

## Chapter 2

# Elementary Statistical Physics

In this chapter, we provide the formalism and the elementary background in statistical physics. We first define the basic postulates of statistical mechanics, and then define various ensembles. Finally, we shall derive some of the thermodynamic potentials and their properties, as well as the relationships among them. The important laws of thermodynamics will also be pointed out. The contents of this chapter has a considerable overlap with Chap. 2 of [1] (though there are also considerable differences). It is provided in this book too, mostly for the sake of completeness.

### 2.1 Basic Postulates

As explained in the Introduction, statistical physics is about a probabilistic approach to systems of many particles. While our discussion here will no longer be specific to the ideal gas as before, we will nonetheless start again with this example in mind, just for the sake of concreteness. Consider then a system with a very large number  $N$  of mobile particles, which are free to move in a given volume. The *microscopic state* (or *microstate*, for short) of the system, at each time instant  $t$ , consists, in this example, of the position vector  $\vec{r}_i(t)$  and the momentum vector  $\vec{p}_i(t)$  of each and every particle,  $1 \leq i \leq N$ . Since each one of these is a vector of three components, the microstate is then given by a  $(6N)$ -dimensional vector  $\vec{x}(t) = \{(\vec{r}_i(t), \vec{p}_i(t)) : i = 1, 2, \dots, N\}$ , whose trajectory along the time axis, in the *phase space*  $\mathbb{R}^{6N}$ , is called the *phase trajectory*.

Let us assume that the system is closed, i.e., *isolated* from its environment, in the sense that no energy flows inside or out. Imagine that the phase space  $\mathbb{R}^{6N}$  is partitioned into very small hypercubes (or cells)  $\Delta \vec{p} \times \Delta \vec{r}$ . One of the basic postulates of statistical mechanics is the following: in the long run, the relative amount of time at which  $\vec{x}(t)$  spends within each such cell, converges to a certain number between 0 and 1, which can be given the meaning of the *probability* of this cell.

Thus, there is an underlying assumption of equivalence between temporal averages and ensemble averages, namely, this is the postulate of *ergodicity*. Considerable efforts were dedicated to the proof of the ergodic hypothesis at least in some cases. As reasonable and natural as it may seem, the ergodic hypothesis should not be taken for granted. It does not hold for every system but only if no other conservation law holds. For example, a single molecule ( $N = 1$ ) of a gas in a box is non-ergodic. The reason is simple: assuming elastic collisions with the walls, the kinetic energy of the molecule is conserved, and hence also the speed  $s$ , rather than sampling the Maxwell distribution over time.

What are then the probabilities of the above-mentioned phase-space cells? We would like to derive these probabilities from first principles, based on as few as possible basic postulates. Our second postulate is that for an isolated system (i.e., whose energy is fixed) all microscopic states  $\{\vec{x}(t)\}$  are equiprobable. The rationale behind this postulate is twofold:

- In the absence of additional information, there is no apparent reason that certain regions in phase space would have preference relative to any others.
- This postulate is in harmony with a basic result in kinetic theory of gases – *the Liouville theorem* (see e.g., [2]), which we will not touch upon in this book, but in a nutshell, it asserts that the phase trajectories must lie along hyper-surfaces of constant probability density.<sup>1</sup>

## 2.2 Statistical Ensembles

### 2.2.1 The Microcanonical Ensemble

Before we proceed, let us slightly broaden the scope of our discussion. In a more general context, associated with our  $N$ -particle physical system, is a certain instantaneous microstate, generically denoted by  $\mathbf{x} = (x_1, x_2, \dots, x_N)$ , where each  $x_i$ ,  $1 \leq i \leq N$ , may itself be a vector of several physical quantities associated with particle number  $i$ , e.g., its position, momentum, angular momentum, magnetic moment, spin, and so on, depending on the type and the nature of the physical system. According to the physical model of the given system, there is a certain energy function, a.k.a. *Hamiltonian*, that assigns to every  $\mathbf{x}$  a certain energy  $\mathcal{E}(\mathbf{x})$ .<sup>2</sup> Now, let us denote by  $A(E)$  the volume of the shell of energy about  $E$ . This means

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<sup>1</sup>This is a result of the energy conservation law along with the fact that probability mass behaves like an incompressible fluid in the sense that whatever mass that flows into a certain region from some direction must be equal to the outgoing flow from some other direction. This is reflected in the equation of continuity, which was demonstrated earlier.

<sup>2</sup>For example, in the case of an *ideal gas*,  $\mathcal{E}(\mathbf{x}) = \sum_{i=1}^N \|\vec{p}_i\|^2 / (2m)$ , where  $m$  is the mass of each molecule, namely, it accounts for the contribution of the kinetic energies only. In more complicated situations, there might be additional contributions of potential energy, which depend on the positions.

$$A(E) = \text{Vol}\{\mathbf{x} : E \leq \mathcal{E}(\mathbf{x}) \leq E + \Delta E\} = \int_{\{\mathbf{x} : E \leq \mathcal{E}(\mathbf{x}) \leq E + \Delta E\}} d\mathbf{x}, \quad (2.2.1)$$

where  $\Delta E$  is a very small (but fixed) energy increment, which is immaterial when  $N$  is large. Then, our above postulate concerning the ensemble of an isolated system, which is called the *microcanonical ensemble*, is that the probability density  $P(\mathbf{x})$  is given by

$$P(\mathbf{x}) = \begin{cases} \frac{1}{A(E)} & E \leq \mathcal{E}(\mathbf{x}) \leq E + \Delta E \\ 0 & \text{elsewhere} \end{cases} \quad (2.2.2)$$

In the discrete case, things are simpler: here,  $A(E)$  is the number of microstates with  $\mathcal{E}(\mathbf{x}) = E$  (exactly) and  $P(\mathbf{x})$  is the uniform probability mass function over this set of states.

Returning to the general case, we next define the notion of the *density of states*,  $\omega(E)$ , which is intimately related to  $A(E)$ . Basically, in simple cases,  $\omega(E)$  is defined such that  $\omega(E)\Delta E = A(E)$  where  $\Delta E$  is very small, but there might be a few minor corrections, depending on the concrete system being addressed. More generally, we define the density of states such that  $\omega(E)\Delta E = \Omega(E)$ , where  $\Omega(E)$  will be the relevant (possibly corrected) function. The first correction has to do with the fact that  $A(E)$  is, in general, not dimensionless: in the above example of a gas, it has the physical units of  $[\text{length} \times \text{momentum}]^{3N} = [\text{J} \cdot \text{s}]^{3N}$ , but we must eliminate these physical units because we will have to apply on it non-linear functions like the logarithmic function. To this end, we normalize the volume  $A(E)$  by an elementary reference volume. In the gas example, this reference volume is taken to be  $h^{3N}$ , where  $h$  is *Planck's constant* ( $h \approx 6.62 \times 10^{-34} \text{ J} \cdot \text{s}$ ). Informally, the intuition comes from the fact that  $h$  is our best available “resolution” in the plane spanned by each component of  $\vec{r}_i$  and the corresponding component of  $\vec{p}_i$ , owing to the *uncertainty principle* in quantum mechanics, which tells that the product of the standard deviations  $\Delta p_a \cdot \Delta r_a$  of each component  $a$  ( $a = x, y, z$ ) is lower bounded by  $\hbar/2$ , where  $\hbar = h/(2\pi)$ . More formally, this reference volume is obtained in a natural manner from quantum statistical mechanics: by changing the integration variable  $\vec{p}$  to  $\vec{k}$  using the relation  $\vec{p} = \hbar\vec{k}$ , where  $\vec{k}$  is the wave vector. This is a well-known relation (one of the de Broglie relations) pertaining to particle–wave duality. The second correction that is needed to pass from  $A(E)$  to  $\Omega(E)$  is applicable when the particles are indistinguishable<sup>3</sup>: In these cases, we do not consider permutations between particles in a given configuration as distinct microstates. Thus, we have to divide also by  $N!$  Taking into account both corrections, we find that in the example of the ideal gas,

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<sup>3</sup>In the example of the ideal gas, since the particles are mobile and since they have no colors and no identity certificates, there is no distinction between a state where particle no. 15 has position  $\vec{r}$  and momentum  $\vec{p}$  while particle no. 437 has position  $\vec{r}'$  and momentum  $\vec{p}'$  and a state where these two particles are swapped.

$$\Omega(E) = \frac{A(E)}{N!h^{3N}}. \quad (2.2.3)$$

Once again, it should be understood that both of these corrections are optional and their applicability depends on the system in question: the first correction is applicable only if  $A(E)$  has physical units and the second correction is applicable only if the particles are indistinguishable. For example, if  $\mathbf{x}$  is discrete, in which case the integral defining  $A(E)$  is replaced by a sum (that counts  $\mathbf{x}$ 's with  $\mathcal{E}(\mathbf{x}) = E$ ), and the particles are distinguishable, then no corrections are needed at all, i.e.,

$$\Omega(E) = A(E). \quad (2.2.4)$$

Now, the *entropy* is defined as

$$S(E) = k \ln \Omega(E), \quad (2.2.5)$$

where  $k$  is *Boltzmann's constant*. We will see later what is the relationship between  $S(E)$  and the classical thermodynamic entropy, due to Clausius (1850), as well as the information-theoretic entropy, due to Shannon (1948). As will turn out, all three are equivalent to one another. Here, a comment on the notation is in order: the entropy  $S$  may depend on additional quantities, other than the energy  $E$ , like the volume  $V$  and the number of particles  $N$ . When this dependence will be relevant and important, we will use the more complete form of notation  $S(E, V, N)$ . If only the dependence on  $E$  is relevant in a certain context, we use the simpler notation  $S(E)$ .

To get some insight into the behavior of the entropy, it should be noted that normally,  $\Omega(E)$  (and hence also  $\omega(E)$ ) behaves as an exponential function of  $N$  (at least asymptotically), and so,  $S(E)$  is roughly linear in  $N$ . For example, if  $\mathcal{E}(\mathbf{x}) = \sum_{i=1}^N \frac{\|\tilde{\mathbf{p}}_i\|^2}{2m}$ , then  $\Omega(E)$  is the volume of a thin shell about the surface of a  $(3N)$ -dimensional sphere with radius  $\sqrt{2mE}$ , divided by  $N!h^{3N}$ , which is proportional to  $(2mE)^{3N/2} V^N / N!h^{3N}$ , where  $V$  is the volume. The quantity  $\omega(E)$  is then associated with the surface area of this  $(3N)$ -dimensional sphere. Specifically (ignoring the contribution of the factor  $\Delta E$ ), we get

$$\begin{aligned} S(E, V, N) &= k \ln \left[ \left( \frac{4\pi m E}{3N} \right)^{3N/2} \cdot \frac{V^N}{N!h^{3N}} \right] + \frac{3}{2} Nk \\ &\approx Nk \ln \left[ \left( \frac{4\pi m E}{3N} \right)^{3/2} \cdot \frac{V}{Nh^3} \right] + \frac{5}{2} Nk. \end{aligned} \quad (2.2.6)$$

Assuming that  $E$  and  $V$  are both proportional to  $N$  ( $E = N\epsilon$  and  $V = N/\rho$ ), it is readily seen that  $S(E, V, N)$  is also proportional to  $N$ . A physical quantity that has a linear dependence on the size of the system  $N$ , is called an *extensive quantity*. Energy, volume and entropy are then extensive quantities. Other quantities, which

are not extensive, i.e., independent of the system size, like temperature and pressure, are called *intensive*.

It is interesting to point out that from the function  $S(E, V, N)$ , one can obtain the entire information about the relevant macroscopic physical quantities of the system, e.g., temperature, pressure, and so on. Specifically, the *temperature*  $T$  of the system is defined according to:

$$\frac{1}{T} = \left[ \frac{\partial S(E, V, N)}{\partial E} \right]_{V, N} \quad (2.2.7)$$

where  $[\cdot]_{V, N}$  emphasizes that the derivative is taken while keeping  $V$  and  $N$  constant. One may wonder, at this point, what is the justification for *defining* temperature this way. We will get back to this point a bit later, but for now, we can easily see that this is indeed true at least for the ideal gas, as by taking the derivative of (2.2.6) w.r.t.  $E$ , we get

$$\frac{\partial S(E, V, N)}{\partial E} = \frac{3Nk}{2E} = \frac{1}{T}, \quad (2.2.8)$$

where the second equality has been shown already in Chap. 1.

Intuitively, in most situations, we expect that  $S(E)$  would be an increasing function of  $E$  for fixed  $V$  and  $N$  (although this is not strictly always the case), which means  $T \geq 0$ . But  $T$  is also expected to increase with  $E$  (or equivalently,  $E$  is increasing with  $T$ , as otherwise, the heat capacity  $dE/dT < 0$ ). Thus,  $1/T$  should decrease with  $E$ , which means that the increase of  $S$  in  $E$  slows down as  $E$  grows. In other words, we expect  $S(E)$  to be a concave function of  $E$ . In the above example, indeed,  $S(E)$  is logarithmic and  $E = 3NkT/2$ , as we have seen.

How can we be convinced, in mathematical terms, that under certain regularity conditions,  $S(E)$  is a concave function in  $E$ ? The answer may be given by a simple superadditivity argument: As both  $E$  and  $S$  are extensive quantities, let us define  $E = N\epsilon$  and for a given density  $\rho$ ,

$$s(\epsilon) = \lim_{N \rightarrow \infty} \frac{S(N\epsilon)}{N}, \quad (2.2.9)$$

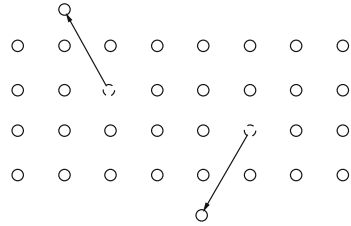
i.e., the per-particle entropy as a function of the per-particle energy, where we assume that the limit exists. Consider the case where the Hamiltonian is additive, i.e.,

$$\mathcal{E}(\mathbf{x}) = \sum_{i=1}^N \mathcal{E}(x_i) \quad (2.2.10)$$

just like in the above example where  $\mathcal{E}(\mathbf{x}) = \sum_{i=1}^N \frac{\|\vec{p}_i\|^2}{2m}$ . Then, the inequality

$$\Omega(N_1\epsilon_1 + N_2\epsilon_2) \geq \Omega(N_1\epsilon_1) \cdot \Omega(N_2\epsilon_2), \quad (2.2.11)$$

**Fig. 2.1** Schottky defects in a crystal lattice



expresses the simple fact that if our system is partitioned into two parts,<sup>4</sup> one with  $N_1$  particles, and the other with  $N_2 = N - N_1$  particles, then every combination of individual microstates with energies  $N_1\epsilon_1$  and  $N_2\epsilon_2$  corresponds to a combined microstate with a total energy of  $N_1\epsilon_1 + N_2\epsilon_2$  (but there are more ways to split this total energy between the two parts). Thus,

$$\begin{aligned} \frac{k \ln \Omega(N_1\epsilon_1 + N_2\epsilon_2)}{N_1 + N_2} &\geq \frac{k \ln \Omega(N_1\epsilon_1)}{N_1 + N_2} + \frac{k \ln \Omega(N_2\epsilon_2)}{N_1 + N_2} \\ &= \frac{N_1}{N_1 + N_2} \cdot \frac{k \ln \Omega(N_1\epsilon_1)}{N_1} + \\ &\quad \frac{N_2}{N_1 + N_2} \cdot \frac{k \ln \Omega(N_2\epsilon_2)}{N_2}. \end{aligned} \quad (2.2.12)$$

and so, by taking  $N_1$  and  $N_2$  to  $\infty$ , with  $N_1/(N_1 + N_2) \rightarrow \lambda \in (0, 1)$ , we get:

$$s(\lambda\epsilon_1 + (1 - \lambda)\epsilon_2) \geq \lambda s(\epsilon_1) + (1 - \lambda)s(\epsilon_2), \quad (2.2.13)$$

which establishes the concavity of  $s(\cdot)$  at least in the case of an additive Hamiltonian, which means that the entropy of mixing two systems of particles is greater than the total entropy before the mix. A similar proof can be generalized to the case where  $\mathcal{E}(\mathbf{x})$  includes also a limited degree of interactions (short range interactions), e.g.,  $\mathcal{E}(\mathbf{x}) = \sum_{i=1}^N \mathcal{E}(x_i, x_{i+1})$ , but this requires somewhat more caution. In general, however, concavity may no longer hold when there are long range interactions, e.g., where some terms of  $\mathcal{E}(\mathbf{x})$  depend on a linear subset of particles.

*Example 2.1 (Schottky defects)* In a certain crystal, the atoms are located in a lattice, and at any positive temperature there may be defects, where some of the atoms are dislocated (see Fig. 2.1). Assuming that defects are sparse enough, such that around each dislocated atom all neighbors are in place, the activation energy,  $\epsilon_0$ , required for dislocation is fixed. Denoting the total number of atoms by  $N$  and the number of defect ones by  $n$ , the total energy is then  $E = n\epsilon_0$ , and so,

<sup>4</sup>This argument works for distinguishable particles. Later on, a more general argument will be presented, that holds for indistinguishable particles too.

$$\Omega(E) = \binom{N}{n} = \frac{N!}{n!(N-n)!}, \quad (2.2.14)$$

or, equivalently,

$$\begin{aligned} S(E) &= k \ln \Omega(E) = k \ln \left[ \frac{N!}{n!(N-n)!} \right] \\ &\approx k[N \ln N - n \ln n - (N-n) \ln(N-n)] \end{aligned} \quad (2.2.15)$$

where in the last passage we have used the Stirling approximation. It is important to point out that here, unlike in the example of the ideal gas, we have not divided  $A(E)$  by  $N!$ . The reason is that we do distinguish between two different configurations where the same number of particles were dislocated but the sites of dislocation are different. Yet, we do not distinguish between two microstates whose only difference is two (identical) particles which are not dislocated but swapped. This is the reason for the denominator  $n!(N-n)!$  in the expression of  $\Omega(E)$ . Now,<sup>5</sup>

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{dn}{dE} \cdot \frac{dS}{dn} = \frac{1}{\epsilon_0} \cdot k \ln \frac{N-n}{n}, \quad (2.2.16)$$

which gives the number of defects as

$$n = \frac{N}{\exp(\epsilon_0/kT) + 1}. \quad (2.2.17)$$

At  $T = 0$ , there are no defects, but their number increases gradually with  $T$ , approximately according to  $\exp(-\epsilon_0/kT)$ . Note also that

$$\begin{aligned} S(E) &= k \ln \binom{N}{n} \approx k N h_2 \left( \frac{n}{N} \right) \\ &= k N h_2 \left( \frac{E}{N \epsilon_0} \right) = k N h_2 \left( \frac{\epsilon}{\epsilon_0} \right), \end{aligned} \quad (2.2.18)$$

where

$$h_2(x) \triangleq -x \ln x - (1-x) \ln(1-x), \quad 0 \leq x \leq 1$$

is the so called binary entropy function. Note also that  $s(\epsilon) = k h_2(\epsilon/\epsilon_0)$  is indeed concave in this example.  $\square$

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<sup>5</sup>Here and in the sequel, the reader might wonder about the meaning of taking derivatives of, and with respect to, integer valued variables, like the number of dislocated particles,  $n$ . To this end, imagine an approximation where  $n$  is interpolated to be a continuous valued variable.

Suppose we have two systems that are initially at certain temperatures (and with corresponding energies). At a certain time instant, the two systems are brought into thermal contact with one another, but their combination remains isolated. What happens after a long time? How does the total energy  $E$ , split and what is the final temperature  $T$  of the combined system? The number of combined microstates where subsystem no. 1 has energy  $E_1$  and subsystem no. 2 has energy  $E_2 = E - E_1$  is  $\Omega_1(E_1) \cdot \Omega_2(E - E_1)$ . As the combined system is isolated, the probability of such a combined macrostate is proportional to  $\Omega_1(E_1) \cdot \Omega_2(E - E_1)$ . Keeping in mind that, normally,  $\Omega_1$  and  $\Omega_2$  are exponential in  $N$ , then for large  $N$ , this product is dominated by the value of  $E_1$  for which it is maximum, or equivalently, the sum of logarithms,  $S_1(E_1) + S_2(E - E_1)$ , is maximum, i.e., it is a **maximum entropy** situation, which is **the second law of thermodynamics**, asserting that an isolated system (in this case, combined of two subsystems) achieves its maximum possible entropy in equilibrium. This maximum is normally achieved at the value of  $E_1$  for which the derivative vanishes, i.e.,

$$S'_1(E_1) - S'_2(E - E_1) = 0 \quad (2.2.19)$$

or

$$S'_1(E_1) - S'_2(E_2) = 0 \quad (2.2.20)$$

which means

$$\frac{1}{T_1} \equiv S'_1(E_1) = S'_2(E_2) \equiv \frac{1}{T_2}. \quad (2.2.21)$$

Thus, in equilibrium, which is the maximum entropy situation, the energy splits in a way that temperatures are the same. Now, we can understand the concavity of entropy more generally:  $\lambda s(\epsilon_1) + (1 - \lambda)s(\epsilon_2)$  was the total entropy per particle when two subsystems (with the same entropy function) were isolated from one another, whereas  $s(\lambda\epsilon_1 + (1 - \lambda)\epsilon_2)$  is the equilibrium entropy per particle after we let them interact thermally.

At this point, we are ready to justify why  $S'(E)$  is equal to  $1/T$  in general, as was promised earlier. Although it is natural to expect that equality between  $S'_1(E_1)$  and  $S'_2(E_2)$ , in thermal equilibrium, is related to equality between  $T_1$  and  $T_2$ , this does not automatically mean that the derivative of each entropy is given by one over its temperature. On the face of it, for the purpose of this implication, this derivative could have been equal any one-to-one function of temperature  $f(T)$ . To see why  $f(T) = 1/T$  indeed, imagine that we have a system with an entropy function  $S_0(E)$  and that we let it interact thermally with an ideal gas whose entropy function, which we shall denote now by  $S_g(E)$ , is given as in Eq. (2.2.6). Now, at equilibrium  $S'_0(E_0) = S'_g(E_g)$ , but as we have seen already,  $S'_g(E_g) = 1/T_g$ , where  $T_g$  is the temperature of the ideal gas. But in thermal equilibrium the temperatures equalize, i.e.,  $T_g = T_0$ , where  $T_0$  is the temperature of the system of interest. It then follows



eventually that  $S'_0(E_0) = 1/T_0$ , which now means that in equilibrium, the derivative of entropy of the system of interest is equal to the reciprocal of its temperature *in general*, and not only for the ideal gas! At this point, the fact that our system has interacted and equilibrated with an ideal gas is not important anymore and it does not limit the generality of this statement. In simple words, our system does not ‘care’ what kind of system it has interacted with, whether ideal gas or any other. This follows from a fundamental principle in thermodynamics, called **the zero-th law of thermodynamics**, which states that thermal equilibrium has a transitive property: If system  $A$  is in equilibrium with system  $B$  and system  $B$  is in equilibrium with system  $C$ , then  $A$  is in equilibrium with  $C$ .

So we have seen that  $\partial S/\partial E = 1/T$ , or equivalently,  $\delta S = \delta E/T$ . But in the absence of any mechanical work ( $V$  is fixed) applied to the system and any chemical energy injected into the system ( $N$  is fixed), any change in energy must be in the form of *heat*,<sup>6</sup> thus we denote  $\delta E = \delta Q$ , where  $Q$  is the heat intake. Consequently,

$$\delta S = \frac{\delta Q}{T}, \quad (2.2.22)$$

This is exactly the definition of the classical thermodynamic entropy due to Clausius. Thus, at least for the case where no mechanical work is involved, we have demonstrated the equivalence of the two notions of entropy, the statistical notion due to Boltzmann  $S = k \ln \Omega$ , and the thermodynamic entropy due to Clausius,  $S = \int dQ/T$ , where the integration should be understood to be taken along a slow (quasi-static) process, where after each small increase in the heat intake, the system is allowed to equilibrate, which means that  $T$  is given enough time to adjust before more heat is further added. For a given  $V$  and  $N$ , the difference  $\Delta S$  between the entropies  $S_A$  and  $S_B$  associated with two temperatures  $T_A$  and  $T_B$  (pertaining to internal energies  $E_A$  and  $E_B$ , respectively) is given by  $\Delta S = \int_A^B dQ/T$  along such a quasi-static process. This is a rule that defines entropy differences, but not absolute levels. A reference value is determined by the **third law of thermodynamics**, which asserts that as  $T$  tends to zero, the entropy tends to zero as well.<sup>7</sup>

We have seen what is the meaning of the partial derivative of  $S(E, V, N)$  w.r.t.  $E$ . Is there also a simple meaning to the partial derivative w.r.t.  $V$ ? Again, let us begin by examining the ideal gas. Differentiating the expression of  $S(E, V, N)$  of the ideal gas w.r.t.  $V$ , we obtain

$$\frac{\partial S(E, V, N)}{\partial V} = \frac{Nk}{V} = \frac{P}{T}, \quad (2.2.23)$$

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<sup>6</sup>Heat is a form of energy that is transferred neither by mechanical work nor by matter. It is the type of energy that flows spontaneously from a system/body at a higher temperature to one with a lower temperature (and this transfer is accompanied by an increase in the total entropy).

<sup>7</sup>In this context, it should be understood that the results we derived for the ideal gas hold only for high enough temperatures: since  $S$  was found proportional to  $\ln E$  and  $E$  is proportional to  $T$ , then  $S$  is proportional to  $\ln T$ , but this cannot be true for small  $T$  as it contradicts (among other things) the third law.

where the second equality follows again from the equation of state. So at least for the ideal gas, this partial derivative is related to the pressure  $P$ . For similar considerations as before, the relation

$$\frac{\partial S(E, V, N)}{\partial V} = \frac{P}{T} \quad (2.2.24)$$

is true not only for the ideal gas, but in general. Consider again an isolated system that consists of two subsystems, separated by a wall (or a piston). Initially, this wall is fixed and the volumes are  $V_1$  and  $V_2$ . At a certain moment, this wall is released and allowed to be pushed in either direction. How would the total volume  $V = V_1 + V_2$  divide between the two subsystems in equilibrium? Again, the total entropy  $S_1(E_1, V_1) + S_2(E - E_1, V - V_1)$  would tend to its maximum for the same reasoning as before. The maximum will be reached when the partial derivatives of this sum w.r.t. both  $E_1$  and  $V_1$  would vanish. The partial derivative w.r.t.  $E_1$  has already been addressed. The partial derivative w.r.t.  $V_1$  gives

$$\frac{P_1}{T_1} = \frac{\partial S_1(E_1, V_1)}{\partial V_1} = \frac{\partial S_2(E_2, V_2)}{\partial V_2} = \frac{P_2}{T_2} \quad (2.2.25)$$

Since  $T_1 = T_2$  by the thermal equilibrium pertaining to derivatives w.r.t. energies, it follows that  $P_1 = P_2$ , which means mechanical equilibrium: the wall will be pushed to the point where the pressures from both sides are equal. We now have the following differential relationship:

$$\begin{aligned} \delta S &= \frac{\partial S}{\partial E} \delta E + \frac{\partial S}{\partial V} \delta V \\ &= \frac{\delta E}{T} + \frac{P \delta V}{T} \end{aligned} \quad (2.2.26)$$

or

$$\delta E = T \delta S - P \delta V = \delta Q - \delta W, \quad (2.2.27)$$

which is the **the first law of thermodynamics**, asserting that the change in the energy  $\delta E$  of a system with a fixed number of particles is equal to the difference between the incremental heat intake  $\delta Q$  and the incremental mechanical work  $\delta W$  carried out by the system. This is nothing but a restatement of the law of energy conservation.

*Example 2.2 (Compression of ideal gas)* Consider again an ideal gas of  $N$  particles at constant temperature  $T$ . The energy is  $E = 3NkT/2$  regardless of the volume. This means that if we compress (slowly) the gas from volume  $V_1$  to volume  $V_2$  ( $V_2 < V_1$ ), the energy remains the same, in spite of the fact that we injected energy by applying mechanical work

$$W = - \int_{V_1}^{V_2} P dV = -NkT \int_{V_1}^{V_2} \frac{dV}{V} = NkT \ln \frac{V_1}{V_2}. \quad (2.2.28)$$

What happened to that energy? The answer is that it was transformed into heat as the entropy of the system (which is proportional to  $\ln V$ ) has changed by the amount  $\Delta S = -Nk \ln(V_1/V_2)$ , and so, the heat intake  $\Delta Q = T \Delta S = -NkT \ln(V_1/V_2)$  exactly balances the work.  $\square$

Finally, we should consider the partial derivative of  $S$  w.r.t.  $N$ . This is given by

$$\frac{\partial S(E, V, N)}{\partial N} = -\frac{\mu}{T}, \quad (2.2.29)$$

where  $\mu$  is called the *chemical potential*. If we now consider again the isolated system, which consists of two subsystems that are allowed to exchange, not only heat and volume, but also particles (of the same kind), whose total number is  $N = N_1 + N_2$ , then again, maximum entropy considerations would yield an additional equality between the chemical potentials,  $\mu_1 = \mu_2$  (chemical equilibrium).<sup>8</sup> The chemical potential should be understood as a kind of a force that controls the ability to inject particles into the system. For example, if the particles are electrically charged, then the chemical potential has a simple analogy to the electrical potential. The first law is now extended to have an additional term, pertaining to an increment of chemical energy, and it now reads:

$$\delta E = T \delta S - P \delta V + \mu \delta N. \quad (2.2.30)$$

Equation (2.2.30) can be used to derive a variety of relations. For example,  $\mu = (\partial E / \partial N)_{S, V}$ ,  $T = (\partial H / \partial S)_N$ , where  $H = E + PV$  is called the enthalpy,  $P = \mu(\partial N / \partial V)_{E, S}$ , and so on.

### 2.2.2 The Canonical Ensemble

So far we have assumed that our system is isolated, and therefore has a strictly fixed energy  $E$ . Let us now relax this assumption and assume instead that our system is free to exchange energy with its very large environment (heat bath) and that the total energy of the system plus heat bath,  $E_0$ , is by far larger than the typical energy of the system. The combined system, composed of our original system plus the heat bath, is now an isolated system at temperature  $T$ .

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<sup>8</sup>Equality of chemical potentials is, in fact, the general principle of chemical equilibrium, and not equality of concentrations or densities. In Sect. 1.3, we saw equality of densities, because in the case of the ideal gas, the chemical potential is a function of the density, so equality of chemical potentials happens to be equivalent to equality of densities in this case.

Similarly as before, since the combined system is isolated, it is governed by the microcanonical ensemble. The only difference is that now we assume that one of the systems (the heat bath) is very large compared to the other (our test system). This means that if our small system is in microstate  $\mathbf{x}$  (for whatever definition of the microstate vector) with energy  $\mathcal{E}(\mathbf{x})$ , then the heat bath must have energy  $E_0 - \mathcal{E}(\mathbf{x})$  to complement the total energy to  $E_0$ . The number of ways that the heat bath may have energy  $E_0 - \mathcal{E}(\mathbf{x})$  is  $\Omega_B(E_0 - \mathcal{E}(\mathbf{x}))$ , where  $\Omega_B(\cdot)$  is the state volume function pertaining to the entropy of the heat bath. In other words, the volume/number of microstates of the *combined* system for which the small subsystem is in microstate  $\mathbf{x}$  is  $\Omega_B(E_0 - \mathcal{E}(\mathbf{x}))$ . Since the combined system is governed by the microcanonical ensemble, the probability of this is proportional to  $\Omega_B(E_0 - \mathcal{E}(\mathbf{x}))$ . More precisely:

$$P(\mathbf{x}) = \frac{\Omega_B(E_0 - \mathcal{E}(\mathbf{x}))}{\sum_{\mathbf{x}'} \Omega_B(E_0 - \mathcal{E}(\mathbf{x}'))}. \quad (2.2.31)$$

Let us focus on the numerator for now, and normalize the result at the end. Then,

$$\begin{aligned} P(\mathbf{x}) &\propto \Omega_B(E_0 - \mathcal{E}(\mathbf{x})) \\ &= \exp\{S_B(E_0 - \mathcal{E}(\mathbf{x}))/k\} \\ &\approx \exp\left\{\frac{S_B(E_0)}{k} - \frac{1}{k} \frac{\partial S_B(E)}{\partial E} \Big|_{E=E_0} \cdot \mathcal{E}(\mathbf{x})\right\} \\ &= \exp\left\{\frac{S_B(E_0)}{k} - \frac{1}{kT} \cdot \mathcal{E}(\mathbf{x})\right\} \\ &\propto \exp\{-\mathcal{E}(\mathbf{x})/(kT)\}. \end{aligned} \quad (2.2.32)$$

It is customary to work with the so called *inverse temperature*:

$$\beta = \frac{1}{kT} \quad (2.2.33)$$

and so,

$$P(\mathbf{x}) \propto e^{-\beta \mathcal{E}(\mathbf{x})}, \quad (2.2.34)$$

as we have already seen in the example of the ideal gas (where  $\mathcal{E}(\mathbf{x})$  was the kinetic energy), but now it is much more general. Thus, all that remains to do is to normalize, and we then obtain the *Boltzmann–Gibbs* (B–G) distribution, or the *canonical ensemble*, which describes the underlying probability law in equilibrium:

$$P(\mathbf{x}) = \frac{\exp\{-\beta \mathcal{E}(\mathbf{x})\}}{Z(\beta)} \quad (2.2.35)$$

where  $Z(\beta)$  is the normalization factor:

$$Z(\beta) = \sum_{\mathbf{x}} \exp\{-\beta\mathcal{E}(\mathbf{x})\} \quad (2.2.36)$$

in the discrete case, or

$$Z(\beta) = \int d\mathbf{x} \exp\{-\beta\mathcal{E}(\mathbf{x})\} \quad (2.2.37)$$

in the continuous case. This function is called the *partition function*. As with the function  $\Omega(E)$ , similar comments apply to the partition function: it must be dimensionless, so if the components of  $\mathbf{x}$  do have physical units, we must normalize by a ‘reference’ volume, which in the case of the (ideal) gas is again  $h^{3N}$ . By the same token, for indistinguishable particles, it should be divided by  $N!$  While the microcanonical ensemble was defined in terms of the extensive variables  $E$ ,  $V$  and  $N$ , in the canonical ensemble, we replaced the variable  $E$  by the intensive variable that controls it, namely,  $\beta$  (or  $T$ ). Thus, the full notation of the partition function should be  $Z_N(\beta, V)$  or  $Z_N(T, V)$ .

**Exercise 2.1** Show that for the ideal gas

$$Z_N(T, V) = \frac{1}{N!h^{3N}} V^N (2\pi mkT)^{3N/2} = \frac{1}{N!} \left( \frac{V}{\lambda^3} \right)^N \quad (2.2.38)$$

where

$$\lambda \triangleq \frac{h}{\sqrt{2\pi mkT}}. \quad (2.2.39)$$

$\lambda$  is called the *thermal de Broglie wavelength*.<sup>9</sup>

The formula of the B–G distribution is one of the most fundamental results in statistical mechanics, obtained solely from the energy conservation law and the postulate of the uniform distribution in an isolated system. As we shall see, the meaning of the partition function is by far deeper than just being a normalization constant. Interestingly, a great deal of the macroscopic physical quantities, like the internal energy, the free energy, the entropy, the heat capacity, the pressure, etc., can be obtained from the partition function. This is in analogy to the fact that in the microcanonical ensemble,  $S(E)$  (or, more generally,  $S(E, V, N)$ ) was pivotal to the derivation of all macroscopic physical quantities of interest.

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<sup>9</sup>The origin of this name comes from the wave–particle de Broglie relation  $\lambda = h/p$  together with the fact that the denominator,  $\sqrt{2\pi mkT}$ , can be viewed as a notion of thermal momentum of the ideal gas, given the fact that the average molecular speed is proportional to  $\sqrt{kT/m}$  (see Sect. 1.1).

Several comments are in order:

- The B–G distribution tells us that the system “prefers” to visit its low energy states more than the high energy states, and what counts is only energy differences, not absolute energies: If we add to all states a fixed amount of energy  $E_0$ , this will result in an extra factor of  $e^{-\beta E_0}$  both in the numerator and in the denominator of the B–G distribution, which of course will cancel out.
- In many physical systems, the Hamiltonian is a quadratic (or “harmonic”) function, e.g.,  $\frac{1}{2}mv^2$ ,  $\frac{1}{2}kx^2$ ,  $\frac{1}{2}CV^2$ ,  $\frac{1}{2}LI^2$ ,  $\frac{1}{2}I\omega^2$ , etc., in which case the resulting B–G distribution turns out to be Gaussian. This is at least part of the explanation why the Gaussian distribution is so frequently encountered in Nature.
- When the Hamiltonian is additive, that is,  $\mathcal{E}(\mathbf{x}) = \sum_{i=1}^N \mathcal{E}(x_i)$ , the various particles are statistically independent: Additive Hamiltonians correspond to non-interacting particles. In other words, the  $\{x_i\}$ ’s behave as if they were drawn from an i.i.d. probability distribution. By the law of large numbers  $\frac{1}{N} \sum_{i=1}^N \mathcal{E}(x_i)$  will tend (almost surely) to  $\epsilon = \langle \mathcal{E}(X_i) \rangle$ . Thus, the average energy of the system is about  $N \cdot \epsilon$ , not only on the average, but moreover, with an overwhelmingly *high probability* for large  $N$ . Nonetheless, this is different from the microcanonical ensemble where  $\frac{1}{N} \sum_{i=1}^N \mathcal{E}(x_i)$  was held *strictly* at the value of  $\epsilon$ .

One of the important principles of statistical mechanics is that the microcanonical ensemble and the canonical ensemble (with the corresponding temperature) are asymptotically equivalent (in the thermodynamic limit) as far as macroscopic quantities go. They continue to be such, even in cases of interactions, as long as these are short range<sup>10</sup> and the same is true with the other ensembles that we will encounter later in this chapter. This is an important and useful fact, because more often than not, it is more convenient to analyze things in one ensemble rather than in others, and so it is appropriate to pass to another ensemble for the purpose of the analysis, even though the “real system” is in the other ensemble. We will use this *ensemble equivalence principle* many times later on. The important thing, however, is to be consistent and not to mix up two ensembles or more. Having moved to the other ensemble, it is recommended to keep all further analysis in that ensemble.

**Exercise 2.2** Consider the ideal gas with gravitation, where the Hamiltonian includes, in addition to the kinetic energy term for each molecule, also an additive term of potential energy  $mgz_i$  for the  $i$ -th molecule ( $z_i$  being its height). Suppose that an ideal gas of  $N$  molecules of mass  $m$  is confined to a room whose floor and ceiling areas are both  $A$  and whose height is  $h$ : (i) Write an expression for the joint pdf of the location  $\vec{r}$  and the momentum  $\vec{p}$  of each molecule. (ii) Use this expression to show that the gas pressures at the floor and the ceiling are given by

$$P_{\text{floor}} = \frac{mgN}{A(1 - e^{-mgh/kT})}; \quad P_{\text{ceiling}} = \frac{mgN}{A(e^{mgh/kT} - 1)}. \quad (2.2.40)$$

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<sup>10</sup>This is related to the concavity of  $s(\epsilon)$  [3, 4].

## Properties of the Partition Function and the Free Energy

Let us now examine more closely the partition function and make a few observations about its basic properties. For simplicity, we shall assume that  $\mathbf{x}$  is discrete. First, let's look at the limits: obviously,  $Z(0)$  is equal to the size of the entire set of microstates, which is also  $\sum_E \Omega(E)$ . This is the high temperature limit, where all microstates are equiprobable. At the other extreme, we have:

$$\lim_{\beta \rightarrow \infty} \frac{\ln Z(\beta)}{\beta} = -\min_{\mathbf{x}} \mathcal{E}(\mathbf{x}) \triangleq -E_{\text{GS}} \quad (2.2.41)$$

which describes the situation where the system is frozen to the absolute zero. Only states with minimum energy – the *ground-state energy*, prevail.

Another important property of  $Z(\beta)$ , or more precisely, of  $\ln Z(\beta)$ , is that it is a cumulant generating function: by taking derivatives of  $\ln Z(\beta)$ , we can obtain cumulants of  $\mathcal{E}(\mathbf{x})$ . For the first cumulant, we have

$$\langle \mathcal{E}(X) \rangle = \frac{\sum_{\mathbf{x}} \mathcal{E}(\mathbf{x}) e^{-\beta \mathcal{E}(\mathbf{x})}}{\sum_{\mathbf{x}} e^{-\beta \mathcal{E}(\mathbf{x})}} = -\frac{d \ln Z(\beta)}{d\beta}. \quad (2.2.42)$$

For example, referring to Exercise 2.1, for the ideal gas,

$$Z_N(\beta, V) = \frac{1}{N!} \left( \frac{V}{\lambda^3} \right)^N = \frac{1}{N!} \frac{V^N}{h^{3N}} \cdot \left( \frac{2\pi m}{\beta} \right)^{3N/2}, \quad (2.2.43)$$

thus,  $\langle \mathcal{E}(X) \rangle = -d \ln Z_N(\beta, V)/d\beta = 3N/(2\beta) = 3NkT/2$  in agreement with the result we obtained both in Chap. 1 and in the microcanonical ensemble, thus demonstrating the ensemble equivalence principle. Similarly, it is easy to show that

$$\text{Var}\{\mathcal{E}(X)\} = \langle \mathcal{E}^2(X) \rangle - \langle \mathcal{E}(X) \rangle^2 = \frac{d^2 \ln Z(\beta)}{d\beta^2}. \quad (2.2.44)$$

This in turn implies that

$$\frac{d^2 \ln Z(\beta)}{d\beta^2} \geq 0, \quad (2.2.45)$$

which means that  $\ln Z(\beta)$  must always be a convex function. Note also that

$$\begin{aligned} \frac{d^2 \ln Z(\beta)}{d\beta^2} &= -\frac{d\langle \mathcal{E}(\mathbf{x}) \rangle}{d\beta} \\ &= -\frac{d\langle \mathcal{E}(\mathbf{x}) \rangle}{dT} \cdot \frac{dT}{d\beta} \\ &= kT^2 C(T) \end{aligned} \quad (2.2.46)$$

where  $C(T) = d\langle \mathcal{E}(\mathbf{x}) \rangle / dT$  is the heat capacity (at constant volume). Thus, the convexity of  $\ln Z(\beta)$  is intimately related to the physical fact that the heat capacity of the system is positive.

Next, we look at the function  $Z(\beta)$  slightly differently. Instead of summing the terms  $\{e^{-\beta \mathcal{E}(\mathbf{x})}\}$  over all states individually, we sum them by energy levels, in a collective manner. This amounts to:

$$\begin{aligned}
 Z(\beta) &= \sum_{\mathbf{x}} e^{-\beta \mathcal{E}(\mathbf{x})} \\
 &= \sum_E \Omega(E) e^{-\beta E} \\
 &\approx \sum_{\epsilon} e^{Ns(\epsilon)/k} \cdot e^{-\beta N\epsilon} \\
 &= \sum_{\epsilon} \exp\{-N\beta[\epsilon - Ts(\epsilon)]\} \\
 &\doteq \max_{\epsilon} \exp\{-N\beta[\epsilon - Ts(\epsilon)]\} \\
 &= \exp\{-N\beta \min_{\epsilon} [\epsilon - Ts(\epsilon)]\} \\
 &\triangleq \exp\{-N\beta[\epsilon^* - Ts(\epsilon^*)]\} \\
 &\triangleq e^{-\beta F}, \tag{2.2.47}
 \end{aligned}$$

where here and throughout the sequel, the notation  $\doteq$  means asymptotic equivalence in the exponential scale. More precisely,  $a_N \doteq b_N$  for two positive sequences  $\{a_N\}$  and  $\{b_N\}$ , means that  $\lim_{N \rightarrow \infty} \frac{1}{N} \ln \frac{a_N}{b_N} = 0$ .

The quantity  $f \triangleq \epsilon^* - Ts(\epsilon^*)$  is the (per-particle) *free energy*. Similarly, the entire free energy,  $F$ , is defined as

$$F \triangleq E - TS = -\frac{\ln Z(\beta)}{\beta} = -kT \ln Z(\beta). \tag{2.2.48}$$

Once again, due to the exponentiality of (2.2.47) in  $N$ , with *very high probability* the system would be found in a microstate  $\mathbf{x}$  whose normalized energy  $\epsilon(\mathbf{x}) = \mathcal{E}(\mathbf{x})/N$  is very close to  $\epsilon^*$ , the normalized energy that minimizes  $\epsilon - Ts(\epsilon)$  and hence achieves  $f$ . Note that the minimizing  $\epsilon^*$  (obtained by equating the derivative of  $\epsilon - Ts(\epsilon)$  to zero), is the solution to the equation  $s'(\epsilon^*) = 1/T$ , which conforms with the definition of temperature. We see then that equilibrium in the canonical ensemble amounts to **minimum free energy**. This extends the second law of thermodynamics from isolated systems to non-isolated ones. While in an isolated system, the second law asserts the principle of maximum entropy, when it comes to a non-isolated system, this rule is replaced by the principle of minimum free energy.



**Exercise 2.3** Show that the canonical average pressure is given by

$$P = -\frac{\partial F}{\partial V} = kT \cdot \frac{\partial \ln Z_N(\beta, V)}{\partial V}.$$

Examine this formula for the canonical ensemble of the ideal gas. Compare to the equation of state.

The physical meaning of the free energy, or more precisely, the difference between two free energies  $F_1$  and  $F_2$ , is the minimum amount of work that it takes to transfer the system from equilibrium state 1 to another equilibrium state 2 in an isothermal (fixed temperature) process. This minimum is achieved when the process is *quasi-static*, i.e., so slow that the system is always almost in equilibrium. Equivalently,  $-\Delta F$  is the maximum amount of energy in the system, that is *free* and useful for performing work (i.e., not dissipated as heat) in fixed temperature.

To demonstrate this point, let us consider the case where  $\mathcal{E}(\mathbf{x})$  includes a term of a potential energy that is given by the (scalar) product of a certain external force and the conjugate physical variable at which this force is exerted (e.g., pressure times volume, gravitational force times height, moment times angle, magnetic field times magnetic moment, voltage times electric charge, etc.), i.e.,

$$\mathcal{E}(\mathbf{x}) = \mathcal{E}_0(\mathbf{x}) - \lambda \cdot L(\mathbf{x}) \quad (2.2.49)$$

where  $\lambda$  is the force and  $L(\mathbf{x})$  is the conjugate physical variable, which depends on (some coordinates of) the microstate. The partition function then depends on both  $\beta$  and  $\lambda$  and hence will be denoted<sup>11</sup>  $Z(\beta, \lambda)$ . It is easy to see (similarly as before) that  $\ln Z(\beta, \lambda)$  is convex in  $\lambda$  for fixed  $\beta$ . Also,

$$\langle L(\mathbf{x}) \rangle = kT \cdot \frac{\partial \ln Z(\beta, \lambda)}{\partial \lambda}. \quad (2.2.50)$$

The free energy is given by<sup>12</sup>

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<sup>11</sup> Since the term  $\lambda \cdot L(\mathbf{x})$  is not considered part of the internal energy (but rather an external energy resource), formally, this ensemble is no longer the canonical ensemble, but a somewhat different ensemble, called the Gibbs ensemble, which will be discussed later on.

<sup>12</sup> At this point, there is a distinction between the *Helmholtz free energy* and the *Gibbs free energy*. The former is defined as  $F = E - TS$  in general, as mentioned earlier. The latter is defined as  $G = E - TS - \lambda L = -kT \ln Z$ , where  $L$  is shorthand notation for  $\langle L(\mathbf{x}) \rangle$  (the quantity  $H = E - \lambda L$  is called the enthalpy). The physical significance of the Gibbs free energy is similar to that of the Helmholtz free energy, except that it refers to the total work of all other external forces in the system (if there are any), except the work contributed by the force  $\lambda$  (**Exercise 2.4** show this!). The passage to the Gibbs ensemble, which replaces a fixed value of  $L(\mathbf{x})$  (say, constant volume of a gas) by the control of the conjugate external force  $\lambda$ , (say, pressure in the example of a gas) can be carried out by another Legendre–Fenchel transform (see, e.g., [5, Sect. 1.14]) as well as Sect. 2.2.3 in the sequel.

$$\begin{aligned}
F &= E - TS \\
&= -kT \ln Z + \lambda \langle L(\mathbf{X}) \rangle \\
&= kT \left( \lambda \cdot \frac{\partial \ln Z}{\partial \lambda} - \ln Z \right). \tag{2.2.51}
\end{aligned}$$

Now, let  $F_1$  and  $F_2$  be the equilibrium free energies pertaining to two values of  $\lambda$ , denoted  $\lambda_1$  and  $\lambda_2$ . Then,

$$\begin{aligned}
F_2 - F_1 &= \int_{\lambda_1}^{\lambda_2} d\lambda \cdot \frac{\partial F}{\partial \lambda} \\
&= kT \cdot \int_{\lambda_1}^{\lambda_2} d\lambda \cdot \lambda \cdot \frac{\partial^2 \ln Z}{\partial \lambda^2} \\
&= \int_{\lambda_1}^{\lambda_2} d\lambda \cdot \lambda \cdot \frac{\partial \langle L(\mathbf{X}) \rangle}{\partial \lambda} \\
&= \int_{\langle L(\mathbf{X}) \rangle_{\lambda_1}}^{\langle L(\mathbf{X}) \rangle_{\lambda_2}} \lambda \cdot d\langle L(\mathbf{X}) \rangle \tag{2.2.52}
\end{aligned}$$

The product  $\lambda \cdot d\langle L(\mathbf{X}) \rangle$  designates an infinitesimal amount of (average) work performed by the force  $\lambda$  on a small change in the average of the conjugate variable  $\langle L(\mathbf{X}) \rangle$ , where the expectation is taken w.r.t. the actual value of  $\lambda$ . Thus, the last integral expresses the total work along a slow process of changing the force  $\lambda$  in small steps and letting the system adapt and equilibrate after this small change every time. On the other hand, it is easy to show (using the convexity of  $\ln Z$  in  $\lambda$ ), that if  $\lambda$  varies in large steps, the resulting amount of work will always be larger.

Let us define

$$\phi(\beta) = \lim_{N \rightarrow \infty} \frac{\ln Z(\beta)}{N} \tag{2.2.53}$$

and, in order to avoid dragging the constant  $k$ , let us define

$$\Sigma(\epsilon) = \lim_{N \rightarrow \infty} \frac{\ln \Omega(N\epsilon)}{N} = \frac{s(\epsilon)}{k}. \tag{2.2.54}$$

Then, the chain of equalities (2.2.47), written slightly differently, gives

$$\begin{aligned}
\phi(\beta) &= \lim_{N \rightarrow \infty} \frac{\ln Z(\beta)}{N} \\
&= \lim_{N \rightarrow \infty} \frac{1}{N} \ln \left\{ \sum_{\epsilon} e^{N[\Sigma(\epsilon) - \beta\epsilon]} \right\} \\
&= \max_{\epsilon} [\Sigma(\epsilon) - \beta\epsilon].
\end{aligned}$$

Thus,  $\phi(\beta)$  is (a certain variant of) the *Legendre–Fenchel transform*<sup>13</sup> of  $\Sigma(\epsilon)$ . As  $\Sigma(\epsilon)$  is (normally) a concave, monotonically increasing function, then it can readily be shown that the inverse transform is:

$$\Sigma(\epsilon) = \min_{\beta} [\beta\epsilon + \phi(\beta)]. \quad (2.2.55)$$

The achiever,  $\epsilon^*(\beta)$ , of  $\phi(\beta)$  in the forward transform is obtained by equating the derivative to zero, i.e., it is the solution to the equation

$$\beta = \Sigma'(\epsilon), \quad (2.2.56)$$

where  $\Sigma'(\epsilon)$  is the derivative of  $\Sigma(\epsilon)$ . In other words,  $\epsilon^*(\beta)$  the inverse function of  $\Sigma'(\cdot)$ . By the same token, the achiever,  $\beta^*(\epsilon)$ , of  $\Sigma(\epsilon)$  in the backward transform is obtained by equating the other derivative to zero, i.e., it is the solution to the equation

$$\epsilon = -\phi'(\beta) \quad (2.2.57)$$

or in other words, the inverse function of  $-\phi'(\cdot)$ . This establishes a relationship between the typical per-particle energy  $\epsilon$  and the inverse temperature  $\beta$  that gives rise to  $\epsilon$  (cf. the Lagrange interpretation above, where we said that  $\beta$  controls the average energy).

*Example 2.3 (Two level system)* Similarly to the earlier example of Schottky defects, which was previously given in the context of the microcanonical ensemble, consider now a system of  $N$  independent particles, each having two possible states: state 0 of zero energy and state 1, whose energy is  $\epsilon_0$ , i.e.,  $\mathcal{E}(x) = \epsilon_0 x$ ,  $x \in \{0, 1\}$ . The  $x_i$ 's are independent, each having a marginal<sup>14</sup>:

$$P(x) = \frac{e^{-\beta\epsilon_0 x}}{1 + e^{-\beta\epsilon_0}} \quad x \in \{0, 1\}. \quad (2.2.58)$$

In this case,

$$\phi(\beta) = \ln(1 + e^{-\beta\epsilon_0}) \quad (2.2.59)$$

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<sup>13</sup>More precisely, the one-dimensional Legendre–Fenchel transform of a real function  $f(x)$  is defined as  $g(y) = \sup_x [xy - f(x)]$ . If  $f$  is convex, it can readily be shown that: (i) The inverse transform has the very same form, i.e.,  $f(x) = \sup_y [xy - g(y)]$ , and (ii) The derivatives  $f'(x)$  and  $g'(y)$  are inverses of each other.

<sup>14</sup>Note that the expected number of ‘activated’ particles  $\langle n \rangle = NP(1) = Ne^{-\beta\epsilon_0}/(1 + e^{-\beta\epsilon_0}) = N/(e^{\beta\epsilon_0} + 1)$ , in agreement with the result of Example 2.1 (Eq. (2.2.17)). This demonstrates the ensemble equivalence principle.

and

$$\Sigma(\epsilon) = \min_{\beta \geq 0} [\beta \epsilon + \ln(1 + e^{-\beta \epsilon_0})]. \quad (2.2.60)$$

To find  $\beta^*(\epsilon)$ , we take the derivative and equate to zero:

$$\epsilon - \frac{\epsilon_0 e^{-\beta \epsilon_0}}{1 + e^{-\beta \epsilon_0}} = 0 \quad (2.2.61)$$

which gives

$$\beta^*(\epsilon) = \frac{\ln(\epsilon_0/\epsilon - 1)}{\epsilon_0}. \quad (2.2.62)$$

On substituting this back into the above expression of  $\Sigma(\epsilon)$ , we get:

$$\Sigma(\epsilon) = \frac{\epsilon}{\epsilon_0} \ln \left( \frac{\epsilon}{\epsilon_0} - 1 \right) + \ln \left[ 1 + \exp \left\{ - \ln \left( \frac{\epsilon}{\epsilon_0} - 1 \right) \right\} \right], \quad (2.2.63)$$

which after a short algebraic manipulation, becomes

$$\Sigma(\epsilon) = h_2 \left( \frac{\epsilon}{\epsilon_0} \right), \quad (2.2.64)$$

just like in the Schottky example. In the other direction:

$$\phi(\beta) = \max_{\epsilon} \left[ h_2 \left( \frac{\epsilon}{\epsilon_0} \right) - \beta \epsilon \right], \quad (2.2.65)$$

whose achiever  $\epsilon^*(\beta)$  solves the zero-derivative equation:

$$\frac{1}{\epsilon_0} \ln \left[ \frac{1 - \epsilon/\epsilon_0}{\epsilon/\epsilon_0} \right] = \beta \quad (2.2.66)$$

or equivalently,

$$\epsilon^*(\beta) = \frac{\epsilon_0}{1 + e^{-\beta \epsilon_0}}, \quad (2.2.67)$$

which is exactly the inverse function of  $\beta^*(\epsilon)$  above, and which when substituted back into the expression of  $\phi(\beta)$ , indeed gives

$$\phi(\beta) = \ln(1 + e^{-\beta \epsilon_0}). \quad (2.2.68)$$

This concludes Example 2.3.

*Comment* A very similar model (and hence with similar results) pertains to non-interacting spins (magnetic moments), where the only difference is that  $x \in \{-1, +1\}$  rather than  $x \in \{0, 1\}$ . Here, the meaning of the parameter  $\epsilon_0$  becomes that of a magnetic field, which is more customarily denoted by  $B$  (or  $H$ ), and which is either parallel or anti-parallel to that of the spin, and so the potential energy (in the appropriate physical units),  $\vec{B} \cdot \vec{x}$ , is either  $Bx$  or  $-Bx$ . Thus,

$$P(x) = \frac{e^{\beta Bx}}{2 \cosh(\beta B)}; \quad Z(\beta) = 2 \cosh(\beta B). \quad (2.2.69)$$

The net *magnetization* per-spin is defined as

$$m \triangleq \left\langle \frac{1}{N} \sum_{i=1}^N X_i \right\rangle = \langle X_1 \rangle = \frac{\partial \phi}{\partial(\beta B)} = \tanh(\beta B). \quad (2.2.70)$$

This is the paramagnetic characteristic of the magnetization as a function of the magnetic field: as  $B \rightarrow \pm\infty$ , the magnetization  $m \rightarrow \pm 1$  accordingly. When the magnetic field is removed ( $B = 0$ ), the magnetization vanishes too. We will get back to this model and its extensions in Chap. 5.  $\square$

Now, observe that whenever  $\beta$  and  $\epsilon$  are related as explained above, we have:

$$\Sigma(\epsilon) = \beta\epsilon + \phi(\beta) = \phi(\beta) - \beta \cdot \phi'(\beta). \quad (2.2.71)$$

The Gibbs entropy per particle is defined in its normalized form as

$$\bar{H} = - \lim_{N \rightarrow \infty} \frac{1}{N} \sum_x P(x) \ln P(x) = - \lim_{N \rightarrow \infty} \frac{1}{N} \langle \ln P(x) \rangle, \quad (2.2.72)$$

which in the case of the B-G distribution amounts to

$$\begin{aligned} \bar{H} &= \lim_{N \rightarrow \infty} \frac{1}{N} \left\langle \ln \frac{Z(\beta)}{e^{-\beta \mathcal{E}(X)}} \right\rangle \\ &= \lim_{N \rightarrow \infty} \left[ \frac{\ln Z(\beta)}{N} + \frac{\beta \langle \mathcal{E}(X) \rangle}{N} \right] \\ &= \phi(\beta) - \beta \cdot \phi'(\beta), \end{aligned}$$

but this is exactly the same expression as in (2.2.71), and so,  $\Sigma(\epsilon)$  and  $\bar{H}$  are identical whenever  $\beta$  and  $\epsilon$  are related accordingly. The former, as we recall, we defined as the normalized logarithm of the number of microstates with per-particle energy  $\epsilon$ . Thus, we have learned that the number of such microstates is of the exponential order of  $e^{N\bar{H}}$ . Another look at this relation is the following:

$$\begin{aligned}
1 &\geq \sum_{\mathbf{x}: \mathcal{E}(\mathbf{x}) \approx N\epsilon} P(\mathbf{x}) = \sum_{\mathbf{x}: \mathcal{E}(\mathbf{x}) \approx N\epsilon} \frac{\exp\{-\beta \sum_i \mathcal{E}(x_i)\}}{Z^N(\beta)} \\
&= \sum_{\mathbf{x}: \mathcal{E}(\mathbf{x}) \approx N\epsilon} \exp\{-\beta N\epsilon - N\phi(\beta)\} \\
&= \Omega(N\epsilon) \cdot \exp\{-N[\beta\epsilon + \phi(\beta)]\}
\end{aligned} \tag{2.2.73}$$

which means that

$$\Omega(N\epsilon) \leq \exp\{N[\beta\epsilon + \phi(\beta)]\} \tag{2.2.74}$$

for all  $\beta$ , and so,

$$\Omega(N\epsilon) \leq \exp\{N \min_{\beta} [\beta\epsilon + \phi(\beta)]\} = e^{N\Sigma(\epsilon)} = e^{N\bar{H}}. \tag{2.2.75}$$

A compatible lower bound is obtained by observing that the minimizing  $\beta$  gives rise to  $\langle \mathcal{E}(X_1) \rangle = \epsilon$ , which makes the event  $\{\mathbf{x} : \mathcal{E}(\mathbf{x}) \approx N\epsilon\}$  a high-probability event, by the weak law of large numbers. A good reference for further study, and from a more general perspective, is the article by Hall [6]. See also [7].

Now, that we identified the Gibbs entropy with the Boltzmann entropy, it is instructive to point out that the B–G distribution could have been obtained also in a different manner, owing to the maximum-entropy principle that stems from the second law, or the minimum free-energy principle. Specifically, let us denote the Gibbs entropy as

$$H(P) = - \sum_{\mathbf{x}} P(\mathbf{x}) \ln P(\mathbf{x}) \tag{2.2.76}$$

and consider the following optimization problem:

$$\begin{aligned}
&\max H(P) \\
&\text{s.t. } \langle \mathcal{E}(\mathbf{X}) \rangle = E
\end{aligned} \tag{2.2.77}$$

By formalizing the equivalent Lagrange problem, where  $\beta$  now plays the role of a Lagrange multiplier:

$$\max \left\{ H(P) + \beta \left[ E - \sum_{\mathbf{x}} P(\mathbf{x}) \mathcal{E}(\mathbf{x}) \right] \right\}, \tag{2.2.78}$$

or equivalently,

$$\min \left\{ \sum_{\mathbf{x}} P(\mathbf{x}) \mathcal{E}(\mathbf{x}) - \frac{H(P)}{\beta} \right\} \tag{2.2.79}$$

one readily verifies that the solution to this problem is the B–G distribution where the choice of the (Lagrange multiplier)  $\beta$  controls the average energy  $E$ . If  $\beta$  is identified with the inverse temperature, the above is nothing but the minimization of the free energy.

Note also that Eq. (2.2.71), which we will rewrite, with a slight abuse of notation as

$$\phi(\beta) - \beta\phi'(\beta) = \Sigma(\beta) \quad (2.2.80)$$

can be viewed in two ways. The first suggests to take derivatives of both sides w.r.t.  $\beta$  and then obtain  $\Sigma'(\beta) = -\beta\phi''(\beta)$  and so,

$$\begin{aligned} s(\beta) &= k\Sigma(\beta) \\ &= k \int_{\beta}^{\infty} \tilde{\beta}\phi''(\tilde{\beta})d\tilde{\beta} \quad \text{3rd law} \\ &= k \int_0^T \frac{1}{k\tilde{T}} \cdot k\tilde{T}^2 c(\tilde{T}) \cdot \frac{d\tilde{T}}{k\tilde{T}^2} \quad c(\tilde{T}) \triangleq \text{heat capacity per particle} \\ &= \int_0^T \frac{c(\tilde{T})d\tilde{T}}{\tilde{T}} \end{aligned} \quad (2.2.81)$$

recovering the Clausius entropy as  $c(\tilde{T})d\tilde{T}$  is the increment of heat intake per particle  $dq$ . The second way to look at Eq. (2.2.80) is as a first order differential equation in  $\phi(\beta)$ , whose solution is easily found to be

$$\phi(\beta) = -\beta\epsilon_{\text{GS}} + \beta \cdot \int_{\beta}^{\infty} \frac{d\hat{\beta}\Sigma(\hat{\beta})}{\hat{\beta}^2}, \quad (2.2.82)$$

where  $\epsilon_{\text{GS}} = \lim_{N \rightarrow \infty} E_{\text{GS}}/N$ . Equivalently,

$$Z(\beta) \doteq \exp \left\{ -\beta E_{\text{GS}} + N\beta \cdot \int_{\beta}^{\infty} \frac{d\hat{\beta}\Sigma(\hat{\beta})}{\hat{\beta}^2} \right\}, \quad (2.2.83)$$

namely, the partition function at a certain temperature can be expressed as a functional of the entropy pertaining to all temperatures lower than that temperature. Changing the integration variable from  $\beta$  to  $T$ , this readily gives the relation

$$F = E_{\text{GS}} - \int_0^T S(T')dT'. \quad (2.2.84)$$

Since  $F = E - ST$ , we have

$$E = E_{\text{GS}} + ST - \int_0^T S(T')dT' = E_{\text{GS}} + \int_0^S T(S')dS', \quad (2.2.85)$$

where the second term amounts to the heat  $Q$  that accumulates in the system, as the temperature is raised from 0 to  $T$ . This is a special case of the first law of thermodynamics. The more general form, as said, takes into account also possible work performed on (or by) the system.

Let us now summarize the main properties of the partition function that we have seen thus far:

1.  $Z(\beta)$  is a continuous function.  $Z(0) = |\mathcal{X}^n|$  and  $\lim_{\beta \rightarrow \infty} \frac{\ln Z(\beta)}{\beta} = -E_{\text{GS}}$ .
2. Generating cumulants:  $\langle \mathcal{E}(X) \rangle = -d \ln Z / d\beta$ ,  $\text{Var}\{\mathcal{E}(X)\} = d^2 \ln Z / d\beta^2$ , which implies convexity of  $\ln Z$ , and hence also of  $\phi(\beta)$ .
3.  $\phi$  and  $\Sigma$  are a Legendre–Fenchel transform pair.  $\Sigma$  is concave.

We have also seen that Boltzmann’s entropy is not only equivalent to the Clausius entropy, but also to the Gibbs/Shannon entropy. Thus, there are actually three different forms of the expression of entropy.

*Comment* Consider  $Z(\beta)$  for an *imaginary temperature*  $\beta = i\omega$ , where  $i = \sqrt{-1}$ , and define  $z(E)$  as the inverse Fourier transform of  $Z(i\omega)$ . It can readily be seen that  $z(E) = \omega(E)$ , i.e., for  $E_1 < E_2$ , the number of states with energy between  $E_1$  and  $E_2$  is given by  $\int_{E_1}^{E_2} z(E) dE$ . Thus,  $Z(\cdot)$  can be related to energy enumeration in two different ways: one is by the Legendre–Fenchel transform of  $\ln Z(\beta)$  for real  $\beta$ , and the other is by the inverse Fourier transform of  $Z(\beta)$  for imaginary  $\beta$ . It should be kept in mind, however, that while the latter relation holds for every system size  $N$ , the former is true only in the thermodynamic limit, as mentioned.

## The Energy Equipartition Theorem

It turns out that in the case of a quadratic Hamiltonian,  $\mathcal{E}(x) = \frac{1}{2}\alpha x^2$ , which means that  $x$  is Gaussian, the average per-particle energy, is always given by  $1/(2\beta) = kT/2$ , independently of  $\alpha$ . If we have  $N$  such quadratic terms, then of course, we end up with  $NkT/2$ . In the case of the ideal gas, we have three such terms (one for each dimension) per particle, thus a total of  $3N$  terms, and so,  $E = 3NkT/2$ , which is exactly the expression we obtained also from the microcanonical ensemble as well as in the previous chapter. In fact, we observe that in the canonical ensemble, whenever we have an Hamiltonian of the form  $\frac{\alpha}{2}x_i^2$  plus some arbitrary terms that do not depend on  $x_i$ , then  $x_i$  is Gaussian (with variance  $kT/\alpha$ ) and independent of the other variables, i.e.,  $p(x_i) \propto e^{-\alpha x_i^2/(2kT)}$ . Hence it contributes an amount of

$$\left\langle \frac{1}{2}\alpha X_i^2 \right\rangle = \frac{1}{2}\alpha \cdot \frac{kT}{\alpha} = \frac{kT}{2} \quad (2.2.86)$$

to the total average energy, independently of  $\alpha$ . It is more precise to refer to this  $x_i$  as a *degree of freedom* rather than a particle. This is because in the three-dimensional world, the kinetic energy, for example, is given by  $p_x^2/(2m) + p_y^2/(2m) + p_z^2/(2m)$ , that is, each particle contributes *three* additive quadratic terms rather than one (just



like three independent one-dimensional particles) and so, it contributes  $3kT/2$ . This principle is called the *energy equipartition theorem*.

Below is a direct derivation of the equipartition theorem:

$$\begin{aligned}
 \left\langle \frac{1}{2} \alpha X^2 \right\rangle &= \frac{\int_{-\infty}^{\infty} dx (\alpha x^2/2) e^{-\beta \alpha x^2/2}}{\int_{-\infty}^{\infty} dx e^{-\beta \alpha x^2/2}} \\
 &= -\frac{\partial}{\partial \beta} \ln \left[ \int_{-\infty}^{\infty} dx e^{-\beta \alpha x^2/2} \right] \\
 &= -\frac{\partial}{\partial \beta} \ln \left[ \frac{1}{\sqrt{\beta}} \int_{-\infty}^{\infty} d(\sqrt{\beta} x) e^{-\alpha (\sqrt{\beta} x)^2/2} \right] \\
 &= -\frac{\partial}{\partial \beta} \ln \left[ \frac{1}{\sqrt{\beta}} \int_{-\infty}^{\infty} du e^{-\alpha u^2/2} \right] \\
 &= \frac{1}{2} \frac{d \ln \beta}{d \beta} = \frac{1}{2\beta} = \frac{kT}{2}.
 \end{aligned}$$

Note that although we could have used closed-form expressions for both the numerator and the denominator of the first line, we have deliberately taken a somewhat different route in the second line, where we have presented it as the derivative of the denominator of the first line. Also, rather than calculating the Gaussian integral explicitly, we only figured out how it scales with  $\beta$ , because this is the only thing that matters after taking the derivative relative to  $\beta$ . The reason for using this trick of bypassing the need to calculate integrals, is that it can easily be extended in two directions at least:

1. Let  $\mathbf{x} \in \mathbb{R}^N$  and let  $\mathcal{E}(\mathbf{x}) = \frac{1}{2} \mathbf{x}^T A \mathbf{x}$ , where  $A$  is a  $N \times N$  positive definite matrix. This corresponds to a physical system with a quadratic Hamiltonian, which includes also interactions between pairs (e.g., harmonic oscillators or springs, which are coupled because they are tied to one another). It turns out that here, regardless of  $A$ , we get:

$$\langle \mathcal{E}(\mathbf{X}) \rangle = \left\langle \frac{1}{2} \mathbf{X}^T A \mathbf{X} \right\rangle = N \cdot \frac{kT}{2}. \quad (2.2.87)$$

2. Back to the case of a scalar  $x$ , but suppose now a more general power-law Hamiltonian,  $\mathcal{E}(x) = \alpha |x|^\theta$ . In this case, we get

$$\langle \mathcal{E}(X) \rangle = \langle \alpha |X|^\theta \rangle = \frac{kT}{\theta}. \quad (2.2.88)$$

Moreover, if  $\lim_{x \rightarrow \pm\infty} x e^{-\beta \mathcal{E}(x)} = 0$  for all  $\beta > 0$ , and we denote  $\mathcal{E}'(x) \triangleq d\mathcal{E}(x)/dx$ , then

$$\langle X \cdot \mathcal{E}'(X) \rangle = kT. \quad (2.2.89)$$

It is easy to see that the earlier power-law result is obtained as a special case of this, as  $\mathcal{E}'(x) = \alpha\theta|x|^{\theta-1}\text{sgn}(x)$  in this case.

*Example 2.4 (Ideal gas with gravitation)* Let

$$\mathcal{E}(x) = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + mgz. \quad (2.2.90)$$

The average kinetic energy of each particle is  $3kT/2$ , as said before. The contribution of the average potential energy is  $kT$  (one degree of freedom with  $\theta = 1$ ). Thus, the total is  $5kT/2$ , where 60% come from kinetic energy and 40% come from potential energy, universally, that is, independent of  $T$ ,  $m$ , and  $g$ .  $\square$

### 2.2.3 The Grand-Canonical Ensemble and the Gibbs Ensemble

A brief summary of what we have done thus far, is the following: we started with the microcanonical ensemble, which was very restrictive in the sense that the energy was held strictly fixed to the value of  $E$ , the number of particles was held strictly fixed to the value of  $N$ , and at least in the example of a gas, the volume was also held strictly fixed to a certain value  $V$ . In the passage from the microcanonical ensemble to the canonical one, we slightly relaxed the first of these parameters,  $E$ : rather than insisting on a fixed value of  $E$ , we allowed energy to be exchanged back and forth with the environment, and thereby to slightly fluctuate (for large  $N$ ) around a certain average value, which was controlled by temperature, or equivalently, by the choice of  $\beta$ . This was done while keeping in mind that the total energy of both system and heat bath must be kept fixed, by the law of energy conservation, which allowed us to look at the combined system as an isolated one, thus obeying the microcanonical ensemble. We then had a one-to-one correspondence between the extensive quantity  $E$  and the intensive variable  $\beta$ , that adjusted its average value. But the other extensive variables, like  $N$  and  $V$  were still kept strictly fixed.

It turns out, that we can continue in this spirit, and ‘relax’ also either one of the other variables  $N$  or  $V$  (but not both at the same time), allowing it to fluctuate around a typical average value, and controlling it by a corresponding intensive variable. Like  $E$ , both  $N$  and  $V$  are also subjected to conservation laws when the combined system is considered. Each one of these relaxations leads to a new ensemble, in addition to the microcanonical and the canonical ensembles that we have already seen. In the case where it is the variable  $V$  that is allowed to be flexible, this ensemble is called the *Gibbs ensemble*. In the case where it is the variable  $N$ , this ensemble is called the *grand-canonical ensemble*. There are, of course, additional ensembles based on this principle, depending on the kind of the physical system.

## The Grand-Canonical Ensemble

The fundamental idea is essentially the very same as the one we used to derive the canonical ensemble: let us get back to our (relatively small) subsystem, which is in contact with a heat bath, and this time, let us allow this subsystem to exchange with the heat bath, not only energy, but also matter, i.e., particles. The heat bath consists of a huge reservoir of energy and particles. The total energy is  $E_0$  and the total number of particles is  $N_0$ . Suppose that we can calculate the number/volume of states of the heat bath as a function of both its energy  $E'$  and amount of particles  $N'$ , and denote this function by  $\Omega_B(E', N')$ . A microstate is now a combination  $(\mathbf{x}, N)$ , where  $N$  is the (variable) number of particles in our subsystem and  $\mathbf{x}$  is as before for a given  $N$ . From the same considerations as before, whenever our subsystem is in state  $(\mathbf{x}, N)$ , the heat bath can be in any one of  $\Omega_B(E_0 - \mathcal{E}(\mathbf{x}), N_0 - N)$  microstates of its own. Thus, owing to the microcanonical ensemble,

$$\begin{aligned}
 P(\mathbf{x}, N) &\propto \Omega_B(E_0 - \mathcal{E}(\mathbf{x}), N_0 - N) \\
 &= \exp\{S_B(E_0 - \mathcal{E}(\mathbf{x}), N_0 - N)/k\} \\
 &\approx \exp\left\{\frac{S_B(E_0, N_0)}{k} - \frac{1}{k} \frac{\partial S_B}{\partial E} \cdot \mathcal{E}(\mathbf{x}) - \frac{1}{k} \frac{\partial S_B}{\partial N} \cdot N\right\} \\
 &\propto \exp\left\{-\frac{\mathcal{E}(\mathbf{x})}{kT} + \frac{\mu N}{kT}\right\}
 \end{aligned} \tag{2.2.91}$$

where  $\mu$  is the chemical potential of the heat bath. Thus, we now have the grand-canonical distribution:

$$P(\mathbf{x}, N) = \frac{e^{\beta[\mu N - \mathcal{E}(\mathbf{x})]}}{\Xi(\beta, \mu)}, \tag{2.2.92}$$

where the denominator is called the *grand partition function*:

$$\Xi(\beta, \mu) \triangleq \sum_{N=0}^{\infty} e^{\beta\mu N} \sum_{\mathbf{x}} e^{-\beta\mathcal{E}(\mathbf{x})} \triangleq \sum_{N=0}^{\infty} e^{\beta\mu N} Z_N(\beta). \tag{2.2.93}$$

*Example 2.5 (Grand partition function of the ideal gas)* Using the result of Exercise 2.1, we have for the ideal gas:

$$\begin{aligned}
 \Xi(\beta, \mu) &= \sum_{N=0}^{\infty} e^{\beta\mu N} \cdot \frac{1}{N!} \left(\frac{V}{\lambda^3}\right)^N \\
 &= \sum_{N=0}^{\infty} \frac{1}{N!} \left(e^{\beta\mu} \cdot \frac{V}{\lambda^3}\right)^N
 \end{aligned}$$

$$= \exp \left( e^{\beta\mu} \cdot \frac{V}{\lambda^3} \right). \quad (2.2.94)$$

It is convenient to change variables and to define  $z = e^{\beta\mu}$  (which is called the *fugacity*) and then, define

$$\tilde{\Xi}(\beta, z) = \sum_{N=0}^{\infty} z^N Z_N(\beta). \quad (2.2.95)$$

This notation emphasizes the fact that for a given  $\beta$ ,  $\tilde{\Xi}(z)$  is actually the  $z$ -transform of the sequence  $\{Z_N(\beta)\}_{N \geq 0}$ . A natural way to think about  $P(\mathbf{x}, N)$  is as  $P(N) \cdot P(\mathbf{x}|N)$ , where  $P(N)$  is proportional to  $z^N Z_N(\beta)$  and  $P(\mathbf{x}|N)$  corresponds to the canonical ensemble as before.

Using the grand partition function, it is now easy to obtain moments of the random variable  $N$ . For example, the first moment is:

$$\langle N \rangle = \frac{\sum_N N z^N Z_N(\beta)}{\sum_N z^N Z_N(\beta)} = z \cdot \frac{\partial \ln \tilde{\Xi}(\beta, z)}{\partial z}. \quad (2.2.96)$$

Thus, we have replaced the fixed number of particles,  $N$ , by a random number of particles, which concentrates around an average controlled by  $\mu$ , or equivalently, by  $z$ . The dominant<sup>15</sup> value of  $N$  is the one that maximizes the product  $z^N Z_N(\beta)$ , or equivalently,  $\beta\mu N + \ln Z_N(\beta) = \beta(\mu N - F_N)$ . Thus,  $\ln \tilde{\Xi}$  is related to  $\ln Z_N$  by another kind of a Legendre–Fenchel transform:  $\ln \tilde{\Xi}(\beta, z, V) \approx \max_N [\beta\mu N + \ln Z_N(\beta, V)]$  or equivalently

$$kT \ln \tilde{\Xi}(\beta, z, V) \approx \max_N [\mu N + kT \ln Z_N(\beta, V)].$$

Note that by passing to the grand-canonical ensemble, we have replaced two extensive quantities,  $E$  and  $N$ , by their respective conjugate intensive variables,  $T$  and  $\mu$ . This means that the grand partition function depends on one remaining extensive variable only, which is  $V$ , and so, under ordinary conditions,  $\ln \Xi(\beta, z)$ , or in its more complete notation,  $\ln \Xi(\beta, z, V)$ , depends linearly on  $V$  at least in the thermodynamic limit, namely,  $\lim_{V \rightarrow \infty} [\ln \Xi(\beta, z, V)]/V$  tends to a constant that depends only on  $\beta$  and  $z$ . What is this constant? Let us examine again the first law in its more general form, as it appears in Eq.(2.2.30). For fixed  $T$  and  $\mu$ , we have the following:

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<sup>15</sup>The best way to understand this is in analogy to the derivation of  $\epsilon^*$  as the minimizer of the free energy in the canonical ensemble, except that now the ‘big’ extensive variable is  $V$  rather than  $N$ , so that  $z^N Z_N(\beta, V)$  is roughly exponential in  $V$  for a given fixed  $\rho = N/V$ . The exponential coefficient depends on  $\rho$ , and the ‘dominant’  $\rho^*$  maximizes this coefficient. Finally, the ‘dominant’  $N$  is  $N^* = \rho^* V$ .

$$\begin{aligned}
P\delta V &= \mu\delta N + T\delta S - \delta E \\
&= \delta(\mu N + TS - E) \\
&= \delta(\mu N - F) \\
&\approx kT \cdot \delta[\ln \Xi(\beta, z, V)] \quad V \text{ large}
\end{aligned} \tag{2.2.97}$$

Thus, the constant of proportionality must be  $P$ . In other words, the grand-canonical formula of the pressure is:

$$P = kT \cdot \lim_{V \rightarrow \infty} \frac{\ln \Xi(\beta, z, V)}{V}. \tag{2.2.98}$$

This is different from the canonical-ensemble formula (Exercise 2.3):  $P = kT \cdot \partial \ln Z_N(\beta, V)/\partial V$ , and to the microcanonical-ensemble formula,  $P = T \cdot \partial S(E, V, N)/\partial V$ .

*Example 2.6 (more on the ideal gas)* Applying formula (2.2.96) to Eq. (2.2.94), we readily obtain

$$\langle N \rangle = \frac{zV}{\lambda^3} = \frac{e^{\mu/kT} V}{\lambda^3}. \tag{2.2.99}$$

We see that the grand-canonical factor  $e^{\mu/kT}$  has the physical meaning of the average number of ideal gas atoms in a cube of size  $\lambda \times \lambda \times \lambda$ , where  $\lambda$  is the thermal de Broglie wavelength. Now, applying Eqs. (2.2.98) to (2.2.94), we get

$$P = \frac{kT \cdot e^{\mu/kT}}{\lambda^3} = \frac{\langle N \rangle \cdot kT}{V}, \tag{2.2.100}$$

recovering again the equation of state of the ideal gas. This also demonstrates the principle of ensemble equivalence.

Once again, it should be pointed out that beyond the obvious physical significance of the grand-canonical ensemble, sometimes it proves useful to work with from reasons of pure mathematical convenience, using the principle of ensemble equivalence. We will see this very clearly in the next chapters on quantum statistics.

## The Gibbs Ensemble

Consider now the case where  $T$  and  $N$  are fixed, but  $V$  is allowed to fluctuate around an average volume controlled by the pressure  $P$ . Again, we can analyze our relatively small test system surrounded by a heat bath. The total energy is  $E_0$  and the total volume of the system and the heat bath is  $V_0$ . Suppose that we can calculate the count/volume of states of the heat bath as function of both its energy  $E'$  and the volume  $V'$ , call it  $\Omega_B(E', V')$ . A microstate is now a combination  $(x, V)$ , where  $V$  is the (variable) volume of our subsystem. Once again, the same line of thought is

used: whenever our subsystem is at state  $(\mathbf{x}, V)$ , the heat bath may be in any one of  $\Omega_B(E_0 - \mathcal{E}(\mathbf{x}), V_0 - V)$  microstates of its own. Thus,

$$\begin{aligned}
 P(\mathbf{x}, V) &\propto \Omega_B(E_0 - \mathcal{E}(\mathbf{x}), V_0 - V) \\
 &= \exp\{S_B(E_0 - \mathcal{E}(\mathbf{x}), V_0 - V)/k\} \\
 &\approx \exp\left\{\frac{S_B(E_0, V_0)}{k} - \frac{1}{k} \frac{\partial S_B}{\partial E} \cdot \mathcal{E}(\mathbf{x}) - \frac{1}{k} \frac{\partial S_B}{\partial V} \cdot V\right\} \\
 &\propto \exp\left\{-\frac{\mathcal{E}(\mathbf{x})}{kT} - \frac{PV}{kT}\right\} \\
 &= \exp\{-\beta[\mathcal{E}(\mathbf{x}) + PV]\}.
 \end{aligned} \tag{2.2.101}$$

The corresponding partition function that normalizes this probability function is given by

$$Y_N(\beta, P) = \int_0^\infty e^{-\beta PV} Z_N(\beta, V) dV = \int_0^\infty e^{-\beta PV} dV \sum_{\mathbf{x}} e^{-\beta \mathcal{E}(\mathbf{x})}. \tag{2.2.102}$$

For a given  $N$  and  $\beta$ , the function  $Y_N(\beta, P)$  can be thought of as the *Laplace transform* of  $Z_N(\beta, V)$  as a function of  $V$ . In the thermodynamic limit,  $\lim_{N \rightarrow \infty} \frac{1}{N} \ln Y_N(\beta, P)$  is the Legendre–Fenchel transform of  $\lim_{N \rightarrow \infty} \frac{1}{N} \ln Z_N(\beta, V)$  for fixed  $\beta$ , similarly to the Legendre–Fenchel relationship between the entropy and the canonical log-partition function.<sup>16</sup> Note that analogously to Eq. (2.2.96), here the Gibbs partition function serves as a cumulant generating function for the random variable  $V$ , thus, for example,

$$\langle V \rangle = -kT \cdot \frac{\partial \ln Y_N(\beta, P)}{\partial P}. \tag{2.2.103}$$

As mentioned in footnote no. 20,

$$G = -kT \ln Y_N(\beta, P) = E - TS + PV = F + PV \tag{2.2.104}$$

is the Gibbs free energy of the system, and for the case considered here, the force is the pressure and the conjugate variable it controls is the volume. In analogy to the grand-canonical ensemble, here too, there is only one extensive variable, this time, it is  $N$ . Thus,  $G$  should be asymptotically proportional to  $N$  with a constant of proportionality that depends on the fixed values of  $T$  and  $P$ .

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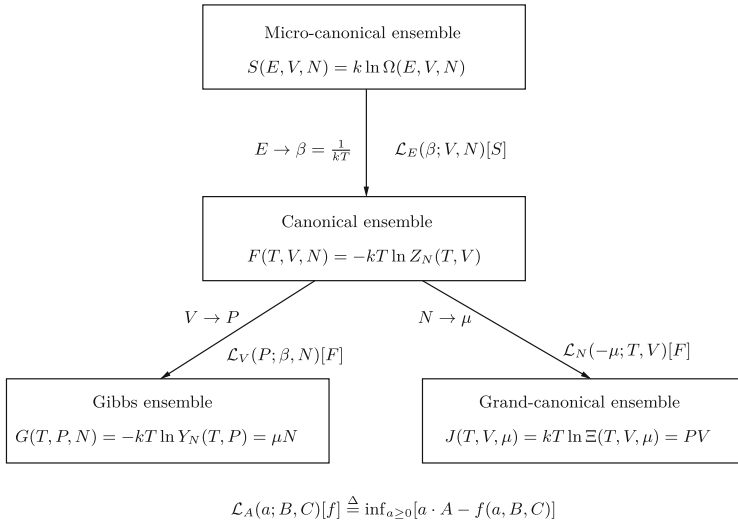
<sup>16</sup>**Exercise 2.5** Write explicitly the Legendre–Fenchel relation (and its inverse) between the Gibbs partition function and the canonical partition function.

**Exercise 2.6** Show that this constant is the chemical potential  $\mu$ .

All this is, of course, relevant when the physical system is a gas in a container. In general, the Gibbs ensemble is obtained by a similar Legendre–Fenchel transform replacing an extensive physical quantity of the canonical ensemble by its conjugate force. For example, magnetic field is conjugate to magnetization, electric field is conjugate to electric charge, mechanical force is conjugate to displacement, moment is conjugate to angular shift, and so on. By the same token, the chemical potential is a ‘force’ that is conjugate to the number of particles in grand-canonical ensemble, and (inverse) temperature is a ‘force’ that controls the heat energy.

Figure 2.2 summarizes the thermodynamic potentials associated with the various statistical ensembles. The arrow between each two connected blocks in the diagram designates a passage from one ensemble to another by a Legendre–Fenchel transform operator  $\mathcal{L}$  that is defined generically at the bottom of the figure. In each passage, it is also indicated which extensive variable is replaced by its conjugate intensive variable.

It should be noted, that at least mathematically, one could have defined three more ensembles that would complete the picture of Fig. 2.2 in a symmetric manner. Two of the additional ensembles can be obtained by applying Legendre–Fenchel transforms on  $S(E, V, N)$ , other than the transform that takes us to the canonical ensemble. The first Legendre–Fenchel transform is w.r.t. the variable  $V$ , replacing it by  $P$ , and the second additional ensemble is w.r.t. the variable  $N$ , replacing it by  $\mu$ . Let us denote the new resulting ‘potentials’ (minus  $kT$  times log-partition functions) by  $A(E, P, N)$  and  $B(E, V, \mu)$ , respectively. The third ensemble, with potential  $C(E, P, \mu)$ , whose only extensive variable is  $E$ , could be obtained by



**Fig. 2.2** Diagram of Legendre–Fenchel relations between the various ensembles

yet another Legendre–Fenchel transform, either on  $A(E, P, N)$  or  $B(E, V, \mu)$  w.r.t. the appropriate extensive variable. Of course,  $A(E, P, N)$  and  $B(E, V, \mu)$  are also connected directly to the Gibbs ensemble and to the grand-canonical ensemble, respectively, both by Legendre–Fenchel-transforming w.r.t.  $E$ . While these three ensembles are not really used in physics, they might prove useful to work with for calculating certain physical quantities, by taking advantage of the principle of ensemble equivalence.

**Exercise 2.7** Complete the diagram of Fig. 2.2 by the three additional ensembles just defined. Can you give physical meanings to  $A$ ,  $B$  and  $C$ ? Also, as said,  $C(E, P, \mu)$  has only  $E$  as an extensive variable. Thus,  $\lim_{E \rightarrow \infty} C(E, P, \mu)/E$  should be a constant. What is this constant?

Even more generally, we could start from a system model, whose micro-canonical ensemble consists of many extensive variables  $L_1, \dots, L_n$ , in addition to the internal energy  $E$  (not just  $V$  and  $N$ ). The entropy function is then  $S(E, L_1, \dots, L_n, N)$ . Here,  $L_i$  can be, for example, volume, mass, electric charge, electric polarization in each one of the three axes, magnetization in each one of three axes, and so on. The first Legendre–Fenchel transform takes us from the micro-canonical ensemble to the canonical one upon replacing  $E$  by  $\beta$ . Then we can think of various Gibbs ensembles obtained by replacing any subset of extensive variables  $L_i$  by their respective conjugate forces  $\lambda_i = T \partial S / \partial L_i$ ,  $i = 1, \dots, n$  (in the above examples: pressure, gravitational force (weight), voltage (or electric potential), electric fields, and magnetic fields in the corresponding axes, respectively). In the extreme case, all  $L_i$  are replaced by  $\lambda_i$  upon applying successive Legendre–Fenchel transforms, or equivalently, a multi-dimensional Legendre–Fenchel transform:

$$G(T, \lambda_1, \dots, \lambda_n, N) = - \sup_{L_1, \dots, L_n} [kT \ln Z_N(\beta, L_1, \dots, L_n) - \lambda_1 L_1 - \dots - \lambda_n L_n]. \quad (2.2.105)$$

Once again, there must be one extensive variable at least.

## 2.3 Suggestions for Supplementary Reading

Part of the presentation in this chapter is similar to a corresponding chapter in [1]. The derivations associated with the various ensembles of statistical mechanics, as well as their many properties, can also be found in any textbook on elementary statistical mechanics, including: Beck [8, Chap. 3], Huang [9, Chaps. 6, 7], Honerkamp [10, Chap. 3], Landau and Lifshitz [2], Pathria [11, Chaps. 2–4], and Reif [12, Chap. 6], among many others.



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Statistical Physics for Electrical Engineering

Merhav, N.

2018, XII, 137 p. 21 illus., 3 illus. in color., Hardcover

ISBN: 978-3-319-62062-6