

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), valid when no external fields are present,

**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 (1878) 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 $1/\rho$. The question of the range of its validity is discussed, briefly, by Fitts (1962) who refers to work by Prigogine (1949). In this paper a fundamental expression for the entropy is shown to be valid in certain situations away from equilibrium.

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 adiabatic equations of motion

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 . What we have so far is this

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

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; it will be discussed in Section III.5.

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

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

Here $f(\rho, T)$ 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 uniform for the time being. The extensive nature of the entropy ¹ 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 density** $S = s/\rho$ is independent of ρ (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 agree 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 ρ and S , with ρ, 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) and in the presence of external forces.

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

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.

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 ρ it is a pre-assigned function of ρ . 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, ρ . We insist on this point because it will help us confront difficult issues later on.

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

$$\left. \frac{\partial f}{\partial T} \right|_{\rho} + s = 0, \quad (3.1.1)$$

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

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

where p is the local version of the pressure. Equivalently

$$\vec{\nabla} \left(\mu + T \frac{\partial s}{\partial \rho} \right) = 0, \quad (3.1.2)$$

where μ is known as the **chemical potential** and is defined by either of two equivalent ways,

$$\mu := \left. \frac{\partial f}{\partial \rho} \right|_T \quad (3.1.3)$$

or

$$\mu := \left. \frac{\partial u}{\partial \rho} \right|_s = 0.$$

Here u is the **internal energy density**; it will be discussed in Section III.7. The first definition is more straight forward; in the second form appears the **adiabatic derivative**, where T is to be eliminated in favor of ρ and S using (3.1.1).

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

$$p = \rho \frac{\partial f}{\partial \rho} - f. \quad (3.1.4)$$

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

$$\vec{\nabla}p = \vec{\nabla}(\rho\mu - f) = \rho\vec{\nabla}\mu + \mu\vec{\nabla}\rho - \left(\frac{\partial f}{\partial\rho}\vec{\nabla}\rho + \frac{\partial f}{\partial T}\vec{\nabla}T\right) = \rho\vec{\nabla}\mu + s\vec{\nabla}T. \quad (3.1.5)$$

We used the adiabatic condition $\partial f/\partial T = -s$. Hence

$$\rho\vec{\nabla}\mu = \vec{\nabla}p - s\vec{\nabla}T$$

and (3.1.2) becomes

$$\rho\vec{\nabla}\left(\mu + T\frac{\partial s}{\partial\rho}\right) = \vec{\nabla}p + \left(\rho\frac{\partial s}{\partial\rho} - s\right)\vec{\nabla}T + \rho T\vec{\nabla}\frac{\partial s}{\partial\rho} = 0, \quad (3.1.6)$$

which is the general form of the **hydrostatic 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. Unless s is a linear function of the density, $s = \rho S$, there is a force proportional to the gradient of the temperature and
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 $\vec{\nabla}p = 0$, is verified when (a) $s = \rho S$, with S independent of ρ (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 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 $\vec{\nabla}S$ 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 so; just as is the case with the pressure.² 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 $\vec{\nabla}p + \vec{\nabla}\phi = 0$, where ϕ is the gravitational potential. This relation is widely used in astrophysics; the fact that it has implications for the entropy is very rarely pointed out, but recent publications show an increased awareness of this important point. It implies 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 Gibbsian 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 significant 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).

²Special situations may call for an additional contribution to the entropy density, independent of the mass density, thus $s = \rho S + s_{\text{ex}}$, the second term is treated as an external field. An idea adapted from Landau and Lifshitz.

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 been adequately explained. If we assume 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 in Eq.(3.1.5), it is necessary to allow for variations of the total 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 a field that extends the pressure on the walls into the bulk. (See Section III.5.) It is this circumstance that justifies referring to p as ‘the pressure’. 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.

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**³,

$$A[\rho, T, S, P, \vec{v}] = \int_{\Sigma} \delta^3x h + VP, \quad h = \rho\lambda + \rho\vec{v}^2/2 + f(\rho, T) + sT, \quad s = \rho S. \quad (3.2.1)$$

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.

³Gibbs’ *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

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 ρ as independent variables off shell, leads as before to

$$\left. \frac{\partial f}{\partial T} \right|_{\rho} + s = 0, \quad (3.1.1bis)$$

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

$$\dot{\rho} = \{\rho, H\} = \partial_i \frac{\partial H}{\partial v_i} = -\vec{\nabla} \cdot (\rho \vec{v}) \quad (3.2.3)$$

and

$$\dot{\vec{v}} = \{\vec{v}, H\} = -\vec{\nabla} \frac{\partial H}{\partial \rho} = -\vec{\nabla} (\vec{v}^2/2 + \frac{\partial f}{\partial \rho} + ST). \quad (3.2.4)$$

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**,

$$\rho \frac{D\vec{v}}{Dt} = -\vec{\nabla} p, \quad p = \rho \frac{\partial f}{\partial \rho} - f, \quad (3.2.5)$$

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 ρ, Φ 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 profound, **statistical interpretation** developed especially by Boltzmann. This valuable insight does not include 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 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 (1698-1759), who was the first to apply a variational principle to a dynamical system away from equilibrium, one of the most important suggestions 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** Φ ,

$$\mathcal{A} = \int d^3x (\mathcal{L} - P), \quad \mathcal{L} = \rho(\dot{\Phi} - \vec{v}^2/2 + \lambda) - f(\rho, T) - sT, \quad (3.3.1)$$

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 statement about 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 λ 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

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

since the derivative term vanishes on shell.⁴ Consequently, 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 adds support for our contention that the entropy is usually linear in the density.

Similarly

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

⁴The 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.

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),

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

and for an ideal gas

$$\dot{\Phi} - \lambda - \vec{v}^2/2 - gz = (n + 1)\mathcal{R}T. \quad (3.3.5)$$

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 $\rho\dot{\Phi}$ in the **Legendre transformation** that defines the Hamiltonian density - is slightly unfamiliar:

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

The variable that is canonically conjugate to Φ is ρ . The inverse transformation is

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

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.⁵

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 have a general 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. 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

⁵This concept of ‘degradation’ was introduced by Lewis and Randall (1938). It is the main idea of their explanation of the second law.

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 $U = n\mathcal{R}T$, this brings about a calculable change in T ; this prediction was confirmed by a crucial set of experiments by Joule and Kelvin. 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 ρ , 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.

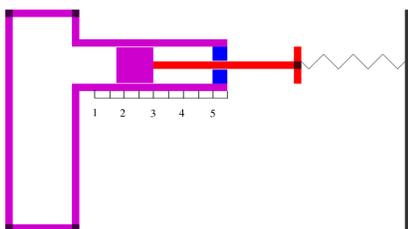


Fig. 3.5.1. Vessel with an addition degree of freedom, including piston with mass m and a spring with spring constant k . See Eq. (3.5.1).

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.⁶

**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

⁶According to Gibbs himself only the total entropy is an adiabatic invariant.

“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.⁷ What happens is that the gas is set in motion. This motion can be 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”. (Callen 1960) 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 $\rho\vec{v}^2/2$. But at the end, when the macroscopic motion has ceased, it is observed that the temperature has not changed. Consequently, neither has U , since $U = n\mathcal{R}T$; 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

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

⁷It 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.

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.⁸ 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 $n\mathcal{R}T$ so the temperature does not change in this type of process. Also, in the case of an ideal gas, $p = \mathcal{R}T/V$, so that

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

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 . 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 variation⁹ of the volume leads to

$$\delta \int d^3x (\mathcal{L} - P) = \delta \int d^3x (p - P) = \int d\sigma p \delta z - AP \delta z = 0, \quad (3.5.1),$$

where the 2-dimensional integral is over the face of the piston and A is the area of the piston. By replacing \mathcal{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

⁸See Callen (1960), page ???, for a very authoritative discussion of this point.

⁹In 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.

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

$$m\dot{z}^2/2 - kz^2/2$$

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.

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

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

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.

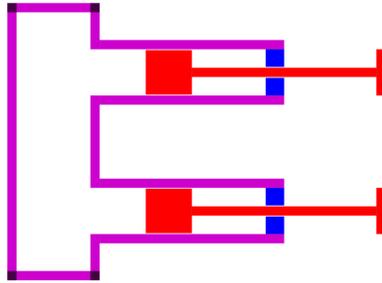


Fig. 3.5.2. A vessel with two pistons.

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. Important lesson

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.¹⁰ 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 another model. We must imagine a system of long polymers of twisting and interlaced molecules, to which a very large set of states is 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 sure 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.¹¹ 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 (2012).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

¹⁰I am not sure how this statement is justified.

¹¹Historically the most important by Joule and Kelvin.

¹²johncarlosbaez.wordpress.com/2012/02/01/entropic-force/

the given energy. 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 statistical mechanics, 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.

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? ¹³ 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

¹³For an answer to this question see the last paragraph of this section.

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 statistical 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 are other paths, quasi-static and ‘reversible’, that connects the two configurations: slow expansion and slow expansion in a heath 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* page 65.

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.

For an answer to the question. No, I do not go so far as to suggest that the increase of entropy takes place, in its entirety and instantly, as a result of the opening of the gate. There is strong intuitive support for the idea that the entropy increases as the temporary convective motion quiets down. But I do think that the question should be asked, and discussed. It was asked, and widely debated, during the second half of the 19th century, but the question remains poorly understood.

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

$$\begin{array}{ccc}
 U(V, S) & ST & F(V, T) \\
 VP & & VP \\
 H(P, S) & ST & G(P, T)
 \end{array}$$

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

$$f(\rho, T) = u(\rho, s) - sT, \quad g(p, T) = h(p, s) - sT, \quad s = -\left.\frac{\partial f}{\partial T}\right|_{\rho} = -\left.\frac{\partial g}{\partial T}\right|_p \quad (3.7.1)$$

and

$$g(p, T) = f + p, \quad h(p, s) = u + p, \quad p = \rho \frac{\partial f}{\partial \rho} - f, \quad \hat{p} = u - \rho \frac{\partial u}{\partial \rho}. \quad (3.7.2)$$

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,

$$\begin{array}{ccc} h(s, \mu) & sT & p(T, \mu) \\ \rho\mu & & \rho\mu \\ u(s, \rho) & sT & f(T, \rho) \end{array}$$

where

$$\mu := \left.\frac{\partial f}{\partial \rho}\right|_T = \left.\frac{\partial u}{\partial \rho}\right|_s. \quad (3.7.3)$$

For historical reasons, this function μ is called the **chemical potential**. It will play an important role in the theory. The natural variables for p are T and μ . 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:

$$\left.\frac{\partial p}{\partial T}\right|_{\mu} = s, \quad \left.\frac{\partial p}{\partial \mu}\right|_T = \rho. \quad (3.7.4)$$

The first one is related to the **Clapeyron equation**. .

In this book we shall rely principally on the density potentials u, s and f , functions of the densities, 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

$$\frac{\partial}{\partial T}(f + sT)\Big|_{\rho, S} = 0, \quad \dot{\Phi} - \bar{v}^2/2 - \frac{\partial}{\partial \rho}(f + sT)\Big|_{T, S} = \text{constant}, \quad (3.7.5)$$

or

$$\frac{\partial f}{\partial T}\Big|_{\rho} + s = 0, \quad \dot{\Phi} - \bar{v}^2/2 - \mu = \text{constant}, \quad (3.7.6)$$

III.8. Conservation laws and the stress tensor

What more than any other property characterize 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 $\delta q_1, \dots, \delta q_n$ then the function

$$\sum_i \delta q_i \frac{d\mathcal{L}}{dq_i}$$

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 \mathcal{L} is a time derivative, $\delta\mathcal{L} = \dot{K}$, then the function

$$\sum_i \delta q_i \frac{d\mathcal{L}}{dq_i} - K$$

is a constant of the motion. 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 Φ, ρ . With $\vec{v} = -\vec{\nabla}\Phi$,

$$\delta A = \int_{t_0}^{t_1} dt \int_{\Sigma} d^3x \frac{d}{dt}\mathcal{L}, \quad \mathcal{L} = \rho(\dot{\Phi} - \lambda - \bar{v}^2/2) - W[\rho].$$

The calculation of δA , on shell, proceeds exactly as in the derivation of the **Euler-Lagrange equations**, with the partial integrations, but in this case only the ‘integrated parts’, or surface integrals, that are ignored in that context, remain, since the Euler-Lagrange equations are satisfied on shell. The result is

$$\int_{t_0}^{t_1} dt \int_{\Sigma} d^3x \frac{d}{dt}\mathcal{L} = \int_{t_0}^{t_1} dt \int_{\Sigma} d^3x \left(\frac{d}{dt}(\rho\dot{\Phi}) + \vec{\nabla} \cdot (\rho\vec{v}\dot{\Phi}) \right).$$

That is,

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

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 boundary term, 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 $d/dt \int d^3x h = 0$.

The structure of (3.8.1) mirrors that of the global formulation of the equation of continuity,

$$\frac{d}{dt} \int_{\Sigma} d^3x \rho = \int_{\Sigma} d^3x \dot{\rho} = - \int_{\partial\Sigma} \rho \vec{v} \cdot d\vec{\sigma}. \quad (3.8.2)$$

The integral on the right of this equation is the total mass flow out of the volume Σ . The local version of this is the equation of continuity,

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

The corresponding local version of (3.8.1) is

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

where the ‘energy flow’ is $(h + p) \vec{v}$.

Next, consider the case that the variation is generated by a translation, $\xi = \vec{\xi} \cdot \vec{\nabla}$ or the infinitesimal rotation $\xi = \vec{\omega} \wedge \vec{x} \cdot \vec{\nabla}$ with $\vec{\xi}$ and $\vec{\omega}$ constant. The variations of a scalar field are

$$\delta\phi = \xi\phi, \quad \delta\dot{\Phi} = \xi\dot{\Phi}, \quad \delta\partial_i\phi = \partial_i\xi\phi.$$

The effect on the action of (3.8.1) is

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

With the help of the equations of motion one obtains

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

or

$$\frac{d}{dt} \int_{\Sigma} d^3x (\rho \vec{\xi} \cdot \vec{v}) + \int_{\partial\Sigma} \left(\rho (\vec{\xi} \cdot \vec{v}) \vec{v} + \mathcal{L} \vec{\xi} \right) \cdot d\vec{\sigma} = 0. \quad (3.8.3)$$

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.(3.8.3). The interpretation is this: to conserve the momentum (resp. angular momentum) in the volume it is not enough that the velocity at the boundary be normal to it, as is the case if the surface Σ moves with the fluid; though that would take care of the first of the two boundary terms. In addition, the total force (resp. total torque) on $\partial\Sigma$ must add to zero also. Equivalently,

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

This equation tells us that the ‘momentum density’ and the density of angular momentum are, respectively

$$\rho \vec{v} \quad \text{and} \quad \vec{\ell} := \rho \vec{x} \wedge \vec{v}$$

and the two ‘conservation laws’ are

$$\frac{D}{Dt} \rho \vec{v} = -\vec{\nabla} p, \quad \frac{D}{Dt} \rho \vec{\ell} = -\vec{x} \wedge \vec{\nabla} p.$$

Here the contributions of the first two terms in (3.8.3) have been combined in the total or co-moving derivative. Neither momentum nor angular momentum is preserved, unless the force, resp. the torque, is zero. To make this absolutely clear; for any volume Σ the integral of the left side over Σ is zero if and only if the total force or torque on Σ vanishes.

Using the equation of continuity we convert (3.8.3) to

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

When $\xi = \vec{\xi} \cdot \vec{\nabla}$, $\vec{\xi}$ constant, this is the **Navier-Stokes equation**,

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

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 she was 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 field theory Lagrangian, a function of a scalar field ϕ and its first order derivatives. Without invoking relativity, we shall use a convenient notation, writing $\partial_\mu\phi = \phi_{,\mu}$, $\mu = 0, 1, 2, 3$ for the "4-vector" $(\dot{\phi}, \vec{\nabla})$. What follows can easily be generalized to the case that there is any number of fields.

The relativistic stress tensor, or **energy-momentum tensor** is defined by

$$T_\mu^\nu = \phi_{,\nu} \frac{\partial \mathcal{L}}{\partial \phi_{,\mu}} - \delta_\mu^\nu \mathcal{L}.$$

Repeating the calculation that led to (3.8.3) in this more general case we get

$$\int d^3x \xi \mathcal{L} = \sum \int d^3x \left(\frac{\delta \mathcal{L}}{\delta \phi} \delta \phi + \frac{\delta \mathcal{L}}{\delta \phi_{,\mu}} \partial_\mu \xi \phi \right)$$

The sum is over all the scalar fields in \mathcal{L} . A partial integration of the second term, and using the equations of motion, leaves the integrated part

$$\int d^3x \xi \mathcal{L} = \sum \int d^3x \partial_\mu \left(\frac{\delta \mathcal{L}}{\delta \phi_{,\mu}} \xi \phi \right)$$

If the variation $\xi \phi$ is an infinitesimal translation (in the time or space coordinate, $\xi = \xi^\nu \partial_\nu$ with ξ^ν constant, then this result takes the form

$$\partial_\nu T_\mu^\nu = 0.$$

The simplest example is

$$\mathcal{L} = \frac{1}{2} g^{\mu\lambda} \phi_{,\mu} \phi_{,\lambda},$$

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

$$T_\mu^\nu = g^{\nu\lambda} \phi_{,\lambda} \phi_{,\mu} - \delta_\mu^\nu \mathcal{L}.$$

A completely straight forward calculation gives

$$\partial_\nu T_\mu^\nu = -\phi_{,\mu} \square \phi = 0, \quad \text{on shell.}$$

The operator \square 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.

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

$$\begin{aligned} T_0^0 &= \rho\dot{\Phi} - \mathcal{L}, & T_0^i &= \dot{\Phi}\rho v_i, & T_i^0 &= \Phi_i\rho, \\ T_i^j &= -\Phi_i\rho v_j - \delta_i^j \mathcal{L}. \end{aligned} \quad (3.8.5)$$

We can verify the conservation law $\partial_\nu T_\mu^\nu = 0$. It splits into these two cases;

$$\partial_0 T_0^0 + \partial_j T_0^j = 0$$

is easy to verify, it reduces to

$$\frac{d}{dt} h + \vec{\nabla} \cdot (\rho\dot{\Phi}\vec{v}) = 0, \quad (3.8.6)$$

which is the statement of **energy conservation**, Eq.(3.8.1). The other one, with $\mu \rightarrow i = 1, 2, 3$, 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**.

$$\frac{d}{dt}\vec{v} + (\vec{v} \cdot \vec{\nabla})\vec{v} = -\frac{1}{\rho}\vec{\nabla}\mathcal{L}, \quad (3.8.7)$$

So we have verified (and re-verified) that the 4-divergence of T is zero, and that the statement relates to 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, the Fetter-Walecka formulation of hydrodynamics is a complete, dynamical field theory (but limited to irrotational velocities).

Quite generally, Noether's discovery is a relation between invariance under a group of transformations and a conservation law. Invariance of what?...

of the Action. And what is conserved: the ‘momentum’ that is canonically conjugate to the coordinate that is being varied under the action of the group. The whole concept assumes that there is an action and without it there is no sense in talking about energy or any other kinematical conservation law.

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 ρ 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 **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, \dots, q_n and

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

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

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

Here we see what we are looking for: If “**equilibrium**” is defined as a solution in which nothing varies with the time, $p_1, \dots, p_n, q_1, \dots, q_n$ being time independent, then Eq.(3.9.2) tells us that the Hamiltonian must be stationary at all equilibrium solutions. 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

$$\int d^3x \mathcal{L} = \int d^3x \rho \dot{\Phi} - H[\rho] \quad (3.9.3)$$

and the canonical equations of motion (3.9.2).

$$\dot{\rho} = \{\rho, H\}, \quad \dot{\Phi} = -\{\Phi, H\}, \quad (3.9.4)$$

This is a close, field theoretic analogue and the conclusion is the same: At equilibrium the Hamiltonian H is extremal (assuming the appropriate definition of the Lagrangian multiplier included in Φ).

Note. Adding a boundary term to (3.9.3) we obtain instead the ‘symmetrized’ expression

$$\int d^3x \mathcal{L} = \int d^3x \left(\frac{\rho \dot{\Phi} - \dot{\rho} \Phi}{2} - H[\rho] \right)$$

The equations of motion are the same as before. In fact nothing has changed. The only difference is that it becomes more evident that the variables ρ, Φ are canonical conjugates.

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 . The Hamiltonian density h , on the other hand is defined by

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

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. A 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 :

$$sT \rightarrow T\rho\dot{\sigma} + j(\sigma). \tag{3.9.5}$$

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

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

This confirms that $\dot{\sigma}$ is the **specific entropy density** under a new name. Variation of the mass density gives the familiar equation with S replaced by $\dot{\sigma}$. We have one new equation, from variation of σ ,

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

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 σ is that it should maintain and justify the assumptions that were made about the ‘isolated’ system. This is exactly the same attitude that validates the way that the pressure is treated in the case of an incompressible gas. the relation of this equation with the Fourier heat equation is obvious but we have not explored that direction.

After the replacement (3.9.5) we have two canonical pairs of dynamical variables and a non-degenerate symplectic structure. The Hamiltonian density is now defined by - instead of (3.2.7):

$$\mathcal{L} = \rho\dot{\Phi} - \rho T\dot{\sigma} = h = \rho\vec{v}^2/2 + f + j(\sigma).$$

The Hamiltonian is extremal for allowed variations of the equilibrium state, variations that do not affect the field $S = \dot{\sigma}$. Finally, the functional $\int d^3x(\rho\vec{v}^2/2 + f)$ 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

$$\mathcal{L} = \rho\dot{\Phi} - \rho T\dot{\sigma} - h, \quad h = \rho\vec{v}^2/2 + f. \quad (3.3.9.6)$$

Finally, just as choosing the value of the total mass leads to fixing the value of $\dot{\Phi}$, the fact that the system is isolated implies fixing the value of $\dot{\sigma}$.

Summary

Prompted by the experimental evidence we have moved the term sT out of the Hamiltonian. The field σ is canonically conjugate to ρT , the canonical structure is non degenerate.

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 the total entropy.¹⁴ 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 $\Delta v = M^{-1}\Delta p$.

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 (1906), who dedicated a monograph to it. 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 ϵ , 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

¹⁴Actually, the highest value of $\int sT$.

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 ϵ 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 \mathcal{R}^3 or a part thereof. Galilei invariance is possible when the system extends over all of space.

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

$$x^i \rightarrow x'^i = x'^i(\vec{x}), \quad (3.11.1)$$

a scalar field transforms as follows,

$$T \rightarrow T',$$

the field T' defined by

$$T'(\vec{x}') = T(\vec{x}).$$

Nothing could be simpler than this fundamental transformation property.

Our theory also employs vector fields, most of them are gradients and transform like gradients of scalar fields. 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 ρ , the temperature T , and the kinetic energy density.¹⁵

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

$$x_i \rightarrow x'_i = x'_i(\vec{x}') = x_i - tu_i, \quad (3.11.2)$$

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,

$$\Phi'(x', t) = \Phi(x, t), \quad \partial'_i \Phi(x', t) = \partial_i \Phi(x, t) + u_i, \quad (3.11.3)$$

and

$$\dot{\Phi}'(x', t) = \dot{\Phi}(x, t) + \vec{u} \cdot \vec{\nabla} \Phi + \vec{u}^2/2. \quad (3.11.4)$$

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

$$x'^\mu = x^\nu \Lambda_\nu^\mu.$$

¹⁵Our use of the term ‘density’ is slightly abusive. Ultimately, our context always involves a metric. If we use non-Cartesian coordinates we shall make it conventional to include a factor \sqrt{g} in the differential volume dv . Then the ‘density’ ρ in $\int dv \rho$ is a scalar field.

Here the Greek indices run over 1,2,3,0 and Λ 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

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

$$\gamma := 1/\sqrt{1 - (u/c)^2}.$$

where c is the velocity of light. Any 4-dimensional, scalar field ψ transforms as follows,

$$\psi'(\vec{x}', t') = \psi(x, t) \quad (3.11.5)$$

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

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

$$\frac{\partial}{dy'} \psi'(\vec{x}') = \frac{\partial}{\partial y} \psi(\vec{x}, t),$$

$$\frac{\partial}{dz'} \psi'(\vec{x}', t') = \frac{\partial}{\partial z} \psi(\vec{x}, t). \quad (3.11.6)$$

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

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

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

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

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

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).

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 define 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. On 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 **space 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: ¹⁶

“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. Its 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 energy.

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,

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

¹⁶See also pages 20, 21, where a clear distinction is made between entropy production and entropy convection by mass flow, and page 39.

And here 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 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 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 entropy density**’ s is a linear function of the densities.

This problematic is not part of the traditional treatment; it is a principal innovation presented in this treatise. lacking was a sufficiently precise specification of the class of allowed variations, as I have tried to explain above. 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 reader may be surprised to find no discussion of “interactions” in the sense of Caratheodory. The first version of this book did develop this subject, but lacking a sufficiently precise specification of the class of allowed variations, the subject was dropped for lack of interest.

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