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## The Fundamental Postulate

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When he woke up, the dinosaur was still there.

—Augusto Monterroso

The aim of statistical mechanics is to describe the thermodynamic properties of complex systems, composed of a large number of particles. The characteristic evolution times of these systems are microscopic, and for this reason, measuring mechanical quantities in an experiment of reasonable length is equivalent to the measurement of these quantities' average during the corresponding time interval. In this manner, it is possible to define the thermodynamic observables as time averages of mechanical quantities. The pressure applied by a fluid on a wall, for example, can be expressed (by analogy with what we saw in chapter 1) as the time average of the force applied on the wall, divided by the surface area of the wall itself.

We have seen, however, that entropy is not a mechanical quantity, in the sense we just expressed. The key to the relation between mechanical and thermodynamic properties is the microscopic expression of entropy. This expression was found by Ludwig Boltzmann, and it has such an important role that we have decided to call it the **fundamental postulate** of statistical mechanics. Since we are dealing with a postulate, it cannot be proven—we can, however, make it plausible by showing that the properties of entropy that derive from it agree with the properties that we postulated in thermodynamics.

In order to make the fundamental postulate more explicit, we must resort to an abstract representation of the dynamics of a system with many particles—this representation uses the concepts of phase space and of a system's representative point.

### 3.1 Phase Space

Let us consider a simple fluid represented as a classical system composed of  $N$  identical particles, of mass  $m$ , interacting with one another and with the walls of the container. Let us suppose that the system is energetically isolated so that there are no exchanges of

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energy between it and the external environment. At each instant, the state of the system can be described by giving each particle's position  $\mathbf{r}$  and momentum  $\mathbf{p}$ :  $6N$  scalar variables in total. These identify a point, the system's **representative point**, within a  $6N$ -dimensional space, called the **phase space**. The evolution of the system is represented by the motion of the representative point within this space and is described by Hamilton's system of  $6N$  differential equations of motion. If we denote the system's Hamiltonian by  $H$ :

$$H = \sum_{i=1}^N \left[ \frac{\mathbf{p}_i^2}{2m} + U(\mathbf{r}_1, \dots, \mathbf{r}_N) \right], \quad (3.1)$$

these equations have the expression

$$\frac{d\mathbf{r}_i}{dt} = \frac{\partial H}{\partial \mathbf{p}_i}, \quad (3.2)$$

$$\frac{d\mathbf{p}_i}{dt} = -\frac{\partial H}{\partial \mathbf{r}_i}. \quad (3.3)$$

Let us denote the generic point of the space phase by  $x = (\mathbf{p}_1, \mathbf{r}_1, \dots, \mathbf{p}_N, \mathbf{r}_N)$ . With the passage of time, the system's representative point moves along a trajectory  $x = x(t; x^0)$ , identified by the initial condition  $x(0; x^0) = x^0 = (\mathbf{p}_1^0, \mathbf{r}_1^0, \dots, \mathbf{p}_N^0, \mathbf{r}_N^0)$ .

Generally speaking, this trajectory is extremely complicated. The only thing we can state a priori is that, if the system is isolated, it lies entirely on the surface defined by the equation

$$H = E = \text{const.} \quad (3.4)$$

The Hamiltonian's constant value  $E$  can be identified with the system's internal energy.

Strictly speaking, for a system of  $6N$  equations of motion, there exist  $6N - 1$  integrals of motion, which define a *line* in phase space along which the system must move. To a very large extent, however, these integrals cannot be measured or theoretically predicted, because a small disturbance to the system causes their values to vary greatly. In a system composed of many particles, a small (experimentally imperceptible) shift of each particle corresponds to a large shift of the system's representative point in phase space. It is obvious that quantities that change a lot due to a shift of this kind cannot be relevant to a thermodynamic description of the system. Therefore, the properties that are dealt with by thermodynamics and statistical mechanics must vary only slightly when the system's representative point is changed slightly. We will make this condition more explicit further on.

In order for our argument to be consistent with thermodynamics, it is necessary that given a certain (not very large) number of these quantities, we can predict their value (and the value of other analogous quantities) after thermodynamic transformations have occurred, at least for sufficiently large systems. How these quantities can be characterized is a well-defined problem, but one that has not yet been satisfactorily resolved in the general case. In order to obtain a microscopic equivalent of the postulates of thermodynamics, however, we can assume that these quantities are the thermodynamic observables, only

this time considered as functions of the *microscopic* state of the system, rather than its thermodynamic state. We shall therefore formulate the following hypothesis:

*The region in phase space in which the system is evolving can be completely identified, for thermodynamic purposes, by the values of certain observable quantities.*

In the case of the simple fluid we considered, for example, this region can be identified by the condition that the positions of all particles be situated inside a region of volume  $V$ , which represents the inside of the container, and by the value  $E$  of internal energy. If the thermodynamics of simple fluids that we discussed in chapter 2 is valid, it is impossible to identify other physically important quantities that vary slowly in the phase space and that would restrict this region in a significant manner.

### 3.2 Observables

Let us call **observables** in statistical mechanics those functions, defined on the phase space, that vary smoothly enough when the representative point varies. The total kinetic energy of a mechanical system, for example, defined by

$$E_c = \sum_{i=1}^N \frac{p_i^2}{2m}, \quad (3.5)$$

is an observable—a particle's variation in momentum causes a relative increase of  $E_c$  on the order of  $N^{-1}$  (which is therefore negligible when  $N$  is large).

An example of a *nonobservable* function is the following:

$$\Theta = \prod_{i=1}^N \theta(r_0^2 - r_i^2). \quad (3.6)$$

This quantity is equal to 1 if *all* the particles are within a sphere of radius  $r_0$  around the origin and is otherwise equal to 0. A shift applied to just one particle is sufficient to change the value of this function by a finite quantity.

As we saw previously, the internal energy corresponds to the observable  $H$  (the Hamiltonian). The number of particles can be expressed as an observable as follows:

$$N = \int d\mathbf{r} \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i). \quad (3.7)$$

We are thus led to formulate the following hypothesis:

*All the extensive thermodynamic variables as a function of which the fundamental equation is expressed are observables.*

Since the fundamental equation is the expression of entropy as a function of extensive variables, what we are missing is a mechanical interpretation of entropy. It will be provided by the fundamental postulate.

### 3.3 The Fundamental Postulate: Entropy as Phase-Space Volume

The fundamental postulate of statistical mechanics expresses entropy as a function of the accessible volume in phase space—in other words, of the volume of the phase space in which the thermodynamic observables have values compatible with a specific thermodynamic state.

Let us assume that the thermodynamic state is determined by the extensive variables  $(X_0, \dots, X_r)$ . Each of these variables— $X_i$ , for example—is represented (in our hypotheses) by a function  $X_i(x)$  defined over the space of microscopic states. The region of phase space that is accessible is defined by the values that these variables assume and that we will denote by  $(X_0, \dots, X_r)$ . In effect, this region is defined by the values  $(X_0, \dots, X_r)$ , up to errors  $\Delta X_i$ ,  $i = 1, \dots, r$ , which can be assumed to be small but macroscopic. The region of phase space in which these observables have those specific values (within the errors) will be denoted by  $\Gamma$ , and its volume by  $|\Gamma|$ . Then the fundamental postulate states that

$$S = k_B \ln |\Gamma|. \quad (3.8)$$

In this formula,

- $S$  is thermodynamic entropy (expressed as a function of extensive variables).
- $k_B$  is Boltzmann's constant ( $1.384 \cdot 10^{-23} \text{ JK}^{-1}$ ).
- The equals sign must be understood as implying “except for nonextensive terms, which become negligible.”

Since it is a postulate, this relation cannot be “proven”—however, one can attempt to justify it by showing that  $\ln |\Gamma|$  has the properties of thermodynamic entropy.

The preceding discussion therefore allows one to give the following expression to thermodynamic entropy, as a function of the extensive variables  $(X_0, \dots, X_r)$ :

$$S(X_0, \dots, X_r) = k_B \ln \int_{\Gamma} dx = k_B \ln \int dx \prod_{i=0}^r [\theta(X_i(x) - (X_i - \Delta X_i)) \theta(X_i - X_i(x))]. \quad (3.9)$$

The product of the theta functions is such that the integrand assumes a value of 1 if the microscopic state  $x$  is such that the values of the observables belong to the interval  $X_i - \Delta X_i \leq X_i(x) \leq X_i$ ,  $i = 0, \dots, r$ , and is otherwise equal to zero.

#### 3.3.1 Other Expressions of Entropy

If we assume that the fundamental postulate is valid, as a corollary we can conclude that the quantity that appears on the left-hand side of equation (3.9) is extensive. As a consequence, it is possible to obtain other expressions of the same quantity, ones that differ from it for terms that grow less rapidly than  $S$  with the system's dimensions. Since in what follows we will make use of these expressions in an interchangeable manner, it is useful to discuss them explicitly here. For simplicity's sake, we will start with a situation in which

all the extensive thermodynamic variables ( $X_1, \dots, X_r$ ) have a well-defined value, and we explicitly consider entropy solely as a function of internal energy  $E$ .

In this situation, equation (3.9) takes the form

$$S(E) = k_B \ln \int dx \theta(H(x) - E + \Delta E) \theta(E - H(x)). \quad (3.10)$$

A fairly surprising first result is that if the energy has a lower bound (we can assume, for example, that it cannot be negative), one obtains the same value for entropy by extending the integral to the entire region  $H(x) \leq E$ :

$$S(E) = k_B \ln \int dx \theta(E - H(x)) + \text{nonextensive terms}. \quad (3.11)$$

In effect, as we know,  $S(E)$  is a monotonically increasing function of  $E$ , and it is extensive. The accessible phase space volume  $|\Gamma(E)| = e^{S(E)/k_B}$  increases with  $E$ , and it increases all the more rapidly the greater the size of the system being considered. As a consequence, the greater part of the accessible phase space volume corresponds to the largest values of  $E$ . In effect, given two values of internal energy  $E$  and  $E'$ , the relation between the corresponding phase space volumes is given by

$$\frac{|\Gamma(E)|}{|\Gamma(E')|} = e^{[S(E) - S(E')]/k_B}, \quad (3.12)$$

and if  $E < E'$ , this relation is exponentially small in the system's size.

We have thus obtained expression (3.11). Given the same hypotheses, we can conclude that entropy can also be expressed as a function of the surface area defined by  $H(x) = E$ :

$$S(E) = k_B \ln \int dx \delta(H(x) - E) + \text{nonextensive terms}, \quad (3.13)$$

where  $\delta(x)$  is the Dirac delta "function." In effect, let us temporarily denote the quantity defined on the right-hand side of equation (3.13) by  $\mathcal{S}(E)$ . By substituting this expression in (3.9), we obtain

$$S(E) = k_B \ln \int_{E-\Delta E}^{E'} dE' e^{S(E')/k_B}. \quad (3.14)$$

If  $\Delta E$  is sufficiently small but finite, the integrand varies slowly in the interval  $E - \Delta E < E' < E$ , and one therefore arrives at

$$S(E) \simeq k_B \ln(e^{S(E)/k_B} \Delta E) = S(E) + \ln \Delta E. \quad (3.15)$$

The last term is obviously negligible in the thermodynamic limit, and therefore  $\mathcal{S}(E) = S(E)$ . By using this result, we can obtain a more explicit derivation of (3.11).

### 3.4 Liouville's Theorem

In the fundamental postulate, entropy is expressed in terms of the accessible volume *in phase space*. One may ask why phase space plays this privileged role, rather than other

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possible spaces that also describe the microscopic state of a mechanical system. Let us consider, e.g., a system composed of identical particles of mass  $m$ . In this case, the momentum  $\mathbf{p}$  of a particle is simply proportional to its velocity  $\mathbf{v}$ , and it is a matter of taste to describe the system in the phase space, i.e., by the collection  $(\mathbf{r}, \mathbf{p})$  of the position and momentum vectors of the particles or by the space of position and velocity vectors. But let us now consider a mixture of particles of two different masses—say,  $m$  and  $m'$ . When particles collide, they exchange momentum in the center-of-mass frame. If they have the same mass, this is tantamount to a velocity exchange. But this is not true when the particles have a different mass. Indeed, we can show that the phase space of positions and momenta possesses a very special property with respect to time evolution. This property is expressed by **Liouville's theorem**.

Let us consider a mechanical system described in the phase space  $x = (\mathbf{r}, \mathbf{p})$ , where  $\mathbf{r} = (\mathbf{r}_1, \dots, \mathbf{r}_N)$  and  $\mathbf{p} = (\mathbf{p}_1, \dots, \mathbf{p}_N)$ . Let the system's Hamiltonian be  $H(\mathbf{r}, \mathbf{p}, t)$ , which may depend on the time  $t$  in an arbitrary way. Then the representative point of the system evolves according to the canonical equations of motion:

$$\dot{\mathbf{r}} = \frac{\partial H}{\partial \mathbf{p}}, \quad \dot{\mathbf{p}} = -\frac{\partial H}{\partial \mathbf{r}}. \quad (3.16)$$

In this way, to each point  $x$  in phase space is assigned a velocity vector  $b(x, t)$  in the same space such that if the representative point of the system lies at  $x$  at a given time  $t$ , it will be at  $x + b(x, t) dt$  at time  $t + dt$ , where  $dt$  is infinitesimal. The vector  $b(x, t)$  has  $6N$  coordinates. To simplify the following discussion, let us identify all pairs  $(r_{i\alpha}, p_{i\alpha})$  of conjugate coordinates and momenta, where  $i$  denotes the particle and  $\alpha = x, y, z$  denotes the coordinate, by a single index  $i$  running from 1 to  $3N$ . Thus the canonical equations of motion assign a local velocity  $b(x) = (b_{r_i}(x), b_{p_i}(x))$  ( $i = 1, \dots, 3N$ ) to each phase-space point  $x = (r_i, p_i)$  ( $i = 1, \dots, 3N$ ) where

$$b_{r_i}(x) = \frac{\partial H}{\partial p_i}, \quad b_{p_i}(x) = -\frac{\partial H}{\partial r_i}, \quad i = 1, \dots, 3N. \quad (3.17)$$

Let us consider a small region  $\Gamma^0$  of phase space, identified by the conditions

$$r_i^0 < r_i < r_i^0 + dr_i, \quad p_i^0 < p_i < p_i^0 + dp_i, \quad i = 1, \dots, 3N.$$

We define the **evolute**  $\Gamma^t$  at time  $t$  as the set of all points that satisfy the following condition: Let  $x(t; x_0)$  be the solution of the canonical equations of motion that satisfies the initial condition  $x(t=0; x_0) = x_0$ . Then,  $\Gamma^t$  contains all the points  $x$  such that  $x = x(t; x_0)$  for some  $x_0 \in \Gamma^0$ . In practice, we can say that all the points that made up  $\Gamma^0$  at time 0 have moved to  $\Gamma^t$  at time  $t$ .

Liouville's theorem states that the volume in phase space of  $\Gamma^t$  is equal to that of  $\Gamma^0$ :

$$|\Gamma^t| = |\Gamma^0|. \quad (3.18)$$

It will be sufficient to prove the result for an infinitesimal time change  $dt$ , since it is clear that if the volume of the evolute remains constant for a small time change, iterating the statement will prove that it remains constant forever.

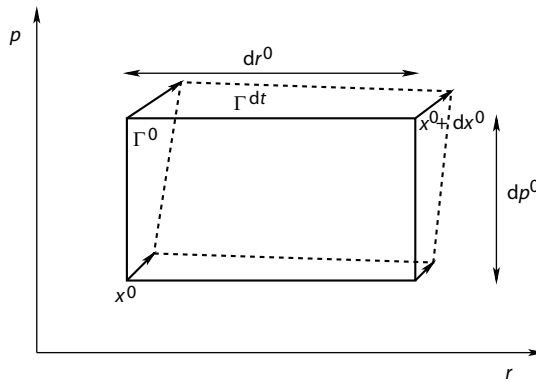


FIGURE 3.1. Evolution of a small phase-space region during an infinitesimal time interval.

To fix one's ideas, it is useful to consider the case of a single particle in one dimension, i.e., of a two-dimensional phase space (see figure 3.1). Then, let the infinitesimal region  $d\Gamma^0$  be defined by the inequalities

$$r^0 < r < r^0 + dr^0, \quad p^0 < p < p^0 + dp^0.$$

Let us denote by  $x^0$  the point  $(r^0, p^0)$  and by  $dx^0$  the vector  $(dr^0, dp^0) = dr^0 \mathbf{i} + dp^0 \mathbf{j}$ , where  $\mathbf{i} = (1, 0)$  and  $\mathbf{j} = (0, 1)$  are the base vectors of the space. The local velocity is given by

$$b_r(r, p) = \frac{\partial H}{\partial p}, \quad b_p(r, p) = -\frac{\partial H}{\partial r}. \quad (3.19)$$

The evoluted region  $d\Gamma^{dt}$  is the parallelogram whose vertices are, respectively, the points  $x^0 + b(x^0)dt$ ;  $x^0 + dp^0 \mathbf{j} + b(x^0 + dp^0 \mathbf{j})dt$ ;  $x^0 + dx^0 + b(x^0 + dx^0)dt$ ; and  $x^0 + dr^0 \mathbf{i} + b(x^0 + dr^0 \mathbf{i})dt$ . Its area is therefore approximately given by

$$\begin{aligned} |d\Gamma^{dt}| &= dr dp = \{dr^0 + [b_r(r^0 + dr^0, p') - b_r(r^0, p')]dt\} \\ &\quad \times \{dp^0 + [b_p(r', p^0 + dp^0) - b_p(r', p^0)]dt\} \\ &\simeq dr^0 dp^0 + dt \left( \frac{\partial b_r}{\partial r} + \frac{\partial b_p}{\partial p} \right) dr^0 dp^0 + \text{higher orders,} \end{aligned}$$

where  $r'$  and  $p'$ , respectively, differ from  $r^0$  and  $p^0$  by less than  $dr^0$  or  $dp^0$ . One has, however, from equations (3.19),

$$\frac{\partial b_r}{\partial r} + \frac{\partial b_p}{\partial p} = \frac{\partial^2 H}{\partial r \partial p} - \frac{\partial^2 H}{\partial p \partial r} = 0. \quad (3.20)$$

Thus  $|d\Gamma^{dt}| = dr^0 dp^0 = |d\Gamma^0|$ , up to terms that are higher order in  $dt$  or in the region's size.

We can now consider the full  $6N$ -dimensional phase space flow. By the same considerations, we obtain, up to higher-order terms,

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$$|d\Gamma^{\text{dr}}| = |d\Gamma^0| \left\{ 1 + dt \sum_{i=1}^{3N} \left[ \frac{\partial b_{r_i}(x, t)}{\partial r_i} + \frac{\partial b_{p_i}(x, t)}{\partial p_i} \right] \right\}. \quad (3.21)$$

By evaluating the derivatives, we obtain

$$\sum_{i=1}^{3N} \left[ \frac{\partial b_{r_i}(x, t)}{\partial r_i} + \frac{\partial b_{p_i}(x, t)}{\partial p_i} \right] = \sum_{i=1}^{3N} \left[ \frac{\partial^2 H(x, t)}{\partial r_i \partial p_i} + \frac{\partial^2 H(x, t)}{\partial p_i \partial r_i} \right] = 0, \quad (3.22)$$

and thus  $|d\Gamma^{\text{dr}}| = |d\Gamma^0|$ . Therefore, for a finite  $t$ , we have

$$|d\Gamma^t| = |d\Gamma^0| = \text{const.} \quad (3.23)$$

which corresponds to Liouville's theorem for an infinitesimal phase space region. The theorem can be extended to arbitrary regions by decomposing them into the union of infinitesimal ones.

The fact that the canonical equations conserve the volume of regions in phase space is the special property of phase space we were looking for.

Liouville's theorem has an important corollary. Let  $\rho(x, t)$  be the local probability density of finding a system in the neighborhood of phase space point  $x$ . Given a small region  $d\Gamma$  of phase space around point  $x$ , the probability of finding the given system in  $d\Gamma$  at time  $t$  is given by

$$dP = \rho(x, t) |d\Gamma|. \quad (3.24)$$

We want to evaluate the way  $\rho(x, t)$  changes if the system evolves according to the canonical equations. Let us consider an arbitrary small region  $d\Gamma^0$  around  $x_0$ , and let  $\rho(x, 0)$  be the initial distribution at  $t = 0$ . Then, the probability  $dP(t)$  that the system is found at time  $t$  within the evolute  $d\Gamma^t$  of  $\Gamma^0$  does not vary by definition, since if its initial condition was lying within  $d\Gamma^0$  at  $t = 0$ , its evolved point must lie within  $d\Gamma^t$  at time  $t$ . We have, therefore,

$$dP = \rho(x(t; x_0), t) |d\Gamma^t| = \rho(x_0, 0) |d\Gamma^0|.$$

Thus,

$$\rho(x(t; x_0), t) = \rho(x_0, 0) \frac{|d\Gamma^0|}{|d\Gamma^t|} = \rho(x_0, 0), \quad (3.25)$$

where in the last equality we have taken into account Liouville's theorem. Therefore, the local probability density does not change if one moves along with the local velocity dictated by the canonical equations.

Let us evaluate the expression of the local probability density change. We have

$$\begin{aligned} \frac{d\rho}{dt} &= \frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left[ \frac{\partial \rho}{\partial r_i} b_{r_i}(x, t) + \frac{\partial \rho}{\partial p_i} b_{p_i}(x, t) \right] \\ &= \frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left( \frac{\partial \rho}{\partial r_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial r_i} \right). \end{aligned}$$

Since Liouville's theorem implies that  $d\rho/dt = 0$ , we obtain



$$\frac{\partial \rho}{\partial t} = - \sum_{i=1}^{3N} \left( \frac{\partial H}{\partial p_i} \frac{\partial \rho}{\partial r_i} - \frac{\partial H}{\partial r_i} \frac{\partial \rho}{\partial p_i} \right) = - [H, \rho]_{\text{PB}}. \quad (3.26)$$

The expression on the right-hand side is called the **Poisson bracket** of the Hamiltonian  $H$  with  $\rho$ , and is usually denoted by  $[ , ]_{\text{PB}}$ . This equation is known as **Liouville's equation**.

Let  $A(x)$  be a function defined on the phase space of the system, e.g., an observable. Let us evaluate the change of its instantaneous value as the system evolves according to the canonical equations of motion. We have

$$A(t) = A(x(t; x_0)),$$

and

$$\frac{dA}{dt} = \sum_{i=1}^{3N} \left[ b_{r_i}(x) \frac{\partial A}{\partial r_i} + b_{p_i}(x) \frac{\partial A}{\partial p_i} \right] = \sum_{i=1}^{3N} \left( \frac{\partial H}{\partial p_i} \frac{\partial A}{\partial r_i} - \frac{\partial H}{\partial r_i} \frac{\partial A}{\partial p_i} \right) = [H, A]_{\text{PB}}. \quad (3.27)$$

Thus, the derivative of  $A$  with respect to time is expressed in terms of its Poisson bracket with the Hamiltonian. Notice, however, the change in sign with respect to Liouville's equation (3.26). In particular, the constants of the motion are characterized by the vanishing of their Poisson bracket with the Hamiltonian.

Let us now assume that  $\rho(x, t)$  is such that, at  $t = 0$ , it depends only on the values of a set  $(X_1, \dots, X_r)$  of constants of the motion, i.e.,

$$\rho(x, 0) = \Phi(X_1(x), \dots, X_r(x)),$$

where, for  $k = 1, \dots, r$ , one has

$$\frac{dX_k}{dt} = [H, X_k]_{\text{PB}} = 0.$$

We then have

$$\frac{\partial \rho}{\partial t} = - \sum_{i=1}^{3N} \left( \frac{\partial H}{\partial p_i} \frac{\partial \rho}{\partial r_i} - \frac{\partial H}{\partial r_i} \frac{\partial \rho}{\partial p_i} \right) = - \sum_{k=1}^r \sum_{i=1}^{3N} \left( \frac{\partial H}{\partial p_i} \frac{\partial X_k}{\partial r_i} - \frac{\partial H}{\partial r_i} \frac{\partial X_k}{\partial p_i} \right) \frac{\partial \Phi}{\partial X_k} = 0.$$

Therefore,  $\rho(x)$  does not change with time. This provides us with a recipe to obtain probability distribution functions that do not change with time—it is sufficient that they depend on  $x$  only via some constants of the motion  $X_k$ .

### 3.5 Quantum States

We know that in classic thermodynamics, entropy would be defined up to an additive constant if one did not add a third postulate to the principles discussed in the preceding chapter, a postulate called either **Nernst's postulate** or the **third law of thermodynamics**, which stipulates the following property:

*The entropy of any system tends to zero for  $T \rightarrow 0$ .*

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According to this postulate, each transformation that is isotherm to  $T = 0$  is also an adiabatic transformation. (From this, it follows that one cannot reach absolute zero.)

On the other hand, from the expression  $S = k_b \ln|\Gamma|$  of the fundamental postulate, it appears obvious that changing the phase space's units of measurement results in the addition of a constant to the entropy. As a consequence, if Nernst's postulate univocally sets the value of entropy (except in cases involving subextensive terms), it must also implicitly fix the unit of measurement for phase space's volume.

The value of this unit is obtained from considerations that involve quantum mechanics and that I will try to describe briefly in this section. We have to keep in mind that we are still far from disposing of a satisfying set of postulates for the foundation of quantum statistical mechanics. The informal remarks that follow have only a heuristic value.

A *microscopic* state in quantum mechanics is described by a vector (normalized and defined up to a phase)  $|\Psi\rangle$  that belongs to a Hilbert space  $\mathcal{H}$ . It evolves according to the time-dependent Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = \widehat{H} |\Psi\rangle, \quad (3.28)$$

where  $\widehat{H}$  is the Hamiltonian operator. (We will always denote quantum operators with a  $\widehat{\phantom{x}}$ .) The **quantum observables**  $A$  are represented by Hermitian operators  $\widehat{A}$  defined on  $\mathcal{H}$ , whose eigenvalues correspond to the possible results of the measurement of  $A$ .

More particularly, if a quantum observable  $\widehat{A}$  commutes with the Hamiltonian  $\widehat{H}$ , it is a constant of motion, and its average value does not change over time—in addition, it is possible to identify some common eigenstates  $|E, A\rangle$  of both the Hamiltonian and  $\widehat{A}$ , and in which both the energy  $E$  and the observable  $A$  have well-defined values. If a system is prepared in one of these eigenstates, the system's evolution (dictated by the Schrödinger equation [3.28]) lets it remain in the same state.

Let us then suppose that it is possible to identify a certain number of quantum observables  $(\widehat{X}_0, \dots, \widehat{X}_r)$  that commute among themselves as well as with the Hamiltonian and that represent the extensive thermodynamic properties  $(X_0, \dots, X_r)$ . Obviously, following our conventions, one has  $\widehat{X}_0 = \widehat{H}$ .

Let us consider the set of all microscopic states in which the thermodynamic observables  $(\widehat{X}_0, \dots, \widehat{X}_r)$  all have a well-defined value, which is equal to  $(X_0, \dots, X_r)$  up to the small uncertainties  $\Delta X_i$ ,  $i = 0, \dots, r$ . These states are the common eigenstates of the Hamiltonian and of the macroscopic observables  $(\widehat{X}_0, \dots, \widehat{X}_r)$ , whose eigenvalues  $\Xi_i$  satisfy the inequalities  $X_i \leq \Xi_i \leq X_i + \Delta X_i$ ,  $i = 0, \dots, r$ . Their number  $\mathcal{N}$  is the quantum analog of the accessible volume of phase space.

The fundamental postulate, in its quantum version, then stipulates that

$$S = k_b \ln \mathcal{N}. \quad (3.29)$$

In this formulation, the arbitrariness associated with the unit of measurement of the phase space's volume has disappeared. More specifically, the Nernst postulate has a clear interpretation: when the temperature tends to zero, only those states that correspond to the lowest energy values become accessible. The number of these states is finite, or grows

more slowly than an exponential when the system's size increases, so that the extensive part of entropy vanishes.<sup>1</sup>

We can now see how in the semiclassical limit, the number  $\mathcal{N}$  of quantum states is proportional to the volume  $|\Gamma|$  of the phase space, and we can calculate the relevant constant of proportionality. In effect, Heisenberg's indeterminacy principle stipulates that for each pair  $(q, p)$  formed by the generalized coordinate  $q$  and the relevant conjugate momentum  $p$ , the quantum uncertainties must satisfy

$$\Delta p \Delta q \geq O(\hbar). \quad (3.30)$$

Each quantum state therefore "occupies" a region of the phase space whose projection on the plane  $(q, p)$  has an area proportional to  $h$ . For a system with  $N$  degrees of freedom, the volume therefore becomes proportional to  $h^N$ , where  $N$  is the number of coordinate pairs and relevant conjugate momenta.

In order to determine the constant of proportionality (which must be universal), one can consider some simple systems. Let us take the harmonic oscillator, for example. The eigenstates of the Hamiltonian of a harmonic oscillator with angular frequency  $\omega$  correspond to the values  $E_n = \hbar\omega(n + 1/2)$  of energy, where  $n = 0, 1, \dots$ . We can evaluate the volume of phase space "occupied" by each eigenstate by calculating the volume included between the curves  $H = n\hbar\omega$  and  $E = (n + 1)\hbar\omega$ . (Since we are in two dimensions, the "volume" is, obviously, an area.) We have

$$H(p, q) = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2, \quad (3.31)$$

and therefore

$$\Delta|\Gamma| = \int_{n\hbar\omega}^{(n+1)\hbar\omega} dE \int dq dp \delta(H(p, q) - E). \quad (3.32)$$

We can now introduce the variables

$$x^2 = \frac{p^2}{m}, \quad y^2 = m\omega^2 q^2, \quad (3.33)$$

and therefore the integral becomes

$$\begin{aligned} \Delta|\Gamma| &= \int_{n\hbar\omega}^{(n+1)\hbar\omega} dE \int \frac{dx dy}{\omega} \delta\left(\frac{1}{2}(x^2 + y^2) - E\right) \\ &= \int_{r^2=2n\hbar\omega}^{r^2=2(n+1)\hbar\omega} \frac{2\pi r}{\omega} dr = 2\pi\hbar = h. \end{aligned} \quad (3.34)$$

The "volume" of each quantum state is therefore equal to  $h$  for a system with only one degree of freedom, as we had anticipated.

<sup>1</sup> One often comes across the statement that Nernst's postulate is a consequence of the fact that the ground state of a quantum system is unique. This is not correct, because the postulate concerns the behavior of the extensive part of  $\ln \mathcal{N}$  for a system with a large  $N$ , in the limit  $T \rightarrow 0$ . (In other words, one *first* passes to the "thermodynamic limit"  $N \rightarrow \infty$ , and one then puts  $T$  to 0.) The uniqueness of the ground state is not sufficient to guarantee that entropy vanishes within this order of limits.

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**Exercise 3.1 (Particle in a Potential Well)** Let us consider a particle of mass  $m$ , constrained to moving in one dimension along a segment of length  $n$ . In this case, the possible energy values are  $E_n = \hbar^2 \pi^2 n^2 / L^2$ , where  $n = 1, 2, \dots$ . Prove that in this case also, the phase space volume “occupied” by each quantum state is equal to  $h$ . (Be careful to calculate the classic volume correctly!)

More generally, one will be able to obtain the correct factor for calculating the volume of quantum states by comparing the entropy calculated classically with the quantum entropy in the semiclassical limit. (Usually, at high temperatures both system behave “classically.”) Since we do not intend to deal with quantum statistical mechanics in this text, we will not delve more deeply into this topic.

### 3.6 Systems in Contact

We will now discuss the extensivity of the entropy. Let us consider two systems, 1 and 2, such that the thermodynamic state of 1 corresponds to the region  $\Gamma^{(1)}$  of phase space, and that of 2 to  $\Gamma^{(2)}$ . Then the Cartesian product  $\Gamma^{(1\cup 2)} = \Gamma^{(1)} \times \Gamma^{(2)}$  will correspond to the region of phase space describing the state of the compound system  $1\cup 2$  (see figure 3.2). The volume of this region is equal to  $|\Gamma^{(1\cup 2)}| = |\Gamma^{(1)}| |\Gamma^{(2)}|$ .

In this manner, the fundamental postulate gives us:

$$\begin{aligned} S &= k_B \ln |\Gamma^{(1\cup 2)}| = k_B \ln (|\Gamma^{(1)}| |\Gamma^{(2)}|) \\ &= k_B \ln |\Gamma^{(1)}| + k_B \ln |\Gamma^{(2)}| = S^{(1)} + S^{(2)}, \end{aligned} \quad (3.35)$$

thus conforming to entropy’s additivity.

One should note that this result implicitly presupposes that no relation between the dynamic states of each of the two subsystems exists, so that the variables that define the overall state of the system are given simply by those that define the state of each subsystem taken separately. This condition of *dynamic independence* of the subsystems is in principle an experimentally based hypothesis, essential for statistical mechanics’ validity, and can be considered as a supplement to the fundamental postulate.

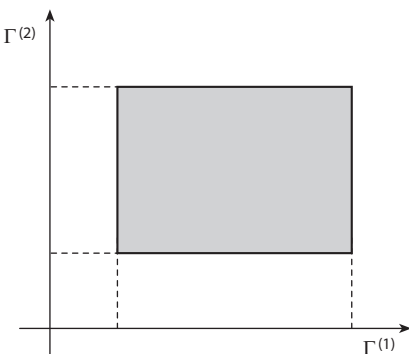


FIGURE 3.2. Schematic representation of the phase-space distribution  $\Gamma^{(1)} \times \Gamma^{(2)}$  of two systems in contact.

In the last analysis, this hypothesis corresponds to the independence of the observables that pertain to systems (in the sense given it by probability theory) in contact. A little later, we will see to what extent it may be possible to justify this hypothesis on the basis of the chaos theory of dynamic systems.

### 3.7 Variational Principle

The other fundamental property of entropy is the **variational principle**, according to which it reaches a maximum at thermodynamic equilibrium. Let us see how this principle is compatible with the interpretation of entropy in terms of accessible volume in phase space.

Let us consider a system whose thermodynamic state is identified by the values of a certain collection ( $X_i$ ) of extensive variables. At thermodynamic equilibrium, certain observables, which we shall collectively denote by  $\xi$ , will have the equilibrium values  $\xi^*$ :

*The variational principle for the entropy states that the equilibrium values  $\xi^*$  correspond to the maximum value of the entropy.*

For example, let us assume that our system is composed of two systems in contact, 1 and 2, that can exchange energy. The total internal energy,  $E_{\text{tot}}$ , has a fixed value: at equilibrium, the value  $E_{\text{eq}}^{(1)}$  of the internal energy of system 1 will also be fixed. This value is determined by the condition that the entropy reaches a maximum. In order to simplify, we will assume that each system's internal energy is determined up to a (macroscopic) uncertainty  $\Delta E$ , and that the thermodynamic states will correspond to discrete values of energy that differ by  $\Delta E$ .

If we consider the two systems as isolated from each other, the accessible volume of the phase space is given by

$$|\Gamma_0| = |\Gamma^{(1)}(E_{\text{in}}^{(1)})||\Gamma^{(2)}(E_{\text{in}}^{(2)})|. \quad (3.36)$$

If we allow for the energy exchange between the two systems, the accessible volume becomes

$$|\Gamma| = \sum_{E^{(1)}} |\Gamma^{(1)}(E^{(1)})||\Gamma^{(2)}(E_{\text{tot}} - E^{(1)})|. \quad (3.37)$$

The sum runs over all possible values of  $E^{(1)}$ . It is obvious that  $|\Gamma| \geq |\Gamma_0|$ , since the term that appears in equation (3.36) is one of the terms that appears in (3.37), and therefore the removal of the constraints leads to an increase of the accessible volume of the phase space—in other words, of the entropy. We thus obtain the property that entropy cannot decrease spontaneously.

At equilibrium, however, the value of the internal energy of system 1 is well determined, while in this equation *all* possible values appear. If we were to take this equation at face value, the result would be disastrous, because the value of the system's entropy would come to depend on its history, and not only on the values of the observables. In effect, this equation implies

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$$|\Gamma| > |\Gamma^{(1)}(E_{\text{eq}}^{(1)})||\Gamma^{(2)}(E_{\text{eq}}^{(2)})|, \quad (3.38)$$

instead of the equality we would expect from thermodynamics.

This problem is solved by considering that the accessible volume of the phase space corresponds *almost entirely* to the states in which  $E^{(1)} = E_{\text{eq}}^{(1)}$ ,  $E^{(2)} = E_{\text{eq}}^{(2)}$ , so that the difference between the two expressions of  $\ln|\Gamma|$  is negligible for large values of  $N$ . This remark is based in its turn on the extensivity of entropy.

Let us in fact make the sum explicit, reading the fundamental postulate backwards. We thus obtain

$$\begin{aligned} |\Gamma| &= \sum_{E^{(1)}} |\Gamma^{(1)}(E^{(1)})||\Gamma^{(2)}(E_{\text{tot}} - E^{(1)})| \\ &= \sum_{E^{(1)}} \exp\left\{\frac{1}{k_B} [S^{(1)}(E^{(1)}) + S^{(2)}(E_{\text{tot}} - E^{(1)})]\right\}. \end{aligned} \quad (3.39)$$

We know that the total entropy—and therefore the summand—reaches its maximum for the equilibrium values of  $E^{(1)}$  and  $E^{(2)}$ . Let us approximate the sum with an integral and expand the exponential's argument into a Taylor series around these values. The first-order term vanishes, and we thus obtain

$$\begin{aligned} |\Gamma| \approx \int \frac{dE^{(1)}}{\Delta E} \exp\left\{\frac{1}{k_B} [S^{(1)}(E_{\text{eq}}^{(1)}) + S^{(2)}(E_{\text{eq}}^{(2)}) \right. \\ \left. + \frac{1}{2} \left( \frac{\partial^2 S^{(1)}}{\partial E^{(1)2}} \Big|_{E_{\text{eq}}^{(1)}} + \frac{\partial^2 S^{(2)}}{\partial E^{(2)2}} \Big|_{E_{\text{eq}}^{(2)}} \right) (E^{(1)} - E_{\text{eq}}^{(1)})^2 \right\}. \end{aligned} \quad (3.40)$$

Due to the extensivity of entropy and internal energy, the derivatives  $\partial^2 S / \partial E^2$  are of order  $1/N$ , where  $N$  is a measure of the two subsystems' sizes, and therefore the contribution of the integral in  $E^{(1)}$  is a factor of order  $N^{1/2}$ . This produces an additive contribution to entropy on the order of  $\ln N$ , and is therefore negligible.

This reasoning gives us another important piece of information: that each system's internal energy values can differ from the equilibrium value of quantities of  $N^{1/2}$  order and are therefore negligible with respect to the value of internal energy, which is of order  $N$ . This is a first step toward a theory of the fluctuations of thermodynamic quantities.

We therefore see that the a priori uncertainty  $\Delta E$  over the value of internal energy is not relevant, at least so long as it is not much smaller than the thermodynamic uncertainty, which is of order  $N^{1/2}$ —in accordance with thermodynamics, we therefore arrive at the conclusion that the value of entropy does not depend on the uncertainty by which we know the values of the thermodynamic variables.

### 3.8 The Ideal Gas

Let us consider the ideal gas. In this case, the extensive variables to be considered are the number of particles  $N$ , the volume  $V$ , and internal energy  $E$ . The system is described by the Hamiltonian:

$$H = \sum_{i=1}^N \left[ \frac{p_i^2}{2m} + u(\mathbf{r}_i) \right], \quad (3.41)$$

where the single particle potential  $u(\mathbf{r})$  is given by

$$u(\mathbf{r}) = \begin{cases} 0, & \text{if } \mathbf{r} \text{ is inside the box of volume } V, \\ \infty, & \text{otherwise.} \end{cases} \quad (3.42)$$

The accessible volume of the phase space is given by

$$|\Gamma| = \frac{1}{N!} \frac{1}{h^{3N}} \int \prod_i d\mathbf{r}_i d\mathbf{p}_i \delta\left(\sum_i \frac{p_i^2}{2m} - E\right). \quad (3.43)$$

In this expression, the integral over the spatial coordinates is extended to the box of volume  $V$ , the delta function in the momenta imposes the internal energy value, and the  $h^{-3N}$  factor is used to normalize the number of states, as previously mentioned. The factor  $1/N!$  take into account the fact that, because of the indistinguishability of identical particles, states that differ only by a permutation of particle indices correspond to the same quantum state and do not need to be counted separately. It is worthy of note that Gibbs was led to introduce this factor on the basis of considerations on entropy's extensivity, well before the introduction of quantum mechanics.

Easily performing the integral over the coordinates, we are led to

$$|\Gamma| = \frac{V^N}{N! h^{3N}} \int \prod_i d\mathbf{p}_i 2m \delta\left(\sum_i p_i^2 - 2mE\right). \quad (3.44)$$

We can interpret the right-hand side integral as the surface area of a sphere of radius  $R = (2mE)^{1/2}$  in a space with  $3N$  dimensions. It is easy to see (see appendix B) that this area is equal to  $1/2\pi^{3N/2} R^{3N-1} / \Gamma_E(3N/2)$ , where  $\Gamma_E$  is Euler's gamma function. We finally obtain

$$|\Gamma| = \frac{V^N \sqrt{\pi} (2mE)^{(3N-1)/2}}{N! h^{3N} \Gamma_E(3N/2)}, \quad (3.45)$$

up to factors that vary more slowly with  $N$ . Shifting to logarithms and taking the asymptotic expression of Euler's function (Stirling's formula; see appendix B) into account, we obtain

$$S = Nk_B \ln \left\{ \left( \frac{eV}{N} \right) \left[ \frac{2\pi m e}{h^2} \left( \frac{2E}{3N} \right) \right]^{3/2} \right\}, \quad (3.46)$$

up to terms that are negligible for large values of  $N$ . We can see from this expression that the entropy thus obtained is actually extensive (while it would not have been so had the factor  $1/N!$  in the definition of  $|\Gamma|$  been absent).

It is interesting to remark that the expression of the entropy of the ideal gas, including the quantum factors  $h$ , has been obtained in the early twentieth century by O. Sackur and H. M. Tetrode [Sack11, Tetr14], before the formulation of quantum mechanics. This expression is therefore known as the **Sackur-Tetrode formula**.

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Having thus arrived at the fundamental equation, we can deduce the equations of state by taking derivatives:

$$\frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_{V,N} = \frac{3}{2} \frac{Nk_B}{E}, \quad (3.47)$$

$$\frac{p}{T} = \left. \frac{\partial S}{\partial V} \right|_{E,N} = \frac{Nk_B}{V}. \quad (3.48)$$

These equations correspond to the usual equations for the ideal monoatomic gas—let us note that they imply that the entropy has the expression  $S = S^{(1)}(E) + S^{(2)}(V)$ , and, moreover, that the internal energy of the ideal gas depends only on the temperature  $E = E(T)$ .

### 3.9 The Probability Distribution

The power of statistical mechanics is highlighted by the possibility of providing predictions for observables that are not explicitly considered in thermodynamics.

Let us assume that the state of our system is identified by a collection  $X = (X_i)$  of extensive variables, which is associated with a region  $\Gamma$  of volume  $|\Gamma|$ . We want to calculate the value taken by another observable,  $A$ , which we will assume is extensive. This observable is defined by a function,  $A(x)$ , over the phase space. According to our hypothesis, in the thermodynamic state specified by the  $(X_i)$ , the observable  $A$  assumes a specific equilibrium value, which we will denote by  $a^*$ . If we impose the constraint that the value of  $A$  be  $a$ , not necessarily identical to the equilibrium value  $a^*$ , on our system, the fundamental hypotheses of thermodynamics tell us that entropy can only decrease:

$$S(X; a) \leq S(X; a^*). \quad (3.49)$$

On the other hand, the fundamental postulate of statistical mechanics relates entropy  $S(X; a)$  to the accessible volume  $|\Gamma(a)|$  of the phase space once the further constraint that the value of  $A$  be equal to  $a$  has also been imposed:

$$S(X; a) = k_B \ln \int_{\Gamma} dx \delta(A(x) - a). \quad (3.50)$$

Since the equilibrium value of  $A$  is equal to  $a^*$ , however, one must get

$$S(X) = S(X; a^*) \geq S(X; a). \quad (3.51)$$

These relations are compatible only if essentially the entire volume of the accessible region  $\Gamma$  of phase space corresponds to the equilibrium value  $a^*$  of the observable  $A$ .

One can become convinced that this is how things stand by calculating the ratio of the volumes of the regions being considered:

$$\begin{aligned} \frac{|\Gamma(a)|}{|\Gamma|} &= \frac{1}{|\Gamma|} \int_{\Gamma} dx \delta(A(x) - a) \\ &= \exp \left\{ \frac{1}{k_B} [S(X; a) - S(X; a^*)] \right\} \\ &\simeq \exp \left\{ \frac{1}{2k_B} \left[ \frac{\partial^2 S}{\partial A^2} \right]_{a^*} (a - a^*)^2 \right\}. \end{aligned} \quad (3.52)$$



The first-order contribution vanishes because of the maximum entropy principle. The second-order derivative is negative and of order  $1/N$ ; the characteristic values of the additive observable  $A$  are also of order  $N$ . The exponential function therefore rapidly becomes negligible as soon as the value of  $A$  differs from the equilibrium value.

But if almost all the accessible volume corresponds to  $A$ 's equilibrium value, we can calculate this value simply by taking  $A$ 's average over the entire accessible region of the phase space:

$$a^* = \langle A(\mathbf{x}) \rangle = \frac{1}{|\Gamma|} \int_{\Gamma} d\mathbf{x} A(\mathbf{x}). \quad (3.53)$$

This gives us a very convenient “recipe” for calculating thermodynamic quantities. Let us observe that the average appearing in equation (3.53) corresponds to the average over a probability distribution that is uniform within  $\Gamma$  and vanishes outside—this distribution is called **microcanonical**. In statistical mechanics, one often uses the word *ensemble* as a synonym for probability distribution in the phase space. The ensemble we have described, in which the internal energy has a fixed value, is called the **microcanonical ensemble** and was introduced by Gibbs.

Let us remark that conceptually, the ensemble is nothing more than a rule to calculate the thermodynamic value of the observables, but that any other distribution, so long as it is fairly smooth within the phase space and only parametrized by the observables, would lead to equivalent results. We will see some additional examples further on.

### 3.10 Maxwell Distribution

Let us consider for example the distribution of velocity in the ideal gas. We define the observable *density of particles having a certain value of velocity*:

$$\mathcal{F}(\mathbf{v}) = \sum_{i=1}^N \delta\left(\frac{\mathbf{p}_i}{m} - \mathbf{v}\right). \quad (3.54)$$

Let us calculate the average value of  $\mathcal{F}$  over the accessible region of phase space:

$$\langle \mathcal{F}(\mathbf{v}) \rangle = \frac{1}{|\Gamma|} \int_{\Gamma} \prod_i d\mathbf{p}_i \delta\left(\frac{\mathbf{p}_i}{m} - \mathbf{v}\right). \quad (3.55)$$

The right-hand-side integrals belong to the type that includes projections onto the axes of a  $3N$ -dimensional sphere and are discussed in appendix B. Using those results, we obtain

$$\langle \mathcal{F}(\mathbf{v}) \rangle = N \left( \frac{2\pi E}{3Nm} \right)^{-3/2} \exp\left[ -\frac{v^2}{2E/(3Nm)} \right], \quad (3.56)$$

which is the Maxwell distribution.

### 3.11 The Ising Paramagnet

Let us now consider a simple model of paramagnet. We can disregard the molecules' translational degrees of freedom as irrelevant to our purposes, and assume that the molecules

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are arranged on a lattice. Let us also assume that each molecule possesses an elementary magnetic moment of magnitude  $\mu$  that can be arranged (for quantum reasons) parallel or antiparallel to the direction of the  $z$  axis. Let us additionally assume that we can disregard all interactions between these magnetic moments and, as a matter of convenience, that we have rescaled the magnetic field  $h$  by the magnetic permeability of the vacuum  $\mu_0$ . These assumptions result in the following definition of the model called the **Ising paramagnet**:

- Each molecule at site  $i$  of the lattice is associated with a variable  $\sigma_i$ , that can assume the values  $+1$  and  $-1$ , depending on whether the corresponding magnetic moment is parallel or antiparallel to the  $z$  axis.
- The energy is due only to the interaction with the magnetic field  $h$  (which we assume is parallel to the  $z$  axis) and is equal to  $-h \sum_{i=1}^N \mu \sigma_i$

In this case, the internal energy vanishes, and the only extensive variable is the total magnetization  $M = \sum_{i=1}^N \mu \sigma_i$ . The relation between entropy and the magnetic field  $h$  can be obtained from

$$dE = TdS + hdM. \quad (3.57)$$

Taking the fact that  $E = 0 = \text{const.}$  into account, we obtain

$$\frac{h}{T} = - \frac{dS}{dM}. \quad (3.58)$$

We must therefore evaluate the entropy as a function of  $M$ . Given  $M$ 's value, the number of molecules  $L$  whose magnetic moment is oriented parallel to the  $z$  axis is determined:

$$L = \frac{1}{2} \left( N + \frac{M}{\mu} \right). \quad (3.59)$$

Strictly speaking, since  $L$  is an integer,  $M$  cannot assume an arbitrary value. Since the quantities we are examining vary slowly with  $L$ , however, it is allowable to consider that  $M$  is known with a small uncertainty, so as to permit the existence of a certain number of possible values of  $L$ . This uncertainty produces a (nonextensive) additive term within entropy, which we will not take into account.

The number of ways in which these  $L$  molecules can be chosen is given by

$$|\Gamma| = \frac{N!}{L!(N-L)!}. \quad (3.60)$$

By using Stirling's formula, therefore, we obtain

$$\begin{aligned} S &= k_B \ln |\Gamma| \\ &= -Nk_B \left[ \frac{1}{2} \left( 1 - \frac{M}{N\mu} \right) \ln \frac{1}{2} \left( 1 - \frac{M}{N\mu} \right) + \frac{1}{2} \left( 1 + \frac{M}{N\mu} \right) \ln \frac{1}{2} \left( 1 + \frac{M}{N\mu} \right) \right]. \end{aligned} \quad (3.61)$$

By taking the derivative of  $S$  with respect to  $M$ , we obtain

$$\frac{h}{T} = Nk_B \cdot \frac{1}{\mu N} \tanh^{-1} \left( \frac{M}{\mu N} \right), \quad (3.62)$$

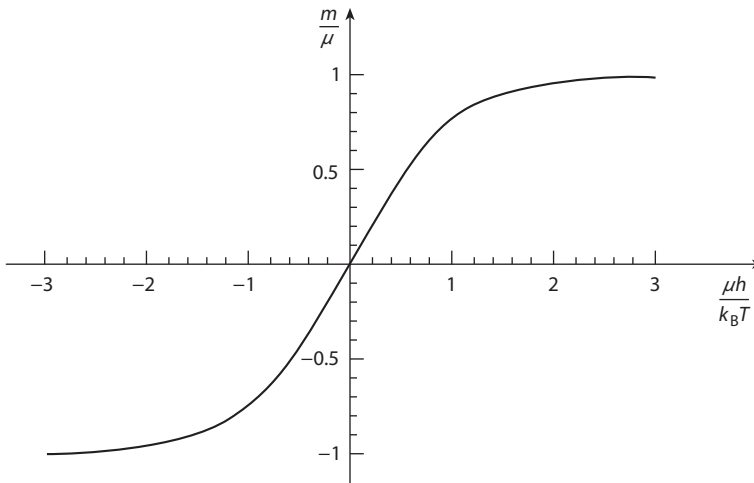


FIGURE 3.3. Equation of state of the Ising paramagnet:  $m/\mu$  as a function of  $\mu h/k_B T$ .

from which the equation of state follows:

$$m = \frac{M}{N} = \mu \tanh\left(\frac{\mu h}{k_B T}\right). \quad (3.63)$$

Figure 3.3 shows the equation of state (3.63)  $m/\mu$  as a function of  $\mu h/k_B T$ . One should note that for  $|\mu h/k_B T| \ll 1$  one has  $m \propto h$ , while for  $|\mu h/k_B T| \gg 1$ ,  $m$  tends to saturate at values of  $m = \pm \mu$ .

The specific heat with magnetic field held constant can be obtained by taking the derivative of the entropy with respect to  $T$ :

$$\frac{C_h}{T} = \frac{\partial S}{\partial T}_h = \frac{dS}{dM} \cdot \frac{\partial M}{\partial T}_h = \frac{1}{T} N k_B \left(\frac{\mu h}{k_B T}\right)^2 \left[1 - \tanh^2\left(\frac{\mu h}{k_B T}\right)\right]. \quad (3.64)$$

Figure 3.4 shows the behavior of  $C_h/Nk_B$  as a function of  $k_B T/\mu h$ .

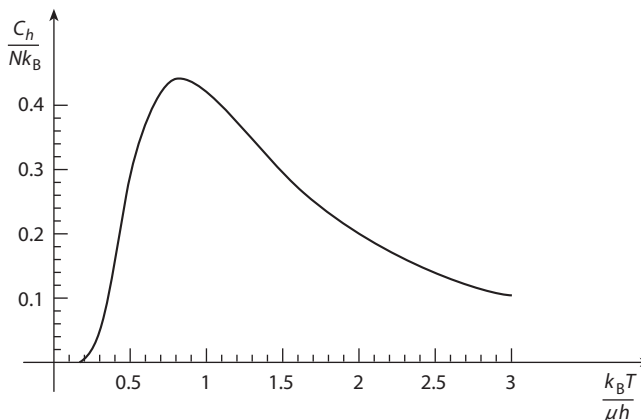


FIGURE 3.4. Specific heat of the Ising paramagnet.  $C_h/Nk_B T$  is plotted versus  $k_B T/\mu h$ .

### 3.12 The Canonical Ensemble

The microcanonical ensemble that we have described in the preceding sections corresponds to the most direct description of thermodynamic systems, in which the thermodynamic equilibrium states are identified by the values of a collection of extensive thermodynamic variables. We have seen that it is possible, in thermodynamics, to provide a different but equivalent description of the same thermodynamic state by considering the values of some intensive variables, rather than those of their conjugate extensive ones, as fixed. In an analogous way, it is possible to define different ensembles in statistical mechanics that correspond to these representations of thermodynamic equilibrium states.

The most important case is that in which the intensive variable we want to introduce is temperature and the corresponding intensive one is internal energy. In this case, we will suppose that we put the system we are interested in, and which we will denote by an  $S$  and call *system*, in contact with a much larger system, which we will denote by an  $R$  and which we will call *reservoir*. System and reservoir can freely exchange energy. At equilibrium, they will have the same temperature—since the reservoir is much larger than the system, however, we can assume that its temperature does not vary independently from the amount of energy it exchanges with the system. In this fashion, we have imposed a fixed temperature value on the system. We want to be able to calculate the average  $a^*$  of any observable  $A$  relative to the system  $S$  only. In order to do this, we observe that the global system's state (SUR) is defined by the pair  $(x_s, x_r)$ , where  $x_s$  is the system's representative point, and  $x_r$  is the reservoir's. Therefore, by applying the rule we derived in the preceding chapter, we obtain:

$$a^* = \frac{1}{|\Gamma|} \int_{\Gamma} dx_s dx_r A(x_s). \quad (3.65)$$

The region  $\Gamma$  is defined by the value  $E$  of total internal energy and by the values of the other extensive variables that we will not specify. Let us rewrite the integral as follows:

$$\langle A \rangle = \frac{1}{|\Gamma|} \int dx_s dx_r A(x_s) \delta(H^{(S)}(x_s) + H^{(R)}(x_r) - E). \quad (3.66)$$

This integral can be rearranged in the following manner:

$$\langle A \rangle = \frac{1}{|\Gamma|} \int dx_s A(x_s) \times \int dx_r \delta(H^{(R)}(x_r) - (E - H^{(S)}(x_s))). \quad (3.67)$$

The integral in  $dx_r$  that appears in this equation is the volume of phase space accessible to the reservoir when its internal energy assumes the value  $E - H^{(S)}$ . This quantity can be expressed by the entropy:

$$\int dx_r \delta(H^{(R)}(x_r) - (E - H^{(S)}(x_s))) \simeq \exp \left\{ \frac{1}{k_B} S^{(R)}(E - H^{(S)}) \right\}. \quad (3.68)$$

When we remember that the system is much smaller than the reservoir, we can expand the exponent into a Taylor series:

$$\exp \left\{ \frac{1}{k_B} S^{(R)}(E - H^{(S)}(x_s)) \right\} \simeq \exp \left[ \frac{1}{k_B} S^{(R)}(E) \right] \exp \left[ - \frac{1}{k_B} \frac{\partial S^{(R)}}{\partial E} \Big|_E H^{(S)}(x_s) \right]. \quad (3.69)$$

At this point, we should note that  $\partial S^{(R)}/\partial E^{(R)} = 1/T$ , and that in our hypotheses, this quantity is fixed. We can then write:

$$\langle A \rangle = \frac{1}{Z} \int dx_s A(x_s) \exp \left[ -\frac{H^{(S)}(x_s)}{k_B T} \right]. \quad (3.70)$$

The normalization constant  $Z$  is called the **partition function** and is equal to:

$$Z = \int dx_s \exp \left[ -\frac{H^{(S)}(x_s)}{k_B T} \right]. \quad (3.71)$$

We see that we can now freely integrate over the system's entire phase space but that the different regions of the phase space are weighed proportionally to the factor

$$\exp \left[ -\frac{H^{(S)}(x_s)}{k_B T} \right], \quad (3.72)$$

which is called the **Boltzmann factor**. We can interpret this factor as the probability density of a certain point in the phase space. In this way, we have defined a new probability distribution—in other words, a new ensemble, which is called the **canonical ensemble**. In order for these results to be compatible with those we obtained from the microcanonical ensemble, it is necessary that the contribution to  $A$ 's average are dominated by the region of phase space in which the system's internal energy assumes the equilibrium value. In order to prove that this is how things stand, let us rearrange the integral according to the values of internal energy. From here on, we will omit the  $S$  indices, because we will be examining only the system itself explicitly. We therefore obtain

$$\langle A \rangle = \frac{1}{Z} \int dE \int dx \delta(H(x) - E) A(x) \exp \left( -\frac{E}{k_B T} \right). \quad (3.73)$$

The integral in  $x$  is proportional to the average microcanonical value of  $A$ , and we will denote it with  $a^*(E)$ , in the state in which the internal energy is equal to  $E$ . The proportionality factor is the corresponding volume of phase space, which we can express by means of the entropy. This integral can therefore be written

$$\langle A \rangle = \frac{1}{Z} \int dE' a^*(E') \exp \left[ -\frac{E' - TS(E')}{k_B T} \right]. \quad (3.74)$$

Since  $a^*(E)$  varies slowly, the integral is determined by the behavior of the exponential, in which the extensive functions  $E'$  and  $S$  appear. If we evaluate it by means of the saddle point method (see appendix B), we notice that it is dominated by a region in which  $E' \simeq E^*$ , where  $E^*$  is the extremal of  $E - TS(E)$  and therefore satisfies

$$\left. \frac{\partial S}{\partial E} \right|_{E^*} = \frac{1}{T}. \quad (3.75)$$

We can therefore identify  $E^*$  with the thermodynamic average value of the energy—in other words, with the internal energy. The contribution of  $E$ 's other values rapidly goes to zero as soon as  $E' - E^*$  is on the order of  $N^{1/2}$ . Considering the integral that defines the partition function, we have

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$$Z \simeq \exp \left[ -\frac{E^* - TS(E^*)}{k_B T} \right] = \exp \left( -\frac{F}{k_B T} \right). \quad (3.76)$$

It is therefore connected to the Helmholtz free energy expressed in the relevant natural variables. Knowledge of the partition function therefore allows us to obtain thermodynamics.

### 3.12.1 Energy Fluctuations

More particularly, the value of internal energy can be obtained by differentiating  $\ln Z$  with respect to  $\beta = 1/k_B T$ :

$$\left. \frac{\partial \ln Z(\beta)}{\partial \beta} \right|_{\beta=1/k_B T} = -\frac{1}{Z} \int dx H(x) \exp \left[ -\frac{H(x)}{k_B T} \right] = -\langle H(x) \rangle = -E. \quad (3.77)$$

The relation one obtains by taking this equation's derivative is even more interesting:

$$\left. \frac{\partial^2 \ln Z}{\partial \beta^2} \right|_{\beta=1/k_B T} = \langle H^2(x) \rangle - \langle H(x) \rangle^2. \quad (3.78)$$

In this manner, we have obtained the variance of internal energy in the canonical ensemble. It is proportional to  $N$ . Moreover, since it cannot be negative, it follows that  $\ln Z$  must be a concave function of its argument  $1/k_B T$ .

It is easy to relate this result to the stability properties of Helmholtz free energy. In fact, by interpreting the derivative differently, we obtain

$$\langle H^2 \rangle - \langle H \rangle^2 = -\frac{\partial E}{\partial (1/k_B T)} = k_B T^2 \frac{\partial E}{\partial T} = k_B T^2 C, \quad (3.79)$$

where  $C$  is the specific heat. We have thus related a *statistical* quantity (variance), connected with the fluctuations of internal energy, to a *thermodynamic* quantity (specific heat). The variance's positiveness implies the specific heat's positiveness. This is the first of a series of important relations that come under the general designation of **fluctuation-dissipation theorems**.

### 3.12.2 The Ideal Gas in the Canonical Ensemble

The advantage of using the canonical ensemble becomes obvious when we are dealing with systems whose Hamiltonian has the form

$$H = \sum_{\alpha} h(x_{\alpha}). \quad (3.80)$$

In other words, it decomposes into terms, each of which is a function of only one or a few degrees of freedom. In fact, while in the microcanonical ensemble, we must satisfy a *global* constraint in which all the degrees of freedom appear, in the canonical ensemble, we can split our integrals into factors in which only a few degrees of freedom appear at each time, and which can be evaluated explicitly.

The ideal gas obviously falls within this category. In fact, we have

$$H = \sum_{\alpha=1}^N \frac{p_{\alpha}^2}{2m} = \sum_{\alpha=1}^N \sum_{i=1}^3 \frac{p_{i\alpha}^2}{2m}. \quad (3.81)$$

Let us calculate the partition function:

$$Z = \frac{1}{N!} \int \prod_{\alpha=1}^N \prod_{i=1}^3 \left( \frac{dr_{i\alpha} dp_{i\alpha}}{h} \right) \exp \left( -\frac{1}{k_B T} \sum_{\alpha=1}^N \sum_{i=1}^3 \frac{p_{i\alpha}^2}{2m} \right). \quad (3.82)$$

The integral over the coordinates yields  $V^N$  as in the microcanonical case, while the integral over momenta can be factorized into  $3N$  identical integrals, which give

$$Z = \frac{V^N}{N!} \left[ \int \frac{dp}{h} \exp \left( -\frac{p^2}{2mk_B T} \right) \right]^{3N} = \frac{V^N}{N!} \left( \frac{2\pi m k_B T}{h^2} \right)^{3N/2}. \quad (3.83)$$

By taking the logarithm and using Stirling's formula, we obtain

$$\ln Z = \frac{F}{k_B T} = N \ln \left[ \frac{eV}{N} \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} \right] = N \ln \left( \frac{e\nu}{\lambda^3} \right), \quad (3.84)$$

where  $e = 2.178\dots$ , i.e., the basis of natural logarithms. In this equation, we introduced the volume per particle  $\nu = V/N$  and the **thermal de Broglie wavelength**:

$$\lambda = \left( \frac{h^2}{2\pi m k_B T} \right)^{1/2}. \quad (3.85)$$

From this equation, it is easy to get free energy  $F$  and, by taking derivatives, obtain the equations of state:

$$F = -Nk_B T \ln \left( \frac{e\nu}{\lambda^3} \right), \quad (3.86)$$

$$S = -\left. \frac{\partial F}{\partial T} \right|_V = Nk_B \ln \left( \frac{e\nu}{\lambda^3} \right) - \frac{3}{2} Nk_B, \quad (3.87)$$

$$p = -\left. \frac{\partial F}{\partial V} \right|_T = \frac{Nk_B T}{V}. \quad (3.88)$$

From the definition  $F = E - TS$  or, equivalently, by taking derivatives of  $\ln Z$  with respect to  $1/k_B T$ , we obtain the value of internal energy:

$$E = \frac{3}{2} Nk_B T. \quad (3.89)$$

By taking further derivatives of this result, we obtain the specific heat at constant volume:

$$C_V = \left. \frac{\partial E}{\partial T} \right|_V = \frac{3}{2} Nk_B. \quad (3.90)$$

### 3.13 Generalized Ensembles

Let us now suppose that we want to keep fixed the value of the variable  $f_i$ , which is conjugated with the extensive variable  $X_i$ . In order to physically realize this constraint, we can

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follow the procedure in the preceding section. We imagine that we are putting our system S (the system) in contact with a system R (the reserve) that is much larger, with which it can exchange the quantity  $X_i$ , and that is characterized by the value  $f_i$  of the corresponding conjugate variable. Keeping in mind that  $f_i$  is determined by the relation

$$\left. \frac{\partial S^{(R)}}{\partial X_i^{(R)}} \right|_E = -\frac{f_i}{T}, \quad (3.91)$$

we can write

$$\begin{aligned} \langle A \rangle &= \frac{1}{|\Gamma|} \int_{\Gamma} dx_R dx_S A(x_S) \\ &= \frac{1}{|\Gamma|} \int dx_S A(x_S) \int dx_R \delta(X_i^{(R)}(x_R) + X_i^{(S)}(x_S) - X_i) \\ &= \frac{1}{|\Gamma|} \int dx_S A(x_S) \exp \left[ -\frac{1}{k_B} S^{(R)}(X_i - X_i^{(S)}(x_S)) \right] \\ &\simeq \frac{1}{Z} \int dx_S A(x_S) \exp \left[ -\frac{1}{k_B} \frac{\partial S^{(R)}}{\partial X_i} X_i^{(S)}(x_S) \right] \\ &= \frac{1}{Z} \int dx_S A(x_S) \exp \left[ \frac{f_i X_i^{(S)}(x_S)}{k_B T} \right]. \end{aligned} \quad (3.92)$$

where  $Z$  is a normalization constant. We can now see that the different points in phase space are weighted proportionally to the factor  $\exp(f_i X_i/k_B T)$ . We have thus introduced a new ensemble, parametrized by the intensive variable  $f_i$ .

It is a consequence of the principles of thermodynamics that practically the entire weight is concentrated in the region of phase space in which  $X_i$  assumes the equilibrium value. One can become convinced of this fact by again following the line of reasoning we just laid out.

The normalization constant  $Z$  can be easily interpreted in thermodynamic terms. We have (omitting the S index):

$$Z = \int dx \exp \left[ \frac{f_i X_i(x)}{k_B T} \right] = \int d\xi \int dx \delta(X_i(x) - \xi) \exp \left( \frac{f_i \xi}{k_B T} \right). \quad (3.93)$$

The integral over phase space in this expression is equal to the entropy expressed as a function of the extensive variable  $X_i$  (as well as of the other extensive thermodynamic variables). Therefore,

$$Z = \int d\xi \exp \left[ \frac{TS(\xi) + f_i \xi}{k_B T} \right]. \quad (3.94)$$

Since both  $S$  and  $X_i$  are extensive variables (and are therefore proportional to  $N$ ), we can calculate this integral with the saddle point method, and we obtain

$$Z \simeq \exp \left[ \frac{TS(X_i^*) + f_i X_i^*}{k_B T} \right]. \quad (3.95)$$

where  $X_i^*$  is the value of  $X_i$  for which the exponent becomes a maximum—in other words,



$$\left. \frac{\partial S}{\partial X_i} \right|_{X'} = -\frac{f_i}{T}. \quad (3.96)$$

We therefore see that the exponential's argument is a Legendre transform of entropy. These thermodynamic functions are known as **Massieu functions**—we will see, however, that in the most useful cases we will end up once again with the usual Legendre internal energy transforms that we saw in chapter 2.

### 3.13.1 Average Values and Fluctuations

The normalization constant allows us to obtain the values for the quantities of interest by simple differentiation. One therefore has

$$\langle X_i \rangle = \frac{1}{Z} \int dx X_i(x) \exp \left[ \frac{f_i X_i(x)}{k_B T} \right] = \frac{\partial \ln Z}{\partial (f_i/k_B T)}. \quad (3.97)$$

By taking the derivative of this expression, we obtain

$$\frac{\partial^2 \ln Z}{\partial (f_i/k_B T)^2} = \langle X_i^2 \rangle - \langle X_i \rangle^2 = k_B T \frac{\partial \langle X_i \rangle}{\partial f_i}, \quad (3.98)$$

which is another fluctuation–dissipation relation. Let us note how the positivity of the variance is reflected in the positivity of  $X_i$ 's derivative with respect to the conjugate variable  $f_i$ , which is in its turn a consequence of stability. In this latest relation, the ratio between the thermodynamic derivative  $\partial X_i / \partial f_i$  and  $X_i$ 's variance contains the Boltzmann constant—therefore, in principle, it is possible to measure Boltzmann's constant (and thus Avogadro's constant) if one finds a way to measure the fluctuations of the thermodynamic variables. This is in effect the core of the first methods used to measure Avogadro's constant.

### 3.13.2 The Paramagnet

In the case of the paramagnet, we want to proceed from the ensemble with a fixed magnetization  $M$  to that in which the magnetic field  $h$  is fixed. According to our rules, we obtain

$$\begin{aligned} Z &= \sum_{\{\sigma_i\}} \exp \left[ \frac{h}{k_B T} M(\{\sigma_i\}) \right] = \sum_{\{\sigma_i\}} \exp \left( \frac{1}{k_B T} \sum_{i=1}^N \mu h \sigma_i \right) \\ &= \prod_{i=1}^N \left[ \sum_{\sigma_i} \exp \left( \frac{1}{k_B T} \sum_{i=1}^N \mu h \sigma_i \right) \right] = [e^{\mu h/k_B T} + e^{-\mu h/k_B T}]^N \\ &= \left[ 2 \cosh \left( \frac{\mu h}{k_B T} \right) \right]^N. \end{aligned} \quad (3.99)$$

The corresponding free energy is given by

$$-\frac{F}{k_B T} = \ln Z = N \ln 2 \cosh \left( \frac{\mu h}{k_B T} \right). \quad (3.100)$$

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The average magnetization is given by

$$\langle M \rangle = \frac{\partial \ln Z}{\partial (h/k_B T)} = N\mu \tanh\left(\frac{\mu h}{k_B T}\right), \quad (3.101)$$

in agreement with what has been obtained from the microcanonical ensemble, while  $M$ 's variance is given by

$$\langle M^2 \rangle - \langle M \rangle^2 = \frac{\partial^2 \ln Z}{\partial (h/k_B T)^2} = N\mu^2 \left[ 1 - \tanh^2\left(\frac{\mu h}{k_B T}\right) \right] = k_B T \chi, \quad (3.102)$$

where  $\chi$  is the isothermal susceptibility:

$$\chi = \frac{\partial \langle M \rangle}{\partial h} \Big|_T. \quad (3.103)$$

We have thus obtained another fluctuation-dissipation relation. From this relation, we can see that isothermal susceptibility at  $h = 0$  is inversely proportional to absolute temperature—this result is known as **Curie's law** and is the basis of the methods used to measure low temperatures.

### 3.14 The $p$ - $T$ Ensemble

Let us now suppose that we fix the value of the temperature  $T$  and of the pressure  $p$  (and therefore let the internal energy and the volume fluctuate). The corresponding ensemble is called the  **$p$ - $T$  ensemble** and is described by the following formula:

$$\langle A \rangle = \frac{1}{Z} \int dx A(x) \exp\left[-\frac{E(x) + pV(x)}{k_B T}\right]. \quad (3.104)$$

The partition function is connected to the Gibbs free energy:

$$\ln Z = -\frac{E - TS + pV}{k_B T} = -\frac{G}{k_B T}. \quad (3.105)$$

We can easily obtain the following relations:

$$E = \langle H \rangle = -\frac{\partial \ln Z}{\partial (1/k_B T)} \Big|_{p/k_B T}, \quad (3.106)$$

$$V = -\frac{\partial \ln Z}{\partial (p/k_B T)} \Big|_{1/k_B T}. \quad (3.107)$$

By taking further derivatives, we obtain:

$$\begin{aligned} \langle H^2 \rangle - \langle H \rangle^2 &= -\frac{\partial E}{\partial \beta} \Big|_{p/k_B T} = k_B T^2 \left[ \frac{\partial E}{\partial T} \Big|_p + \frac{\partial E}{\partial p} \Big|_T \frac{\partial p}{\partial T} \Big|_{p/k_B T} \right] \\ &= k_B T^2 \left[ \frac{\partial E}{\partial T} \Big|_v - \frac{1}{T} \frac{\partial E}{\partial V} \Big|_T \frac{\partial V}{\partial p} \Big|_T \right] \geq k_B T^2 C_V, \end{aligned} \quad (3.108)$$

$$\langle V^2 \rangle - \langle V \rangle^2 = \frac{\partial^2 \ln Z}{\partial (p/k_B T)^2} = -k_B T \left( \frac{\partial V}{\partial p} \right)_T = k_B T V \kappa_T, \quad (3.109)$$

where

$$\kappa_T = -\frac{1}{V} \left. \frac{\partial V}{\partial p} \right|_T, \quad (3.110)$$

is the isothermal compressibility.

In order to obtain the expression in the second line, we can make use of the fact that, in the  $p$ - $T$  ensemble, the fluctuations of internal energy are also induced by fluctuations in volume. A small fluctuation  $\delta V$  in volume therefore causes a corresponding fluctuation  $\partial E / \partial V|_T \delta V$  in energy. As a consequence, the first term of the expression (3.108) corresponds to fluctuations in  $H$  at constant volume, while second term corresponds to the contribution of the volume fluctuations—in other words to  $\partial E / \partial V|_T^2 (\langle V^2 \rangle - \langle V \rangle^2)$ , as can be seen by comparing with equation (3.109). Let us remark that these equations imply that fluctuations in energy are larger than in the canonical ensemble—we removed some constraints, and therefore the fluctuations can only increase.

**Exercise 3.2** Making use of the Maxwell relations and the expression  $p = -\partial F / \partial V|_T$  of pressure, prove the validity of the third equality in equation (3.108).

Last, we have the mixed derivatives:

$$\begin{aligned} \langle HV \rangle - \langle H \rangle \langle V \rangle &= \frac{\partial^2 \ln Z}{\partial (1/k_B T) \partial (p/k_B T)} \\ &= k_B T^2 \left( \frac{\partial V}{\partial T} \right)_p = k_B T \left( \frac{\partial E}{\partial p} \right)_T. \end{aligned} \quad (3.111)$$

We see that the Maxwell relations are connected to the symmetry of correlations. Moreover, the fact that the correlation matrix is positive definite is related to the concavity of the partition function.

### 3.14.1 One-Dimensional Hard Sphere Gas

As an application of the  $p$ - $T$  ensemble, we can solve our first problem with interacting particles. Let us suppose that we have some particles arranged on a straight line. Each particle is a hard sphere of diameter  $\ell$ . Two particles that do not touch do not interact.

The particles' potential energy is therefore given by

$$U(\{r_i\}) = \frac{1}{2} \sum_{(i \neq j)} \phi(r_i - r_j), \quad (3.112)$$

where

$$\phi(r) = \begin{cases} \infty, & \text{if } |r| \leq \ell, \\ 0, & \text{otherwise.} \end{cases} \quad (3.113)$$

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We will see that calculating the partition function becomes very simple in the  $p$ - $T$  ensemble.

Since the particles cannot exchange position, we can imagine numbering them consecutively starting with the one situated most to the left. If we additionally assume that we put the origin in correspondence of the particle with the number zero, then the system's volume can be expressed as the coordinate of the last particle. We thus obtain the following expression of the partition function:

$$Z = \int \prod_{i=1}^N \frac{dp_i}{h} \int_{\ell}^{\infty} dr_1 \int_{r_1+\ell}^{\infty} dr_2 \cdots \int_{r_{N-1}+\ell}^{\infty} dr_N \times \exp\left(-\frac{1}{k_B T} \sum_{i=1}^N \frac{p_i^2}{2m} - \frac{pr_N}{k_B T}\right). \quad (3.114)$$

One can evaluate first the integral over momentum, and this gives us as a contribution  $\lambda^{-N}$ , where  $\lambda$  is the thermal de Broglie wavelength. We still have to calculate the integral over the  $r$ 's, which is also called the configuration integral. Let us change integration variables:

$$\xi_1 = r_1, \quad \xi_i = r_i - r_{i-1}, \quad i > 1. \quad (3.115)$$

The partition function can then be written

$$Z = \lambda^{-N} \int_{\ell}^{\infty} d\xi_1 \int_{\ell}^{\infty} d\xi_2 \cdots \int_{\ell}^{\infty} d\xi_N \exp\left(-\frac{p}{k_B T} \sum_{i=1}^N \xi_i\right). \quad (3.116)$$

The integral then factorizes into  $N$  identical integrals:

$$Z = \lambda^{-N} \left[ \int_{\ell}^{\infty} d\xi \exp\left(-\frac{p\xi}{k_B T}\right) \right]^N = \left[ \frac{1}{\lambda} \frac{k_B T}{p} \exp\left(-\frac{p\ell}{k_B T}\right) \right]^N. \quad (3.117)$$

By taking the derivative of  $\ln Z$  with respect to  $p/k_B T$ , we obtain the equation of state:

$$V = -\frac{\partial \ln Z}{\partial (p/k_B T)} = N \left( \frac{k_B T}{p} + \ell \right). \quad (3.118)$$

In other words,

$$p(V - N\ell) = k_B T. \quad (3.119)$$

The internal energy is obtained by taking the derivative of  $\ln Z$  with respect to  $1/k_B T$  (at  $p/k_B T$  constant) and is equal to  $3k_B T/2$ .

**Exercise 3.3** Extend the preceding result to the case in which, in addition to the hard core, there is an interaction  $u(r)$ , between the particles, with a range between  $\ell$  and  $2\ell$  (such that only close nearest-neighbor particles can interact).

### 3.15 The Grand Canonical Ensemble

The generalized ensemble in which the number of particles fluctuates and the chemical potential is fixed is called the **grand canonical ensemble**. We can directly write

$$\langle A \rangle = \frac{1}{Z} \sum_{N=1}^{\infty} \int dx A(x) \exp \left[ -\frac{H_N(x) - \mu N}{k_B T} \right]. \quad (3.120)$$

The grand canonical partition function is connected to the potential  $\Omega$ :

$$\ln Z = -\frac{E - TS - \mu N}{k_B T} = -\frac{\Omega}{k_B T}. \quad (3.121)$$

As a reminder, let me add that it follows from Euler's equation that  $\Omega = -pV$  for simple fluids (see equation [2.118]). The average values of  $H$  and  $N$  are obtained, as usual, by taking derivatives:

$$E = -\left. \frac{\partial \ln Z}{\partial \left( \frac{1}{k_B T} \right)} \right|_{\frac{\mu}{k_B T}}, \quad (3.122)$$

$$N = \left. \frac{\partial \ln Z}{\partial (\mu/k_B T)} \right|_{1/k_B T}. \quad (3.123)$$

By taking further derivatives, we obtain the expressions for the variances and the corresponding correlations. This derivation is left as an exercise.

**Exercise 3.4** Consider a simple fluid, described by a grand canonical ensemble. Express the following quantities in terms of the grand canonical partition function:

$$\begin{aligned} \langle \Delta E^2 \rangle &= \langle E^2 \rangle - \langle E \rangle^2; \\ \langle \Delta N^2 \rangle &= \langle N^2 \rangle - \langle N \rangle^2; \\ \langle \Delta E \Delta N \rangle &= \langle EN \rangle - \langle \Delta E \rangle \langle \Delta N \rangle. \end{aligned}$$

Interpret the quantities thus obtained in terms of thermodynamic derivatives.

**Exercise 3.5** Show that the energy fluctuations in the grand canonical ensemble are always greater than the corresponding fluctuations in the canonical ensemble:

$$\langle \Delta E^2 \rangle_{\text{GC}}(\mu) \geq \langle \Delta E^2 \rangle_{\text{C}}(N),$$

where  $N$  is the average value of the number of particles corresponding to  $\mu$ .

Since one usually tries to obtain the thermodynamic properties of gases as a function of the number of particles  $N$  rather than of the thermodynamic potential  $\mu$ , it is worthwhile to adopt the following strategy. One calculates the grand canonical partition function, thus obtaining  $\ln Z(T, \mu, V)$ . One then calculates the average number of particles  $N$  as a function of  $\mu$ ,  $T$  and  $V$  using equation (3.123). One inverts this relation, obtaining  $\mu$  as a function of  $N$ ,  $T$ , and  $V$ . This is always possible, since stability implies that  $N$  is a monotonically increasing function of  $\mu$  when the other quantities are kept fixed. One performs the substitutions in equations (3.121) and (3.122) so as to obtain the equation of state for the pressure  $p$  and the internal energy  $E$ .

Let us calculate the properties of the ideal gas in the grand canonical ensemble:

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$$\begin{aligned}
Z &= \sum_{N=1}^{\infty} e^{\mu N/k_B T} \frac{1}{N!} \int \prod_{i=1}^N \left( \frac{d\mathbf{r}_i d\mathbf{p}_i}{h^3} \right) \exp\left(-\frac{1}{k_B T} \sum_{i=1}^N \frac{p_i^2}{2m}\right) \\
&= \sum_{N=1}^{\infty} z^N Z_N,
\end{aligned} \tag{3.124}$$

where  $Z_N$  is a function of the canonical partition of a gas of  $N$  particles (calculated in section 3.12) and where we have also introduced the **fugacity**  $z$ :

$$z = \exp\left(\frac{\mu}{k_B T}\right). \tag{3.125}$$

From section 3.12.2 we obtain:

$$Z_N = \frac{V^N}{N! \lambda^{3N}}, \tag{3.126}$$

and therefore,

$$Z = \sum_{N=1}^{\infty} \frac{1}{N!} \left(\frac{zV}{\lambda^3}\right)^N = \exp\left(\frac{zV}{\lambda^3}\right). \tag{3.127}$$

By taking the logarithm, we obtain the equation of state expressed as a function of  $z$ :

$$\frac{pV}{k_B T} = \ln Z = \frac{zV}{\lambda^3}. \tag{3.128}$$

In order to express it in terms of the usual variables, let us calculate the average value of the number of particles as a function of fugacity:

$$N = \left. \frac{\partial \ln Z}{\partial (\mu/k_B T)} \right|_{1/k_B T} = z \frac{\partial \ln Z}{\partial z} = \frac{zV}{\lambda^3}. \tag{3.129}$$

From this equation, we can obtain  $z$  as a function of  $N$  and substitute it in the preceding equation, so as to obtain the usual equation of state. Obviously, in this case it is trivial, and we immediately obtain the equation of state for ideal gases.

### 3.16 The Gibbs Formula for the Entropy

In this section, we want to show how in any generalized ensemble, entropy can be expressed in terms of the probability density that defines the ensemble. In order to simplify the notations, let us assume that we are dealing with a discrete phase space.

Let us assume that our generalized ensemble is obtained by setting the value of the intensive variable  $f$ , which is conjugated with the extensive variable  $X$ . The expression of any observable's average is

$$\langle A \rangle = \frac{1}{Z} \sum_v A_v \exp\left(\frac{fX_v}{k_B T}\right), \tag{3.130}$$

where the partition function  $Z$  is given by

$$Z = \sum_{\nu} \exp\left(\frac{fX_{\nu}}{k_B T}\right), \quad (3.131)$$

and the sum runs over all of the system's  $\nu$  microstates. As we saw, the relation between the partition function and the thermodynamic potentials is

$$\ln Z = \frac{TS + f\langle X \rangle}{k_B T}, \quad (3.132)$$

where we make explicit the fact that the thermodynamic value of the extensive variable  $X$  is given by its average.

A microstate's  $\nu$  probability is therefore given by:

$$p_{\nu} = \frac{1}{Z} \exp\left(\frac{fX_{\nu}}{k_B T}\right). \quad (3.133)$$

Let us evaluate the logarithm of this expression:

$$\ln p_{\nu} = \frac{fX_{\nu}}{k_B T} - \ln Z = \frac{1}{k_B T} (fX_{\nu} - TS - f\langle X \rangle). \quad (3.134)$$

If we calculate the average of both sides of this equation, we obtain

$$\langle \ln p_{\nu} \rangle = \sum_{\nu} p_{\nu} \ln p_{\nu} = \frac{1}{k_B T} (f\langle X \rangle - TS - f\langle X \rangle) = -\frac{S}{k_B}. \quad (3.135)$$

We have thus obtained the **Gibbs formula for the entropy**:

$$S = -k_B \sum_{\nu} p_{\nu} \ln p_{\nu}. \quad (3.136)$$

This elegant equation is at the origin of modern information theory. One of the most obvious reasons of its interest is the fact that, although it was derived only in the context of generalized ensembles, its right-hand side is defined for any probability distribution. In effect, the quantity defined as *entropy* in information theory is defined precisely by this expression. The temptation to use it to define the thermodynamic entropy of any probability distribution over the phase space is great, even outside thermodynamic equilibrium. One has to resist this temptation as much as possible. In fact, the probability distribution in phase space is only a conceptual instrument that we introduced to calculate the values of the thermodynamic observables, and not a physically observable quantity.

In information theory, it is in principle possible to sample the probability distribution  $p_{\nu}$  and therefore provide a reliable estimate of  $S$ . In our case, the phase space is simply too vast to allow us to perform this program even for the simplest system. We must therefore estimate entropy by resorting to some hypotheses about the independence of degrees of freedom and so on that are valid only if the state we want to describe is close to thermodynamic equilibrium.

Another objection against the generalized use of this relation is that the quantity  $S$  obtained in this way is a constant of the motion for an isolated system, with an arbitrary initial probability distribution. This is a consequence of Liouville's theorem. This is of course

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at variance with the behavior of thermodynamic entropy, which, as we know, increases as the system approaches equilibrium.

### 3.17 Variational Derivation of the Ensembles

One can use the Gibbs formula with the necessary care, being careful that we consider only thermodynamic equilibrium and states close to it. In this section, we show how the ensembles' probability distributions can be derived from a variational principle over the  $S$  defined by the Gibbs formula.

Let us prove the variational principle for the microcanonical ensemble. Let us define the functional  $\mathcal{S}$  of the probability distribution  $p_v$ :

$$\mathcal{S} = -k_B \sum_v p_v \ln p_v. \quad (3.137)$$

This functional is maximum for the (uniform) microcanonical distribution among all the distributions that are supported (in other words, that do not vanish) only within the accessible region  $\Gamma$  of the phase space. In this fashion, we can relate the choice of distribution associated with the ensembles to a principle of maximum entropy.

This is a typical problem of constrained extrema. The constraint is due to probability's normalization condition:

$$\sum_{v \in \Gamma} p_v = 1. \quad (3.138)$$

By introducing the Lagrange multiplier  $\alpha$ , we look for the functional's unconstrained extremum:

$$\Phi = \mathcal{S} - \alpha \left( \sum_v p_v - 1 \right). \quad (3.139)$$

We obtain

$$0 = \frac{\partial \Phi}{\partial p_v} = -k_B (\ln p_v + 1) - \alpha. \quad (3.140)$$

The solution is obviously

$$p_v = \text{const} = \frac{1}{|\Gamma|} \quad (3.141)$$

(the constant's value follows from the normalization condition), which corresponds to

$$\mathcal{S} = k_B \ln |\Gamma|. \quad (3.142)$$

If we consider a generalized ensemble defined by the extensive variable  $X$ , we must take the following constraint into account

$$\langle X_v \rangle = \sum_v p_v X_v = X. \quad (3.143)$$

Let us introduce the Lagrange multiplier  $\lambda$  and look for the extremal of



$$\Phi = S - \alpha \left( \sum_v p_v \right) - \lambda \left( \sum_v p_v X_v \right). \quad (3.144)$$

(We omitted some inessential additive constants.) We obtain

$$\ln p_v = \text{const.} - \lambda X_v, \quad (3.145)$$

which corresponds to the distributions of the generalized ensembles. It is easy to see that, in the case in which  $X$  is the internal energy, the corresponding Lagrange multiplier (usually denoted by  $\beta$ ) is equal to  $1/k_B T$ .

### 3.18 Fluctuations of Uncorrelated Particles

In this section, we attempt to explain the universality of the equation of state of ideal gases by showing that it is a consequence of some very simple hypotheses about the particle distribution.

Let us suppose in fact that the phase space can be considered a product of single-particle states and that the global system's state can be defined by giving the **occupation number** for each single-particle's state. For example, in the ideal quantum gas, the global system's state is determined when the number of particles that possess a specific (quantized) value of momentum has been determined. Let us additionally assume that the occupation numbers of the single-particle states are independent random variables (not necessarily identically distributed!) and that its average is small (so that for every state  $i$ , it is possible to disregard  $\langle n_i \rangle^2$  with respect to  $\langle n_i \rangle$ ). From these hypotheses, it follows that the system obeys the equation of state of ideal gases.

Let us note that nothing is said in these hypotheses about the nature of single-particle states—we can assume that they correspond to larger or smaller cells in configuration space, or in phase space, or in momentum space. One cannot even say with absolute certainty that the occupation numbers define the system's microstate **univocally**—there is nothing to prevent different microstates from corresponding to the same occupation numbers, and so on.

Let us consider the grand canonical ensemble and express the total number of particles by means of the  $n_i$ :

$$N = \sum_i \langle n_i \rangle. \quad (3.146)$$

We can now calculate  $N$ 's variance:

$$\langle N^2 \rangle - \langle N \rangle^2 = \sum_{ij} (\langle n_i n_j \rangle - \langle n_i \rangle \langle n_j \rangle). \quad (3.147)$$

In this sum, all the terms with  $i \neq j$  vanish because of the hypothesis about the  $n_i$ 's independence. On the other hand, if  $\langle n_i \rangle$  is small, the greatest contributions are those for which  $n_i$ 's value is 0 or 1, and therefore  $n_i^2 = n_i$ . We thus obtain

$$\langle N^2 \rangle - \langle N \rangle^2 = \sum_i (\langle n_i \rangle - \langle n_i \rangle^2). \quad (3.148)$$

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If we can neglect  $\langle n_i \rangle^2$  with respect to  $\langle n_i \rangle$ , this relation gives us

$$\langle N^2 \rangle - \langle N \rangle^2 = \sum_i \langle n_i \rangle = N. \quad (3.149)$$

The variance  $N$  is therefore equal to its average. (Here, we recognize a property of the Poisson distribution.) This relation implies the state equation for ideal gases. In fact, one has

$$\begin{aligned} \langle N^2 \rangle - \langle N \rangle^2 &= \left. \frac{\partial^2 \ln Z}{\partial (\mu/k_B T)^2} \right)_{1/k_B T} \\ &= \left. \frac{\partial N}{\partial (\mu/k_B T)} \right)_{1/k_B T} = V k_B T \left. \frac{\partial (N/V)}{\partial \mu} \right)_{T, V}. \end{aligned} \quad (3.150)$$

Then, by introducing the volume per particle  $\nu = V/N$ , one gets

$$\left. \frac{\partial \mu}{\partial \nu} \right)_{T, V} = -\nu^2 \left. \frac{\partial \mu}{\partial (N/V)} \right)_{T, V} = \frac{V k_B T}{N} = \nu k_B T. \quad (3.151)$$

As a consequence of the Gibbs-Duhem equation, on the other hand, we have

$$\left. \frac{\partial \mu}{\partial \nu} \right)_{T, V} = -p. \quad (3.152)$$

Therefore,

$$p = \frac{k_B T}{\nu} = \frac{N k_B T}{V}. \quad (3.153)$$

## Recommended Reading

I have followed the point of view laid forth in S.-K. Ma, *Statistical Mechanics*, Singapore: World Scientific, 1985, which is close to that in L. D. Landau and E. M. Lifshitz, *Statistical Physics*, 3rd ed., Part I, Oxford, UK: Pergamon Press, 1980. Another point of view can be found in R. Balian, *From Microphysics to Macrophysics: Methods and Applications of Statistical Physics* (Berlin/New York: Springer, 1991).

In this volume, I have chosen not to discuss the many subtle problems posed by the foundations of statistical mechanics. An interesting discussion can be found in chapter 26 of Ma's text, *Statistical Mechanics*. Another point of view is expressed in G. Gallavotti, *Statistical Mechanics: A Short Treatise*, Berlin: Springer, 1999.