

## Chapter 2

# The Different Statistical Ensembles. General Methods in Statistical Physics

In the first chapter we convinced ourselves that the macroscopic properties of a physical system can only be analyzed through a statistical approach, in the framework of Statistical Physics.

Practically, the statistical description of a system with a very large number of particles in equilibrium, and the treatment of any *exercise* or *problem* of Statistical Physics, *always* follow the two steps (see the section General method for solving exercises and problems, at the end of Ch. 9) :

- *First, determination of the microscopic states* (microstates) accessible by the  $N$ -particles system : this is a Quantum Mechanics problem, which may be reduced to a Classical Mechanics one in some specific cases. § 2.1 will schematically present the most frequent situations.

- *Second, evaluation of the probability for the system to be in a particular microstate*, in the specified physical conditions : it is at this point that the statistical description comes in.

To solve this type of problem, one has to express that *in equilibrium the statistical entropy is maximum, under the constraints* defined by the physical situation under study : the system may be isolated, or in thermal contact

with a heat reservoir (a very large system, which will dictate its temperature), the system may exchange particles or volume with another system, and so forth. The experimental conditions define the constraint(s) from the conservation laws adapted to the physical situation (conserved total energy, conserved number of particles, etc.). In this chapter, the most usual statistical ensembles will be presented : “microcanonical” ensemble in § 2.2, “canonical” ensemble in § 2.4, “grand canonical” ensemble in § 2.5, using the names introduced at the end of the 19th century. In all these statistical ensembles, one reproduces the considered system in a thought experiment, thus realizing an assembly of macroscopic objects built under the same initial conditions, which allows average values of fluctuating physical parameters to be defined. For a given physical condition, one will decide to use the statistical ensemble most adapted to the analysis of the problem.

However, as will be shown, for systems with a *macroscopic* number of particles (the only situation considered in this book), there is equivalence, to a extremely small relative fluctuation, between the various statistical ensembles that will be described here : in the case of a macroscopic system, a measurement will not distinguish between a situation in which the energy is fixed and another one in which the temperature is given. It is only the convenience of treatment of the problem that will lead us to choose one statistical ensemble rather than another. (On the contrary for systems with a small number of particles, or of size intermediate between the microscopic and macroscopic ranges, the so-called “mesoscopic systems,” nowadays much studied in Condensed Matter Physics, the equivalence between statistical ensembles is not always valid.)

## 2.1 Determination of the Energy States of an $N$ -Particle System

For an individual particle  $i$  in translation, of momentum  $\vec{p}_i$  and mass  $m$ , under a potential energy  $V_i(\vec{r}_i)$ , the time-independent Schroedinger equation (eigenvalues equation) is

$$\begin{aligned}\hat{h}_i|\psi_i^{\alpha_i}\rangle &= \left(\frac{\hat{p}_i^2}{2m} + V_i(\vec{r}_i)\right)|\psi_i^{\alpha_i}\rangle \\ &= \varepsilon_i^{\alpha_i}|\psi_i^{\alpha_i}\rangle\end{aligned}\tag{2.1}$$

where  $\alpha_i$  expresses the different states accessible to this particle.

As soon as several particles are present, one has to consider their interactions, which leads to a several-body potential energy. Thus, the hamiltonian for  $N$  particles in motion, under a potential energy and mutual interactions, is given

by

$$\hat{H} = \sum_i \frac{\hat{p}_i^2}{2m} + V_i(\vec{r}_i) + \sum_{i < j} V_{ij}(\vec{r}_i, \vec{r}_j) \quad (2.2)$$

This is the case, for example, for the molecules of a gas, confined within a limited volume and mutually interacting through Van der Waals interactions; this is also the situation of electrons in solids in attractive Coulombic interaction with the positively charged nuclei ( $V_i$  term), and in repulsion between themselves ( $V_{ij}$  term). The latter interactions, expressed in the  $V_{ij}$ 's, are essential in the approach toward thermal equilibrium through the transitions they induce between microscopic states, but they complicate the solution of the  $N$ -particle eigenstate problem. Now they mostly correspond to energy terms very small with respect to those associated with the remaining part of the hamiltonian.

An analogous problem is faced when one is concerned by the magnetic moments of a ferromagnetic material : the hamiltonian of an individual electronic intrinsic magnetic moment located in a magnetic field is given by

$$\hat{h} = -\hat{\vec{\mu}}_B \cdot \vec{B} \quad (2.3)$$

where the Bohr magneton operator  $\hat{\vec{\mu}}_B$  is related to the spin operator  $\hat{\vec{S}}$  by :

$$\hat{\vec{\mu}}_B = -\frac{e}{m} \hat{\vec{S}} \quad (2.4)$$

and has for eigenvalues  $\mp e\hbar/2m$  (see a course of Quantum Mechanics). The hamiltonian of an ensemble of magnetic moments in a magnetic field  $\vec{B}$  contains, in addition to terms similar to  $\hat{h}$ , other terms expressing their mutual interactions, i.e.

$$\hat{H} = -\sum_i \hat{\vec{\mu}}_{Bi} \cdot \vec{B} + \sum_{i < j} J_{ij} \hat{\vec{\mu}}_{Bi} \cdot \hat{\vec{\mu}}_{Bj} \quad (2.5)$$

where  $J_{ij}$  is the coupling term between the moments localized at sites  $i$  and  $j$ . According to the site  $i$  or  $j$ , the moment orientation is different.

All these types of hamiltonians, in which several-particle terms appear, are generally treated through approximations, which allow them to be reduced to the simplest situation where  $\hat{H}$  is written as a *sum of similar hamiltonians*, each concerning a single particle. There are several methods to achieve such a reduction :

– either neglecting the interactions between particles in the equilibrium state, as they correspond to very small energies. As a consequence, in the above example of the gas molecules, the only term included in the potential energy

expresses the confinement with a box (confinement potential) or an external field (gravity); the particles are then considered as “free”;

– or using the so-called “mean field” treatment : each particle is subjected to a mean effect from the other ones. This will be a repulsive potential energy in the case of the Coulombic interaction between electrons in a solid, an effective magnetic field equivalent to the interactions from the other magnetic moments in the case of a ferromagnetic material;

– or changing of variable in the hamiltonian  $\hat{H}$ , in order to decouple the variables, so that  $\hat{H}$  may be re-written as a sum of terms (“normal modes” defining quasi-particles, for example, in the problem of the atomic vibrations in a crystal at a given temperature).

From now on, let us assume that the total-system hamiltonian is indeed expressed as the sum of similar individual-particle hamiltonians

$$\hat{H} = \sum_i \hat{h}_i, \quad \text{with } \hat{h}_i \psi_i^{\alpha_i}(\vec{r}_i) = \varepsilon_i^{\alpha_i} \psi_i^{\alpha_i}(\vec{r}_i) \quad (2.6)$$

Then it will only be necessary to solve the problem for an individual particle : indeed you learnt in Quantum Mechanics that the solution of

$$\hat{H} \psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = E \psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \quad (2.7)$$

is

$$\left( \sum_j \hat{h}_j \right) \left( \prod_{i=1}^N \psi_i^{\alpha_i}(\vec{r}_i) \right) = \left( \sum_j \varepsilon_j^{\alpha_j} \right) \left( \prod_{i=1}^N \psi_i^{\alpha_i}(\vec{r}_i) \right) \quad (2.8)$$

i.e.,

$$E = \sum_i \varepsilon_i^{\alpha_i}, \quad \psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \prod_{i=1}^N \psi_i^{\alpha_i}(\vec{r}_i) \quad (2.9)$$

The total energy of the system is the sum of the individual particle energies and the  $N$ -particle eigenfunction is the product of the eigenfunctions for each single particle.

In the first three chapters of this book, the problems studied will concern discrete variables (for example, spin magnetic moments) or particles distinguishable by their *fixed* coordinates, like the atoms of a solid vibrating around their equilibrium position at finite temperature. The systems with translation degrees of freedom will be analyzed in the classical framework in chapter 4 (ideal gas), or in the framework of the Quantum Statistics from chapter 5 until the end of the course : in the Quantum Statistics description of the accessible

microstates, one has to account for the indistinguishability of the particles, as expressed by the Pauli principle.

In all that follows, we will assume that the microscopic states of the considered system are known. We are going to rely on the hypothesis of maximum entropy, as introduced in chapter 1, § 1.3 and § 1.4, under the specific physical constraints due to the given experimental conditions ; we will then deduce the system macroscopic properties, using Statistical Physics.

## 2.2 Isolated System in Equilibrium : “Microcanonical Ensemble”

In such a system one assumes that there is no possible exchange with its surroundings (Fig. 2.1) : the volume is fixed, the number of particles  $N$  is given, the total energy assumes a fixed value  $E$ , i.e., its lies in the range between  $E$  and  $E + \delta E$ , where  $\delta E$  is the uncertainty. This situation is called “*microcanonical ensemble*.” It is the framework of application of the Boltzmann hypothesis of equiprobability of the  $W(E)$  accessible microstates (§ 1.3.3). The probability to realize any of these microstates is equal to  $1/W(E)$  ; the statistical entropy  $S$  is maximum under these conditions (with respect to the situation where the probabilities would not be equal) and is given by

$$S = k_B \ln W(E) \quad (2.10)$$

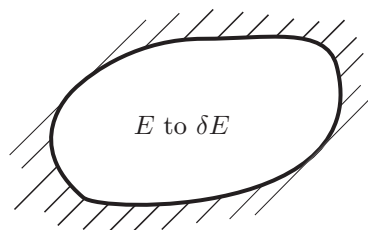


FIG. 2.1 : Isolated system. Its energy has a fixed value.

To solve this type of problem, one has to determine  $W(E)$  : this means performing a combinatory calculation of the number of occurrences of the macroscopic energy  $E$  from the various configurations of the microscopic components of the system. For example, for an ensemble of localized magnetic moments located in an external magnetic field, to each fixed value of  $E$  corresponds a value of the macroscopic magnetization. The corresponding number of microstates  $W(E)$  was evaluated in § 1.3.1. The other physical macroscopic parameters

are deduced from  $S$  and its partial derivatives (see § 3.5). In particular a microcanonical temperature is defined from the partial derivative of  $S$  versus  $E$  :  $1/T = \partial S / \partial E$ .

## 2.3 Equilibrium Conditions for Two Systems in Contact, Only Exchanging Energy

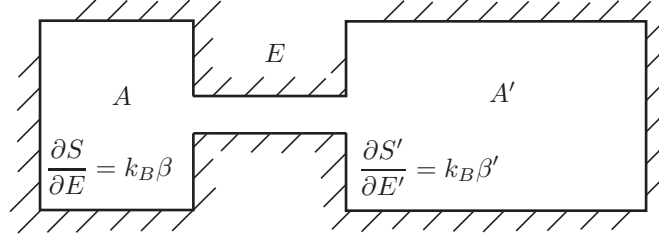


FIG. 2.2: The systems  $A$  and  $A'$  only exchange energy, the combined system  $A_0 = A + A'$  is isolated.

Two distinct systems  $A$  and  $A'$  are brought into thermal contact. The system  $A_0$ , made up of the combination of  $A$  and  $A'$  (Fig. 2.2) is the isolated system, to which we can apply the above approach, i.e. look for the maximum of its statistical entropy. The systems in contact,  $A$  and  $A'$ , can only exchange energy and are weakly coupled, which means that a possible interaction energy is neglected. We can also say that the system  $A$  under study has the constraint to be coupled to  $A'$ , the total energy  $E + E'$  being conserved. This is a very common situation, like the one of a drink can in a refrigerator, the ensemble (can-refrigerator) being taken as thermally insulated from the room in which the refrigerator stands, the room representing the surroundings.

### 2.3.1 Equilibrium Condition : Equal $\beta$ Parameters

The total energy and the total statistical entropy are shared between  $A$  and  $A'$  :

$$E_0 = E + E' \quad (2.11)$$

$$S_{A_0}(E_0, E) = S_A(E) + S_{A'}(E_0 - E) \quad (2.12)$$

From the Boltzmann relation (2.10), the equation (2.12) is equivalent to

$$W_0(E_0, E) = W_A(E) \cdot W_{A'}(E_0 - E) \quad (2.13)$$

since for weakly coupled systems the number of microstates of the combined system is the product of the numbers of microstates of the two subsystems.

After a long enough time has elapsed, the combined system (can-refrigerator)  $A_0$  reaches an equilibrium situation. Since the combination  $A_0$  of the two systems  $A$  and  $A'$  is an isolated system, in equilibrium its entropy is maximum with respect to the exchange of energy between  $A$  and  $A'$  :

$$S_{A_0}(E_0, E) = S_A(E) + S_{A'}(E_0 - E) \quad (2.14)$$

$$\frac{\partial S_{A_0}(E_0, E)}{\partial E} = 0, \text{ i.e., } \frac{\partial S_{A_0}(E_0, E)}{\partial E} = \frac{\partial S_A(E)}{\partial E} + \frac{\partial S_{A'}(E_0 - E)}{\partial E} = 0 \quad (2.15)$$

Once the equilibrium has been reached :

$$\frac{\partial S_A(E)}{\partial E} = - \frac{\partial S_{A'}(E_0 - E)}{\partial E} = \frac{\partial S_{A'}(E')}{\partial E'} \quad (2.16)$$

The obtained equilibrium condition is that the *partial derivative of entropy versus energy* takes the *same value* in *both systems* in contact,  $A$  and  $A'$ , all the other parameters (volume, etc.) being kept constant. This derivative will be written :

$$\frac{\partial S}{\partial E} = k_B \beta \quad (2.17)$$

where  $k_B$  is the Boltzmann constant.

In equilibrium, reached for an energy value of system  $A$  equal to  $E = \tilde{E}$ , one thus has

$$\beta = \beta' \quad (2.18)$$

We know that the entropy  $S$  and the energy  $E$  are both *extensive\** parameters : by definition the values of extensive parameters are doubled when the system volume  $\Omega$  is doubled together with the number  $N$  of particles, while the density  $N/\Omega$ , an *intensive\** parameter, is maintained in such a transformation. In such a process, the parameter  $\beta$  is not changed, it is an *intensive* parameter having the dimension of reciprocal energy, the dimension of  $k_B \beta$  being a reciprocal temperature. In § 3.3 the partial derivative of the entropy versus energy will be identified with  $1/T$ , where  $T$  is the absolute temperature, so that (2.18) expresses that in equilibrium  $T = T'$ .

### 2.3.2 Fluctuations of the Energy Around its Most Likely Value

The number of microstates of the total system  $A_0$  realizing the splitting of the energies [ $E$  in  $A$ ,  $E_0 - E$  in  $A'$ ] is proportional to the product

$W_A(E) \cdot W_{A'}(E_0 - E)$ . The probability of occurrence of the corresponding microstate is

$$p(E, E_0 - E) = \frac{W_A(E)W_{A'}(E_0 - E)}{\sum_E W_A(E)W_{A'}(E_0 - E)} = \frac{W_A(E)W_{A'}(E_0 - E)}{W_{\text{tot}}(E_0)} \quad (2.19)$$

Let us consider the *variation* of this probability versus  $E$  around the value  $\tilde{E}$  achieving the entropy maximum with respect to an energy exchange between  $A$  and  $A'$ . In (2.19), only the numerator is a function of  $E$ , since the denominator is a sum over all the possible values of  $E$ .

For a macroscopic system,  $W(E)$  increases very fast with  $E$ , as already verified on the example of free particles in Appendix 3 of Chapter 1. On the other hand,  $W_{A'}(E_0 - E)$  strongly decreases with  $E$  if  $A'$  is macroscopic. Their product goes through a very steep maximum, corresponding to the state of maximum probability of the combined system, reached for  $E = \tilde{E}$ . This energy is very close to the average value  $\langle E \rangle$  of the energy in system  $A$ , as the probability practically vanishes outside the immediate vicinity of  $\tilde{E}$ . The probability variation around  $\tilde{E}$  is much faster than that of its logarithm, which varies versus  $E$  in the same way as

$$S_{A_0}(E) = k_B \ln[W_A(E)W_{A'}(E_0 - E)] \quad (2.20)$$

because the combined system  $A_0$  is isolated.

Note that in the particular case of a free-particle system, where  $W(E) \sim E^N$  (see Appendix 3, Chapter 1),  $\beta = \left( \frac{\partial S}{\partial E} \right)_\Omega$  is of the order of  $N/E$ . Since the total energy is of the order  $\tilde{E}$ , the average energy per particle is of the order  $1/\beta = k_B T$ , to a numerical factor of order unity. The average energy of a free particle at temperature  $T$  is thus of order  $k_B T$ .

Now we look for the probability *variation* versus the energy of system  $A$  for  $E$  close to the most likely value  $\tilde{E}$ . The logarithm of this probability is proportional to the entropy of the combined system  $S_{A_0}(E)$ , considered as a function of  $E$ , as  $A_0$  is an isolated system to which the Boltzmann formula  $S_{A_0}(E) = k_B \ln W_0(E)$  applies.

In equilibrium, the entropy of the combined system  $A_0$  is maximum with respect to an energy exchange between the two systems; the entropy of  $A_0$  can be developed around this maximum, for  $E - \tilde{E}$  small :

$$S_{A_0}(E) = S_{A_0}(\tilde{E}) + \left( \frac{\partial S_{A_0}}{\partial E} \right)_{\tilde{E}} (E - \tilde{E}) + \frac{1}{2} \left( \frac{\partial^2 S_{A_0}}{\partial E^2} \right)_{\tilde{E}} (E - \tilde{E})^2 + O((E - \tilde{E})^3) \quad (2.21)$$



Here the first derivative is equal to zero and the second derivative is negative, as the extremum is a maximum. This second derivative includes the contributions of both  $A$  and  $A'$  and is equal to :

$$\frac{\partial^2 S_{A_0}}{\partial E^2} = \frac{\partial^2 S_A}{\partial E^2} + \frac{\partial^2 S_{A'}}{\partial E'^2} = k_B \left( \frac{\partial \beta}{\partial E} + \frac{\partial \beta'}{\partial E'} \right) = -k_B \lambda_0 \quad (2.22)$$

All these terms are calculated for  $E = \tilde{E}$ . In fact, since  $\beta = 1/k_B T$ , stating that  $\partial \beta / \partial E$  is negative means that the internal energy increases with temperature : this is always realized in practical cases.<sup>1</sup>

From the entropy properties (2.21) and (2.22), using the Boltzmann relation one deduces those of the number of accessible microstates :

$$W_0(E) \approx W_0(\tilde{E}) \exp \left[ -\lambda_0 (E - \tilde{E})^2 / 2 \right] \quad (2.23)$$

The probability of realizing the state with the sharing of the energies [ $E$  in system  $A$  and  $E_0 - E$  in system  $A'$ ] is proportional to  $W_0(E)$ . It is given by

$$p(E, E_0 - E) \approx p(\tilde{E}, E_0 - \tilde{E}) \exp \left( -\lambda_0 (E - \tilde{E})^2 / 2 \right) \quad (2.24)$$

This is a Gaussian function around the equilibrium state  $\tilde{E}$ . Its width  $\Delta E = 1/\sqrt{\lambda_0}$  depends of the size of the total system like

$$\left( \frac{\partial \beta}{\partial E} + \frac{\partial \beta'}{\partial E'} \right)^{-1/2} \quad (2.25)$$

that is, like the square root of a number of particles, since  $E$  and  $E'$  are extensive and the parameters  $\beta$  and  $\beta'$  intensive. The *relative* width  $\Delta E / \tilde{E}$  varies as a reciprocal number of particles. For a macroscopic system, where  $N$  and  $N' \sim 10^{23}$ , this relative width is of the order of  $10^{-11}$ , thus unmeasurable : the fluctuations of the energy of system  $A$  around its equilibrium value are practically null. This is equivalent to saying that, for a system with a very large number of particles, situations *i*), in which the energy of  $A$  is exactly equal to the value  $\tilde{E}$ , and *ii*), in which system  $A$  reached an equilibrium energy  $\tilde{E}$  through exchanges with a heat reservoir, lead to the same physical measurement of the energy.

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<sup>1</sup>When the total energy has an upper bound, as in the case of the spins in a paramagnetic solid, the maximum energy is reached when all the magnetic moments are antiparallel to the applied magnetic field. In the vicinity of this maximum, adding energy produces a decrease in entropy, so that (2.17) leads to a negative  $\beta$ , thus to a “negative temperature.” However in the situation of a *real* paramagnetic solid, the spin degree of freedom is in equilibrium with the other degrees of freedom, like the ones related to the atoms’ vibrations around their equilibrium positions. For the latter ones, the energy is not limited and for the whole solid, the total energy indeed increases with temperature.

## 2.4 System in Contact with a Heat Reservoir, “Canonical Ensemble”

When two systems are brought into thermal contact, one being much larger than the other (the can is much smaller than the refrigerator) (Fig. 2.3), the larger system behaves like a heat reservoir of energy  $E_0 - E$  close to  $E_0$ , the energy  $E$  of the other system thus being very small. The statistical entropy, and, consequently, the parameter  $\beta$  of the larger system, are close to those of the total system :

$$\left( \frac{\partial S_{A'}}{\partial E'} \right)_{E_0-E} = \left( \frac{\partial S_{A'}(E)}{\partial E} \right)_{E_0} - E \left( \frac{\partial^2 S_{A'}(E)}{\partial E^2} \right)_{E_0} + O(E^2) \quad (2.26)$$

$$= k_B \beta_0 - E \left( \frac{\partial^2 S_{A'}(E)}{\partial E^2} \right)_{E_0} + O(E^2) \quad (2.27)$$

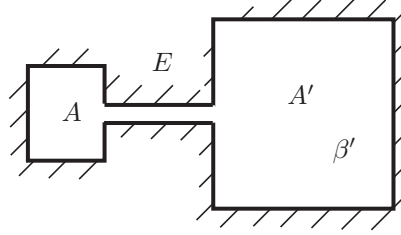


FIG. 2.3: The system  $A$  is in contact with the heat reservoir  $A'$  which dictates its parameter  $\beta'$  to  $A$ .

When the equilibrium is reached, the parameter  $\beta$  of the smaller system is adjusted to the parameter  $\beta'$  of the larger system, which itself takes a value close to that of the parameter  $\beta_0$  of the ensemble : the larger system acts as a *heat reservoir* or *thermostat*, a body that keeps its value of  $\beta$  and dictates this parameter to the smaller system (we will see in chapter 3 that this is equivalent to saying that it keeps its temperature when put in thermal contact : for example, in equilibrium the can takes the temperature of the refrigerator). The smaller system  $A$  can be a macroscopic system, sufficiently smaller than  $A'$ , or even a single microscopic particle, like an individual localized magnetic moment inside a paramagnetic solid, with respect to which the rest of the macroscopic solid plays the role of a reservoir.

The situation in which the system under study is in thermal contact with a heat reservoir that gives its temperature  $T$  to the system is called “canonical,” since it is a very frequent situation among the studied problems. The ensemble

of systems in contact with the heat reservoir, on which we will calculate the ensemble average, is the “canonical ensemble.”

### 2.4.1 The Boltzmann Factor

We are thus in the situation where a smaller system  $A$  is coupled to a larger system  $A'$  that dictates its value of the parameter  $\beta$ , which is close to the value for the combined isolated system.

First consider the probability  $p_i$  that a *specific microstate*  $i$  of system  $A$ , of energy  $E_i$ , is produced. It only depends on the properties of the *heat reservoir* and is the ratio of the number of microstates  $W_{\text{res}}(E_0 - E_i)$  of the reservoir with this energy to the sum of all the numbers of microstates for all the reservoir energies  $E_0 - E_i$  :

$$p_i = \frac{W_{\text{res}}(E_0 - E_i)}{\sum_i W_{\text{res}}(E_0 - E_i)} \quad (2.28)$$

$W_{\text{res}}(E_0 - E_i)$  is calculated in the microcanonical ensemble for the given energy  $E_0 - E_i$  and is related to  $S_{\text{res}}(E_0 - E_i)$  through the Boltzmann relation

$$\ln W_{\text{res}}(E_0 - E_i) = \frac{1}{k_B} S_{\text{res}}(E_0 - E_i) \quad (2.29)$$

Indeed, once the reservoir energy  $E_0 - E_i$  is fixed, the different microstates in this situation are equally likely.

Since

$$S_{\text{res}}(E_0 - E_i) = S_{A'}(E_0) - E_i \left( \frac{\partial S_{A'}}{\partial E'} \right)_{E'=E_0} + \dots \quad (2.30)$$

$$\begin{aligned} \ln W_{\text{res}}(E_0 - E_i) &= \ln W_{A'}(E_0) - E_i \beta_0 + \dots \\ &= \text{constant} - \beta_0 E_i + \dots \end{aligned} \quad (2.31)$$

the probability of occurrence of this microstate is proportional to  $W_{\text{res}}(E_0 - E_i)$ , i.e.,

$$p_i = C \exp(-\beta_0 E_i) \quad (2.32)$$

In the probability  $p_i$  there appears the exponential of the energy  $E_i$  of the system. This is the so-called “Boltzmann factor” (1871), or “canonical distribution,” an expression that will be used very often in this course, every time we will study an *ensemble of distinguishable particles*, in *fixed number*  $N$ , of *given temperature*  $T = \frac{1}{k_B \beta}$  (the case of indistinguishable particles will

be treated in the framework of the Quantum Statistics in chapter 5 and the following ones). As an example, Fig. 2.4 schematizes the Boltzmann factor for a 4-microstate system.

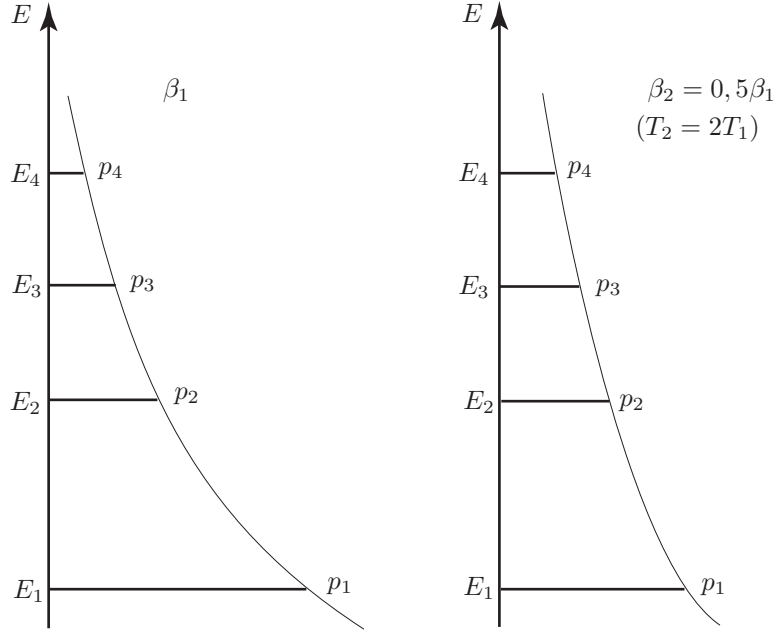


FIG. 2.4: The considered system has four microstates of energies  $E_1$  to  $E_4$ . The abscissae are proportional to the probabilities of occurrence of one of the microstates, for two different values of  $\beta$  (or of the temperature).

If the *total number* of microstates of system  $A$  corresponding to the *same energy*  $E$  is  $W(E)$ , then the probability that system  $A$ , coupled to  $A'$ , has the *energy*  $E$ , is equal to :

$$p(E) = C' W(E) \exp(-\beta_0 E) \quad (2.33)$$

where  $W(E)$  is the degeneracy (the number of ways to realize this energy) of the state of energy  $E$ . The probability  $p(E)$  is the product of the function  $W(E)$ , very rapidly increasing with energy for a macroscopic system, by a decreasing exponential : the probability has a very steep maximum for  $E = \tilde{E}$ .

### 2.4.2 Energy, with Fixed Average Value

We now show that another condition, i.e., the constraint of a given average value  $\langle E \rangle$  of the energy of a system  $A$ , leads to a probability law analogous to

the one just found. The only difference is that the value of  $\beta$ , now a parameter, should be adjusted so that the average of energy indeed coincides with the given value  $\langle E \rangle$ .

We have to maximize the statistical entropy of  $A$  while the value  $\langle E \rangle$  is given. We thus have to realize

$$S_A = -k_B \sum_i p_i \ln p_i \text{ maximum, under the constraints} \quad (2.34)$$

$$\begin{cases} \sum_i p_i = 1 \\ \sum_i p_i E_i = \langle E \rangle \end{cases}$$

A general mathematical method allows one to solve this type of problem, it is the method of Lagrange multipliers explained in Appendix 2.1 : parameters are introduced, which are the Lagrange multipliers (here  $\beta$ ). These parameters are adjusted at the end of the calculation, in order that the average values be equal to those given by the physical properties of the system, here the value of the average energy.

One thus obtains for the probability of occurrence of the microstate of energy  $E_i$  :

$$p_i = \frac{\exp(-\beta E_i)}{\sum_i \exp(-\beta E_i)} \quad (2.35)$$

that is, an expression of the “Boltzmann-factor” type (2.32) but here  $\beta$  does not characterize the temperature of a real heat reservoir. It is rather determined by the condition that the average energy of the system  $A$  should be the one given by the problem conditions, that is :

$$\frac{\sum_i E_i \exp(-\beta E_i)}{\sum_i \exp(-\beta E_i)} = \langle E \rangle \quad (2.36)$$

This method of the Lagrange multipliers is followed in some Statistical Physics courses to obtain the general expression of the Boltzmann factor (for example, those given at Ecole polytechnique by R. Balian, E. Brézin, or A. Georges and M. Mézard).

### 2.4.3 Partition Function $Z$

The probability for the system in contact with a heat reservoir to be in a state of energy  $E_i$  is

$$p_i = \frac{e^{-\beta E_i}}{Z_N}, \text{ with } \beta = \frac{1}{k_B T} \quad (2.37)$$

The term

$$Z_N = \sum_i e^{-\beta E_i} \quad (2.38)$$

which allows one to norm the Boltzmann factors is called the “canonical partition function for  $N$  particles” (in German “Zustandssumme,” which means “sum over the states”).

**Formulae (2.37) and (2.38) are among the most important ones of this course !**

The complete statistical information on the considered problem is contained in its partition function, since from  $Z$  and its partial derivatives all the average values of the physical macroscopic parameters of the system can be calculated. We will show this property now on the examples of the average energy and the energy fluctuation around its average (for the entropy see § 2.4.5). Indeed, the average energy is given by

$$\begin{aligned} \langle E \rangle &= \sum_i p_i E_i = \sum_i E_i \frac{\exp(-\beta E_i)}{Z} \\ &= -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta} \end{aligned} \quad (2.39)$$

It appears here that  $\ln Z$  is extensive like  $\langle E \rangle$ .

To determine the energy fluctuation around its average value, one calculates

$$(\Delta E)^2 = \langle E - \langle E \rangle \rangle^2 = \langle E^2 \rangle - \langle E \rangle^2 \quad (2.40)$$

A procedure similar to that of (2.39) is followed to find  $\langle E^2 \rangle$  :

$$\langle E^2 \rangle = \sum_i p_i E_i^2 = \sum_i E_i^2 \frac{\exp(-\beta E_i)}{Z} = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} \quad (2.41)$$

$$(\Delta E)^2 = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \frac{1}{Z^2} \left( \frac{\partial Z}{\partial \beta} \right)^2 = \frac{\partial}{\partial \beta} \left( \frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) = \frac{\partial^2 \ln Z}{\partial \beta^2} \quad (2.42)$$

One verifies here that, since  $\ln Z$  varies as the number of particles of the system and  $\beta$  is intensive,  $\Delta E$  varies as  $N^{1/2}$  and  $\Delta E/E$  as  $N^{-1/2}$  (in agreement

with the result of § 2.3.2), which corresponds to an extremely small value in a macroscopic system : for  $N = 10^{23}$ ,  $\Delta E/E$  is of the order of  $10^{-11}$  !

*Note 1 :* A demonstration (outside the framework of the present course, see, for example, R. Balian chapter 5 § 5) can be done of the equivalence between all the statistical ensembles in the case of macroscopic systems : it is valid in the “thermodynamical limit,” which consists in simultaneously having several parameters tending toward infinity : the volume  $\Omega$  (which means in particular that it is very much larger than typical atomic volumes), the particle number  $N$  and the other extensive parameters, while keeping constant the particle density  $N/\Omega$  and the other intensive parameters. In such a limit, it is equivalent to impose an exact value of a physical parameter (like the energy in the microcanonical ensemble) or an average value of the same parameter (the energy in the canonical ensemble).

In fact, the technique is simpler in the canonical ensemble, where  $\ln Z$  is calculated on *all the states* without any restriction, than in the microcanonical ensemble, where the calculation of  $\ln W(E)$  requires the limitation to the range of energies between  $E$  and  $E + \delta E$ . Besides, for macroscopic systems one understands that the predicted physical results, using either the microcanonical or the canonical statistical ensemble, cannot be distinguished through measurements.

*Note 2 :* The value of  $Z_N$  “gives a hint” at the number of microstates that can be achieved at the experiment temperature. Indeed at very low temperature, where  $\beta E_i \rightarrow \infty$ , only the fundamental state  $E_0$  is realized and  $Z_N = 1$ . On the other hand, at high temperature where  $\beta E_i \rightarrow 0$ , many terms are of the order of unity, corresponding to practically equally likely states.

#### 2.4.4 Entropy in the Canonical Ensemble

We just showed that, using the partition function, we can calculate the average energy of system  $A$  at temperature  $T$ , together the fluctuation around this average energy. We now have to express the statistical entropy of  $A$  in these conditions. Here the probabilities of occurrence of the different microstates are not equal, since they depend of their respective energies through Boltzmann factors. Thus the definition of the statistical entropy to be used is no longer that of Boltzmann, but rather the one of Gibbs :

$$S_A = -k_B \sum_i p_i \ln p_i \quad (2.43)$$

with

$$p_i = \frac{1}{Z} e^{-\beta E_i}, \quad \sum_i p_i = 1 \quad (2.44)$$

Consequently,

$$S_A = -k_B \sum_i p_i (-\ln Z - \beta E_i) \quad (2.45)$$

$$S_A = k_B (\ln Z + \beta \langle E \rangle) = k_B \ln Z + k_B \beta U \quad (2.46)$$

The average energy  $\langle E \rangle$  of the macroscopic system is identified to the internal energy  $U$  of Thermodynamics (see § 3.2).

Note that, for a large system in which the energy fluctuation is relatively very small around  $\langle E \rangle$ , the probability of occurrence of this energy value is very close to unity. The number of occurrences of this average energy is  $W(\langle E \rangle)$ , so that the Gibbs entropy (2.43) practically reduces to the Boltzmann entropy (2.10) for this value  $\langle E \rangle$ .

#### 2.4.5 Partition Function of a Set of Two Independent Systems with the Same $\beta$ Parameter (Same $T$ )

In § 2.1 we saw that, in the  $N$ -particle problems solved in this book, we always decompose the hamiltonian of the total system into a sum of hamiltonians for individual particles; a particle may have several degrees of freedom, whence another sum of hamiltonians. The energy of a microstate is thus a sum of energies and now we see the consequence of this property on the partition function of such a system in thermal equilibrium.

This situation is schematized by simply considering a system  $A$  made up of two independent subsystems  $A_1$  and  $A_2$ , both in contact with a heat reservoir at temperature  $T$ . A particular microstate of  $A_1$  has the energy  $E_{1i}$ , while the energy of  $A_2$  is  $E_{2j}$  and the energy of  $A$  is  $E_{ij}$ . Then

$$\left\{ \begin{array}{l} E_{ij} = E_{1i} + E_{2j} \\ Z = Z_1 Z_2 = \sum_{ij} \exp\{-\beta(E_{1i} + E_{2j})\}, \text{ with } \beta = \frac{1}{k_B T} \\ \ln Z = \ln Z_1 + \ln Z_2 \\ \langle E \rangle = \langle E_1 \rangle + \langle E_2 \rangle \\ S = S_1 + S_2 \end{array} \right. \quad (2.47)$$



This property is very often used : when the *energies* of two independent systems at the same temperature *sum*, the corresponding *partition functions multiply*. Consequently, in the case of distinguishable independent particles with several degrees of freedom, one will separately calculate the partition functions for the various degrees of freedom of an individual particle ; then one will multiply the factors corresponding to the different degrees of freedom and particles to obtain the partition function  $Z$  of the total system. Finally, in the special case of the ideal gas, one will introduce the factor  $C_N$  into  $Z$  (see § 4.4.3 and 6.7).

Take the example of the vibrations of atoms around their equilibrium positions, owing to thermal motion, in a solid in thermal equilibrium at temperature  $T$  : this is a very classical exercise and here we only sketch its solution. In the model proposed by Einstein (1907), one assumes that the atoms, in number  $N$ , are points and that they are all attracted toward their respective equilibrium position with the same restoring constant, that is, with the same frequency  $\omega$ . The value of  $\omega$  depends of the mechanical properties of the solid, in particular of its stiffness. Then the hamiltonian for a particular atom in motion is given by

$$\hat{h}_i = \frac{\hat{p}_i^2}{2m} + \frac{1}{2}m\omega^2\vec{r}_i^2 = \hat{h}_{xi} + \hat{h}_{yi} + \hat{h}_{zi} \quad (2.48)$$

It is the sum of three hamiltonians of the “harmonic-oscillator” type, identical for each coordinate. The eigenvalues of the hamiltonian  $\hat{h}_{xi}$  relative to the coordinate  $x$  of site  $i$  are

$$E_{xi}^n = (n_{xi} + \frac{1}{2})\hbar\omega \quad (2.49)$$

The contribution to the partition function of this degree of freedom is equal to

$$z_{xi} = \sum_n \exp(-\beta(n_{xi} + 1/2)\hbar\omega) \quad (2.50)$$

The partition function for the total system is the product of  $3N$  terms similar to this one. The average energy is deduced using (2.39), it is equal to  $3N$  times the average value for the coordinate  $x$  of site  $i$ .

The parameter accessible to experiment is the specific heat at constant volume  $C_v$ , defined as the derivative of the average energy with respect to temperature. The above solution gives for this lattice contribution

$$C_v = \frac{3Nk_B(\Theta/T)^2}{(e^{\Theta/T} - 1)^2}, \text{ taking } \frac{\hbar\omega}{k_B} = \Theta \quad (2.51)$$

This expression is sketched on Fig. 2.5.

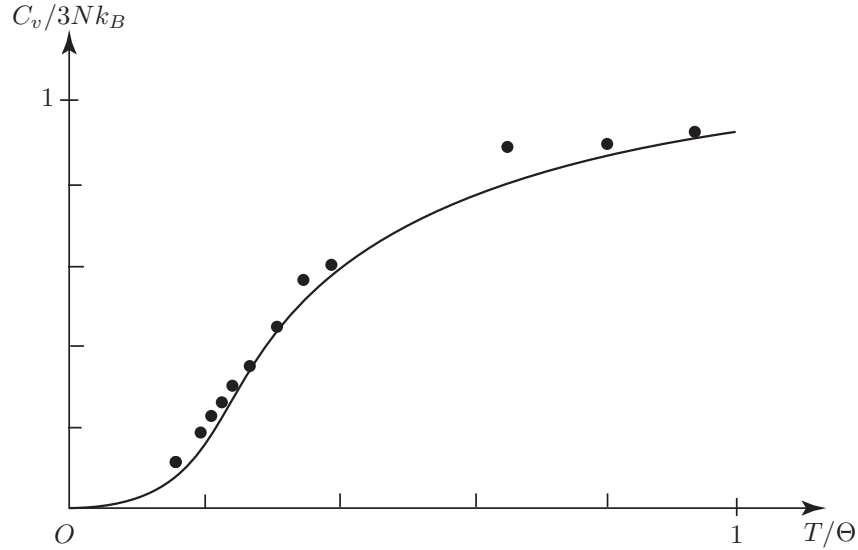


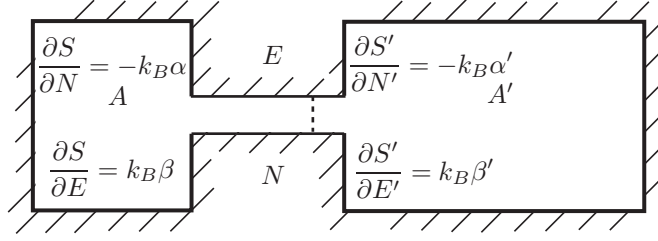
FIG. 2.5: Variation of  $C_v$  versus temperature, according to the Einstein model. The dots are experimental data for diamond, the solid line is calculated for  $\Theta = 1320$  K (after A. Einstein, *Annalen der Physik* vol.22, p.186 (1907)).

Its high temperature limit  $C_v = 3Nk_B = 25 \text{ J.K}^{-1}\text{mol}^{-1}$  is independent of  $\omega$ , thus universal : this is the Dulong and Petit law (1819), valid for metals at room temperature.

The low temperature limit  $C_v \rightarrow 0$  for  $T \rightarrow 0$  is in agreement with experiment. However, the above law of variation of  $C_v$  is not experimentally verified. The Einstein model is improved by introducing a repartition of characteristic frequencies in a solid instead of a single  $\omega$  : this is the Debye model (1913), in which  $C_v$  is proportional to  $T^3$  at very low temperatures. The agreement with experiment then becomes excellent for insulators, whereas for metals an additional term is due to the mobile electron contribution to the specific heat (see § (7.2.2)).

## 2.5 Exchange of Both Energy and Particles : “Grand Canonical Ensemble”

Here we consider two coupled systems  $A$  and  $A'$ , separated by a porous partition through which energy and particles can be exchanged, the combined system  $A_0$  being isolated from its surroundings (Fig. 2.6). An example of such a situation is water molecules under two phases, liquid and gas, contained in

FIG. 2.6 : The two systems  $A$  and  $A'$  exchange energy and particles.

a thermally insulated can of fixed volume, the water molecules belonging to either phase. One can also study hydrogen molecules as a free gas in equilibrium with hydrogen molecules adsorbed on a solid palladium catalyst surface together with the total system being thermally insulated and the total number of molecules fixed.

We have to state that the entropy is maximum at equilibrium, following an approach very similar to the one of 2.3.1.

### 2.5.1 Equilibrium Condition : Equality of Both Temperatures and Chemical Potentials

One writes that the maximum of entropy for the combined system  $A_0 = A + A'$  takes place at constant total energy and fixed total number of particles, i.e.,

$$S_{A_0}(E_0, N_0) = S_A(E, N) + S_{A'}(E', N') \text{ maximum} \quad (2.52)$$

under the two constraints

$$\begin{cases} E_0 = E + E' \\ N_0 = N + N' \end{cases} \quad (2.53)$$

Let us express the condition of entropy maximum of  $A_0$  :

$$S_{A_0}(E_0, N_0) = S_A(E, N) + S_{A'}(E_0 - E, N_0 - N) \quad (2.54)$$

With respect to an energy exchange between the two systems :

$$\left( \frac{\partial S_{A_0}(E, N)}{\partial E} \right)_N = 0, \quad \text{i.e.,} \quad \left( \frac{\partial S_{A_0}(E, N)}{\partial E} \right)_N = \left( \frac{\partial S_A(E, N)}{\partial E} \right)_N + \left( \frac{\partial S_{A'}(E_0 - E, N_0 - N)}{\partial E} \right)_N = 0 \quad (2.55)$$

With respect to a particles exchange :

$$\left( \frac{\partial S_{A_0}(E, N)}{\partial N} \right)_E = 0$$

$$\text{i.e., } \left( \frac{\partial S_{A_0}(E, N)}{\partial N} \right)_E = \left( \frac{\partial S_A(E, N)}{\partial N} \right)_E + \left( \frac{\partial S_{A'}(E_0 - E, N_0 - N)}{\partial N} \right)_E = 0. \quad (2.56)$$

The thermal equilibrium condition (2.55) again provides the results of § 2.3.1, that is,  $\beta = \beta'$ . The condition (2.56) on  $N$  implies that

$$\left( \frac{\partial S_A(E, N)}{\partial N} \right)_E = - \left( \frac{\partial S_{A'}(E_0 - E, N_0 - N)}{\partial N} \right)_E = \left( \frac{\partial S_{A'}(E', N')}{\partial N'} \right)_{E'} \quad (2.57)$$

The second equilibrium condition is the equality, in the systems  $A$  and  $A'$  in contact, of the partial derivatives of the entropy versus the number of particles, all the other parameters being kept constant. This derivative will be written

$$\left( \frac{\partial S}{\partial N} \right)_{\Omega, E} = -k_B \alpha \quad (2.58)$$

where  $k_B$  is the Boltzmann constant. It will be seen in § 3.5.1 that the parameter  $\alpha$  is related to the chemical potential  $\mu$  through  $\alpha = \beta\mu = \mu/k_B T$ .

The equilibrium condition between systems  $A$  and  $A'$  thus simultaneously implies

$$\begin{cases} \beta = \beta' , \text{ i.e., } T = T' \\ \alpha = \alpha' , \text{ i.e., } \frac{\mu}{T} = \frac{\mu'}{T'} \end{cases} \quad (2.59)$$

that is, the equality of *both* the temperatures and the chemical potentials in both systems. Thus in equilibrium the chemical potential of hydrogen is the same, whether in gas phase or adsorbed on the catalyst, and the temperatures are the same in both phases.

## 2.5.2 Heat Reservoir and Particles Reservoir; Grand Canonical Probability and Partition Function

Similarly to the approach of § 2.4, one now considers that the system  $A$  under study is macroscopic, but much smaller than the system  $A'$  (Fig. 2.7). Consequently, the parameters  $\alpha'$  and  $\beta'$  of system  $A'$  are almost the same as those

of the combined system  $A_0$ , and are very little modified when system  $A$  varies in energy or in number of particles : with respect to  $A$  the system  $A'$  behaves like a heat reservoir and a particle reservoir, it dictates both its temperature  $\beta' = 1/k_B T'$  and its chemical potential  $\alpha' = \mu/k_B T'$  to  $A$ .

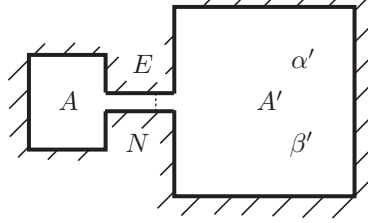


FIG. 2.7: The system  $A$  is in contact with the heat reservoir and particles reservoir  $A'$ , which dictates its parameters  $\alpha'$  and  $\beta'$  to  $A$ .

This situation in Statistical Physics, in which the system under study  $A$  is coupled to a heat reservoir that dictates its value of  $\beta$ , i.e., its temperature, and to a particle reservoir that gives the value of  $\alpha$ , is called the “grand canonical ensemble.”

### 2.5.3 Grand Canonical Probability Law and Partition Function

Now both the energy  $E_i$  and the number of particles  $N_i$  of the considered system enter into the Boltzmann-type probability  $p_i$ . Indeed, consider the probability  $p_i$  to reach a *particular microstate*  $i$  of  $A$ , of energy  $E_i$  and particle number  $N_i$ . It is related to the ability for the *reservoir* to realize this physical situation at given energy and number of particles, that is, to the number  $W_{\text{res}}(E_0 - E_i, N_0 - N_i)$  of equally likely microstates, and thus to the reservoir entropy, through the Boltzmann entropy relation. Now

$$S_{\text{res}}(E_0 - E_i, N_0 - N_i) = S_{A_0}(E_0, N_0) - E_i \left( \frac{\partial S_{\text{res}}}{\partial E} \right)_{E_0, N_0} - N_i \left( \frac{\partial S_{\text{res}}}{\partial N} \right)_{E_0, N_0} + \dots \quad (2.60)$$

thus

$$\ln W_{\text{res}}(E_0 - E_i, N_0 - N_i) = \ln W_{\text{res}}(E_0, N_0) - E_i \beta_0 + N_i \alpha_0 + \dots \quad (2.61)$$

The probability of occurrence of this microstate is proportional to  $W_{\text{res}}$ , i.e.,

$$p(E_i, N_i) = \frac{1}{Z_G} \exp(-\beta_0 E_i + \alpha_0 N_i) \quad (2.62)$$

which defines the grand partition function  $Z_G$ , the quantity which norms the probabilities. It is now a sum over all energies and numbers of particles that can be achieved; this sum can also be regrouped according to the different numbers of particles :

$$Z_G = \sum_i e^{-\beta E_i + \alpha N_i} = \sum_N e^{\alpha N} Z_N \quad (2.63)$$

The canonical partition function  $Z_N$  for  $N$  particles, as defined in (2.38),

$$Z_N = \sum_i e^{-\beta E_i} \quad (2.64)$$

thus appears in  $Z_G$  with a weight equal to  $\exp \alpha N$ .

(Note that in (2.63) the sum is performed over all microstates  $i$  with an *arbitrary number* of particles, whereas in (2.64) the sum is only over the states with  $N$  particles, with  $N$  *fixed*.)

### 2.5.4 Average Values

Using  $p(E_i, N_i)$  one calculates the average energy and the average number of particles of system  $A$  : this is conveniently performed from the partial derivatives of  $Z_G$ . The approach is the same as in (2.39) :

$$\langle E \rangle = \sum_i E_i p(E_i, N_i) = \sum_i E_i \frac{\exp(-\beta E_i + \alpha N_i)}{Z_G} = -\frac{1}{Z_G} \frac{\partial Z_G}{\partial \beta} = -\frac{\partial \ln Z_G}{\partial \beta} \quad (2.65)$$

$$\langle N \rangle = \sum_i N_i p(E_i, N_i) = \sum_i N_i \frac{\exp(-\beta E_i + \alpha N_i)}{Z_G} = +\frac{1}{Z_G} \frac{\partial Z_G}{\partial \alpha} = \frac{\partial \ln Z_G}{\partial \alpha} \quad (2.66)$$

To determine the energy fluctuations around its average value, one proceeds in a way similar to the calculation in the canonical ensemble (eqs. (2.41) and (2.42)). Let us calculate the fluctuation of the particle number in system  $A$  :

$$\langle N^2 \rangle = \sum_i N_i^2 p(E_i, N_i) = \frac{1}{Z_G} \frac{\partial^2 Z_G}{\partial \alpha^2} \quad (2.67)$$

$$\begin{aligned} (\Delta N)^2 &= \langle N^2 \rangle - \langle N \rangle^2 = \frac{1}{Z_G} \frac{\partial^2 Z_G}{\partial \alpha^2} - \left( \frac{1}{Z_G} \frac{\partial Z_G}{\partial \alpha} \right)^2 \\ &= \frac{\partial}{\partial \alpha} \left( \frac{1}{Z_G} \frac{\partial Z_G}{\partial \alpha} \right) = \frac{\partial^2 \ln Z_G}{\partial \alpha^2} \end{aligned} \quad (2.68)$$

Since  $\ln Z_G$  is extensive as it increases like  $\langle E \rangle$  or  $\langle N \rangle$  (see (2.65) and (2.66)),  $(\Delta N)^2$  varies proportionally with the size of the system, or with its average number of particles. Consequently,  $\Delta N/N$  is of the order  $\langle N \rangle^{-1/2}$ , it is thus very small for a macroscopic system.

Thus by differentiating  $Z_G$  one obtains the average physical parameters  $\langle E \rangle$  and  $\langle N \rangle$  and their fluctuations around these averages : in fact  $Z_G$ , which expresses the probabilities, contains the complete information on the system.

### 2.5.5 Grand Canonical Entropy

Using the Gibbs definition

$$S = -k_B \sum_i p_i \ln p_i \quad (2.69)$$

one calculates the entropy in the grand canonical ensemble. Here

$$p_i = \frac{1}{Z_G} e^{-\beta E_i + \alpha N_i}, \quad \sum_i p_i = 1 \quad (2.70)$$

Consequently,

$$S = -k_B \sum_i p_i (-\ln Z_G - \beta E_i + \alpha N_i) \quad (2.71)$$

$$S = k_B (\ln Z_G + \beta \langle E \rangle - \alpha \langle N \rangle) = k_B \ln Z_G + k_B \beta U - k_B \alpha \langle N \rangle \quad (2.72)$$

In the present definition of the grand canonical ensemble, we have considered a macroscopic system in contact with a heat reservoir and a particle reservoir. The grand canonical ensemble is also used when the system under study is specified by the average values of both its energy and its particle number and one then needs to determine  $\beta$  and  $\alpha = \beta\mu$  : the argument is the extension of the one in § 2.4.2. We will use the grand canonical ensemble in particular for the study of the Quantum Statistics : the Pauli principle introduces limitations to the occupation of the quantum states, which will be more conveniently expressed in this ensemble.

## 2.6 Other Statistical Ensembles

As you imagine, one can generalize to various physical situations the approach consisting of considering two weakly coupled systems  $A$  and  $A'$ , the combined system being isolated, i.e., the total parameters being fixed. In particular one

can study systems  $A$  and  $A'$  exchanging both energy and volume, the total volume  $\Omega_0 = \Omega + \Omega'$  being fixed.

The equilibrium condition now implies that the partial derivatives of the entropy

$$\left(\frac{\partial S}{\partial E}\right)_{N,\Omega} = k_B\beta \quad \text{and} \quad \left(\frac{\partial S}{\partial \Omega}\right)_{N,E} = k_B\gamma \quad (2.73)$$

take the same value in both systems. Thermodynamics will show, in § 3.5.1, that  $k_B\gamma = P/T$  where  $P$  is the pressure, so that the new equilibrium condition will be

$$\begin{cases} T = T' \\ P = P' \end{cases} \quad (2.74)$$

that is, in equilibrium the systems  $A$  and  $A'$  will have the same temperature and the same pressure. If  $A'$  is much larger than  $A$ , it will give its pressure to  $A$ .

The chemistry experiments performed in isothermal and isobar conditions (for example, at room temperature and under the atmospheric pressure) are in such a condition. Then

$$p(E_i, \Omega_i) = \frac{1}{Z_{T,P}} \exp(-\beta E_i - \gamma \Omega_i) = \frac{1}{Z_{T,P}} \exp\left(-\frac{E_i}{k_B T} - \frac{P \Omega_i}{k_B T}\right) \quad (2.75)$$

$i$  represents the microstate in which the system has the energy  $E_i$  and occupies the volume  $\Omega_i$ . A new partition function  $Z_{T,P}$  is defined by

$$Z_{T,P} = \sum_i \exp(-\beta E_i - \gamma \Omega_i) \quad (2.76)$$

(In fact the sum over the volume, a continuous variable, is rather an integral.) The entropy is deduced :

$$S = -k_B \sum_i p(E_i, \Omega_i) (-\ln Z_{T,P} - \beta E_i - \gamma \Omega_i) \quad (2.77)$$

$$S = k_B (\ln Z_{T,P} + \beta \langle E \rangle + \gamma \langle \Omega \rangle) \quad (2.78)$$



# Summary of Chapter 2

In this chapter the general method for solving problems in Statistical Physics is presented.

– First one needs to determine the quantum states of the system. In the cases we will consider, the system hamiltonian can be decomposed into a sum of similar one-particle terms

$$\hat{H} = \sum_i \hat{h}_i$$

Until chapter 4, the particles will be assumed to be distinguishable.

– Only in a second step does one choose a statistical ensemble adapted to the physical conditions of the problem (or the most convenient to solve the problem, since for macroscopic systems one cannot measure the fluctuations resulting from the choice of a specific ensemble rather than another one). One expresses that the entropy is maximum in equilibrium, under the constraints set by the physical conditions.

According to the chosen ensemble, a mathematical quantity deduced from the probabilities allows one to obtain the macroscopic physical parameters that can be measured in experiments :

– *the microcanonical ensemble* is used to treat the case of an isolated system : the number of microstates  $W(E)$  all producing the same macrostate of energy in the range between  $E$  and  $E + \delta E$ , allows the entropy to be obtained

$$S = k_B \ln W(E)$$

– *the canonical ensemble* is adapted to the case of a system with a fixed number of particles  $N$ , in contact with a heat reservoir at temperature  $T$ .

The probability to be in a microstate of energy  $E_i$  is then given by the Boltzmann factor :

$$p_i = \frac{e^{-\beta E_i}}{Z_N}, \text{ with } \beta = \frac{1}{k_B T}$$

The canonical partition function for  $N$  particles is defined by

$$Z_N = \sum_i e^{-\beta E_i}$$

It is related to the average energy through

$$\langle E \rangle = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}$$

– the *grand canonical ensemble* corresponds to the situation of a system in contact with a heat reservoir and a particle reservoir. The grand canonical partition function is introduced :

$$Z_G = \sum_N e^{\alpha N} Z_N$$

The probability to be in a microstate of both energy  $E_i$  and number of particles  $N_i$  is given by

$$p(E_i, N_i) = \frac{1}{Z_G} \exp(-\beta E_i + \alpha N_i)$$

The average energy and the average number of particles are then deduced :

$$\langle E \rangle = -\frac{1}{Z_G} \frac{\partial Z_G}{\partial \beta} = -\frac{\partial \ln Z_G}{\partial \beta}, \quad \langle N \rangle = \frac{1}{Z_G} \frac{\partial Z_G}{\partial \alpha} = \frac{\partial \ln Z_G}{\partial \alpha}$$

# Appendix 2.1

## Lagrange Multipliers

One looks for the extremum of a function with several variables, satisfying constraints. Here we just treat the example of the entropy maximum with a fixed average value of the energy, i.e.,

$$S = -k_B \sum_i p_i \ln p_i \text{ maximum, under the constraints}$$
$$\begin{cases} \sum_i p_i = 1 \\ \sum_i p_i E_i = \langle E \rangle \end{cases} \quad (2.79)$$

The process consists in introducing constants, the Lagrange multipliers, here  $\lambda$  and  $\beta$ , the values of which will be determined at the end of the calculation. Therefore one is looking for the maximum of the auxiliary function :

$$F(p_1, \dots, p_i, \dots) = - \sum_i p_i \ln p_i + \lambda (\sum_i p_i - 1) - \beta (\sum_i E_i p_i - \langle E \rangle) \quad (2.80)$$

which expresses the above conditions, with respect to the variables  $p_i$ . This is written

$$\frac{\partial F}{\partial p_i} = -(\ln p_i + 1) + \lambda - \beta E_i = 0 \quad (2.81)$$

The solution is

$$\ln p_i = -\beta E_i + \lambda - 1 \quad (2.82)$$

Consequently,

$$p_i = (e^{\lambda-1}) e^{-\beta E_i} \quad (2.83)$$

The constants  $\lambda$  and  $\beta$  are then obtained by expressing the constraints :

$$\bullet \quad \sum_i p_i = 1, \text{ whence}$$

$$e^{\lambda-1} \sum_i e^{-\beta E_i} = 1 \quad (2.84)$$

$$e^{\lambda-1} = \frac{1}{\sum_i e^{-\beta E_i}} = \frac{1}{Z} \quad (2.85)$$

$$\bullet \quad \sum_i p_i E_i = \langle E \rangle, \text{ i.e.,} \quad (2.86)$$

$$\frac{1}{Z} \sum_i E_i e^{-\beta E_i} = \langle E \rangle \quad (2.87)$$

which is indeed expression (2.36).

Note that, if the only constraint is  $\sum_i p_i = 1$ , the choice of the  $p_i$  maximizing  $S$  indeed consists in taking all the  $p_i$  equal ; this is what is done for an isolated system using the Boltzmann formula.

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