ADIABATIC THERMODYNAMICS OF FLUIDS

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.

A monograph

TABLE OF CONTENTS

III. LOCALIZATION

IV. APPLICATIONS TO SIMPLE SYSTEMS

X. CONSERVATIVE HYDRODYNAMICS

XI. ROTATING PLANETS

XII. SPECIAL RELATIVITY

XIII. GENERAL RELATIVITY

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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 extensive literature on adiabatic, non equilibrium thermodynamics 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 a 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 announce 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 Prigogine (1949) 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 configurations but between adiabatic and non-adiabatic processes. 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 (1825), 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 interpreted in full accord with Gibbs' formulation of the minimum energy principle, but more precisely. 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 was Laplace's theory of adiabatic sound propagation finally accepted, 50 years after publication.

A strong imperative characterizes the presentation adopted for this book: an exclusive 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 sacrified, 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 is introduced in Chapter 10. It is only then that interesting problems in hydrodynamics can be addressed.

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, and 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 statement that characterizes 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 often 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, in thermodynamics if not in statistical mechanics. 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 Process, 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 our attention by Fetter and Walecka (1980). This 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 a 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 some times 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 is approached in a manner, not entirely orthodox, that is implied by the reliance on action principles.

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, electromagnetic fluids and wind tunnels. 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 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, it appears to be completely responsible for the existence of certain interesting convective 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 and developed in Chapters X- XIII.

A major struggle has been to find a variational principle for hydrodynamics that allows for rotational motion and vortices. The problem found a solution in 2015. The non-relativistic theory is presented in Chapter X. The special-relativistic version has been published on arXive and IJGMMP and summarized in Chapter XII. An application to rotating planets is presented in chapter XI. Plans for the future are presented on the last 3 chapters.

The need for Conservative Hydrodynamics in General Relativity is based, in the first place, on the constraint imposed on General Relativity by the Bianchi identity, and the associated Bianchi constraint on the source, as is explained in Chapter XIII.

The discovery of Conservative Hydrodynamics, presented in the last Chapters, was realized through an examination of popular applications of the Navier - Stokes equation. The reliance on the concept of 'energy' and, especially, 'kinetic potential' contains a contradiction. Two kinds of velocity fields are involved, a gradient and a time derivative. The energy density is not $\rho/2(\dot{\vec{X}} + \vec{\bigtriangledown}\Phi)^2$ but $(\rho/2)(\dot{\vec{X}}^2 + \vec{\bigtriangledown}\Phi)^2)$ and the kinetic potential is $(-\dot{\vec{X}}^2 + \vec{\bigtriangledown}\Phi^2)/2$. The full theory is a field theory with two independent vector fields.

This explains why hydrodynamics is poorly represented in the first nine chapters of this book. What was missing was the creation of 'Conservative Hydrodynamics', a formulation of hydrodynamics, free of the restriction to potential flows.

The successful creation of Conservative Hydrodynamics, during the last 3 years of the preparation of this book, is the culmination of a pursuit that has occupied me for the last 12 years. A more complete title for this book would have been *'Adiabatic Thermodynamics and Conservative Hydrodynamics'*.

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