

I. INTRODUCTION

Re-order Sections I.6 to end. Figures? Indexed.

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 reaches 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 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, $1 \text{ MPa} = 1 \text{ J/cm}^3$. 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**,

$$1 \text{ bar} = 10^5 Pa = 10^{-1} \text{ MPa},$$

is used for pressure; it is essentially the same as one standard atmosphere; precisely $1 \text{ bar} = .986 \text{ atm}$ or $1 \text{ atm} = 101325 Pa$, 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.

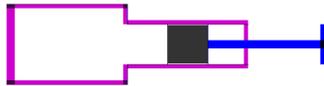


Fig.1.1.1. Vessel with piston.

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

$$dV = A dx.$$

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 these 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. See Clausius (1859).

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.¹ 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 usually preserved. This law is expressed locally by the **equation of continuity**,

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

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

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

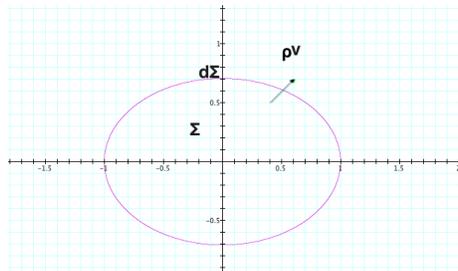


Fig.1.1.2. The equation of continuity. Σ is a region (a domain) in space, $\partial\Sigma$ is the boundary of Σ and the arrow suggest a current $\rho\vec{v}$ flowing out of Σ . See Eq(1.1.2)

By **Gauss' theorem** the second term can be converted into an integral over the boundary $\partial\Sigma$ of the volume Σ , so that the last equation is the same as

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

that is, the increase of mass in Σ 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** .

The equation of continuity is the very soul of hydrdynamics; it has equally important expressions in the related disciplines of quantum mechanics and quantum field theories where it is the condition of unitarity.

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,

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

¹But see Section III.4.

This is the simplest case of an equation attributed to Bernoulli (1738) but already used by 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 scalar field ψ . Thus

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

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 hydrdynamics are presented in Sections 7 and 8 of this chapter.

I.2. Hamiltonian and Lagrangian formulations of hydrdynamics

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 hydrdynamics**. But experience has shown and continues to show the value of the Hamiltonian and Lagrangian formulations in many fields of physics. Helmholtz and Maxwell are two of the many physicists who sought action principle formulations for every branch of physics.² One conclusion of our work is that hydrdynamics 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:³

“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.

²For references to papers of this period see the review by Bordoni (2014).

³See works on ‘extended thermodynamics’, e.g. Müller (1980).

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 ρ 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 a density field ρ ,

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

The total energy is

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

The problem is to determine the density that minimizes the total energy, this implies that this functional be stationary with respect to variations of the density, namely

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

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 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 λ be a real number and consider the modified action

$$E_\lambda = \int d^3x (W(\rho) + \lambda \rho).$$

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 λ 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 ⁴

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

The velocity field is restricted to be of potential type, the velocity vector field is the gradient of a scalar field Φ . This is a very strong restriction. Since Lagrange (or Euler?) first discovered this action principle the search for a generalization has not born fruit until quite recently. In this book we shall work with irrotational flows, $\vec{\nabla} \wedge \vec{v} = 0$, in the first 9 chapters.

The Lagrange density (1.2.2) includes **kinetic energy density** $\rho\vec{v}^2/2$, as well as a Lagrange multiplier λ 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 λ -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**.

As we said, we follow Fetter and Walecka and suppose that

$$\vec{v} = -\vec{\nabla}\Phi.$$

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 significant 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

⁴ \mathcal{L} is the Lagrangian density, ‘the Lagrangian’ is the space integral $\int d^3x \mathcal{L}$ and ‘ A ’ is ‘the action’.

of notice. It will be shown that the appearance of the Lagrange multiplier as an adjunct to the **velocity potential** Φ is appropriate.

Now we have two scalar fields to vary, therefore two Euler-Lagrange equations. The variation of Φ 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 Φ . 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,

$$\dot{\rho} + \vec{\nabla} \cdot (\rho \vec{v}) = 0. \quad (1.2.3)$$

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,

$$\rho \dot{\vec{v}} + \rho \vec{\nabla} v^2/2 = -\vec{\nabla} p, \quad p := \rho \frac{\partial W}{\partial \rho} - W. \quad (1.2.4)$$

The fact that the combination $D\vec{v}/Dt$ appears here, as it should, is due to the identity

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

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

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

The Hamiltonian is

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

and the **Poisson bracket**

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

Here A, B are functionals of \vec{v} and Φ , 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.

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. .

This very brief account of the foundations of hydrodynamics will allow us to introduce our main subject, thermodynamics. Some additional elements of hydrodynamics that will be needed much later are relegated to the end of this chapter.

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. .

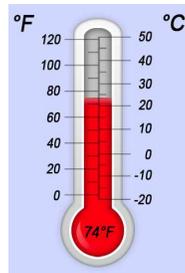


Fig.1.3.1. Thermometer.

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),

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

where \mathcal{R} is a constant and ρ is the molar density.⁵ Since our densities shall be given in grams (not mols) per cm^3 we shall have

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

where m is the molecular weight. Sometimes \mathcal{R}_i will stand for \mathcal{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 often called an ideal gas. When this relation holds, when this or some other relation is used to express T in terms of ρ , 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 $.0012\text{g}/\text{cm}^3$, thus, with the density $\rho = .0012\text{g}/\text{cm}^3$,

$$p = \frac{.8314}{29} \times 10^8 \times .0012 \times 293 = 1.008 \times 10^6 \textit{ergs},$$

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

$$p = .08314 \times 10^5 \times \frac{1.2}{29} \times 293 = 1.008 \textit{bars}.$$

I.4. The internal energy and the first law

Heat and Internal Energy

The first treatise on thermodynamicist 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

⁵If the densities are measured in mols per cm^3 then it is a universal constant,

$$\mathcal{R} = .8314 \times 10^8 (\text{cm}/\text{sec})^2 / K = 8.314 \text{Joule}/K.$$

The Joule is an energy unit equal to 10^7 erg.

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.⁶ 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 , "the **internal energy**" depending on the volume and on a second variable, the "**heat content**" Q , such that, for variations of the equilibrium configurations,

$$dU = dQ - pdV. \quad (1.4.1)$$

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 theory of heat; it is not a state variable of 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.

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**: instead, there is a variable S , related to dQ by $dQ = TdS$ at constant V , and a function $U(V, S)$ such that

$$dU(V, S) = TdS - pdV. \quad (1.4.2)$$

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,

$$\left. \frac{\partial U}{\partial V} \right|_S = -p, \quad \left. \frac{\partial U}{\partial S} \right|_V = T. \quad (1.4.3 - 4)$$

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.

⁶This is an oversimplification; much more will be said about this comparison later on.

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 ⁷, thus

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

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 **Carnot cycle** is taken from Holman (1974).

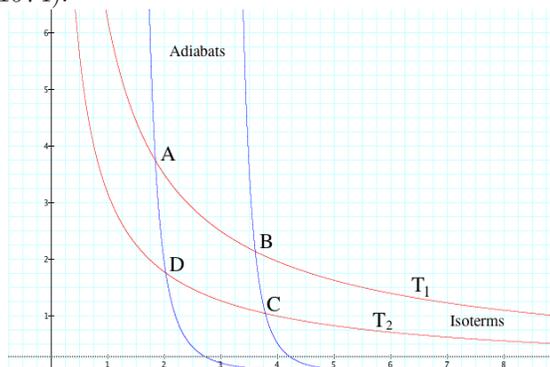


Fig.1.4.1. The Carnot cycle. See the paragraph above figure for a description of the cycle $ABCD$. Heat engines reach maximum efficiency when operating in a Carnot Cycle.

This very abbreviated account of one of the most dramatic development 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

⁷We 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.

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.⁸ But a definition of entropy that applies to irreversible processes is still being debated.⁹ 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.

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

assume that volume and temperature form a complete set of independent variables that suffices to fix the state of the system.

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

⁸An adiabatic configuration is a solution of the Euler - Lagrange equations associated to a Lagrangian.

⁹See for example the discussion after a conference contribution by J.Meixner. (Meixner 1970), as well as references to Prigogine given below.

as a function of V and T . Call this "free 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,

$$-S := \left. \frac{\partial F}{\partial T} \right|_V. \tag{1.4.5}$$

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**,

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

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 .

The remaining sections of this chapter collect some additional remarks about hydrodynamics.

I.5. The **kinetic potential**, and a warning

Eq. (1.2.4),

$$\rho \dot{\vec{v}} + \rho \vec{\nabla} v^2 / 2 = -\vec{\nabla} p, \quad p := \rho \frac{\partial W}{\partial \rho} - W,$$

like Newton’s equation, relates the time derivative of the momentum to various forces. There is the negative pressure gradient $-\vec{\nabla} p$ as well as the term $-\rho \vec{\nabla}(\vec{v}^2/2)$. This makes the expression $-\vec{\nabla}(\vec{v}^2/2)$ appear much like a conserved force derived from a potential

$$K := \vec{v}^2 / 2$$

and this latter expression has been called the ‘kinetic potential’; it is analogous to the centrifugal potential of particle mechanics.

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.

Assume that the density is defined over the complement M of a discrete set of lines in \mathbb{R}^3 , that the field Φ is a section of a line bundle over M and that $\vec{v} = -\text{grad } \Phi$ 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 Φ and ρ 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 Φ is a constant of the motion. It follows that the singular line moves with the fluid. The centrifugal force,

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

is directed outwards, as it must be

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

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

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

$$-\vec{\nabla}K = -\vec{r},$$

directed towards the center, against all experience. Clearly, it is dangerous to transplant equations from their natural domain 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 aestetical 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 $-\vec{\nabla}K$ of the kinetic potential (multiplied by the density) 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**

Perhaps, here at the end of the chapter, a simple example like a glass on a turntable with some remarks about a straw in the middle, may be instructive.

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

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

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 Poincaré¹⁰ 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. An important example 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 of any complex analytic function of $z = x + iy$, such as

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

where r, θ are polar variables. Then

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

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

¹⁰I have not found the references. But see Kaufman (1984) and references given there.

for the fluid to execute the motion considered. In the case of circular flow the pressure must be radial, originating from a cylindrical boundary wall.

Note that, by fixing the value of one of the canonical variables, we have a description of incompressible flows that is not formulated as an action principle.

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

$$\Phi = \Re(\ln z + z^4). \tag{1.7.1}$$

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

$$\Phi = \ln r + x^4 - 6x^2y^2 - 6x^2y^2 + y^4 = -5, -3, -2, -1.3, -.9, -.75., \tag{1.7.2}$$

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

$$\Phi = \Re(\ln z + z^4 + .24z^8) = -.597; \tag{1.7.3}$$

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 ?

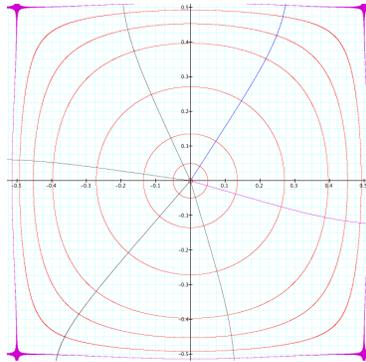


Fig.1.7.1. The red lines are the flow lines in Eq.(1.7.2). The outermost line shows the locus of (1.7.3).The other lines are the loci (anti clockwise) $\Phi = 1$ (blue), 2, 3, 4, 5 (black) and 6 (purple).

I.8. The ‘Lagrangian’ formulation of hydrdynamics

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

Another version of hydrodynamics is more directly related to the particle concept; it is known as the ‘Lagrangian version’ and this suggests that it is equivalent to the Eulerian version. But in fact the two theories 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,

$$\vec{v} = \dot{\vec{x}}.$$

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

$$\mathcal{L} = \rho \dot{\vec{X}}^2 / 2 - W[\rho]. \tag{1.8.1}$$

Variation of the density gives

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

and variation of \vec{X} ,

$$\frac{d}{dt}(\rho \dot{\vec{X}}) = 0.$$

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.

The limitations of potential hydrodynamics

Among the most important applications of hydrodynamics are: the flow of water, oil and gas in pipes, and aerodynamic lift. One would expect that, though our subject is thermodynamics, some space should be devoted to those

applications. The reason that this is not the case is that neither can be treated adequately in terms of irrotational flow.

Aerodynamic lift is an important, classical subject, treated in many books and perhaps most revealingly in a little treatise by Birkhof. Here the subject is treated as a collection of paradoxes of the following type.

In a **wind tunnel**, insert a wing, or more precisely an obstruction that may have the shape of a sphere, a cylinder or, indeed, an airplane wing. The **lifting force** to which this object is subject, as a result of the horizontal air stream, is easily measured, and the result used to design wing shapes with the greatest lift.

To develop a theory that would explain the experiments, and thus make them unnecessary, recourse was taken to the theory of potential flow. This theory, as was seen, is formulated as an action principle, which makes the calculations relatively simple and implies a high degree of predictability. It implies, in fact, that there is no lift: Paradox! Paradox? No, the only conclusion that can be made is that the flow around an object is not irrotational.

Again according to Birkhof, a generalization is needed and what is proposed is that the three-dimensional flow is only piecewise irrotational. We are presented with examples where the flow domain is divided into several parts with individual, irrotational flows, separated by two-dimensional surfaces of discontinuity. Vorticity is thus restricted to these surfaces. This new assumption turns out to be fairly successful, but it is posterior to the experiments; it is not predicted.

Nor does it help to refer to the Navier-Stokes equation, for that equation, even if supplemented by an equation of continuity, is not a complete theory. Other assumptions are needed and most frequently an expression for an ‘energy’ density is invoked, an expression that is necessarily *ad hoc* since no action principle is available; see Section I.?

A simpler phenomenon (because of symmetry) is cylindrical Couette flow. Here the Navier-Stokes equation has an initial success, but when it comes to understanding the limits of stability of the simplest flows it has nothing to offer.

When it comes to understanding turbulence the book by G.K. Batchelor (1952) offers an interesting glimpse into the state of affairs. In the preface he says: “...we have got down to the bedrock difficulty of solving non-linear partial differential equations.” Unfortunately, we are not there yet – the equations are almost certainly not known.

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