

“Een experimentator die niet an de tweede hoofdwet gelooft zal men medelijdend aankijken...” G.E. Uhlenbeck, “Van der Waals revisited”, talk presented on the occasion of the creation of the Van der Waals chair at the University of Amsterdam in 1964.

## II. Action principle for global thermodynamics

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

The role of an action functional as a depository of all information about a system is ubiquitous in theoretical physics, including Eulerian thermodynamics. In statistical physics the partition function plays a similar role. It has been maintained that a full expression for the internal energy as a function of the natural variables  $V$  and  $S$  provides a complete definition of a global thermodynamic system (Massieu 1876).

The internal energy does not reign without competition; a number of Legendre transformations lead to other possibilities that, according to Gibbs (1878), and Callen (1960), contain precisely the same information.

## II.1. The internal energy and the free energy

### Fundamental relations. Legendre transformations

Because of the very abstruse nature of the entropy we shall begin the discussion of the potentials with the free energy  $F$ , a function that, like the **internal energy**  $U$ , contains all intrinsic information about the system. The natural variables of  $F$  are  $V$  and  $T$ , much easier to grasp than  $V$  and  $S$ . The relation between  $F$  and  $U$  is a **Legendre transformation**<sup>1</sup>

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

The inverse transformation is

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

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

$$T = \frac{\partial U}{\partial S} \Big|_V, \quad p = -\frac{\partial U}{\partial V} \Big|_S, \quad (2.1.2a)$$

we obtain

$$p = -\frac{\partial F}{\partial V} \Big|_T, \quad S = -\frac{\partial F}{\partial T} \Big|_V. \quad (2.1.2b)$$

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

The **free energy** was introduced by Helmholtz (1883).<sup>2</sup> The two other potentials that make up the complete collection, first discussed comprehensively by Massieu (1876) and by Gibbs (1878), are **the Gibbs function**  $G(P, T)$  and **the enthalpy**  $H(P, S)$ . Two potentials with one common natural variable are related by a Legendre transformation.

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

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

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<sup>1</sup>As indicated, the variable  $V$  can be eliminated by using the relation  $S = -\partial F/\partial T$ . It is thus assumed that this equation implies a unique value for  $T$ , when  $V$  and  $S$  are given. It is useful to keep this in mind; see Section IV.3.

<sup>2</sup>See Section IV.3.

The two  $dS$  terms cancel, showing that

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

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

### Normalization of the energy

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

## II.2. The ideal gas

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

$$F(V, T) = -\mathcal{R}T \ln(VT^n), \quad \mathcal{R} = \frac{1}{m}.8314 \times 10^8, \quad (2.2.1)$$

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

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

According to the statistical interpretation  $2n$  is the number of degrees of freedom of the molecules that make up the gas; in our present framework it is a number:  $n = 3/2$  for a monatomic gas,  $n = 5/2$  for a diatomic gas.<sup>3 4</sup>

In some texts the ideal gas is defined by the gas law alone, while the formula for the internal energy is derived. But this “derivation” appeals to concepts that are outside our context.<sup>5</sup> To remain within our subject we shall define **the ideal gas** in terms of the formula for the free energy, from which both the gas law (the thermal equation of state) and the formula for the internal energy (the caloric equation of state) are derived, as we shall see.

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

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

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

$$p = \mathcal{R}T/V \tag{2.2.2}$$

and

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

The first is what is called **the ideal gas law**. The expression for the entropy implies that the **polytropic relation**,  $VT^n = \text{constant}$ , is valid for any fixed value of the entropy and this is confirmed experimentally for some gases. When this expression is substituted into the definition  $U := F + ST$  one gets

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<sup>3</sup>Only translational and rotational degrees of freedom are counted in this connection. Vibrational and other degrees of freedom and other types of excited states are less relevant. See Clausius (1859), Landau and Lifschitz (1959) and Brush 1976.

<sup>4</sup>The ideal gas is a product of the kinetic theory of gases, first proposed by Herapath in a paper that was rejected by the Royal Society in 1820. See Brush (1976).

<sup>5</sup>An attempt at a derivation within the context fails to convince. Reif (1965).

the statement that  $U = n\mathcal{R}T$ .<sup>6</sup> This result is often accompanied by the confusing comment that, for an ideal gas, the internal energy is independent of the volume. It must be remembered that the natural variables for  $U$  are  $V$  and  $S$  and not  $V$  and  $T$ .<sup>7</sup> In terms of  $V$  and  $S$  the internal energy of an ideal gas is

$$U(V, S) = n\mathcal{R}V^{-1/n} \exp\left(\frac{S}{n\mathcal{R}} - 1\right) \quad (2.2.4)$$

and not independent of the volume.

In this book we shall follow the practice of defining a fluid by its free energy and derive all required properties from that. An ideal gas is a gas that has the free energy given by Eq.(2.2.1).

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

### II.3. The two **time scales** of thermodynamics

The traditional point of view (and ours) envisages two quite different types of processes, with two different time scales. For the first type of process the time scale is relatively short and certain phenomena, as radiation and dissipation are often neglected. The propagation of sound in an ideal gas is an example of this type of adiabatic process. It is characterized by the fact that the entropy remains constant, thus in the case of an ideal gas,  $VT^n$  is constant in time. When treating such phenomena one usually assumes that there is no interaction with the environment or, rather, that any such interaction is weak enough to be neglected. Processes of the second kind are usually characterized by much longer time scales; they can be ignored over short time intervals, but over longer time periods their effects are often cumulative. For simplicity, by choice, we limit our consideration of dissipative

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<sup>6</sup>More simply but less clear,

$$U = (1 - T/\partial T)(F + ST) = (1 - T/\partial T)F = n\mathcal{R}T$$

<sup>7</sup>See for example Rowlinson (1959) page 13 for a collection of statements that are difficult to interpret.

processes to the case when the system can be considered to be in equilibrium with respect to the faster adiabatic processes; the system passes through a sequence of equilibrium states. A process that is considered to be slow in this sense does not necessarily involve interactions with the environment. Consider a fluid in some kind of regular motion, as in flowing through a circular tube. If the energy and the entropy are both preserved then the adiabatic equations of motion apply (see below). But experience shows that the motion will eventually slow down and finally cease altogether. What happens is that the kinetic energy gradually converts to heat by a process that we shall refer to as internal dissipation. This too is a comparatively slow process, neglected in the context of processes of the first type. See Prigogine (1970), where the existence of two time scales is related to the short reaction time and the much longer relaxation time in collision theory. For a rare example of a text that discusses the same point see Palatnik and Landau (1961), p 17. Most textbooks take much less care to explain the meaning of the ubiquitous ‘variations’ and this is one of the reasons why the study of thermodynamics can be painful.

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

#### **Adiabatic process**

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

#### **Dissipative process**

A **dissipative process** is one in which dissipation (or conduction or other slow processes) is the only change that is taking place. In practice one prepares a state that is as near to equilibrium as one can; ideally this means that the configuration is at equilibrium with respect to all adiabatic changes. Then dissipation can be viewed as progressing sedately through a sequence of adiabatic equilibria. A slow process is not necessarily dissipative; when

a piston is removed slowly no flow of consequence results and the system effectively moves along a continuous family of adiabatic equilibria indexed by the pressure.

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

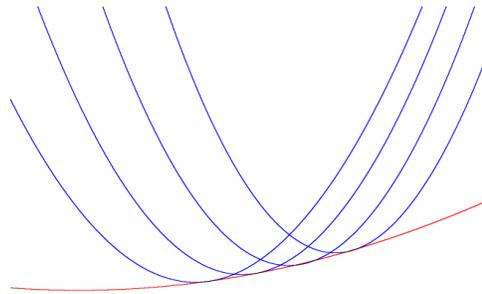


Fig 2.3.1. In this sketch of a 3-dimensional ‘space of configurations’ is associated with a fixed expression for the Lagrangian. Each parabola represents states with fixed Lagrangian, entropy and pressure. The red line represents the set of equilibrium states.

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

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

## II.4. Towards an Action for Thermodynamics

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

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

For any chosen set of values of the pair  $(S, P)$  they constrain the possible equilibrium values of the pair  $(V, T)$ . Taken together, the set of allowed values of  $(S, P, V, T)$  defines a 2-dimensional surface in the total 4-dimensional Euclidean space with coordinates  $V, T, S, P$ . According to Maxwell, one of the most inspiring ideas in Gibbs' thermodynamics is to call attention to these two spaces: the total, 4-dimensional space and the two-dimensional surface of physical states defined by the Fundamental Relations. See Rukeiser (1942).

Gibbs' axiom of minimal energy (or the equivalent axiom of maximal entropy) aims to identify the actual equilibrium states on a two-dimensional surface.

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

As the title of Gibbs' paper, *On the equilibrium of heterogeneous substances*, makes clear, it is not about simple systems. After stating the axioms he seems to take the application to simple systems for granted and, without further clarification, he applies them in a context that is a collection of simple systems, each with its own independent variables

$$(V, T, P, S), (V', T', P', S'), (V'', T'', P'', S''), \dots .$$

This leaves a large gap for the reader to fill and the result has been that the potential impact of the paper has not been realized. The most important void to fill is the associated Action Principle.

The remainder of this chapter attempts to fill the gaps that were left by Gibbs' paper; we shall see that its full implications have been to a large extent overlooked.

### An Action Functional

The following action will serve us well,

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

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

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

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

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

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

#### Interpretation of the action principle

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

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

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

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

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

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

Gibbs postulates that, at equilibrium, among states with fixed entropy and pressure, the energy must be at a minimum. That is; it is at a (local) minimum with respect to certain virtual changes. The proper interpretation of this statement is a difficult question. It is the central issue in equilibrium thermodynamics and it occupies an important place in adiabatic thermodynamics as well.

Gibbs' geometrical formulation of thermodynamics was enthusiastically promoted by Maxwell; see Rukeyser (1942). Its major role is to introduce the raw and mutually independent variables. The action functional is, to use a term from quantum mechanics and quantum field theory, “**off shell**” and subject to no constraints. The laws of adiabatic thermodynamics are the equations of motion of the variational principle and it is of no interest to

use these laws to transform or evaluate the action functional. To approach a specific thermodynamical problem we must determine the off-shell action functional, choose the expression for the free energy and the values of entropy and pressure; here experience and physical insight are most important. From then on the only equations that can and should be invoked are the equations of motion. There is no danger that a crucial relation has been overlooked and there is less need for ingenuity or additional intuitive insight.<sup>8</sup> What has just been said applies to adiabatic processes with fixed entropy and pressure. For non adiabatic processes the situation is much more difficult.

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

$$U(S, V) = \left( F(T, V) + ST \right) \Big|_{S=-\partial F/\partial T|_V}. \quad (2.4.4)$$

but note that this defines the internal energy on shell.<sup>9</sup> Similarly, since  $A$  is stationary with respect to variations of  $V$  and  $T$ , the values of  $A$  at stationary points,

$$A(V, T, P, S) \Big|_{\text{on shell}},$$

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

### Free energy and Gibbs function

The function  $F$  plays a central and distinguished role in this formulation of adiabatic thermodynamics. Other formulations are possible, that give this prominent place to one of the other potentials. In the limited context that is being envisaged at this stage all four choices give rise to exactly the same variational equations, modulo Legendre transformations, and all four versions are absolutely equivalent, according to Gibbs (1878) and to Callen (1960). With localization, the functions  $F(T, V)$  and  $U(S, V)$  become densities  $f(T, \rho)$  and  $u(s, \rho)$ ; both have the density  $\rho$  as one of their two natural variables and that is clearly advantageous since the density is a major variable of hydrodynamics. Rowlinson (1959) page 79 works with  $F$

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<sup>8</sup>This is an overstatement but it shall stand, for it is a succinct summary of the attitude that is adopted in this book. But see Section III.5.

<sup>9</sup>See above.

and gives some hints as to why this choice is preferred. In Landau and Lifshitz “energy” usually means free energy; the practice of referring to “energy” without precision is wide spread. Callen and others emphasize the equivalence of formulations based on either of the four potentials, but his context is global thermodynamics. The integration with hydrodynamics that follows in the next chapter favors the present formulation, based on  $F$ .

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

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

## II.5. Lowest energy and maximal entropy

Gibbs axioms of **minimum energy** and **maximal entropy** are stated in the opening of his monumental paper (Gibbs 1878):

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

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

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

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

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

The nature of the proof is of interest:

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

This is very abstract, but the last sentence gives a hint of a quantity of the nature of “energy plus entropy” that is invariant with respect to the joint variation of energy and entropy. We shall see that this quantity is the action. How shall we interpret Gibbs’ “energy”? In modern thermodynamics

of isolated systems the functional that is minimal at equilibrium is usually the free energy  $F$  or the Gibbs energy  $G$ .<sup>10</sup> Thus, at equilibrium  $F$  can only increase. When we take this to be valid it follows that the  $A - ST$  can only increase and a variation for which the action is stationary can only decrease the entropy, or at least it can only decrease the value of  $ST$ .

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

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<sup>10</sup>It is sometimes assumed that experiments are carried out over a long time, long enough that the system can be seen as being in thermal equilibrium with the environment. On this basis a case has been made for assuming that it is the enthalpy that is minimized. For simplicity we shall restrict ourselves to deal with isolated systems and assign the role of energy to  $F$ .

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