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Anton Bovier
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Part I

Statistical mechanics

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Introduction

> L'analyse mathématique, n'est elle donc qu'un vain jeu d'esprit? Elle ne peut donner au physicien qu'un langage commode; n'est-ce pas là un médiocre service, dont on aurait pu se passer à la rigueur; et même n'est il pas à craindre que ce langage artificiel ne soit un voile interposé entre la réalité et l'œil du physicien? Loin de là, sans ce langage, la pluspart des analogies intimes des choses nous seraient demeurées à jamais inconnues; et nous aurions toujours ignoré l'harmonie interne du monde, qui est, nous le verrons, la seule véritable réalité objective.[1]
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> *Henri Poincaré, La valeur de la science.*

Starting with the Newtonian revolution, the eighteenth and nineteenth centuries saw with the development of analytical mechanics an unprecedented tool for the analysis and prediction of natural phenomena. The power and precision of Hamiltonian perturbation theory allowed even the details of the motion observed in the solar system to be explained quantitatively. In practical terms, analytical mechanics made the construction of highly effective machines possible. Unsurprisingly, these successes led to the widespread belief that, ultimately, mechanics could explain the functioning of the entire universe. On the basis of this confidence, new areas of physics, outside the realm of the immediate applicability of Newtonian mechanics, became the target of the new science of theoretical (analytical) physics. One of the most important of these new fields was the theory of heat, or *thermodynamics*. One of the main principles of Newtonian mechanics was that of the conservation of energy. Now, such a principle could not hold entirely, due to the ubiquitous loss of energy through friction. Thus, all machines on earth require some source of energy. One convenient source of energy is heat, obtainable, e.g., from the burning of wood, coal, or petrol. A central objective of the theory of thermodynamics was to understand how the two types of energy, mechanical and thermal, could be converted into each other. This was originally a completely pragmatic theory, that introduced new concepts related to the phenomenon of heat, *temperature* and *entropy*, and coupled these to mechanical concepts of energy and force. Only towards the end of the nineteenth century, when the success of mechanics reached a peak, was Boltzmann, following earlier work by Bernoulli, Herapath, Joule, Krönig, Claudius,

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[1] Approximately: So is mathematical analysis then not just a vain game of the mind? To the physicist it can only give a convenient language; but isn't that a mediocre service, which after all we could have done without; and, is it not even to be feared that this artificial language be a veil, interposed between reality and the physicist's eye? Far from that, without this language most of the intimate analogies of things would forever have remained unknown to us; and we would never have had knowledge of the internal harmony of the world, which is, as we shall see, the only true objective reality.

and Maxwell, able to give a mechanical interpretation of the thermodynamic effects on the basis of the atomistic theory. This *kinetic theory of gases* turned into what we now know as *statistical mechanics* through the work of Gibbs in the early twentieth century. It should be mentioned that this theory, that is now perfectly accepted, met considerable hostility in its early days. The first part of this book will give a short introduction to the theory of statistical mechanics.

It is not a coincidence that at the same time when statistical mechanics was created, another new discipline of physics emerged, that of *quantum mechanics*. Quantum mechanics was concerned with the inadequacies of classical mechanics on the level of microscopic physics, in particular the theory of atoms, and thus concerned the opposite side of what statistical mechanics is about. Interestingly, quantum mechanical effects could explain some deviations of the predictions of statistical mechanics from experimental observation (e.g. the problem of black body radiation that was resolved by Planck's quantum hypothesis). The basic principles of statistical mechanics can be well reconciled with quantum mechanics and give rise the the theory of *quantum statistical mechanics*. However, in many cases, a full quantum mechanical treatment of statistical mechanics turns out to be unnecessary, and much of classical mechanics applies with just some minor changes. In any case, we will here consider only the classical theory. Before approaching our main subject, let us have a very brief look at thermodynamics.

1.1 Thermodynamics

A mechanical system is characterized by essentially geometric quantities, the positions and velocities of its components (which are points of mass). If solid objects are described, the assumption of rigidity allows us to reduce their description to essentially the same kind of coordinates. Such a description does not, however, do complete justice to all the objects we can observe. Even solids are not really rigid, and may change their shape. Moreover, there are liquids, and gases, for which such a description breaks down completely. Finally, there are properties of real objects beyond their positions or velocities that may interfere with their mechanical properties, in particular their *temperature*. In fact, in a dissipative system one may observe that the temperature of a decelerating body often increases. Thermodynamics introduces a description of such new *internal* variables of the system and devises a theory allowing us to control the associated flow of energy.

The standard classical setting of thermodynamics is geared to the behaviour of a gas. A gas is thought to be enclosed in a container of a given (but possibly variable) volume, $V > 0$. This container provides the means of coupling the system to an external mechanical system. Namely, if one can make the gas change the volume of the container, the resulting motion can be used to drive a machine. Conversely, we may change the volume of the container and thus change the properties of the gas inside. Thus, we need a parameter to describe the state of the gas that reacts to the change of volume. This parameter is called the *pressure*, p. The definition of the pressure is given through the amount of mechanical energy needed to change the volume:[2]

$$\mathrm{d}E_{\text{mech}} = -p\mathrm{d}V \tag{1.1}$$

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[2] The minus sign may appear strange (as do many of the signs in thermodynamics). The point, however, is that if the volume increases, work is done by the system (transfered somewhere), so the energy of the system decreases.

Pressure is the first *intensive* variable of thermodynamics that we meet. Clearly, the relation (1.1) is not universal, but depends on further parameters. An obvious one is the total amount of gas in the container, N. Originally, N was measured in *moles*, which could be defined in terms of chemical properties of the gases. Nowadays, we know that a mole corresponds to a certain number of molecules ($\sim 6 \times 10^{23}$), and we think of N as the number of molecules in the gas. It is natural to assume that, if $V(N) = Nv$, then $p = p(v)$ should not depend on N. Hence the term *intensive*. By contrast, V is called *extensive*. It follows that E is also an extensive quantity. Like V, N can be a variable, and its change may involve a change of energy. This may not seem natural, but we should think of chemical reactions (and the possibility of having several types of molecules). By such reactions, the number of molecules will change and such a change will create or diminish a reservoir of external chemical energy (e.g. energy stored in the form of carbon). Again, we need a parameter to relate this energy change to the change in mass. We call this the *chemical potential*, μ. Then

$$\mathrm{d}E_{\text{chem}} = \mu \mathrm{d}N \tag{1.2}$$

Now comes heat. Contrary to the two previous variables, volume and mass, heat is a less tangible concept. In fact, in this case the intensive variable, the *temperature*, T, is the more intuitive one. This is something we can at least feel, and to some extent also measure, e.g., using a mercury thermometer. However, we could abstract from this sensual notion and simply observe that, in order to have energy conservation, we must take into account a further internal variable property of the gas. This quantity is called *entropy*, S, and the temperature is the coefficient that relates its change to the change in energy. An important assumption is that this quantity is always non-negative. Traditionally, this *thermal energy* is called *heat* and denoted by Q, so that we have

$$\mathrm{d}Q = T\mathrm{d}S \tag{1.3}$$

The principle of conservation of energy then states that any change of the parameters of the system respect the **first law of thermodynamics**:

$$\mathrm{d}E_{\text{mech}} + \mathrm{d}E_{\text{chem}} + \mathrm{d}Q = \mathrm{d}E \tag{1.4}$$

respectively

$$\mathrm{d}E = -p\mathrm{d}V + \mu\mathrm{d}N + T\mathrm{d}S \tag{1.5}$$

Moreover, for closed systems, i.e. for any processes that do not involve exchange of energy with some additional external system, $\mathrm{d}E = 0$.

The main task of thermodynamics is to understand how the total energy of the system can be transformed from one type to the other in order to transform, e.g., heat into mechanical energy.

We will postulate that the state of a thermodynamic system (in equilibrium!) is described by giving the value of the three extensive variables V, N, S. Therefore we can assume that the thermodynamic state space is a three-dimensional manifold. In particular, the total energy,

$$E = E_{\text{mech}} + E_{\text{chem}} + Q \tag{1.6}$$

will be given as a function, $E(V, N, S)$. Such a function defines the particular thermodynamic system. It then follows that the intensive variables (in equilibrium!) can be expressed as functions of the extensive variables via

$$\begin{aligned} -p(V, N, S) &= \frac{\partial E(V, N, S)}{\partial V} \\ \mu(V, N, S) &= \frac{\partial E(V, N, S)}{\partial N} \\ T(V, N, S) &= \frac{\partial E(V, N, S)}{\partial S} \end{aligned} \tag{1.7}$$

These equations are called equations of state.

Remark 1.1.1 The statements above can be interpreted as follows: Suppose we fix the intensive variables p, T, μ by some mechanism to certain values, and set the extensive variables V, S, N to some initial values V_0, S_0, N_0. Then the time evolution of the system will drive these parameters to equilibrium, i.e. to the values for which equations (1.7) hold. Such processes are called *irreversible*. In contrast, *reversible* processes vary intensive and extensive parameters in such a way that the equations of state (1.7) hold both in the initial and in the final state of the process, i.e. the process passes along equilibrium states of the system. Note that this statement contains the formulation of the second law of thermodynamics.

One of the main pleasures of thermodynamics is to re-express the equations of state in terms of different sets of variables, e.g. to express V, N, S as a function of p, N, T, etc. To ensure that this is possible, one always assumes that E is a *convex* function. The function $E(V, S, N)$ is usually called the *internal energy*. Then, the desired change of variables can be achieved with the help of *Legendre transformations*.

In the example mentioned, we would like to express the energy as a function of p, T, N and to introduce a new function G with the property that $\partial G/\partial p = V$. That is, we must have that

$$\begin{aligned} \mathrm{d}G(p, T, N) &= +V\mathrm{d}p - S\mathrm{d}T + \mu\mathrm{d}N \\ &= +\mathrm{d}(Vp) - \mathrm{d}(ST) - p\mathrm{d}V + T\mathrm{d}S + \mu\mathrm{d}N \\ &= \mathrm{d}(Vp - ST + E) \end{aligned} \tag{1.8}$$

Thus, we get

$$G(p, T, N) = pV(p, T, N) - TS(p, T, N) + E(V(p, T, N), N, S(p, T, N)) \tag{1.9}$$

where the functions V and S are obtained from inverting (1.7). However, this inversion often need not be done, since an expression of the energy in the new variables is readily available. The important observation is that the fundamental function, whose derivatives provide the equations of state, is not always the energy, but its various Legendre transforms. All these functions carry interesting names, such as internal energy, free energy, enthalpy, free enthalpy, etc., which are difficult to remember. The importance of these different forms of these *thermodynamic potentials* lies in the fact that one is interested in processes where some parameters of the system are changed, while others are fixed. Computing the resulting changes is most easily done with the help of the corresponding natural potential,

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which typically corresponds to the conserved energy when its variables are kept fixed while the others are varied.

The function G is called the *Gibbs free energy*. Other potentials whose name it is useful to remember are

(i) the Helmholtz *free energy*,

$$F(T, V, N) = E - TS \tag{1.10}$$

(ii) the *enthalpy*,

$$H(p, S, N) = E + pV \tag{1.11}$$

Let us note that thermodynamics, contrary to what its name suggests, is not a theory of dynamics, but rather one of statics, or *equilibrium*. For example, the values that the intensive parameters take on when the extensive ones are fixed are equilibrium values. When performing thermodynamic calculations, one always assumes that the system takes on these equilibrium values, which is perhaps a reasonable approximation if the motion is performed very slowly. In reality, things are much more difficult.

At one point we said that the assumption of convexity allows us to invert the equations of state and to express, e.g., V as a function of p, T, N. But this is not true. It is only true if E is a *strictly convex* function. If in some region E depends linearly on V, then $p = \partial E/\partial V = const.$ on that set, and we cannot compute V as a function of p; all we know is that, for this value of p, V must lie in the said interval. In other words, V as a function of p has a jump at this value of p. If something of this type happens, we say that the system undergoes a *first-order phase transition* at this value of the parameters. Interestingly, real systems do exhibit this phenomenon. If the pressure of, say, water vapour is increased, while the temperature is not too low, at some specific value of p the volume drops down, i.e. the vapour condenses to water. It is remarkable that the formalism of thermodynamics easily allows the incorporation of such striking phenomena. If there is a phase transition, then the equations of state represent discontinuous functions. This is an unexpected feature that we are not familiar with from mechanics. This seems to indicate that classical dynamics and thermodynamics are quite different and should not have much to do with each other, as it seems inconceivable that these discontinuities should result from motions governed by Newton's equations. Therefore, phase transitions are the most remarkable phenomena in statistical mechanics, and they will be at the centre of our attention throughout this book. Even today, they represent one of the most lively topics of research in the field.

Jumps in the equations of state are the most severe singularities that are admitted in the theory, due to the convexity assumption. There are milder forms of singularities that are very interesting, where only higher derivatives of the equations of state are discontinuous. According to the order of the discontinuous derivative, such phase transitions are called second order, third order, etc. They are associated with interesting physical phenomena.

The main problem of thermodynamics is that we do not understand what entropy and temperature are, which represents the main difficulty in understanding what the thermodynamic potentials should be as functions of their parameters. In practice, they are often obtained empirically from experimental data. A derivation from first principles is of course desirable.

The preceding discussion of thermodynamics is of course very cursory. There are numerous in-depth presentations in the literature. A recent attempt to give an axiomatic foundation of thermodynamics was made in a paper by Lieb and Yngvason [169], which also contains a wealth of references.

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Principles of statistical mechanics

> Qu'une goutte de vin tombe dans un verre d'eau; quelle que soit la loi du mouvement interne du liquide, nous le verrons bientôt se colorer d'une teinte rose uniforme et à partir de ce moment on aura beau agiter le vase, le vin et l'eau ne paraîtront plus pouvoir se séparer. Tout cela, Maxwell et Boltzmann l'ont expliqué, mais celui qui l'a vu le plus nettement, dans un livre trop peu lu parce qu'il est difficile à lire, c'est Gibbs, dans ses principes de la Mécanique Statistique.[1]
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> *Henri Poincaré. La valeur de la science.*

About 1870, Ludwig Boltzmann proposed that the laws of thermodynamics should be derivable from mechanical first principles on the basis of the atomistic theory of matter. In this context, N moles of a gas in a container of volume V should be represented by a certain number of *atoms*, described as point particles (or possibly as slightly more complicated entities), moving under Newton's laws. Their interaction with the walls of the container is given by elastic reflection (or more complicated, partially idealized constraint-type forces), and would give rise to the observed *pressure* of the gas. In this picture, the thermal variables, temperature and entropy, should emerge as effective parameters describing the macroscopic essentials of the microscopic dynamics of the gas that would otherwise be disregarded.

2.1 The ideal gas in one dimension

To get an understanding of these ideas, it is best to consider a very simple example which can be analyzed in full detail, even if it is unrealistic. Consider N particles, all of mass m, that move on a one-dimensional line $\mathbb{R}$ and that absolutely do not interact with each other; in particular they penetrate each other freely upon impact. We denote the position and momentum of particle i by q_i and p_i. Assume further that they are confined to an interval $[0, V]$.

When reaching the boundary of this interval, they are perfectly reflected. Now let the top boundary of the interval (the piston) be movable; assume that a constant force f is acting on

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[1] Approximately: Let a drop of wine fall into a glass of water; whatever be the law that governs the internal movement of the liquid, we will soon see it tint itself uniformly pink and from that moment on, however we may agitate the vessel, it appears that the wine and the water can separate no more. All this, Maxwell and Boltzmann have explained, but the one who saw it in the cleanest way, in a book that is too little read because it is difficult to read, is Gibbs, in his *Principles of Statistical Mechanics*.

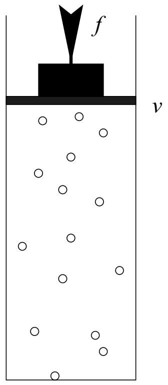

Figure 2.1 Weight on the piston exerting a force f on the piston.

this piston, as shown in Fig. 2.1. Then the container has energy $E_{\text{ext}} = fV$, if the piston's position is V. At some initial time 0 let the momenta of the particles be p_i such that

$$\frac{1}{2m}\sum_{i=1}^{N} p_i^2 = E \tag{2.1}$$

The total (conserved) energy of the system is then

$$H = fV + E \tag{2.2}$$

We will now assume that the dynamics of the system is such that (after a long time) it runs uniformly over all configurations that are compatible with the constraint that the energy of the system is constant (this is probably not the case in our system, but ...). Since the kinetic energy of the particles, E, is non-negative, the position of the piston can only range over the finite interval $[0, V_{\max}]$, where $V_{\max} = H/f$. Then, the total available state space of our system is $[0, V_{\max}] \times [0, V]^N \times S^N_{\sqrt{2m(H-fV)}}$, where S^N_r denotes the $(N-1)$-dimensional sphere of radius r. Our assumptions correspond to saying that we start the process initially at random on any point of this set with equal probability, and that we will find ourselves, in the long run, uniformly distributed on this set (this distribution is called the *micro-canonical distribution* of our system). As we have explained, thermodynamics is concerned with the macroscopic observables only, and in our case this is the position of the piston, V. Finding the *equilibrium position* of this variable amounts to computing the probability distribution of the parameter V, to wit

$$\mathbb{P}[V \in dV] \equiv \frac{\mathrm{d}V \int_{S^N_{\sqrt{2m(H-fV)}}} \mathrm{d}p_1 \cdots \mathrm{d}p_N \int_0^V \mathrm{d}q_1 \cdots \mathrm{d}q_N}{\int_0^{V_{\max}} \mathrm{d}V \int_{S^N_{\sqrt{2m(H-fV)}}} \mathrm{d}p_1 \cdots \mathrm{d}p_N \int_0^V \mathrm{d}q_1 \cdots \mathrm{d}q_N} \tag{2.3}$$

Now $\int_0^V \mathrm{d}q_1 \cdots \mathrm{d}q_N = V^N$, and the surface area of the $(N-1)$-dimensional sphere being $|S^N_r| = \frac{2\pi^{N/2}}{\Gamma(N/2)} r^{N-1}$, we have that

$$\begin{aligned}\int_{S^N_{\sqrt{2m(H-fV)}}} \mathrm{d}p_1 \cdots \mathrm{d}p_N \int_0^V \mathrm{d}q_1 \cdots \mathrm{d}q_N \\ = V^N \frac{2\pi^{N/2}}{\Gamma(N/2)} (2m(H-fV))^{(N-1)/2}\end{aligned} \tag{2.4}$$