whose formulation is greatly simplified in a variational setting. 1. INTRODUCTION Ice-sheet flow is typically modeled as an incompressible gravitationally forced Stokes flow, albeit for a non-Newtonian fluid with a power-law rheology. This is combined with an energy equation describing the evolution of internal temperature. Here we are concerned only with the dynamical part of the problem, the equations of incompressible, nonlinear Stokes flow, with the assumption that the internal temperature distribution is known. The Stokes problem for ice sheets has certain properties with important consequences for both the physical fidelity and numerical solvability of an ice-sheet model: namely, the system of incompressible Stokes equations is self-adjoint and is characterized by positive-definite dissipation (i.e. internal deformational heating). These properties can be traced to the existence of a variational principle (or an that is physically meaningful for this problem: namely, a measure of ice-sheet dissipation plus the rate of loss of potential energy is minimized under the constraint of incompressible flow. At present, the numerical solution of the full Stokes problem is not practical or routine for large-scale modeling of ice sheets. Various approximations are employed to produce simpler models that are easier and cheaper to solve. These include the (Hunke and Dukowicz, 2002). In particular, there is no guarantee that the associated system matrix will be symmetric or positive-definite, in which case numerical solution techniques will be less than optimal. Such problems may be avoided by deriving both approximations and discretizations within a variational framework, ensuring that the numerical model inherits the favorable properties of the underlying variational principle. Variational or action principles are ubiquitous in physics. A famous example is Hamiltonian mechanics and its many extensions to modern field theories. The existence of a variational principle is advantageous for both the analytical and numerical formulation of a problem for a number of reasons, including: 1. A variational principle is a concise statement of a problem in terms of a single scalar quantity, the functional, that is unchanged in all coordinate systems. Thus, the dynamical equations obtained from the variation of the functional naturally incorporate metric terms associated with any given coordinate system (e.g. Hunke and Dukowicz, 2002). A coordinate system is not even required since an unstructured grid may be used. 2. The functional
involves lower-order partial derivatives that are easier to discretize than the higher-order derivatives in the corresponding PDEs. 3. Given an action functional in discrete form, the variational process automatically yields symmetric, often positive-definite matrix systems that, as a result, are generally easier to solve efficiently (e.g. Newton methods). In fact, the variational principle may often be cast as an optimization problem, the minimization of an action functional, in which case a number of efficient 480 Journal of Glaciology, Vol. 56, No. 197, 2010

Title: Thermodynamic inconsistency of the modified Saha equation at high pressures

The cosmic century: a history of astrophysics and cosmology - Google Books Result
books.google.com/books?isbn=0521474361...M. S. Longair - 2006 - Science - 545 pages
These considerations led to the Saha equation, which describes the state of ... a pupil of Milne’s, who carried out these studies at Harvard under the ...

New quests in stellar astrophysics: the link between stars and cosmology ... By Miguel Ch


Appendix 1.80. Sound speed in Helium

Data from Sychev, Speed in Helium versus pressure, density not given, calculated from the cubic equation of state. measured speeds are in the middle row.

<table>
<thead>
<tr>
<th>$p$</th>
<th>.01</th>
<th>.1</th>
<th>1.0</th>
<th>3.0</th>
<th>7.0</th>
<th>15</th>
<th>30</th>
<th>50</th>
<th>Ideal</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho$</td>
<td>.00094</td>
<td>.011</td>
<td>.1656</td>
<td>.2007</td>
<td>.2254</td>
<td>.244</td>
<td>.257</td>
<td>.2635</td>
<td>gas:</td>
</tr>
<tr>
<td>$T = 5.19$</td>
<td>133.2</td>
<td>123.5</td>
<td>263.1</td>
<td>381.1</td>
<td>505.6</td>
<td>663.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cubic</td>
<td>132.8</td>
<td>122.0</td>
<td>273.1</td>
<td>438.7</td>
<td>683.3</td>
<td>1128.1</td>
<td>1839.7</td>
<td>2737.9</td>
<td>134.1</td>
</tr>
</tbody>
</table>

| $\rho$ | .0005 | .005 | .0605 | .1337 | .1823 | .2165 | .24 | .252 |       |
| $T = 10K$ | 185.9 | 184.5 | 197.8 | 322.7 | 479.0 | 643.1 | 816.4 | 1020.3 |       |
| Cubic | 185.8 | 183.5 | 198.0 | 314.5 | 506.2 | 823.11 | 1373.0 | 2047.1 | 186.1 |

| $\rho$ | .00024 | .0024 | .0246 | .068 | .1217 | .1713 | .2088 | .23 |       |
| $T = 20$ | 263.2 | 263.9 | 275.4 | 320.5 | 430.2 | 615.4 | 799.3 | 996.7 |       |
| Cubic | 263.2 | 263.4 | 272.7 | 320.6 | 438.2 | 661.8 | 1047.0 | 1534.0 | 263.2 |

| $\rho$ | .0001 | .001 | .0095 | .0273 | .0576 | .1008 | .1476 | .1807 |       |
| $T = 50$ | 416.2 | 417.1 | 427.3 | 451.9 | 501.8 | 599.0 | 766.4 | 957.2 |       |
| Cubic | 416.7 | 417.1 | 426.2 | 450.9 | 509.1 | 635.1 | 827.1 | 1180.0 | 416.2 |

| $\rho$ | .00005 | .0005 | .0053 | .0154 | .034 | .0643 | .105 | .139 |       |
| $T = 90$ | 558.3 | 559.0 | 566.7 | 584.2 | 619.9 | 687.93 | 808.1 | 952.3 |       |
| Cubic | 558.4 | 559.2 | 567.2 | 586.0 | 627.3 | 714.5 | 884.9 | 1106.6 | 558.4 |

| $\rho$ | .00003 | .0003 | .0034 | .01 | .0224 | .0443 | .0768 | .108 |       |
| $T = 140$ | 696.3 | 696.9 | 702.9 | 716.6 | 744.3 | 799.3 | 895.0 | 1044.8 |       |
| Cubic | 696.5 | 697.1 | 704.0 | 719.5 | 752.1 | 820.4 | 952.8 | 1130.0 | 697.4 |

| $\rho$ | .000024 | .00024 | .0024 | .0071 | .016 | .0323 | .058 | .085 |       |
| $T = 200$ | 832.2 | 832.7 | 837.7 | 848.8 | 871.4 | 917.1 | 999.1 | 1126.0 |       |
| Cubic | 832.4 | 833.0 | 839.0 | 852.4 | 879.8 | 936.3 | 1044.7 | 1191.6 | 832.4 |

| $\rho$ | .000017 | .00017 | .0017 | .0051 | .0116 | .0237 | .044 | .066 |       |
| $T = 280$ | 984.6 | 985.0 | 989.2 | 998.5 | 1017.1 | 1055.1 | 1125.5 | 1235.2 |       |
| Cubic | 984.9 | 985.4 | 990.6 | 1002.2 | 1025.6 | 1072.9 | 1164.8 | 1235.7 | 984.9 |

| $\rho$ | .000012 | .00012 | .0012 | .0036 | .0082 | .017 | .0321 | .05 |       |
| $T = 400$ | 1176.8 | 1177.2 | 1180.6 | 1188.3 | 1203.6 | 1234.6 | 1293.5 | 1388.3 |       |
| Cubic | 1177.2 | 1177.6 | 1182.0 | 1192.0 | 1211.6 | 1251.4 | 1327.2 | 1431.1 | 1177.1 |

| $\rho$ | .000007 | .00007 | .0007 | .002 | .0047 | .01 | .019 | .031 |       |
| $T = 700$ | 1556.8 | 1557.1 | 1559.6 | 1565.3 | 1576.6 | 1599.4 | 1642.8 | 1715.8 |       |
| Cubic | 1557.2 | 1557.6 | 1561.1 | 1568.2 | 1583.4 | 1614.2 | 1669.7 | 1750.3 | 1557.2 |

Data from Sychev, Speed in Helium versus pressure, density not given, calculated from the cubic equation of state. measured speeds are in the middle row.
<table>
<thead>
<tr>
<th>$p$</th>
<th>.01</th>
<th>.1</th>
<th>1.0</th>
<th>3.0</th>
<th>7.0</th>
<th>15</th>
<th>30</th>
<th>50</th>
<th>Ideal</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho$</td>
<td>.00094</td>
<td>.011</td>
<td>.1656</td>
<td>.2007</td>
<td>.2254</td>
<td>.244</td>
<td>.257</td>
<td>.2635</td>
<td>gas:</td>
</tr>
<tr>
<td>$T = 5.19$</td>
<td>133.2</td>
<td>123.5</td>
<td>263.1</td>
<td>381.1</td>
<td>505.6</td>
<td>663.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cubic</td>
<td>132.8</td>
<td>122.0</td>
<td>273.1</td>
<td>438.7</td>
<td>683.3</td>
<td>1128.1</td>
<td>1503.7</td>
<td>2047.1</td>
<td>143.1</td>
</tr>
<tr>
<td>$\rho$</td>
<td>.0005</td>
<td>.005</td>
<td>.0605</td>
<td>.1337</td>
<td>.1823</td>
<td>.2165</td>
<td>.24</td>
<td>.252</td>
<td></td>
</tr>
<tr>
<td>$T = 10K$</td>
<td>185.9</td>
<td>184.5</td>
<td>197.8</td>
<td>322.7</td>
<td>479.0</td>
<td>643.1</td>
<td>816.4</td>
<td>1020.3</td>
<td></td>
</tr>
<tr>
<td>Cubic</td>
<td>185.8</td>
<td>183.5</td>
<td>198.0</td>
<td>314.5</td>
<td>506.2</td>
<td>823.11</td>
<td>1373.0</td>
<td>2047.1</td>
<td>146.2</td>
</tr>
<tr>
<td>$\rho$</td>
<td>.00024</td>
<td>.0024</td>
<td>.0246</td>
<td>.068</td>
<td>.1217</td>
<td>.1713</td>
<td>.2088</td>
<td>.23</td>
<td></td>
</tr>
<tr>
<td>$T = 20$</td>
<td>263.2</td>
<td>263.9</td>
<td>275.4</td>
<td>320.5</td>
<td>430.2</td>
<td>615.4</td>
<td>799.3</td>
<td>996.7</td>
<td></td>
</tr>
<tr>
<td>Cubic</td>
<td>263.2</td>
<td>263.4</td>
<td>272.7</td>
<td>320.6</td>
<td>438.2</td>
<td>661.8</td>
<td>1047.0</td>
<td>1534.0</td>
<td>263.2</td>
</tr>
<tr>
<td>$\rho$</td>
<td>.0001</td>
<td>.001</td>
<td>.0095</td>
<td>.0273</td>
<td>.0576</td>
<td>.1008</td>
<td>.1476</td>
<td>.1807</td>
<td></td>
</tr>
<tr>
<td>$T = 50$</td>
<td>416.2</td>
<td>417.1</td>
<td>427.3</td>
<td>451.9</td>
<td>501.8</td>
<td>599.0</td>
<td>766.4</td>
<td>957.2</td>
<td></td>
</tr>
<tr>
<td>Cubic</td>
<td>416.7</td>
<td>417.1</td>
<td>426.2</td>
<td>450.9</td>
<td>509.1</td>
<td>635.1</td>
<td>827.1</td>
<td>1180.</td>
<td></td>
</tr>
<tr>
<td>$\rho$</td>
<td>.00005</td>
<td>.005</td>
<td>.053</td>
<td>.0154</td>
<td>.034</td>
<td>.0643</td>
<td>.105</td>
<td>.139</td>
<td></td>
</tr>
<tr>
<td>$T = 90$</td>
<td>558.3</td>
<td>559.0</td>
<td>566.7</td>
<td>584.2</td>
<td>619.9</td>
<td>687.93</td>
<td>808.1</td>
<td>952.3</td>
<td></td>
</tr>
<tr>
<td>Cubic</td>
<td>558.4</td>
<td>559.2</td>
<td>567.2</td>
<td>586.0</td>
<td>627.3</td>
<td>714.5</td>
<td>884.9</td>
<td>1106.6</td>
<td>558.4</td>
</tr>
<tr>
<td>$\rho$</td>
<td>.00003</td>
<td>.003</td>
<td>.034</td>
<td>.01</td>
<td>.0224</td>
<td>.0443</td>
<td>.0768</td>
<td>.108</td>
<td></td>
</tr>
<tr>
<td>$T = 140$</td>
<td>696.3</td>
<td>696.9</td>
<td>702.9</td>
<td>716.6</td>
<td>744.3</td>
<td>799.3</td>
<td>895.0</td>
<td>1044.8</td>
<td></td>
</tr>
<tr>
<td>Cubic</td>
<td>696.5</td>
<td>697.1</td>
<td>704.0</td>
<td>719.5</td>
<td>752.1</td>
<td>820.4</td>
<td>952.8</td>
<td>1130.0</td>
<td>697.4</td>
</tr>
<tr>
<td>$\rho$</td>
<td>.000024</td>
<td>.0024</td>
<td>.0071</td>
<td>.016</td>
<td>.023</td>
<td>.0258</td>
<td>.058</td>
<td>.085</td>
<td></td>
</tr>
<tr>
<td>$T = 200$</td>
<td>832.2</td>
<td>832.7</td>
<td>837.7</td>
<td>848.8</td>
<td>871.4</td>
<td>917.1</td>
<td>999.1</td>
<td>1126.0</td>
<td></td>
</tr>
<tr>
<td>Cubic</td>
<td>832.4</td>
<td>833.0</td>
<td>839.0</td>
<td>852.4</td>
<td>879.8</td>
<td>936.3</td>
<td>1044.7</td>
<td>1191.6</td>
<td>832.4</td>
</tr>
<tr>
<td>$\rho$</td>
<td>.000017</td>
<td>.0017</td>
<td>.0017</td>
<td>.0051</td>
<td>.0116</td>
<td>.0237</td>
<td>.044</td>
<td>.066</td>
<td></td>
</tr>
<tr>
<td>$T = 280$</td>
<td>984.6</td>
<td>985.0</td>
<td>989.2</td>
<td>998.5</td>
<td>1017.1</td>
<td>1055.1</td>
<td>1125.5</td>
<td>1235.2</td>
<td></td>
</tr>
<tr>
<td>Cubic</td>
<td>984.9</td>
<td>985.4</td>
<td>990.6</td>
<td>1002.2</td>
<td>1025.6</td>
<td>1072.9</td>
<td>1164.8</td>
<td>1235.7</td>
<td>984.9</td>
</tr>
<tr>
<td>$\rho$</td>
<td>.000012</td>
<td>.0012</td>
<td>.0012</td>
<td>.0036</td>
<td>.0082</td>
<td>.017</td>
<td>.0321</td>
<td>.05</td>
<td></td>
</tr>
<tr>
<td>$T = 400$</td>
<td>1176.8</td>
<td>1177.2</td>
<td>1180.6</td>
<td>1188.3</td>
<td>1203.6</td>
<td>1234.6</td>
<td>1293.5</td>
<td>1388.3</td>
<td></td>
</tr>
<tr>
<td>Cubic</td>
<td>1177.2</td>
<td>1177.6</td>
<td>1182.0</td>
<td>1192.0</td>
<td>1211.6</td>
<td>1251.4</td>
<td>1327.2</td>
<td>1431.1</td>
<td>1177.1</td>
</tr>
<tr>
<td>$\rho$</td>
<td>.000007</td>
<td>.0007</td>
<td>.0007</td>
<td>.002</td>
<td>.0047</td>
<td>.01</td>
<td>.019</td>
<td>.031</td>
<td></td>
</tr>
<tr>
<td>$T = 700$</td>
<td>1556.8</td>
<td>1557.1</td>
<td>1559.6</td>
<td>1565.3</td>
<td>1576.6</td>
<td>1599.4</td>
<td>1642.8</td>
<td>1715.8</td>
<td></td>
</tr>
<tr>
<td>Cubic</td>
<td>1557.2</td>
<td>1557.6</td>
<td>1561.1</td>
<td>1568.2</td>
<td>1583.4</td>
<td>1614.2</td>
<td>1669.7</td>
<td>1750.3</td>
<td>1557.2</td>
</tr>
<tr>
<td>$\rho$</td>
<td>.000005</td>
<td>.0005</td>
<td>.0048</td>
<td>.014</td>
<td>.033</td>
<td>.07</td>
<td>.137</td>
<td>.22</td>
<td></td>
</tr>
<tr>
<td>$T = 1000$</td>
<td>1860.7</td>
<td>1860.9</td>
<td>1863.0</td>
<td>1867.8</td>
<td>1877.2</td>
<td>1896.0</td>
<td>1931.7</td>
<td>1992.2</td>
<td></td>
</tr>
<tr>
<td>Cubic</td>
<td>1861.2</td>
<td>1861</td>
<td>1864.4</td>
<td>1870.5</td>
<td>1883.3</td>
<td>1908.7</td>
<td>1956.6</td>
<td>2019.7</td>
<td>1861.2</td>
</tr>
</tbody>
</table>

mm
| $\rho$ | .000005 | .0005 | .0048 | .014 | .033 | .07 | .137 | .22 |
| $T = 1000$ | 1860.7 | 1860.9 | 1863.0 | 1867.8 | 1877.2 | 1896.0 | 1931.7 | 1992.2 |
| Cubic | 1861.2 | 1861 | 1864.4 | 1870.5 | 1883.3 | 1908.7 | 1956.6 | 2019.7 | 1861.2 |

438
Vocabulary

Assigned entropy
Carnot cycle p 20
Density usually means mass density, in \( g/cm^3 \) or some other units.
D/Dt, pp 14, 16
Dissipation p 29
Equilibrium p 9
Eulerian p 7
Gibbs-Dalton hypothesis p 9
Hydrodynamics p 11
Ideal gas p 26
Immiscible p9
Internal energy p 19
Irrotational flow
Lagrange multiplier p 16
Legendre transformation
Multiplier, p8
Natural variables
Potential flow p 9
Potential
Thermodynamics p 3
Unary system p 8
Uniform, constant in space.
Units, see p 11
van der Waals p 9
VIII.3. Model vs He II

The condition of equilibrium can be examined by plotting both sides of Eq. (8.2.10), adjusting the parameters to make a best fit. Several good fits can be found; in what follows we have restricted attention to the measurements at \( p = 0 \). The simplest is to take \( b = 0, \)

\[
\frac{\ln \rho_2}{\rho_1} = 10 - 5.25 T. \tag{8.3.1}
\]

This is a very good fit for \( T \) in the upper interval \( .8 < T < \lambda \). Since, for He II, \( c_2^2 \) is close to unity, we may take

\[
a = c = 0, \quad b = -6 \tag{8.3.2}
\]

A very good fit for the entire range of temperatures is obtained with

\[
\ln \left( \frac{T}{\lambda - T} \right) = 6 \ln \frac{\rho_1}{\rho_2}, \tag{8.3.3}
\]

Fig. 8.3.1. First fit to concentration vs. temperature with Eq.(8.3.1). The ordinate is \( \ln \rho_2/\rho_1 \). Pressure =0?

Fig. 8.3.2. Second fit to concentration vs. temperature, with Eq.(8.3.3).
But a good fit to the equilibrium condition (8.2.10) that at the same time gives a good fit to the specific heat, Eq.(8.2.11) is

\[ \ln \frac{\rho_2}{\rho_1} = -1.5 \ln |T - .64| - 4T + 7.6. \]  \hspace{1cm} (8.3.4)

As seen in Fig.8.3.3 and Fig.8.3.4 it reproduces the behavior of Helium in the upper interval of temperatures, \( .6 < T < 2.1 \). At the same time it requires that

\[ \frac{C_V}{12\rho_1} = \frac{1.5}{|T - .64|} + 4, \quad c_2^2 = 12. \]

This is compared with experiments in Fig 8.3.5)

Fig.8.3.3. Best fit, with Fig.8.3.4, to concentration vs. temperature.

Fig.8.3.4. \( C_V/\rho_1 \) vs. temperature, Eq.(8.3.4.new). See SuperCV.Jan.1.gcf

A better model of He II must take into account that \( S_2 \) is not quite zero; in fact, it is quite significant at the lowest temperatures.
All of the functions vary over many orders of magnitude, which makes it difficult to bring out detailed structure. But the function \( C_V/s \) varies little, and the plot, Fig.8.3.3, reveals a cusp at \( T = 1 \) or slightly lower, close to the bend in Fig.8.3.1.

**The physical interpretation; temperature**

We have shown that some of the stationary properties of the model show a marked affinity to super fluid Helium. What is more remarkable is that some dynamical features are also represented, in spite of a very different physical interpretation.

The model incorporates London’s insight concerning entropy, and it agrees with Landau’s approach to two-fluid dynamics, up to a point. What is not clear in Landau’s theory is the thermodynamic interpretation. A set of equations is produced to account for the phenomena, but the dynamics that they describe appears to be non adiabatic. To explain that statement consider the propagation of sound, in normal thermodynamics and according to the model.

The Gibbsean action principle regards the pressure and the entropy as fixed parameters. It is not usual to lump both variables together in this way, but we have found it instructive to do so. To generate a sound wave in an ideal gas we interfere with the adiabatic system by driving a periodic variation of the pressure locally at one of the walls. A periodic variation of the density is generated, the thermodynamic pressure in the bulk is determined by the equations of motion. The motion is adiabatic away from the wall, in the sense that the Euler Lagrange equations are satisfied. Included in this system of equations is the adiabatic condition that relates the temperature to the density, and the specific entropy is fixed.

To generate normal sound in the super fluid the same procedure can be used. Second sound can also be generated mechanically, by vibrating a membrane that is permeable to the superfluid. But historically what is more significant is that second sound can be generated by temperature fluctuations at the wall. In Landau’s theory the temperature is one of the dynamical variables that appear in the equations of motion, so a traveling wave is quite naturally excited. In the model the interpretation is more precise. Adiabatic dynamics has \( S_1 \) and \( S_2 \) fixed, the latter equal to zero. The adiabatic condition fixes the temperature in terms of \( S_1 \). The presence of a heat source at a wall perturbs the adiabatic system by providing an oscillating input and withdrawal of heat, changing the entropy. More significantly, this produces a fluctuation of the densities. As this density waves propagates adiabatically it obeys the adiabatic equations of motion with fixed entropy parameters, and with fixed temperature. It is worth pointing out that the relation (8.2.10) between concentration and temperature is not adiabatic; it holds only at equilibrium. It is not inconsistent to hold that a density wave can exist at a fixed temperature.

**The physical interpretation; concentration**

In Landau’s theory the concentration seems to be reduced to a parameter; more precisely to a fixed function of the density and the temperature. This function is often referred to as an equation of state; nothing in the dynamics gives an indication of what it is. This situation is analogous to hydrodynamics, derived from thermodynamics by eliminating the temperature using the adiabatic condition. The reduced theory is capable of describing some of the dynamics, but it is lacking in that it gives only a partial view of the more
complete, underlying thermodynamics. Since, in Landau’s theory, the concentration is not an independent adiabatic variable the propagation of dual sounds relies on oscillations of the temperature.

To compare our model with the phenomenological approach of Arp and others we can use the equilibrium condition to eliminate the concentration, to produce a partially on shell theory in which the concentration does not appear. In this formulation one can define, somewhat arbitrarily, all the thermodynamic machinery of a unary system, but of course second sound cannot be accounted for. The model is in no way in conflict with the phenomenological approach, but it does include the more complete dynamics of a binary system. As to Landau’s theory, in spite of many similarities, there are real differences. Both have a certain amount of latitude and we have not yet found a good way to distinguish between them experimentally. So far, Landau’s 2-fluid theory has been able to account for all the facts. It remains to be seen if the model can be improved to do as much while preserving its basic simplicity. If it can, then the choice between the two approaches becomes an aesthetic one. The difference in the treatment of the pressure may favor the model.

**Dynamical equations of the model**

Since Landau’s theory an be presented as a collection of formulas, let us list the equations of the model:

- Two equations of continuity, derived from variation of the action with respect to the velocity potentials.

- An adiabatic condition, from variation of \( T \), one of the fundamental relations of thermodynamics. In the simplest model it fixes the temperature in terms of the specific entropies.

- Variation of the densities gives the Bernoulli equations

\[
-\frac{D\vec{v}_1}{Dt} = \text{grad} \left( \frac{\partial f}{\partial \rho_1} + S_1 T \right) = 0, \quad -\frac{D\vec{v}_2}{Dt} = \text{grad} \left( \frac{\partial f}{\partial \rho_2} \right).
\]

Finally, at equilibrium,

\[
\frac{\partial f}{\partial \rho_1} + S_1 T = \frac{\partial f}{\partial \rho_2};
\]

this from variation of the densities holding \( \rho \) fixed. That is all.

**Fountain effect revisited**

We promised to show that the model incorporates the fountain effect. Indeed, the last two equations inform us that, if the entropy is increased (by adding heat to the system at rest), the normal fluid will accelerate in the normal manner, while at least to begin with,
the acceleration of the superfluid will be in the opposite direction. At the mouth of the capillary \( \vec{v}_1 = 0 \). At equilibrium \( \vec{v}_2 = 0 \) as well, and then

\[
\text{grad } p = -\rho_1 \text{grad } \frac{\partial f}{\partial \rho_1} - \rho_2 \text{grad } \frac{\partial f}{\partial \rho_2} = \rho_1 S_1 \text{ grad } T.
\]

At the entrance to the capillary there is a discontinuity, and

\[
\Delta p = \rho_1 S_1 \Delta T.
\]

This is the fountain pressure.
Final remark

Except for the reference to the fountain pressure, and the propagation of sound, have treated only stationary configurations. But one of the most fascinating properties of superfluid helium has to do with turbulence, such as in the rotating bucket experiment, when a cylindrical vessel filled with superfluid is rotated about a fixed axis. This situation is otherwise known as Couette flow; in fact other fluids behave much the same way. We cannot take up the study of rotational flow at this time, because we are limited to describe only potential (gradient) flows. But Couette flow shall be discussed in Chapter XI, and then we shall show how our variational principle can be generalized to include rotating flows. This will enable us to return to the superfluids for a more general treatment.

Of course, $T$ is assumed to be uniform. Eliminating $\rho^2$ in favor of $x$ we get

$$p_1(\rho_1) = R_1 \rho_1 T + a(k - 1) \rho_1^k \left( \frac{R_1 \rho_1 - x}{R_2} \right)^k.$$ 

Some simplification can be achieved by interpreting the densities as molar densities in which case $x = n_1 - n_2$ and after renomalization of the constant $a$,

$$p_1(\rho_1, x) = \rho_1 T + a(k - 1) \rho_1^k (\rho_1 - x)^k.$$

In order that this equation admit more than one value for $\rho_1$ there must be a stationary point, at which

$$\frac{\partial}{\partial \rho_1} p_1(\rho_1, x) = T + ak(k - 1) \rho_1^{k-1} (\rho_1 - x)^{k-1} (\rho_1 - x + \rho_1) = 0$$

or

$$T = ak(1 - k)(\rho_1 \rho_2)^{k-1}(\rho_1 + \rho_2).$$

$$\det\left(\frac{\partial p_i}{\partial \rho_j}\right)_{i,j=1,2} = 0.$$ 

Hence if $a > 0, k$ must lie in the interval $(0,1)$.

The highest temperature at which this can happen is reached when

$$k \rho^2 = \rho_1^2 + \rho_2^2,$$

with $\rho := \rho_1 + \rho_2$. Hence $k < 1$ and $a > 0$. The molar densities are equal if $k = .5$; if $k$ is close to one or the other is much smaller than the other and if $k = 1$ there is free mixing at all temperatures.

The maximal temperature at which there are two phases is

$$T_{cr} = 2^{1-k} ak(1 - k)^k \rho^{2k-1}$$

The existence of the phenomenon depends on finding a pair of gases for which the interaction free energy has the the form $a(\rho_1 \rho_2)^k$, with $a > 0$ and $k < 1$. Immiscible gases are known but the temperature has to be near the gas-liquid critical point and the treatment
in terms of ideal gases is not appropriate. It is usual to use the van der Waals equation of state, as we shall do next. But first, a remark.

We have been describing a system at constant pressure and constant total masses \( M_1, M_2 \). If suffices \( a, b \) denote the two parts of the separated system we have \( M_i = V^a \rho^a_i + V^b \rho^b_i, i = 1, 2 \). These relations fix the two volumes once the densities (here in grams/cm\(^3\)). Any change in volumes must lead to a change in densities, even if the temperature is kept constant. The amount of heat required depends on the heat of mixing, if any, and can be calculated from the change in entropy. The maximum entropy principle tells us that, at equilibrium, the value of the free energy ??

**Determination of the critical point**

Separation implies the existence of 2 distinct points in \( \mathbb{R} \) of \((\rho_1, \rho_2)\) for fixed values of \( p_1, p_2 \). We are interested in the limiting case when these two points flow together. At this point there is a direction \( \vec{a} \) in tangent space such that, if \( p_{ij} = \partial_j p_i \),

\[
\vec{a} \cdot \nabla p_i = p_{ij} a^j = 0, \quad i = 1, 2.
\]

in other words, \( \vec{a} \) is a null eigenvector of the matrix \( p = (p_{ij}) \). The determinant of this matrix is thus zero; in accord with the implied function theorem.

In the calculation we made use of the fact that \( p_1 - p_2 \) evidently satisfies

\[
(R_2 \partial_1 + R_1 \partial_2)(p_1 - p_2) = 0,
\]

so that the vector \( \vec{a} = (R_1, R_2) \). Instead of eliminating \( \rho_2 \) in favor of \( x \) we could have varied \( p_1 \) along this direction;

\[
(R_2 \partial_1 + R_1 \partial_2)p_1(\rho_1, \rho_2) = 0
\]

gives the same result as \( \partial_1 p(\rho_1, x) = 0 \).

According to the general theory, a critical point is one where there is a tangent vector with the properties

\[
p_{ij} a^i a^j = 0, \quad p_{ijk} a^i a^j a^k = 0,
\]

where \( p_{ijk} = \partial_k \partial_j p_i(\rho_1, \rho_2) \). The direction of \( \vec{a} \) is gotten from the first equation and can be inserted into the third equation to produce a complicated polynomial of the fourth order in the components of these tensors. But since, in this case, we know the direction of \( \vec{a} \) this amounts to

\[
(R_2 \partial_1 + R_1 \partial_2)^2(R_1 p_1 + R_2 p_2) = 0,
\]

and since the operator \( R_2 \partial_1 + R_1 \partial_2 \) annihilates \( p_1 - p_2 \)

\[
(R_2 \partial_1 + R_1 \partial_2)^2 p_1(\rho_1, \rho_2) \propto \partial_1^3 p_1(\rho_1, x) = 0.
\]

To work this out we introduce some abbreviations:

\[
p_{11} = q_1 + w/\rho_1, \quad p_{12} = w/\rho_2,
\]

447
\[
p_{21} = \frac{w}{\rho_1}, \quad p_{22} = q_2 + \frac{w}{\rho_2}.
\]
and \( w = \alpha k(k-1)(\rho_1\rho_2)^k \). Then
\[
\vec{q} \cdot \vec{p} \det p = q_1^2q_{21} + q_1q_{21} \frac{w}{\rho_2} + (k-1)q_1^2 \frac{w}{\rho_1^2} + kq_1q_2 \frac{w}{\rho_1\rho_2} + q_2^2q_{12} + q_2q_{12} \frac{w}{\rho_1} + (k-1)q_2^2 \frac{w}{\rho_2^2} + kq_2q_1 \frac{w}{\rho_1\rho_1}.
\]

To simplify further suppose that the temperature is much higher than the evaporation temperature of the second fluid, so that it can be treated as an ideal gas, \( a_2 = b_2 = 0 \). Then \( q_1 = RT \) and
\[
\vec{q} \cdot \vec{p} \det p = q_1^2q_{21} + q_1q_{21} \frac{w}{\rho_2} + 2kq_1q_2 \frac{w}{\rho_1\rho_2} + (k-1)q_1^2 \frac{w}{\rho_1^2} + (k-1)q_2^2 \frac{w}{\rho_2^2}.
\]
This is a cubic polynomial in \( T \).

But thermodynamic considerations presented in Gibbs\%UTF00D5groundbreaking paper from 1875-8 show that equilibrium cannot in general be identified with a state of minimum energy. A system doesn\%UTF00D5t attain equilibrium by minimising energy simpliciter, but under the condition that the entropy is constant.

Note that \( ?S \) is not necessarily positive under isothermal conditions; the principle that equilibrium corresponds to an entropy maximum holds under the condition that the energy is constant, whereas what is now under consideration are conditions of constant temperature and pressure. Duhem warns of drawing erroneous consequences if the restriction is not observed. %UTF00D2It is quite certain, for example, that the entropy of a mass of water decreases when it is vaporises at constant temperature%UTF00D3 (1887, p. 164).

\[ \beta = 0. \] Lower critical point

\[
T= .2, p= .00525, T= .3, p=.0122, T= .4, p= .0223, T= .5, p=.0361, T=.6, p=.0539, \quad T= .7, p=.0762 \quad T= .8, p= .1039, T=.9, p= .138, T=1, p= .1803
\]
Up to \( T=1.07 \) lines of constant \( p \) include a ring around the critical point.

Upper critical point.

\[
T=1.07, p= .13, T=1.1, p= .234 \quad The \ ring \ forms \ at \ p= .21. \quad T=1.15, p= .267 \ the \ ring \ forms \ at \ p= .26 \ T=1, p= .01, T=1, \ negative \ pressure
\]

Now let us turn on the interaction. If it is attractive, \( \alpha < 0 \), the oval regions in Fig.\_Symmx shrink and soon disappear.

It the interaction is repulsive, \( \alpha > 0 \) the oval regions expand as they fill the domain \( 0 < x, y < 1 \); that is, the liquids become more and more miscible. Let us fix \( b \) at a relatively strong value, and vary the temperature. At very low temperatures the liquids are miscible.
As the temperature is increased they coexist in a domain that shrinks, to disappear as the temperature reaches the value 1.9.

Reading the pressure from the Figure we obtain the following vapor pressure curve for $\beta = 5$,

$T=.1$, $p=.0014$, $T=.2$, $p=.0057$, $T=.4$, $p=.204$, $T=.6$, $p=.057$, $T=.8$, $p=.108$, $T=.9$, $p=.141$, $T=1$, $p=.18$, $T=1.1$, $p=.227$, $T=1.2$, $p=.344$, $T=1.3$, $p=.418$, $T=1.4$, $p=.505$, $T=1.5$, $p=.610$, $T=1.6$, $p=.735$, $T=1.7$, $p=.893$, $T=1.8$, $p=1.11$, $T=1.9$, $p=1.5$, $T=2$, $p=1.8$

The other line yields

$T=.01$, $p=.00013$, $T=.152$, $p=0$, $T=.2$, $p=.35$, $T=.4$, $p=1.35$, $T=.6$, $p=1.96$, $T=.8$, $p=2.32$, $T=1$, $p=2.55$, $T=1.1$, $p=2.62$, $T=1.2$, $p=2.66$, $T=1.3$, $p=2.67$, $T=1.4$, $p=2.65$, $T=1.5$, $p=2.61$, $T=1.6$, $p=2.53$, $T=1.7$, $p=2.4$, $T=1.8$, $p=\lambda 2$, $T=1.9$, $p=1.88$

Taking $\beta = 1$:


$T=.83$, $p=0$, $T=.9$, $p=.15$, $T=1$, $p=.33$, $T=1.1$, $p=.47$, $T=1.2$, $p=.57$, $T=1.3$, $p=.61$, $T=1.4$, $p=.6$

Taking $\beta = 2$ is a weak interaction. The oval region exists for $T < 1.2$. The pressure is positive when $x, y$ are not too different

At $\beta = .2$, Lower critical point,


Upper $T=1.4$, $p=1.00$, $T=1.45$, $p=.95$, $T=1.47$, $p=.94$, $T=1.1$, $p=.89$, $T=1.2$, $p=.97$, $T=1.3$, $p=1.02$, $T=1$, $p=.77$, $T=.9$, $p=.63$, $T=.8$, $p=.44$, $T=.7$, $p=.2$, $T=.63$, $p=0$. 

449
What follows should be incorporated in the preceding pages.

A. Symmetric solutions

We begin by mapping the saturation region for a range of values of the parameters $\hat{a}$ and $\beta$. This is done most easily by looking for solutions of the equation

$$q(x, y) = \ln \frac{x}{1 - x} + \frac{1}{1 - x} - 2\hat{a}x + \frac{k\beta}{x} (xy)^k = q(y, x), \quad (\text{Ducie1})$$

excluding the trivial solution $x = y$. Earlier studies suggest that the most likely value for the power is $k = 1$; we limit ourselves to that case.

Unexpectedly, immiscibility between two van der Waals gases is not confined to the case of repulsive interactions between unlike particles. A most interesting case occurs when there is none. This case is the easiest one to study; we shall explore weak interactions on either side, $\beta = -1, 0$ and 1.

The range of the parameter $\hat{a}$ that corresponds to the saturation region of either pure liquid is from 3.4 to 4; higher values are possible but then the pressure is not everywhere positive.

Fig.s Ducie1 and Dulcie 1a, 1b show the loci of solutions of Eq. (Ducie1) for the case $\beta = -1$.

A point of the purple curve, $x \neq y$, $0 < x, y < 1$ corresponds to a separation of the mixture into two parts, with densities $\rho_1, \rho_2 = x/b, y/b$, resp. $y/b, x/b$. The green line is the locus of scaled pressure equal to .1

Fig.Ducie1. Loci of solutions of Eq.(Ducie1) for the value $\beta = -1, \hat{a} = 4$. The green curve is the locus $\hat{p} = .1$, where $\hat{p}$ is the scaled pressure.
Fig.Ducie1a. Loci of solutions of Eq.(Ducie1) for the value $\beta = -1, \hat{a} = 5$. The region of positive pressure is painted green.

Fig.s Dulcy2 and 2a give analogous results for the case of no interaction between unlike particles.

Fig.Ducie2. Loci of solutions of Eq.(Ducie1) for the case $\beta = 0, \hat{a} = 4$. The green line is a locus of constant pressure.

Fig.Ducie2a. Loci of solutions of Eq.(Ducie1) for the case $\beta = 0, \hat{a} = 4$.

Fig.Ducie3. Loci of solutions of Eq.(Ducie) for the case $\beta = 1, \hat{a} = 4$.

Fig.Ducie3a. Loci of solutions of Eq.(Ducie) for the case $\beta = 1, \hat{a} = 4$. Here there are 4 coexistent concentrations. Are they stable?

To confirm the calculations we plot the free energy, for example, in Fig.Dulcie4, for the case $\beta = 1, \hat{a} = 4$. For the value of $f = -1.582$ and $x + y = .82$ locate the two minima at $x = .102$ and $x = .702$ and verify that the densities correspond to the coordinates of a point on the symmetry curve. Show the point.

As the value of the pressure is varied the loci (green lines) shift. Where a green curve touches a purple line is a critical point. We shall not go into details at this point because, the temperature having been scaled away, the physics is not clear.

B. Non-symmetric solutions

These solutions are directly related to the saturated states of the individual components. The structure is complicated but this is to some extent alleviated by the fact that they exist even in the absence of the inter component interaction, when $\alpha = 0$. The three conditions
that determine equilibrium are then easily solved by adjusting the values assigned to \( q_1, q_2 \) and \( p \), as in

\[
q_1 = \ln \frac{x}{1 - x} + \frac{1}{1 - x} - \frac{27}{8T} x = -1.853,
\]

\[
q_2 = \ln \frac{y}{1 - y} + \frac{1}{1 - y} - \frac{27}{8T} y = -1.874,
\]

\[
p = \frac{x}{1 - x} - \frac{a}{T} x^2 + \frac{y}{1 - y} - \frac{27}{8T} y^2 = .158.
\]

Fig.31. Maria1. No interaction. Loci of \( q_1 \) (blue) and \( q_2 \) (red) and \( p \) (green curve) for the case that \( T_r = 27/32 \). The critical temperature for the second liquid is \( T = 1 \). This curve is known as the spinoidal.

One of the curves is wrong.

Let \( \alpha = \beta = 0 \). The locus \( q_1 = C_1 = \) constant is a vertical line in the \( x,y \)-plane as shown in Fig.31. Maria1 or, for a range of values of \( C_1 \), 3 vertical lines.. The locus \( q_2 = C_2 \) consists of 3 horizontal lines. In the illustration the chosen values of the chemical potentials are in the saturation regions of both fluids. The green line is a locus of evaluation of the pressure. The value of \( q_2 \) was adjusted until two intersections of the horizontal lines with one of the vertical lines have the same pressure. The coordinates of the intersections are the densities of two coexistent mixtures. The saturated state of the second liquid is exactly as if this liquid were alone, but in order to mix with this state the density of the first liquid must have a uniquely determined value of .615. Note that the first component is in the liquid phase in both mixtures. So much for the case of no interaction between the two liquids.

Stability!

Fig.Maria2 Weak interaction, \( \beta = .05 \).

Fig.Maria3. The case \( \beta = .5 \).

452
When an interaction is present this simple picture is deformed as illustrated in Fig.Maria2 for the case $\beta = .05$. The appearance of two nearly vertical purple lines represent the gaseous and the unstable phases of the first liquid. The two mixtures appear virtually unchanged, but now there is a similar set of mixtures in which the roles of the two liquids are reversed, with a lower pressure (blue line). The illustration Fig.Maria3 is drawn for the stronger interaction $\beta = .5$. This is a critical point, see below. Stability may be a problem here.

Critical points are points in the space of parameters and variables that mark the onset of a new kind of coexistence.
VI.3. Critical points This section is dubious.

With changing parameter values the two points in density space get displaced. Some times they collide and annihilate each other. This happens whenever there is a tangent vector at which the first and the second differential of the function $f$ vanish, where the cotangent 2-vectors

$$(q_1, q_2), (f_{11}, f_{21}), (f_{12}, f_{22})$$

are parallel. Thus

$$q_1 f_{21} - q_2 f_{11} = q_1 f_{22} - q_2 f_{21} = 0.$$ 

What about constant terms in the $q$’s? In terms of our scaled densities these equations read

$$\beta (\ln x + \frac{1}{1-x} - 2\hat{a}x + \beta y) = (\frac{1}{x(1-x)^2} - 2\hat{a}) (\ln y + \frac{1}{1-y} - 2\hat{a}y + \beta x),$$

$$\beta (\ln y + \frac{1}{1-y} - 2\hat{a}y + \beta x) = (\frac{1}{y(1-y)^2} - 2\hat{a}) (\ln x + \frac{1}{1-x} - 2\hat{a}x + \beta y).$$

When $\beta = 0$ they are satisfied at the 9 intersections in Fig.1. When $\beta = .5$ (the interparticle interaction repulsive) the figure is deformed as in Fig.2. Only 4 intersections remain, the additional intersections in Fig.1 are spurious. The pressure locus - light blue curve - corresponds a $p = .14223$. Stability again!

We list the 4 intersections in the order of increasing pressure.

1. Coordinates $x, y = .5347, .1788$ (or vice versa). The values of the chemical potentials are $q_1 = -1.900, q_2 = -1.470$. These values were chosen as input values in Fig.3. Here we see that the red and the purple lines that crossed at right angles in Maria1, and at oblique angles in the case of a weak interaction in Maria2, are about to end their commerce. That is, the two intersections have coalesced, with a further deformation there will be no intersections. so indeed we have located a critical point of the mixture.

Fig.1. Critical points, no interaction.

Fig.2. To Fig.1 we have changed $\beta$ to .5 and added the lines $p = .14223$ and $p = .1935$.

2. $1.436 < p < 1467$. When the pressure is in this interval the pressure locus is connected to form a figure 8. The accuracy of the calculation does not allow us to determine whether the interval may be smaller and even reduce to a single point. We do not know what may be the interpretation of this phenomenon.
3. $p = .1464$ - greencurve - intersection at $x = y = .527938$ and $p = .1935$- light blue curve- intersection at $x = y = .17132$. These are the two star points in Fig.Dulcie3a. The same information in Fig.Action4. These points are what we have called symmetric solutions, in the limit of equal densities.

Fig.Action3. Same as FigDulcie3a with pressure loci added.

Fig.Action4. Same as FigDulcie3a with pressure loci added.

The structure of critical points is thus much simpler than that of coexistent regions.

We have seen that there are 2 kinds of critical points. The first, defined by the symmetrical solution, occurs at a certain value of the concentration, at comparable densities, and will usually involve 2 liquids or two gases. The other arises in a situation where one of the fluids is nearly critical and the other is all gas or all liquid. But the scheme of our calculation is not the most natural one. Instead we should fix a value of $\alpha$ and vary the temperature. We shall examine a particular case.

<table>
<thead>
<tr>
<th></th>
<th>1.363</th>
<th>0.03219</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon</td>
<td>0.03457</td>
<td>0.0237</td>
</tr>
<tr>
<td>Helium</td>
<td>0.2135</td>
<td>0.01709</td>
</tr>
<tr>
<td>Neon</td>
<td>4.250</td>
<td>0.05105</td>
</tr>
<tr>
<td>Xenon</td>
<td>1.385</td>
<td>0.03219</td>
</tr>
</tbody>
</table>

One may try to try to replace $\alpha$ by $\alpha T$. The potential is then

$$V = \sum R_i \rho_i T \ln \frac{\rho_i}{T^m k_{0i}} + \alpha T \sqrt{\rho_1 \rho_2}.$$  

The new term may be considered as an addition to the free energy, and the expression for the entropy density is affected; it is possible to retain the homogenous entropy predicted by Gibbs-Dalton theory. Thus we retain the former values of the parameters $k_{0i}$.

Variation of the temperature gives

$$\sum R_i \rho_i \ln \frac{\rho_i}{(eT)^{n_i} k_{0i}} + \alpha \sqrt{\rho_1 \rho_2} = 0.$$  

The individual gases are no longer polytropic, even at equilibrium. The expression for the internal energy is independent of $\alpha$ and the sum formula (2.6) for the total pressure also remains valid.
Adiabatic changes obey
\[
\frac{dT}{T} \sum R_i \rho_i n_i = \sum R_i d\rho_i \left( \ln \frac{\rho_i}{(eT)^{n_i k_0i}} + 1 \right) + \frac{\alpha}{2} \sqrt{\rho_1 \rho_2} \sum \frac{d\rho_i}{\rho_i}.
\]

Define
\[
N_i = R_i \rho_i \ln \frac{\rho_i}{(eT)^{n_i k_0i}}, \quad N = \frac{N_1 - N_2}{2},
\]
then
\[
\frac{dT}{T} \sum R_i \rho_i n_i = \sum R_i d\rho_i + N \left( \frac{d\rho_1}{\rho_1} - \frac{d\rho_2}{\rho_2} \right).
\]

The linearized equation of motion is
\[
\frac{d\ddot{\rho}_1}{\rho_1} = -\dot{v}'_1 = \partial_x^2 \partial V, \quad \frac{\partial V}{\partial \rho_1} = T R_1 (\ln \frac{\rho_1}{(eT)^{n_1 k_01}} + 1) + \frac{\alpha}{2} \sqrt{\rho_2 \rho_1},
\]
with
\[
\frac{d\partial V}{\partial \rho_1} = \frac{dT (R_1 + \frac{N}{\rho_1}) + R_1 T \frac{d\rho_1}{\rho_1} + \frac{\alpha}{4} \sqrt{\frac{\rho_2}{\rho_1}} \left( \frac{d\rho_2}{\rho_2} - \frac{d\rho_1}{\rho_1} \right)}{\sum R_i \rho_i n_i} \left( R_1 + \frac{N}{\rho_1} \right) \left( \sum R_i d\rho_i + N \left( \frac{d\rho_1}{\rho_1} - \frac{d\rho_2}{\rho_2} \right) \right)
\]
\[
+ R_1 T \frac{d\rho_1}{\rho_1} + \frac{\alpha}{4} \sqrt{\frac{\rho_2}{\rho_1}} \left( \frac{d\rho_2}{\rho_2} - \frac{d\rho_1}{\rho_1} \right).
\]

This time, \( e^2 \) is an eigenvalue of the matrix
\[
\begin{pmatrix}
1 + A_1 (\rho_1 + N/R_1) - \beta \tau^{-1/2} & A_1 \kappa (\rho_2 - N/R_2) + \beta \tau^{-1/2} \\
A_2 (\rho_1 + N/R_1) + \beta \tau^{1/2} & \kappa + A_2 \kappa (\rho_2 - N/R_2) - \beta \tau^{1/2}
\end{pmatrix},
\]
where
\[
A_1 = \sum R_i \rho_i n_i \left( R_1 + \frac{N}{\rho_1} \right)
\]
and \( \beta = (\alpha/4 R_1) \). For large \( \alpha \) the eigen vector has \( d\rho_1/\rho_1 = d\rho_2/\rho_2 \) and \( \alpha \) is eliminated by adding \( \rho_1 \) times the sum of the elements in the first row and \( \rho_2 \) times the sum of the elements in the second row, with the result
\[
A_1 R_1 \rho_1^2 + R_1 T \rho_1 + A_2 R_2 \rho_2^2 + R_2 T \rho_2 - v^2 (\rho_1 + \rho_2) = 0,
\]
which again agrees with (3.10).

Both models can account for the experiments within a range of temperatures and frequencies. The only observation at a temperature other than room temperature that is
known to us is that of Smorenburg et al (Smorenburg 1995). At a molar concentration of 3:1 in He/Ar (Type 2), \( \rho_1/\rho_2 = .3 \), at 160K and 370 bar, they observe the same sound speed as in pure helium. This may indicate that, of our two models, the second one is closer to observation. The main difference is that the first model, with a moderate value of the coupling strength \( \alpha \), predicts 2 speeds at high temperatures.

Lists of pairs, and some triples, of gases with nearly equal vDW parameters

1. Argon (40), \( T_c = 150K, p_c = 4.9MPa \), and oxygen (32), \( T_c = 155K, p_c = 5MPa \).
2. Carbon monoxide (28) and nitrogen (34), \( T_c = 126K, p_c = 3.4MPa \).
3. Carbon dioxide (44), boils at 82K and hydrogen chloride (36.5), boils at 188K.
4. Hydrogen bromide (81) and hydrogen sulfide (34)
5. Fluoromethane (34) \( T_c = 318K, p_c = 6.28MPa \) and phosphine (34), boils at 185K.
6. Hydrogene selelenide (81) and nitrogen dioxide (46)
7. Chlorine (35.5) and sulfur dioxide (64)
8. Chloromethane (50.5), boils at 249K and cyanogen (52), toxic, boils at 252K and dimethyl ether (46)
9. Chloroethane (64.5) and ethylamine (45)
10. Acetonitrile (41) and benzene (78)
11. Acetic anhydride (102) and fluorobenzene (96) and carbon tetrachloride (154)
12. Cyclohexane (84) and germanium tetrachloride (214.5)

If the normal component could be represented as an ideal gas,

\[
f = \mathcal{R} \rho_1 T \ln \frac{\rho_1}{\rho_1^n_1} + f_2(\rho_2),
\]

then the internal energy density would be that of an ideal gas for temperatures above the \( \lambda \) point, where \( \rho_2 = 0 \),

\[
u = n_1 \mathcal{R} \rho_1 T + \frac{df_2}{d\rho_2}.
\]

The observed specific energy differs from that of a perfect gas in a small region near the \( \lambda \) point. This can not be accounted for by the second term in the above expression, so we are going to need a correction to \( f_1 \),

\[
f = \mathcal{R} \rho_1 T \ln \frac{\rho_1}{\rho_1^n_1} + \Delta(\rho_1, T) + f_2(\rho_2).
\]

The internal energy density is then

\[
u = n_1 \mathcal{R} T + (1 - T \frac{\partial}{\partial T}) \Delta.
\]

We can reproduce the experimental form of the specific heat by adjusting the function \( \Delta \). The most attractive guess is that

\[
\Delta = b(T/\lambda - 1)^{-2}.
\]

457
The adiabatic condition is affected, and so is the equilibrium condition.

\[ f_2 = 1.1 \mathcal{R} \left( \frac{5a}{2} \left( \frac{\rho_2}{5a} \right)^2 - \rho_2 \right) - 2b \left( \frac{T}{\lambda} - 1 \right)^{-3}. \]

or

\[ f_2 = 1.1 \mathcal{R} \left( \frac{5a}{2} \left( \frac{\rho_2}{5a} \right)^2 - \rho_2 \right) + 2b \left( \frac{\rho_2}{5a} \right)^{-6}. \]
In order to implement the idea that the entropy of the super fluid component is zero we have to try to express the total free energy in terms of those of the components, as in $f = f_1 + f_2 + f_{\text{int}}$, with $f_{\text{int}} = 2c\rho_1\rho_2$ and

$$f_1 = a_1 + b\rho_1 \ln \rho_1 + c\rho_1^2 + A_1(T)\rho_1,$$

$$f_2 = a_2 + b\rho_2 \ln \rho_2 + c\rho_2^2.$$  

We have made $A_1$ independent of $x$ and $c_2 = 0$.

The condition for equilibrium of the mixture is that

$$q_1 = q_2, \quad q_i = \frac{\partial f + sT}{\partial \rho_i}
\bigg|_{\rho_j, T}, \quad j \neq i, \quad s = S_1\rho_1 + S_2\rho_2.$$  

where the specific entropy $S$ is uniform; but it will change with the temperature. The adiabatic condition is

$$\frac{\partial f}{\partial T} + s = 0.$$  

The values to be assigned to the specific entropies must be obtained from an underlying atomic theory and we shall not attempt it.
The simplest model,

\[ f_1 = a_1 + b_1 \rho_1 + c_1 \rho_1^2, \quad f_2 = a_2 + b_2 \rho_1 + c_2 \rho_2^2, \]

\[ f = f_1 + f_2 + \alpha \rho_1 \rho_2, \]

with coefficients that depend on \( T \) only.

\[ p = -a + c_1 \rho_1^2 + c_2 \rho_2^2 + \alpha \rho_1 \rho_2, \quad a = a_1 + a_2. \]

Since \( p \), to a very good approximation, depends only on \( \rho \) and \( T \) we take

Simplification 1: \( c_1 = c_2 = \alpha/2. \)

Now

\[ f_1 = a_1 + b_1 \rho_1 + c_1 \rho_1^2, \quad f_2 = a_2 + b_2 \rho_2 + c_2 \rho_2^2, \]

\[ f = f_1 + f_2 + 2c \rho_1 \rho_2 = a + b_1 \rho_1 + b_2 \rho_2 + c \rho^2. \]

\[ p = -a + c \rho^2. \]

Next,

\[ q_1 + S_1 T = b_1 + 2c \rho + S_1 T, \quad q_2 + S_2 T = b_2 + 2c \rho + S_2 T. \]

The equation of equilibrium now becomes

\[ \dot{\Phi}_1 - \dot{\Phi}_2 + b_1 - b_2 - T(S_1 - S_2) = 0, \]

and if the last term cancels the first, as in the case of saturation, then it becomes \( b_1 = b_2 \). This does nothing to fix the configuration, so we must turn to the adiabatic equation, using a dot to denote \( T \)-differentiation, and setting the \( b \)'s equal,

\[ \dot{f} = \dot{a} + \dot{b} \rho + \dot{c} \rho^2 = -\rho_1 S_1 - \rho_2 S_2. \]

Since the superfluid carries no entropy we set \( S_2 = 0 \) The value of the entropy density, known by measurements, is thus

\[ s = S_1 \rho_1 = -\dot{a} - \dot{b} \rho - \dot{c} \rho^2, \]

which can be used to get the coefficients. For this to fix the state \( S_1 \) must be fixed once and for all (below the \( \lambda \) point).

Simplification 2: \( b_1 = b_2, S_2 = 0 \) and \( S_1 \) now fixed.
Now
\[ f_1 = a_1 + b\rho_1 + c\rho_1^2, \quad f_2 = a_2 + b\rho_2 + c\rho_2^2, \]
\[ f = a + b\rho + c\rho^2, \quad p = -a + c\rho^2, \quad S_1 = S_{\text{fixed}}, \quad S_2 = 0. \]

With this we try to calculate the speeds of sound.

\[ q_1 + ST = b + 2c\rho + ST, \quad q_2 = b + 2c\rho. \]

Clearly \( c \) does not vanish. Let us try to take \( a = b = 0 \), then

\[ dq_1 + ST = 2c \, d\rho + (2\dot{c}\rho + S) dT, \quad dq_2 = 2c \, d\rho + 2\dot{c}\rho \, dT. \]

The adiabatic condition is now

\[ \ddot{c}\rho^2 \, dT + 2\dot{c}\rho \, d\rho - S \, d\rho_1 = 0, \quad dT = \frac{-2\dot{c}}{c\rho} \, d\rho + \frac{S}{c\rho^2} \, d\rho_1, \]

so that

\[ dq_1 + ST = \left( 2c - (2\dot{c} + S) \frac{2\dot{c}}{c\rho} \right) d\rho + (2\dot{c}\rho + S) \frac{S}{\rho^2} d\rho_1, \]

\[ dq_2 = \left( 2c - (2\dot{c} + S) \frac{2\dot{c}}{c\rho} \right) d\rho. \]

If we write this as

\[ dq_1 + ST = Ad\rho + B \, d\rho_1, \quad dq_2 = A \, d\rho, \]

then the speed-squared matrix is

\[ M = \begin{pmatrix} A\rho_1 & A\rho_2 + B\rho_2 \\ A\rho_1 & A\rho_2 \end{pmatrix} \]

and the eigenvalues are

\[ c^2 = A(1 \pm \sqrt{1 + B}). \]

There is a mode that, if \( B \) is small, has \( c^2 \approx A\rho \), for which \( d\rho_1 \approx d\rho_2 \), and a slower mode, with \( c^2 \approx B\rho_1\rho_2/\rho \) for which \( d\rho_1 \approx -d\rho_2 \). Check this.

Functions with this property are

\[ \alpha = k\sqrt{a_1 - \rho_1\sqrt{a_2 - \rho_2} - k\sqrt{a_1a_2}} \quad (8.2.6) \]

with \( k, a_1, a_2 \) constant.

The principle sound mode has unaltered speed while the squared speed of second sound is

\[ c_2^2 = c^2 - \frac{k}{4} \left( \rho_1(a_2 - \rho_2)^{1/2}(a_1 - \rho_1)^{-3/2} + \rho_2(a_1 - \rho_1)^{1/2}(a_2 - \rho_2)^{-3/2} \right). \]

But we need a large Experimentally, this second sound is found to be about \( c^2/100 \), nearly flat from \( T = 0 \) until it falls abruptly to zero near the \( \lambda \) point. To achieve this, the strong
variations of the individual densities have to cancel over most of the range and especially for small $T$; this requires that we take $a_1 = a_2$. Then

$$c_2^2 = c^2 - \frac{k}{4} \left( \frac{\rho_1(a - \rho_2)^{1/2}}{(a - \rho_1)^{3/2}} + \frac{\rho_2(a - \rho_1)^{1/2}}{(a - \rho_2)^{3/2}} \right)$$  \hspace{1cm} (8.2.7)

Since $\rho$ does not vary much, we can set $\rho_2 = .15 - \rho_1$, express $\rho_1$ as $T^5$ and find the values of $k$ and $a$ that makes the speed of second sound about $20 \text{ m/sec}$.

Expansion in powers of $a_1/\rho$ and $a_2/\rho$ give the approximation

$$c_2^2 = c^2 - \frac{k\rho}{4a} \left( 1 - \frac{\rho_1 \rho_2}{a \rho} + \frac{3}{2a\rho}(\rho_1^2 + \rho_2^2) \right).$$

One set of parameters that gives a good result is

$$a = 2 \times 10^6, \quad k = 4.224 \times 10^{10}. \quad (8.2.8)$$

Let us now see what is the effect on the equilibrium condition of including the interaction term in the Lagrangian. Our analysis of entropy and heat capacity are not affected.

The adiabatic condition is now

$$\frac{\partial f}{\partial T} + s = -b\rho_1 \left[ 1 + \ln(\lambda - T) \right] + \rho_1 S_1 = 0$$

Hence

$$S_1 = b \left[ 1 + \ln(\lambda - T) \right]. \quad (8.2.6)$$

In the case of He II $\lambda$ varies with the pressure. We can achieve a closer approach to the real situation by letting $\lambda$ depend on the density, but to keep the model simple we fix it once and for all.

**TABLE 8.1.1**

<table>
<thead>
<tr>
<th>$p$</th>
<th>$s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>11.10$\rho_1 + .0400 T^3 \rho_2$,</td>
</tr>
<tr>
<td>0.05</td>
<td>9.45$\rho_1 + .0275 T^3 \rho_2$,</td>
</tr>
<tr>
<td>10.0</td>
<td>8.60$\rho_1 + .0195 T^3 \rho_2$,</td>
</tr>
<tr>
<td>15.0</td>
<td>7.80$\rho_1 + .0150 T^3 \rho_2$,</td>
</tr>
<tr>
<td>20.0</td>
<td>7.05$\rho_1 + .0110 T^3 \rho_2$,</td>
</tr>
<tr>
<td>25.0</td>
<td>6.50$\rho_1 + .0100 T^3 \rho_2$,</td>
</tr>
</tbody>
</table>

Table 8.1.1. Relation between measured entropy and the equilibrium values of densities and temperature, covering the whole interval from .1K to 2.1K.
This is original fopr of table. I interpreted entropy in MacDonnelly as density, but it is specific density. To make this right I must multiply by the mean density at each p:

p=0, .14547, p=5, .1534, p=10, .16, p=15, .1652, p=20, .1693, p = 25, .1737

### Table 8.2.1

<table>
<thead>
<tr>
<th>$T$</th>
<th>$T + \lambda \ln(\lambda - T)$</th>
<th>.25 − .24 ln($\rho_1/\rho_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p=0</td>
<td>1.67</td>
<td>3.04</td>
</tr>
<tr>
<td>p=25</td>
<td>3.04</td>
<td>2.77</td>
</tr>
<tr>
<td>$T = .5$</td>
<td>1.54</td>
<td>1.95</td>
</tr>
<tr>
<td>$T = .8$</td>
<td>1.4</td>
<td>1.45</td>
</tr>
<tr>
<td>$T = 1$</td>
<td>.909</td>
<td>.848</td>
</tr>
<tr>
<td>$T = 1.4$</td>
<td>.476</td>
<td>.634</td>
</tr>
<tr>
<td>$T = 1.6$</td>
<td>-.216</td>
<td>.426</td>
</tr>
<tr>
<td>$T = 1.8$</td>
<td>-.154</td>
<td>.171</td>
</tr>
<tr>
<td>$T = 2$</td>
<td>1.54</td>
<td></td>
</tr>
<tr>
<td>$T = 2.1$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 8.2.1. Comparing both sides of the relation (8.2.1) in the case of He II.

Here there is no parameter to adjust. Comparison with He II, in Table 8.2.2, shows a very similar behavior. The numerical value of $c_2^2$, is Joules, is slightly less than unity.

### Table 8.2.1

<table>
<thead>
<tr>
<th>$p$</th>
<th>$\ln(\rho_1/\rho_2)$</th>
<th>$s$</th>
<th>$p$</th>
<th>$\ln(\rho_1/\rho_2)$</th>
<th>$s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>T=.1</td>
<td>0</td>
<td>.000007</td>
<td>0</td>
<td>.000016</td>
<td></td>
</tr>
<tr>
<td>T=.5</td>
<td>0</td>
<td>.00008</td>
<td>.0502</td>
<td>.000233</td>
<td></td>
</tr>
<tr>
<td>T= 1</td>
<td>.0066</td>
<td>.01556</td>
<td>.0265</td>
<td>.0309</td>
<td></td>
</tr>
<tr>
<td>T=1.4</td>
<td>.0796</td>
<td>.1330</td>
<td>.2206</td>
<td>.2362</td>
<td></td>
</tr>
<tr>
<td>T= 1.8</td>
<td>.3921</td>
<td>.5416</td>
<td>2.302</td>
<td>.9919</td>
<td></td>
</tr>
<tr>
<td>T=2.1</td>
<td>1.4680</td>
<td>1.239</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 8.2.2. The entropy density against $\ln(\rho_1/\rho_2)$ for He II. Verify, clean up and make tables. Data, from Putterman, range of $\rho$ from .146 to .177, range of $T$ from 1.3 to 2K.

\[
\rho_2 = A(T) + B(T)(\rho_2 - .13) + C(T)((\rho - .13)^2,
\]

\[
A(T) = .0055T^4, \quad B(T) = .6 + \frac{2.1x^{20}}{3000 + x^{20}} \approx .6 + .977T,
\]

\[
C(T) = 15 + \frac{85x^{13}}{400 + x^{13}} \approx 15 + 38.6T.
\]

463
For small values of $\rho$ this extrapolation of the data gives a small, negative value for $\rho_2$. Better data may change that. The linear approximation for the functions $B$ and $C$ bring large errors near the middle of the temperature range.

The boundary conditions are maintained by heating the bottom wall. We have found that the temperature gradient can be changed by adding a density independent term to the entropy density,

$$s = \rho S + s_{ex}. $$

This is a further departure from the classical analysis, a slight generalization. To compare, we must take $s_{ex} = 0$.

**The basis state**

We are led to the following equations of motion, for the system in the basis state, at rest, with no flow, $\vec{J} = 0$ and therefore

$$\vec{v}_0 = \nu \vec{\nabla} \ln \rho_0, \quad \Phi_0 = -\nu \ln \rho_0.$$  

$$R(\ln \frac{\rho}{T^n} - n) + S + \frac{s_{ex}}{\rho} = 0 \quad (9.6.3)$$

(this adiabatic condition holds in general), and

$$gz + R T_0 (\ln \frac{\rho_0}{T_0} + 1) + ST_0 = \text{constant}, \quad (9.2.129.6.4)$$

Terms involving $\vec{v}_0$ or $\Phi_0$ are second order in $\nu$ and have been dropped; the analysis is valid for low values of the viscosity.

After elimination of the logarithm,

$$gz + R T_0 (n + 1) = T_0 \frac{s_{ex}}{\rho_0} + \text{constant}. \quad (9.2.139.6.5)$$

We shall follow the classical analysis in asking that the temperature gradient of the ground state be constant in the vertical direction. This is the case if

$$s_{ex} = \beta \frac{\rho_0}{T_0} (z - z_0),$$

with $\beta$ constant. For the basis state, (9.6.3) gives

$$T_0 = c + \lambda z, \quad \lambda = \frac{\beta - g}{R(n + 1)}, \quad (9.6.6)$$

with the constant gradient favored by the classical analysis. We suppose that $z = 0$ at the lower plate and $z = d$ of upper boundary; then the term $\lambda z$ is small compared to the constant $c$ and terms of second order will be dropped. Our $\lambda d$ is what Koschmieder denotes $\Delta T$.  

464
Note that the theory of an ideal gas does not allow to fix this quantity at will. If $\beta = 0$ the basic state is isentropic and $\Delta T = d g / R (n + 1)$. If we want an isothermal basic state we must take $\beta = g$ and $\Delta T = 0$. See Section 3 of this chapter. And if we want to be able to adjust $\Delta T$ then we have to do so by selecting the appropriate value of $\beta$:

$$\Delta T = \lambda d = \frac{\beta - g}{R(n + 1)}d.$$

Eq. (9.6.3) gives

$$\rho_0 = k T_0^n e^{-\beta z / R T_0}.$$

For air, with molecular weight 29, $R = 2.87 \times 10^6 \text{ergs/gK}$ and $n = 2.5$. At sea level, $g = 980 \text{cm/sec}^2$, the density is $\rho = 1.2 \times 10^{-3} \text{g/cm}^3$, the pressure $p = 1.013 \times 10^6 \text{dyn/cm}^2$. Thus, if $\beta = 0$,

$$p / \rho = .844 \times 10^9 \text{cm}^2 / \text{sec}^2, \quad T = T_0 = 294 K, \quad d = 3.014 \times 10^6 \text{cm} \approx 30 \text{km},$$

and the dry lapse rate at low altitudes is $-T' = 294 / d = 9.75 K / \text{km}$. The opacity that is implied by this is mainly due to the presence of $\text{CO}_2$ in the atmosphere. Humidity increases the opacity and decreases the lapse rate by as much as a factor of 2. (A temperature difference of 70 degrees over 12 000 m was observed on a recent flight over Europe.)
**Perturbation**

A first order perturbation is governed by the following dynamical equations.

1. The adiabatic condition (9.6.3),
   \[
   \frac{\delta \rho}{\rho_0} - n \frac{\delta T}{T_0} = \frac{\beta z}{RT_0} \frac{\delta \rho}{\rho_0}.
   \]
   It is difficult to see where the right hand side can become significant. To first order in \(\beta z/RT_0\), it is
   \[
   \frac{\delta \rho}{\rho_0} = n(1 - \frac{\beta z}{RT_0}) \frac{\delta T}{T_0},
   \]
   This corresponds to Koschmieder’s \(\delta \rho/\rho_0 = \alpha \delta T\).

2. The equation of continuity
   \[
   \delta \mathbf{J} = \rho_0 \delta \mathbf{v} + \mathbf{v}_0 \delta \rho - \nu \mathbf{\nabla} \delta \rho,
   \]
   where the last term is the additional term that turns the process into an adiabatic one.
   \[
   -\text{div} \delta \mathbf{J} = \mathbf{\nabla} \rho_0 \cdot \mathbf{\nabla} \delta \Phi + \rho_0 \Delta \delta \Phi - \nu (\Delta \ln \rho_0) \delta \rho - \nu \mathbf{\nabla} \ln \rho_0 \cdot \mathbf{\nabla} \delta \rho + \nu \Delta \delta \rho = 0.
   \]

3. Eq.(9.6.2)
   \[
   \dot{\Phi} - \vec{v}^2/2 + \nu \Delta \Phi - gz = \frac{\partial}{\partial \rho}(f + sT) + \text{constant}.
   \]
   By virtue of the adiabatic condition this reduces to
   \[
   \dot{\Phi} - \vec{v}^2/2 + \nu \Delta \Phi - gz = RT(n + 1) - \frac{s_{ex}}{\rho} T + \text{constant}.
   \]
   To first order in a time independent perturbation,
   \[
   -\mathbf{\nabla} \Phi_0 \cdot \mathbf{\nabla} \delta \Phi + \nu \Delta \delta \Phi = \left(\mathcal{R}(n + 1) - \frac{s_{ex}}{\rho_0}\right) \delta T + \frac{s_{ex}}{\rho_0} T_0 \frac{\delta \rho}{\rho_0} + \text{constant \(\delta \rho\)}.
   \]
   Combining these last 2 equations we can eliminate the function \(\delta \Phi\) to get
   \[
   \nu^2 \left((\Delta \rho_0) \delta \rho + \nabla \ln \rho_0 \cdot \nabla \delta \rho - \nabla \Delta \rho_0\right) = \rho_0 \left(\mathcal{R}(n + 1) - \frac{\beta z}{T_0}\right) \delta T + \beta z \delta \rho.
   \]
   Here the absence of rotation (\(\text{curl} \vec{v} = 0\)) is a great simplification. The left hand side reduces to \(\nu^2\) times
   \[
   \left(\frac{\rho_0'}{\rho_0}\right) \delta \rho + \frac{\rho_0'}{\rho_0} \delta \rho' - \Delta \delta \rho = -\partial_z \left(\rho_0 \partial_z \frac{\delta \rho}{\rho_0}\right) - \Delta_2 \delta \rho.
   \]

466
Let us get a preliminary sense of this result by approximating the density $\rho_0$ by a constant. The boundary conditions require that $\delta T$ and $\delta \rho$ vanish at the boundaries and the lowest mode that satisfies this condition is

$$\delta \rho \propto \cos \frac{2\pi z}{d} \sin(\hat{k} \cdot \vec{x}),$$

then the equation reduces to

$$(2\pi)^2 + (dk)^2 = \frac{R(n + 1)T_0 d^2}{\nu^2}.$$ 

According to the classical calculations, in reasonable agreement with experiments, the left side is of order 1700. This can be reached only for extreme values of the viscosity, for which the approximations that were made are not valid.

It seems that the original analysis of Reynolds, and the more complete work of Chandrasekhar, comes closer to predict the observed phenomena. Indeed the success of that very impressive work seems almost miraculous. And the hope of an explanation in terms if irrotational velocities with isolated vortices is dashed.

The linear approximation to the Lagrangian model is thus ruled out. It cannot account for the benard cells, since the velocity field is locally irrotational. %UTF00C5s a matter of fact, the standard approach is also unsatisfactory when subjected to linear analysis. Only a nonlinear treatment is able to account for the facts.
<table>
<thead>
<tr>
<th>Substance</th>
<th>a (L2bar/mol2)</th>
<th>b (L/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>17.71</td>
<td>0.1065</td>
</tr>
<tr>
<td>Acetic anhydride</td>
<td>20.158</td>
<td>0.1263</td>
</tr>
<tr>
<td>Acetone</td>
<td>16.02</td>
<td>0.1124</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>17.81</td>
<td>0.1168</td>
</tr>
<tr>
<td>Acetylene</td>
<td>4.516</td>
<td>0.0522</td>
</tr>
<tr>
<td>Ammonia</td>
<td>4.225</td>
<td>0.0371</td>
</tr>
<tr>
<td>Argon</td>
<td>1.355</td>
<td>0.0320</td>
</tr>
<tr>
<td>Benzene</td>
<td>18.24</td>
<td>0.1154</td>
</tr>
<tr>
<td>Bromobenzene</td>
<td>28.94</td>
<td>0.1539</td>
</tr>
<tr>
<td>Butane</td>
<td>14.66</td>
<td>0.1226</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>3.640</td>
<td>0.04267</td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td>11.77</td>
<td>0.07685</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>1.505</td>
<td>0.03985</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>19.7483</td>
<td>0.1281</td>
</tr>
<tr>
<td>Chlorine</td>
<td>6.579</td>
<td>0.05622</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>25.77</td>
<td>0.1453</td>
</tr>
<tr>
<td>Chloroethane</td>
<td>11.05</td>
<td>0.08651</td>
</tr>
<tr>
<td>Chloromethane</td>
<td>7.570</td>
<td>0.06483</td>
</tr>
<tr>
<td>Cyanogen</td>
<td>7.769</td>
<td>0.06901</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>23.11</td>
<td>0.1424</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>17.61</td>
<td>0.1344</td>
</tr>
<tr>
<td>Diethyl sulfide</td>
<td>19.00</td>
<td>0.1214</td>
</tr>
<tr>
<td>Dimethyl ether</td>
<td>8.180</td>
<td>0.07246</td>
</tr>
<tr>
<td>Dimethyl sulfide</td>
<td>13.04</td>
<td>0.09213</td>
</tr>
<tr>
<td>Ethane</td>
<td>5.562</td>
<td>0.0638</td>
</tr>
<tr>
<td>Ethanol</td>
<td>12.18</td>
<td>0.08407</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>20.72</td>
<td>0.1412</td>
</tr>
<tr>
<td>Ethylamine</td>
<td>10.74</td>
<td>0.08409</td>
</tr>
<tr>
<td>Fluorobenzene</td>
<td>20.19</td>
<td>0.1286</td>
</tr>
<tr>
<td>Fluoromethane</td>
<td>4.692</td>
<td>0.05264</td>
</tr>
<tr>
<td>Freon</td>
<td>10.78</td>
<td>0.0998</td>
</tr>
<tr>
<td>Germanium tetrachloride</td>
<td>22.90</td>
<td>0.1485</td>
</tr>
<tr>
<td>Helium</td>
<td>0.03457</td>
<td>0.0237</td>
</tr>
<tr>
<td>Hexane</td>
<td>24.71</td>
<td>0.1735</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>2.283</td>
<td>0.04278</td>
</tr>
<tr>
<td>Hydrogen chloride</td>
<td>3.716</td>
<td>0.04081</td>
</tr>
<tr>
<td>Hydrogen selenide</td>
<td>5.338</td>
<td>0.04637</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>4.490</td>
<td>0.04287</td>
</tr>
<tr>
<td>Iodobenzene</td>
<td>33.52</td>
<td>0.1656</td>
</tr>
<tr>
<td>Krypton</td>
<td>2.349</td>
<td>0.03978</td>
</tr>
<tr>
<td>Mercury</td>
<td>8.200</td>
<td>0.01696</td>
</tr>
<tr>
<td>Methane</td>
<td>2.283</td>
<td>0.04278</td>
</tr>
<tr>
<td>Methanol</td>
<td>9.649</td>
<td>0.06702</td>
</tr>
<tr>
<td>Neon</td>
<td>0.2135</td>
<td>0.01709</td>
</tr>
<tr>
<td>Nitric oxide</td>
<td>1.358</td>
<td>0.02789</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.408</td>
<td>0.03913</td>
</tr>
<tr>
<td>Nitrogen dioxide</td>
<td>5.354</td>
<td>0.04424</td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>3.832</td>
<td>0.04415</td>
</tr>
<tr>
<td>Oxygen</td>
<td>1.378</td>
<td>0.03183</td>
</tr>
<tr>
<td>Pentane</td>
<td>19.26</td>
<td>0.146</td>
</tr>
<tr>
<td>Phosphine</td>
<td>4.692</td>
<td>0.05156</td>
</tr>
<tr>
<td>Propane</td>
<td>8.779</td>
<td>0.08445</td>
</tr>
<tr>
<td>Silane</td>
<td>4.377</td>
<td>0.05786</td>
</tr>
<tr>
<td>Silicon tetrafluoride</td>
<td>4.251</td>
<td>0.05571</td>
</tr>
<tr>
<td>Sulfur dioxide</td>
<td>6.803</td>
<td>0.05636</td>
</tr>
<tr>
<td>Tin tetrachloride</td>
<td>27.27</td>
<td>0.1642</td>
</tr>
<tr>
<td>Toluene</td>
<td>24.38</td>
<td>0.60</td>
</tr>
<tr>
<td>Water</td>
<td>5.536</td>
<td>0.03049</td>
</tr>
<tr>
<td>Xenon</td>
<td>4.250</td>
<td>0.05105</td>
</tr>
</tbody>
</table>