

## Chapter 2

# The System in Thermal Contact with a Reservoir: The Canonical and Grand Canonical Ensembles

In this chapter, we shall study a system in contact with a very large system which stays at constant temperature  $T$ . We shall call it the reservoir. In the first case, the contact is purely thermal; it means that the temperature of the system is fixed by contact with the reservoir. In the second case, the contact is thermal but there is also the possibility of exchange of particles between the system and the reservoir. Since it is supposed that the system and the reservoir are in equilibrium, there are equalities of the temperatures and of the chemical potentials, as explained above. Our goal is always to find the relation between the microscopic properties of the particles of the system and its macroscopic properties.

The fundamental hypotheses are:

- (a) The system and the reservoir are seen together as a grand system which is isolated from the rest of the world. The results of the preceding chapter can be applied to the grand system. In particular, its energy  $E_0$  is constant and the entropy is given by (1.1).
- (b) The system is much smaller than the reservoir itself. In particular the energy  $E_S$  of the system is much smaller than the energy  $E_R$  of the reservoir and that of the grand system. Thus one will be

able to apply approximations concerning small quantities versus large ones.

## 2.1 The Canonical Ensemble

### 2.1.1 *The partition function*

As revealed above, the system with volume  $V$  and number of particles  $N$  is in thermal contact with the reservoir, which imposes on the system the temperature. However, the energy of the system is not fixed by the contact with the reservoir and can fluctuate over all the possible energies of the system. Our first goal will be to determine, in the ensemble of a huge number of identical systems which constitutes the canonical ensemble, the probability to find a system in a microstate labeled  $s$  with energy  $E_S$ . Once this probability is known, we shall be able to calculate the mean energy, which is the macroscopic energy of the system and other quantities.

If one picks at random a system in the ensemble, the probability  $p_s$  to find this system in a microstate  $s$  with energy  $E_S$  is the ratio of two quantities: the number of microstates of the system with energy  $E_S$  against the total number of microstates of the grand system. A probability is defined as the number of “favorable” cases (here a favorable case is the system is a microstate with energy  $E_S$ ) divided by the number of all the possible cases (here the number of microstates of the grand ensemble, irrespective they are favorable or not).

If the energy of the system is  $E_S$  and that of the grand system is  $E_0$ , the energy of the reservoir is  $E_0 - E_S$  and the number of microstates in which the system has energy  $E_S$  is equal to the number of microstates in which the reservoir has the energy  $E_0 - E_S$ . One writes

$$p_s = \frac{\Omega_R(E_0 - E_S)}{\Omega_{GS}(E_0)}, \quad (2.1)$$

where  $\Omega_R$  indicates the number of microstates of the reservoir and  $\Omega_{GS}$  those of the grand system. From the previous chapter, we know

that the entropies  $S_{GS}$  of the grand system and that  $S_R$  of the reservoir are respectively

$$S_{GS} = k_B \text{Ln } \Omega_{GS}(E_0),$$

$$S_R = k_B \text{Ln } \Omega_R(E_0 - E_S),$$

and we have

$$\Omega_{GS}(E_0) = \exp[S_{GS}(E_0)/k_B], \quad (2.2)$$

$$\Omega_R(E_0 - E_s) = \exp[S_R(E_0 - E_S)/k_B]. \quad (2.3)$$

For the grand system there is no problem in applying the preceding formula since it is a closed system. For the reservoir, it is only an approximation since it is in contact with the system and is not a closed system. It is a good approximation since it is much larger than the system and is practically unperturbed by the system.

From (2.1)–(2.3) one gets

$$p_s = \frac{\exp[S_R(E_0 - E_S)/k_B]}{\exp[S_{GS}(E_0)/k_B]}. \quad (2.4)$$

One can expand  $S_R(E_0 - E_S)$  as a Taylor expansion<sup>1</sup> and terminate after the second term since  $E_0 \gg E_S$ , and

$$S_R(E_0 - E_S) = S_R(E_0) - E_S(\partial S_R/\partial E)_0, \quad (2.5)$$

but  $(\partial S_R/\partial E) = 1/T$ ,

$$S_R(E_0 - E_s) = S_R(E_0) - E_S/T. \quad (2.6)$$

The probability  $p_s$  can be written as

$$p_s = \frac{\exp[S_R(E_0)/k_B - E_S/(k_B T)]}{\exp[S_{GS}(E_0)/k_B]}$$

or

$$p_s = \frac{\exp[S_R(E_0)/k_B] \exp[-E_S/(k_B T)]}{\exp[S_{GS}(E_0)/k_B]}. \quad (2.7)$$

Since the sum of all the probabilities is equal to 1, equivalently

$$\sum_S p_s = \sum_S \frac{\exp[S_R(E_0)/k_B] \exp[-E_S/(k_B T)]}{\exp[S_{GS}(E_0)/k_B]} = 1 \quad (2.8)$$

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<sup>1</sup>The Taylor expansion of a function  $f(x)$  is given by  $f(x+h) = f(x) + h df/dx(x) + (h^2/2!) d^2 f/dx^2(x) + \dots + (h^n/n!) d^n f/dx^n(x) + \dots$ .

or

$$\sum_S p_s = \frac{\exp[S_R(E_0)/k_B]}{\exp[S_{GS}(E_0)/k_B]} \sum_S \exp\left[-\frac{E_S}{k_B T}\right] = 1,$$

thus,

$$\exp[S_{GS}(E_0)/k_B] = \exp[S_R(E_0)/k_B] \sum_S \exp\left[-\frac{E_S}{k_B T}\right]. \quad (2.9)$$

Substituting (2.9) into (2.7), we get the final result for  $p_s$ :

$$p_s = \exp\left[-\frac{E_S}{k_B T}\right] / \sum_S \exp\left[-\frac{E_S}{k_B T}\right], \quad (2.10)$$

when the sums in (2.8)–(2.10) are over all the possible microstates and not only on the possible values of the energies. The probability  $p_s$  is the probability to find the system in a microstate or shortly in a state with energy  $E_S$ . It is an important result and we shall use it several times.

The sum

$$Z = \sum_S \exp\left[-\frac{E_S}{k_B T}\right] \quad (2.11)$$

is called the partition function. In the context of the canonical ensemble, this is the most important result. We shall see that it will give the link between the microscopic and the macroscopic points of view.  $Z$  is a function of the parameters  $T$ ,  $V$ , and  $N$ , that define the system. The temperature  $T$  appears explicitly, but the possible energies of the system depend in general on  $V$  and  $N$ .

It is common to take the Greek letter  $\beta$  as the inverse of the temperature  $\beta = 1/(k_B T)$  and to write  $Z$  as

$$Z = \sum_s \exp(-\beta E_S). \quad (2.12a)$$

It is possible that several different microstates have the same energy, thus there is a function  $g(E_S)$ , giving the number of microstates for a given energy  $E_S$ . Such states with the same energy are called degenerate states. The partition function can be written as a sum over the energies:

$$Z = \sum_E g(E_S) \exp(-\beta E_S). \quad (2.12b)$$

We stress the difference between, (2.11) or (2.12a), and (2.12b). In (2.11) the sum is over all the microstates and in (2.12b) it is over the energies.

### 2.1.2 *Energy, entropy and thermodynamic potential*

**Part A.** With the knowledge of  $p_s$ , it is possible to calculate the mean energy  $E$  as

$$E = \sum_S p_s E_S, \quad (2.13a)$$

or

$$E = \frac{\sum_S E_S \exp(-\beta E_S)}{\sum_S \exp(-\beta E_S)}. \quad (2.13b)$$

The formula (2.13a) is the standard formula for the mean value of a quantity which has different probability to appear in different states of respective energies.

The numerator of (2.13b) is minus the derivative of the dominator relatively to  $\beta$ , and the energy can be written, using  $Z$ , as

$$E = - \left[ \frac{\partial Z}{\partial \beta} \right] / Z = - \frac{\partial \text{Ln } Z}{\partial \beta}. \quad (2.14)$$

**Part B.** The energy  $E$  is given as a function of  $T$ ,  $V$  and  $N$ . The derivative  $(\partial E / \partial T)_{V,N}$  is the specific heat at constant volume,  $C_V$ . The entropy is given by<sup>2</sup>  $S = \int C_V (dT/T) = \int (\partial E / \partial T)_V (dT/T)$ . One uses the following relations linking  $T$  and  $\beta$  to get:

$$\begin{aligned} T &= \frac{1}{k_B \beta}, \\ dT &= - \frac{d\beta}{k_B \beta^2}, \\ \frac{\partial E}{\partial T} &= \frac{\partial E}{\partial \beta} \frac{d\beta}{dT} = -k_B \beta^2 \frac{\partial E}{\partial \beta}, \end{aligned}$$

giving  $S = \int (\partial E / \partial T)_V (dT/T) k_B = k_B \int \beta (\partial E / \partial \beta)_V d\beta$ .

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<sup>2</sup>The fundamental relation between the entropy  $dS$  and the heat  $dQ$  in an infinitesimal process is  $dS = dQ/T$ . If the process takes place at constant volume  $dQ = C_V dT$  and  $dS = (C_V/T) dT$ .

Performing integration by parts, one writes

$$u = \beta, \quad dv = \left( \frac{\partial E}{\partial \beta} \right)_V d\beta, \quad \int u dv = uv - \int v du,$$

$$du = d\beta, \quad v = E.$$

One gets, using (2.14), that

$$S = k_B \left[ \beta E - \int E d\beta \right] = k_B \left[ \beta E + \int \frac{\partial \text{Ln } Z}{\partial \beta} d\beta \right], \quad (2.15)$$

or

$$S = E/T + k_B \text{Ln } Z. \quad (2.16)$$

From (2.16) we find the link that we are looking for:

$$E - TS = F = -k_B T \text{Ln } Z. \quad (2.17)$$

We recall that  $F$  is the Helmholtz free energy and a function of  $T$ ,  $V$  and  $N$ . We mentioned above that from the knowledge of  $F$  we can get all the possible data about the system. The relation (2.17) is one of the most important in this course of study.

We close this section by another formulation of the entropy:

$$S = -k_B \sum_S p_s \text{Ln } p_s. \quad (2.18a)$$

To verify, one introduces in (2.18a) the expression (2.10) for  $p_s$  and one obtains

$$S = -k_B \sum_S \left[ -\beta E_S - \text{Ln } Z \right] \frac{\exp(-\beta E_S)}{Z}, \quad (2.18b)$$

or

$$S = k_B \sum_S [\beta E_S \exp(-\beta E_S)] / Z + k_B [\text{Ln } Z / Z] \sum_S \exp(-\beta E_S). \quad (2.18c)$$

Taking into account (2.13b), one sees that the first term in (2.18b) is equal to  $E/T$ . Since  $\sum_S \exp(-\beta E_S) = Z$ , the second term becomes equal to  $k_B \text{Ln } Z$ . Finally (2.18c) is equal to  $E/T + k_B \text{Ln } Z$ . One recovers the expression (2.16) for the entropy.

The expression (2.18a) is very general and can be used for the closed system of the microcanonical ensemble. In this case, the probability to find the system in a microstate with the chosen energy is

$1/\Omega$ , since all the microstates, in number  $\Omega$ , have the same probability to be found in the ensemble. Putting  $p_s = 1/\Omega$  in (2.17) gives again the Boltzmann formula (1.1),  $S = k_B \text{Ln } \Omega$  since the number of terms in the sum is merely  $\Omega$ .

**Part C.** We consider  $N$  particles without interaction in a volume  $V$  at temperature  $T$ . We add also that it is possible to distinguish between the particles. This implies that it is always possible (in principle) to follow an individual particle. In such case, the permutation of two particles between their respective states introduces a new microstate for the system. This cannot be true for gas in which there are constant collisions between the particles such that their “individuality” is lost.

In the expression of  $Z$  will appear all the energies of the system. These energies are all the possible sums of the individual energies (of the microstates)<sup>3</sup> of the  $N$  particles. We note by  $\{e_i\}$  one of these possible sums (with  $N$  terms), and the partition function is  $Z = \sum \exp(-\beta\{e_i\})$  over all these  $\{e_i\}$ .

The one-particle partition function is  $Z_1 = \sum \exp(-\beta e_i)$ , where the sum is on the possible energies of one particle. Now consider the following expression  $B$ :

$$B = (Z_1)^N = \left[ \exp(-\beta \sum_i e_i) \right]^N. \quad (2.19)$$

One can write

$$\begin{aligned} B &= \left[ \exp(-\beta \sum_i e_i) \right]^N \\ &= \left[ \exp(-\beta \sum_i e_i) \right] \left[ \exp(-\beta \sum_i e_i) \right] \left[ \exp(-\beta \sum_i e_i) \right] \dots \end{aligned} \quad (2.20a)$$

when the right hand contains  $N$  identical terms. More explicitly (2.20a) is

$$\begin{aligned} & \left[ \exp(-\beta e_1) + \exp(-\beta e_2) + \exp(-\beta e_3) \dots \right] \left[ \exp(-\beta e_1) + \exp(-\beta e_2) \right. \\ & \quad \left. + \exp(-\beta e_3) \dots \right] \left[ \exp(-\beta e_1) + \exp(-\beta e_2) + \exp(-\beta e_3) \dots \right]. \end{aligned} \quad (2.20b)$$

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<sup>3</sup>One can sort the energies of the microstates of one particle as  $e_1, e_2, e_3, \dots$ . The energies  $e_i$  are not necessarily all different since it is possible that some microstates have the same energy.

If one expands these products, one finds that  $B$  will be given by a sum of terms of the form  $\exp[-\beta\{e_i\}]$ . As above  $\{e_i\}$  mentions one of the possible sums of the energies of the particles. This gives

$$B = \sum \exp[-\beta\{e_i\}],$$

and one sees that  $B$  is the partition function of the system. Consequently,

$$Z = (Z_1)^N. \quad (2.21)$$

We shall take a simple example of a system with two particles, each with two possible energies  $e_1$  and  $e_2$ . The possible energies of the system or the different  $\{e_i\}$  are:  $e_1 + e_1$ ,  $e_1 + e_2$ ,  $e_2 + e_1$  and  $e_2 + e_2$ . One has

$$\begin{aligned} Z = & \exp[-\beta(e_1 + e_1)] + \exp[-\beta(e_1 + e_2)] \\ & + \exp[-\beta(e_2 + e_1)] + \exp[-\beta(e_2 + e_2)]. \end{aligned} \quad (2.22)$$

or noticing that  $\exp[-\beta(e_1 + e_1)] = \exp(-\beta e_1) \exp(-\beta e_1)$  one has, for  $a_i = \exp(-\beta e_i)$ , that  $Z = a_1 a_1 + 2a_1 a_2 + a_2 a_2 = (a_1 + a_2)^2 = (Z_1)^2$ .

### 2.1.3 A two-level system

We take the same example that we solved at the end of the preceding chapter. We recall that there are, for each particle, two possible states, one with energy 0 and the other with energy  $e$ .

We determine the partition function by the following two ways. The first is to calculate  $Z$  for the system of  $N$  particles. The second is to use (2.21) and to calculate the one particle partition function.

To be able to compute the partition function, we need to know the number of microstates with a given energy  $E = ne$ . This number has already been calculated and is equal to  $C_{nN} = N! / [(N - n)! n!]$ . Thus  $Z$  is using (2.12b),

$$Z = \sum_n C_{nN} \exp(-\beta ne) = \sum_n \frac{N!}{(N - n)! n!} x^n, \quad (2.23)$$

with

$$x = \exp(-\beta ne).$$

The sum in (2.23) is the development of the quantity  $(1+x)^N$ . Thus the final result is

$$Z = [1 + \exp(-\beta e)]^N. \quad (2.24)$$

This result agrees with what we said about the partition function of independent particles,  $Z = Z_1^N$ . The one-particle partition function is  $Z_1 = 1 + \exp(-\beta e)$ , since for a single particle there are only two states.

The free energy  $F$  is  $-k_B T \text{Ln } Z = -k_B T N \text{Ln}[1 + \exp(-\beta e)]$ . Now it is straightforward to get the energy and the entropy using the formulas (2.14) and (2.16) or from the derivatives of  $F$ , that they are  $E = F - T(\partial F/\partial T)_N$  and  $S = -(\partial F/\partial T)_N$ . One gets

$$E = \frac{Ne}{1 + \exp(\beta e)},$$

and

$$S = k_B N \left[ \frac{\frac{e}{k_B T}}{(1 + \exp(\frac{e}{k_B T}))} + \text{Ln} \left( 1 + \exp \left( -\frac{e}{k_B T} \right) \right) \right],$$

as founded above. (Eqs. (1.31) and (1.32b)).

Finally one calculates the chemical potential  $\mu = (\partial F/\partial N)_{T,V}$ :

$$\mu = \frac{\partial}{\partial N} \{-k_B T N \text{Ln}[1 + \exp(-\beta e)]\} = -k_B T \text{Ln}[1 + \exp(-\beta e)]. \quad (2.25)$$

#### 2.1.4 *The ideal gas; equipartition of energy in classical mechanics*

In this section we consider particles in classical mechanics. The energy of one particle is the sum of two terms, the kinetic energy  $E_K$  and the potential energy  $V_p$ , when  $E_K$  is a quadratic function of the particle velocities or the angular momentums and  $V$  is function of the particle positions. In one dimension (particles on a line of

length  $L$ ) the kinetic energy of one particle is  $E_K = p_x^2/2m$  and the partition function is

$$Z = \frac{1}{Q} \iint \exp[-\beta(E_K + V_p)] dp_x dx, \quad (2.26)$$

where the lower and upper limits of the integrals for the two variables ( $p_x, x$ ) are respectively  $-\infty$  and  $\infty$  for the momentum, and 0 and  $L$  for the position. It is the application of the general expression of the partition function (2.11)

$$Z = \sum_S \exp\left[-\frac{E_S}{k_B T}\right]$$

to the case of a single particle in classical mechanics. The introduction of the quantity  $Q$  is needed, since by definition  $Z$  is a quantity without dimension, but the double integral in (2.26) has the dimensionality of (momentum)(length). This is the reason why one has to introduce the quantity  $Q$  with this dimension. In fact the dimensionality of the product (momentum)(length) is the product (mass)(velocity)(length) or  $[M][v][L]$ . This product has the dimension of (energy)(time) =  $[E][T]$ . One can see by the following transformations  $[M][v][L] = [M[v][L][T]/[T] = [M][v]^2[T] = [E][T]$ . We shall see below which constant was chosen for  $Q$ .

The expression (2.26) can be transformed in the product of two integrals

$$Z = (1/Q) \int_{-\infty}^{\infty} \exp\left[-\frac{\beta p_x^2}{2m}\right] dp_x \int_0^L \exp[-\beta V_p(x)] dx. \quad (2.27)$$

Now we consider the case of particles without potential energy and only with kinetic energy. It is the case of the monatomic ideal gas where the atoms have only kinetic energy and there is no interaction between them. This absence of interaction is characteristic of the concept of ideal gas. The one-particle partition function becomes

$$\begin{aligned} Z_1 &= \frac{1}{Q} \int_{-\infty}^{\infty} \exp\left[-\frac{\beta p_x^2}{2m}\right] dp_x \int_0^L dx \\ &= \frac{L}{Q} \int_{-\infty}^{\infty} \exp\left\{-\left[\frac{p_x^2}{2m k_B T}\right]\right\} dp_x. \end{aligned}$$

To calculate  $Z_1$  we use the following trick: we divide the integral by  $(2m k_B T)^{0.5}$  and multiply it by the same factor. This gives

$$Z_1 = (2m k_B T)^{0.5} \frac{L}{Q} \int_{-\infty}^{\infty} \exp \left\{ - \left[ \frac{p_x^2}{2m k_B T} \right] \right\} d[p_x / (2m k_B T)^{0.5}]. \quad (2.28)$$

The integral is now a definite integral of the variable  $u = p_x / (2m k_B T)^{0.5}$  with the same limits ( $-\infty$  and  $\infty$ )

$$Z_1 = (2m k_B T)^{0.5} \frac{L}{Q} \int_{-\infty}^{\infty} \exp(-x^2) dx.$$

If there is no potential energy for the particle the partition function becomes

$$Z_1 = A(2m k_B T)^{0.5} \frac{L}{Q} \quad (2.29)$$

where  $A = \int_{-\infty}^{\infty} \exp(-x^2) dx = \sqrt{\pi}$ . The energy is calculated through the formulas  $E = F - T \frac{\partial F}{\partial T}$  and  $F = -k_B T \ln Z_1$ . Note that we do not need to need the value of  $A$  to calculate the energy. One gets

$$E = \frac{1}{2} k_B T. \quad (2.30)$$

This energy is the mean kinetic energy of the particle and is called the thermal energy of the particle. It is a remarkable result that this mean kinetic energy is proportional to the temperature. For  $N$  particles one multiplies the above result by  $N$ .

In the case of a particle in three dimensions the kinetic energy is  $E_K = (p_x^2 + p_y^2 + p_z^2) / 2m$ . The partition function is now a multiple integral

$$Z_1 = \left( \frac{1}{Q^3} \right) \int \exp \left\{ -\beta \left[ \frac{p_x^2 + p_y^2 + p_z^2}{2m} + V_p(x, y, z) \right] \right\} dp_x dp_y dp_z dx dy dz. \quad (2.31)$$

If there is no potential energy it reduces to

$$Z_1 = \left( \frac{1}{Q^3} \right) \int \exp \left\{ -\beta \left[ \frac{p_x^2 + p_y^2 + p_z^2}{2m} \right] \right\} dp_x dp_y dp_z dx dy dz. \quad (2.32)$$

This can be written as the product of three integrals (when the integral on the variables  $x, y$  and  $z$  is equal to  $V$ )

$$Z_1 = \left(\frac{V}{Q^3}\right) \int_{-\infty}^{\infty} \exp\left[-\frac{\beta p_x^2}{2m}\right] dp_x \int_{-\infty}^{\infty} \exp\left[-\frac{\beta p_y^2}{2m}\right] dp_y \\ \times \int_{-\infty}^{\infty} \exp\left[-\frac{\beta p_z^2}{2m}\right] dp_z, \quad (2.33)$$

and from the above results we conclude

$$Z_1 = \frac{V}{Q^3} (2\pi m k_B T)^{3/2}, \quad (2.34)$$

and finally

$$E = \frac{3}{2} k_B T. \quad (2.35)$$

The preceding results can be generalized in the following formulation. If in the total energy of a system there is a term which is quadratic in some parameter like the momentum or the position, this term contributes to the energy by the amount  $(1/2)k_B T$ . The parameter is called a degree of freedom.

A simple application of this theorem of equipartition is the one-dimensional harmonic oscillator. Its energy is  $E = p^2/(2m) + Kx^2/2$ . In thermal contact with a reservoir at temperature  $T$ , its thermal energy is  $k_B T$ , since there are two degrees of freedom.

Now we come back to the value of  $Q$ . The expression (2.34) is the one-particle partition function of the ideal gas (in three dimensions). Below in the Chapter 4, we shall calculate this partition function from the quantum mechanical principles. In order to make the two results identical (in this chapter and in Chapter 4) one has to choose  $Q = h$ , the Planck constant, the Planck constant has effectively the dimension of (energy)(time).

## 2.2 The Grand Canonical Ensemble

In the present case, one supposes that the system and the reservoir are made by the same type of particles. The system is in thermal

contact with the reservoir, but now the walls, which delimitate the volume  $V$  of the system, are permeable to the particles. The state of the system is determined by the temperature, volume and chemical potential of the reservoir. The energy and density are fluctuating quantities and one looks for their mean values that we consider equal to the macroscopic values.

### 2.2.1 *The grand partition function*

As above, we consider a large ensemble of identical systems. We are looking for the probability  $p_s$  to find the system in a microstate  $s$  with energy  $E_S$  and number of particles  $n_s$ . We begin with the same expressions as above by writing  $p_s$  as given in (2.1), but in specifying that the number of microstates are functions of the energy and the number of particles:

$$p_s = \frac{\Omega_R(E_0 - E_S, N_0 - n_s)}{\Omega_{GS}(E_0, N_0)}. \quad (2.36)$$

Let  $N_0$  is the number of particles in the grand system, a constant, and  $N_0 - n_s$  the number of particles in the reservoir. We write again as above

$$\begin{aligned} S_{GS} &= k_B \text{Ln } \Omega_{GS}(E_0, N_0), \\ S_R &= k_B \text{Ln } \Omega_R(E_0 - E_S, N_0 - n_s), \end{aligned}$$

or

$$\Omega_{GS}(E_0) = \exp\left[\frac{S_{GS}(E_0, N_0)}{k_B}\right], \quad (2.37)$$

$$\Omega_R(E_0 - E_S) = \exp\left[\frac{S_R(E_0 - E_S, N_0 - n_s)}{k_B}\right]. \quad (2.38)$$

In the following steps we use the thermodynamic relation  $E = TS - PV + \mu N$  to write  $S$  in the following form

$$S = \frac{PV}{T} + \frac{E - \mu N}{T}. \quad (2.39)$$

Substituting into (2.37) and (2.38) one gets

$$\begin{aligned}
 \Omega_{GS}(E_0, N_0) &= \exp\left[\frac{P_{GS}V_{GS}}{T} + \frac{E_0 - \mu N_0}{k_B T}\right] \\
 &= \exp\left[\frac{P_{GS}V_{GS}}{k_B T}\right] \exp\left[\frac{E_0 - \mu N_0}{k_B T}\right] \\
 &= A_{GS} \exp\left[\frac{E_0 - \mu N_0}{k_B T}\right], \tag{2.40}
 \end{aligned}$$

with  $A_{GS} = \exp[(P_{GS}V_{GS})/(k_B T)]$ .

For  $\Omega_R(E_0 - E_s, N_0 - n_s)$ , one has

$$\begin{aligned}
 \Omega_R(E_0 - E_s, N - n_s) &= \exp\left[\frac{P_R V_R}{k_B T}\right] \exp\left[\frac{E_0 - E_S}{k_B T} - \frac{\mu(N_0 - n_s)}{k_B T}\right] \\
 &= A_R \exp\left[\frac{E_0 - E_S}{k_B T} - \frac{\mu(N_0 - n_s)}{k_B T}\right] \\
 &= A_R \exp\left[\frac{E_0 - \mu N_0}{k_B T}\right] \exp\left[-\frac{E_S - \mu n_s}{k_B T}\right], \tag{2.41}
 \end{aligned}$$

with  $A_R = \exp[(P_R V_R)/(k_B T)]$ .

Putting (2.40) and (2.41) in (2.36) gives

$$p_s = \frac{A_R}{A_{GS}} \exp\left[-\frac{E_S - \mu n_s}{k_B T}\right]. \tag{2.42}$$

The sum of the probabilities over all the microstates  $\sum_S p_s = 1$ .

Thus

$$\sum_S p_s = \frac{A_R}{A_{GS}} \sum_S \exp\left[-\frac{E_S - \mu n_s}{k_B T}\right] = 1,$$

and this means that

$$\frac{A_{GS}}{A_R} = \sum_S \exp\left[-\frac{E_S - \mu n_s}{k_B T}\right].$$

Finally we arrive at the final result for  $p_s$ ,

$$p_s = \frac{\exp\left[-\frac{E_s - \mu n_s}{k_B T}\right]}{\sum_S \exp\left[-\frac{E_s - \mu n_s}{k_B T}\right]}. \tag{2.43}$$

We stress again that the sum is over all the possible microstates of the system with all the possible energies and number of particles. The values of the mean energy and the mean number of particles are  $E = \sum_S p_S E_S$  and  $N = \sum_S p_S n_S$ . But we can get these values through the grand partition function  $Z_G$  defined by

$$Z_G = \sum_s \exp[-\beta(E_S - \mu n_s)], \quad (2.44)$$

with  $\beta = 1/(k_B T)$ . The sum (2.44) is in fact a double sum, on the microstates and on the number of particles.  $Z_G$  is a function of  $T, V$  and  $\mu$ .

### 2.2.2 *The number of particles, energy, entropy and the grand potential*

The mean number of the particles  $N$  in the system is given by

$$N = \sum_s n_s p_S = \frac{\sum_s n_s \exp[-\beta(E_S - \mu n_s)]}{\sum_s \exp[-\beta(E_S - \mu n_s)]}. \quad (2.45)$$

Recalling that that the numerator of (2.45) is the derivative of the denominator, relatively to  $\mu$ , divided by  $\beta$ , and with a change in the sign, (2.45) can be written as

$$N = \frac{\frac{1}{\beta} \frac{\partial Z_G}{\partial \mu}}{Z_G} = \frac{1}{\beta} \frac{\partial \text{Ln } Z_G}{\partial \mu}. \quad (2.46)$$

The energy  $E = \sum_s p_S E_S$  can be calculated with the help of the derivative  $\frac{\partial \text{Ln } Z_G}{\partial \beta}$ , which is

$$\frac{\partial \text{Ln } Z_G}{\partial \beta} = - \frac{\sum_s (E_S - \mu n_s) \exp[-\beta(E_S - \mu n_s)]}{\sum_s \exp[-\beta(E_S - \mu n_s)]}. \quad (2.47)$$

The numerator of (2.47) is

$$- \sum_s E_S \exp[-\beta(E_S - \mu n_s)] + \sum_s \mu n_s \exp[-\beta(E_S - \mu n_s)],$$

and consequently  $\partial \text{Ln } Z_G / \partial \beta$  is the sum of two terms. The first is

$$- \frac{\sum_s E_S \exp[-\beta(E_S - \mu n_s)]}{\sum_s \exp[-\beta(E_S - \mu n_s)]}, \quad (2.48)$$

which is  $-\sum_s p_s E_s = -E$ . The second term is

$$\frac{\sum_s \mu n_s \exp[-\beta(E_s - \mu n_s)]}{\sum_s \exp[-\beta(E_s - \mu n_s)]}$$

which is equal to

$$\begin{aligned} & \mu \frac{\sum_s n_s \exp[-\beta(E_s - \mu n_s)]}{\sum_s n_s \exp[-\beta(E_s - \mu n_s)]} \\ & = \mu \sum_s p_s n_s = \mu N. \end{aligned} \quad (2.49)$$

Finally one gets  $\partial \text{Ln } Z_G / \partial \beta = -E + \mu N$ , and for  $E$  one has

$$E = -\frac{\partial \text{Ln } Z_G}{\partial \beta} + \mu N = -\frac{\partial \text{Ln } Z_G}{\partial \beta} + \frac{\mu}{\beta} \frac{\partial \text{Ln } Z_G}{\partial \mu}, \quad (2.50)$$

when  $N$  was replaced by its value in (2.46),  $(1/\beta)(\partial \text{Ln } Z_G / \partial \mu)$ .

Since  $E$  is equal to  $-\partial \text{Ln } Z / \partial \beta$ , we have the following relation between the grand partition function and the partition function  $Z$  of a system with the same temperature, the same mean energy and a number of particles equal to the mean number of particles of our present system,

$$\frac{\partial \text{Ln } Z_G}{\partial \beta} = \frac{\partial \text{Ln } Z}{\partial \beta} + \mu N. \quad (2.51)$$

The entropy is determined using (2.51). We saw above, in the section on the canonical ensemble expression (2.16),

$$S = \frac{E}{T} + k_B \text{Ln } Z.$$

Integrating (2.51) gives

$$\text{Ln } Z_G = \text{Ln } Z - \int \mu N d\beta = \text{Ln } Z - \mu N \beta. \quad (2.52)$$

From (2.16) one gets

$$\text{Ln } Z = \frac{S - E/T}{k_B}. \quad (2.53)$$

Introducing this expression of  $\text{Ln } Z$  in (2.52) gives

$$S = \frac{E - \mu N}{T} + k_B \text{Ln } Z_G. \quad (2.53)$$

From (2.50),  $E - \mu N = -\partial \text{Ln } Z_G / \partial \beta$ , and upon introducing it in (2.53),

$$S = \frac{-\frac{\partial \text{Ln } Z_G}{\partial \beta}}{T} + k_B \text{Ln } Z_G,$$

$$S = -k_B \beta \frac{\partial \text{Ln } Z_G}{\partial \beta} + k_B \text{Ln } Z_G. \quad (2.54)$$

It is not difficult to verify the relation  $S = -k_B \sum_s p_s \text{Ln } p_s$ , in analogy with the established cases.

From the preceding results, one deduces the grand potential  $\Psi$  given by

$$\Psi(T, V, N) = -PV = E - TS - \mu N \quad (2.55a)$$

$$= -k_B T \text{Ln } Z_G, \quad (2.55b)$$

where its differential is  $d\Psi = -S dT + P dV - N d\mu$ . To get (2.55b), one inserts in (2.55a) the value of  $E - \mu N = \frac{\partial \text{Ln } Z_G}{\partial \beta}$  (see (2.50)), and  $S$  from (2.54). The expression (2.55) is the third link between the macroscopic thermodynamic description and the microscopic side.

### 2.2.3 *An example*

One considers a system in contact with a reservoir in the conditions of the grand canonical ensemble. This system is made of particles without interaction with energies  $0, e, 2e, 3e, \text{ etc.}$  The grand partition function is the double sum

$$Z_G = \sum_s \exp[-\beta(E_S - \mu n_s)],$$

which can be written as

$$Z_G = \sum_s [\exp(\beta \mu n_s) \sum_s \exp(-\beta E_S)]. \quad (2.56)$$

First one performs the sum over the microstates of a system with  $n_s$  particles and then to sum over the number of particles, from 0 to the infinity. The sum  $\sum_s \exp(-\beta E_S)$  is the partition function of  $n_s$  particles (with the same volume  $V$  and temperature  $T$ ). It is not possible to use the expression (2.21),  $Z = (Z_1)^N$ , since now the

particles are indistinguishable. In the case of the grand canonical ensemble, the particles may leave the system to enter the reservoir, and vice versa, as a gas. This prevents the case when they are viewed as distinguishable. This fact makes the determination of the partition function difficult.

We shall consider a particular situation that we shall call the *classical limit* which in the next chapter we shall explain why. We suppose that particles are distributed among their possible energies or levels as follows: either one particular level is populated by one particle or it is not, i.e. there is no particle with this energy. When one considers a given repartition of the  $n_s$  particles in the energy levels, a particular microstate is defined. If now one changes the position of some particles, keeping the same occupied levels, one has the same microstate. To take into account this fact one divides the partition function by the number of possible permutations of the particles between the occupied levels, i.e. by  $n_s!$ . Thus the partition function of the  $n_s$  particles is

$$Z = \frac{(Z_1)^{n_s}}{n_s!}. \quad (2.57)$$

We shall find again this expression by another method in Chapter 3.

The grand partition function is now

$$Z_G = \sum_s \left\{ \exp(\beta\mu n_s) \frac{[\sum_i \exp(-\beta e_i)]^{n_s}}{n_s!} \right\}, \quad (2.58)$$

with  $e_i = 0, e, 2e, 3e, \text{etc.}$

The sum  $\sum_i \exp(-\beta e_i)$  is equal to  $[1 - \exp(-\beta e)]^{-1}$ , this gives

$$Z_G = \sum_s \frac{\exp(\beta\mu n_s) [1 - \exp(-\beta e)]^{-n_s}}{n_s!} \quad (2.59)$$

$$= \sum_s \frac{\{\exp(\beta\mu) [1 - \exp(-\beta e)]^{-1}\}^{n_s}}{n_s!}, \quad (2.60)$$

or with  $x = \exp(\beta\mu) [1 - \exp(-\beta e)]^{-1}$ ,

$$Z_G = \sum_s \frac{x^{n_s}}{n_s!} = \exp(x), \quad (2.61)$$

where we used the series expansion of the function  $\exp(x)$ . Our final result is

$$Z_G = \exp\{\exp(\beta\mu)[1 - \exp(-\beta e)]^{-1}\}, \quad (2.62)$$

$$\text{Ln } Z_G = \exp(\beta\mu)[1 - \exp(-\beta e)]^{-1}, \quad (2.63)$$

$$\Psi = -k_B T \text{Ln } Z_G = -k_B T \exp(\beta\mu)[1 - \exp(-\beta e)]^{-1}. \quad (2.64)$$

Now one can calculate the mean number of particles  $N$

$$N = \frac{1}{\beta} \frac{\partial \text{Ln } Z_G}{\partial \mu} = \exp(\beta\mu)[1 - \exp(-\beta e)]^{-1}. \quad (2.65)$$

Putting this expression in (2.64) gives the equation of state

$$-\Psi = PV = N k_B T. \quad (2.66)$$

From (2.65) one gets an expression for the chemical potential  $\mu$

$$\mu = k_B T [\text{Ln}(N) + \text{Ln}(1 - \exp(-\beta e))]. \quad (2.67)$$

The derivative of  $\text{Ln } Z_G$  relatively to  $\beta$  is, following (2.50),

$$\frac{\partial \text{Ln } Z_G}{\partial \beta} = \mu N - E. \quad (2.68)$$

One has

$$\frac{\partial \text{Ln } Z_G}{\partial \beta} = \mu \exp(\beta\mu)[1 - \exp(-\beta e)] - \frac{\exp(\beta\mu) e \exp(-\beta e)}{[1 - \exp(-\beta e)]^2} \quad (2.69)$$

Taking into account of (2.65) one can write

$$\frac{\partial \text{Ln } Z_G}{\partial \beta} = \mu N - N e \frac{\exp(-\beta e)}{1 - \exp(-\beta e)} \quad (2.70)$$

Comparing (2.68) and (2.70) gives

$$E = N e \frac{\exp(-\beta e)}{1 - \exp(-\beta e)} = \frac{N e}{\exp(\beta e) - 1}. \quad (2.71)$$

The entropy can be calculated through the formula  $E = TS - PV + \mu N$ , giving

$$S = \frac{E}{T} + \frac{PV}{T} - \frac{\mu N}{T}.$$

Taking into consideration (2.66), (2.67) and (2.71) one gets

$$\frac{S}{k_b N} = \frac{\frac{e}{k_B T}}{\exp(e/k_B T) - 1} + 1 - \text{Ln } N - \text{Ln} \left[ 1 - \exp\left(-\frac{e}{k_B T}\right) \right]. \quad (2.72)$$

In the next chapter we shall show that, in the conditions we choose, the chemical potential is negative such that the entropy is

always positive. It is also possible to verify that  $S$  is an increasing function of the temperature.

The condition that  $\mu < 0$  gives the regime of validity of this problem. Writing, from (2.67), that

$$\frac{\mu}{k_B T} = \text{Ln } N + \text{Ln}(1 - \exp(-\beta e)) < 0$$

gives

$$\text{Ln } N + \text{Ln}[1 - \exp(-\beta e)] = \text{Ln}[N(1 - \exp(-\beta e))] < 0$$

or

$$N[1 - \exp(-\beta e)] < 1.$$

Since  $N$  is very large, this means that  $1 - \exp(-\beta e)$  is very small. In other words,  $\exp(-\beta e)$  is very close to 1, i.e.  $\beta e$  is very small. Using the approximation  $\exp(-\beta e) \approx 1 - \beta e$ , the inequality  $N[1 - \exp(-\beta e)] < 1$  becomes  $\beta e < 1/N$  or  $T > eN/k_B$ . This means that the temperature is large enough and/or  $e$  (the distance between two consecutive levels) is very small. We shall see later that this situation is called the classical case.

## 2.3 Summary

We summarize the developments of the two last chapters. We exposed three methods, which establish the links between the microscopic description and the thermodynamics or macroscopic description of a system.

**The microcanonical ensemble.** The system is defined by the knowledge of the extensive variables like the energy  $E$ , the volume  $V$ , the number of particles  $N$ , etc. The thermodynamic potential is the entropy and the link is made by the relation

$$S(E, V, N) = k_B \text{Ln } \Omega,$$

where  $\Omega$  is the number of microstates of the system associated with the chosen values of the extensive variables. In general it is not an easy task to find  $\Omega(E, V, N)$  and it is why the method of the microcanonical is not frequently used.

**The canonical ensemble.** The system is defined through knowledge of the temperature, the volume and the number of particles. The thermodynamic potential is the Helmholtz free energy  $F$  and

the link is the partition function  $Z$ :

$$F(T, V, N) = -k_B T \text{Ln } Z$$

with  $Z$  equal to  $\sum_s \exp(-\beta E_S)$ . The sum is over all the microstates of the system. In this method, we need to determine the energies of all the microstates of the system. In the following, we shall use very often this method.

**The grand canonical ensemble.** In this case, the temperature, the volume and the chemical potential define the system. The thermodynamic potential is the grand potential  $\Psi$  and the link is the grand partition function  $Z_G$ :

$$\Psi(T, V, \mu) = -k_B T \text{Ln } Z_G$$

with  $Z_G = \sum_s \exp[-\beta(E_S - \mu n_s)]$ . The sum is a double sum over the possible energies of the microstates and the number of particles. This method seems complicated but it permits the introduction of a very important variable: the chemical potential. We shall see in the following chapters the usefulness of this variable.

In the last two methods, the goal is to calculate mean values of the variables that we take as the macroscopic values, neglecting fluctuations. This is possible, in general, because we deal with a very large number of particles. But near a critical point or a phase transition of second kind, this is not correct and the fluctuations need to be taken into account.

Nevertheless, the expressions that we got for  $p_s$  the probability to find the system in a given microstate  $s$  is correct whatever the number of particles is, even for one particle in the case of the canonical ensemble. Of course, in such a case, the fluctuations are important.

**The entropy.** The most general expression for the entropy, in these three approaches is

$$S = -k_B \sum_s p_s \text{Ln } p_s$$

where  $p_s$  is the probability to find the system in the microstate  $s$ .

### 2.3.1 *Fluctuations*

We have supposed that the mean value of the energy (and other quantities) is equal to its macroscopic value although we know that this

quantity fluctuates in the case of the canonical and grand canonical ensembles.

In the case of the thermal contact of the system with the reservoir, it was stated that the temperature is fixed when the energy is fluctuating. This means that there is constant transfer of energy from the reservoir to the system and vice versa. How is this possible if there is no temperature difference between the system and the reservoir? One possibility is the transfer of potential energy through the variations of the distances between particles since this kind of energy is dependant on distances. But in fact there are changes in the temperatures although they are so small that one does not consider them and accepts to say that the temperature is constant.

In thermodynamics, it is possible to calculate the mean standard deviations of the temperature and the energy in the system. It is the mean value of the squared difference between the fluctuating quantity and its mean value. We give the results without derivations. For the temperature one has  $(\Delta T)^2 = k_B T^2 / C_v$  where  $C_v$  is the constant volume specific heat, and for the energy one has  $(\Delta E)^2 = k_B T^2 C_v$ . The dimensionless ratio  $\delta = k_B [(\Delta T)^2 / (\Delta E)^2]^{0.5}$  can give a feeling of the relative magnitude of the fluctuations. One finds that  $\delta = k_B / C_v$ . We take as an example the monatomic ideal gas. In this case  $C_v$  is equal to  $(3/2) N k_B$  and the ratio  $\delta$  is equal to  $2/(3N)$ . For a mole,  $N$  is of order of  $10^{23}$  and  $\delta$  is very small. The fluctuation of the temperature is much smaller than those of the energy. The conclusion is that minuscule changes in the temperature may bring important changes in the energy.

### 2.3.2 *Final remark*

One can point out the analogy between the formulas giving the three thermodynamic potentials,  $-S$ ,  $F$  and  $\Psi$ :

$$\begin{aligned} -S &= -k_B \text{Ln } \Omega; \\ F &= -k_B T \text{Ln } Z; \\ \Psi &= -k_B T \text{Ln } Z_G. \end{aligned}$$