

# Introduction

In thermodynamics it is shown that the thermal properties of a system composed of a very large number of particles is characterized by a relatively small number of quantities such as the internal energy, the temperature, the entropy, the volume, the pressure *etc.* These are the macroscopic parameters of the matter. Thermodynamics was developed without any hypothesis about a microscopic picture of the matter in its three forms: solid, liquid or gas. However with the development of the atomic theory, it began to be possible to look for the link between the macroscopic world and a microscopic picture. At the end of the 19th and at the beginning of the 20th century, the first steps toward a theory relating the macroscopic world and a microscopic picture were proposed by Boltzmann and Gibbs. At this time the term *Statistical Mechanics* was coined by Gibbs.

The basic problem in statistical mechanics is to find the macroscopic properties of a system of particles from the knowledge of their microscopic properties. But at the microscopic level, the number of parameters is enormous. It is impossible, to follow each particle individually and to calculate the properties of the system by some average over all the particles. In front of this impossible task, it was necessary to proceed in another way. One has to leave the microscopic individual picture and to rely on a statistical approach.

The theory is based on a fundamental hypothesis. It is possible to formulate it as follows. The matter, whatever its state, is compounded of microscopic entities which have specific characteristics. The state of each entity does not remain the same but changes with

the time. In other words, the microscopic world is disordered. However it is admitted that the collective properties do remain stationary. For example, the molecules of a gas change constantly their velocities because of the collisions between them, but their mean velocity is well defined.

A particular theory which is based on some postulates was developed. The test of the validity of this method is the comparison between the consequences drawn from the postulates and the experimental results. The close agreement, which was found, is a guarantee of the validity of the method.

An important consequence of this approach is that thermal phenomena have their origin in mechanics. It is not an obvious thinking and the reader must be ready to adopt it. If a system is made of a relatively small number of bodies, one can apply the law of mechanics like in the planetary system. But if now the system is compounded of a very large number of units, one has the thermal phenomena. Some subtle points remain in this approach and in the past they were subjects of intense debate. In this book we shall not consider them except in the historical part. We think that in a first contact with this field, it is better to consider only the basic concepts. We hope that this first encounter with statistical mechanics will help the reader to be able to read more advanced books.

The book is divided into two parts: first the principles of the theory and in the second some applications. This does not correspond to the historical development of statistical mechanics as it is frequently presented. In order to follow the history, we added a chapter which presents those scientists who contributed to the main steps in the development of the theory.

## **The Thermodynamic Potentials.**

Before embarking on the exposition of the theory and its applications, important results concerning the thermodynamic potentials are revised.

If the equilibrium state of the system is defined by the knowledge of some variables, there exists a function of these variables from which

all the properties of the system can be deduced. These functions play the role of a potential for the following reason. If a perturbation appears in the system and the chosen variables are kept constant, the equilibrium state is reached when the potential is in a minimum. We shall consider three cases, which are important for the theory of statistical mechanics.

### 1. The entropy as a thermodynamic potential

In the first case, the state of the system is controlled by the extensive variables like the energy  $E$ , the volume  $V$ , the number of particles  $N$ , etc. (we took only these three variables by convenience). In such case, one considers the system as a closed system since no energy or no particle can enter or leave the system. The extensive variables are those which are proportional to the size of the system. The thermodynamic potential associated with such a state is the entropy  $S(E, V, N)$ . We recall that in a closed system, equilibrium is reached when  $S$  is maximum or when  $-S$  is minimum. Entropy is a complex concept which may be presented in several ways. In the framework of this book, entropy is defined as a thermodynamic potential in the particular context of the closed system.

The entropy is a homogeneous function such that

$$S(\lambda E, \lambda V, \lambda N) = \lambda S(E, V, N), \quad (1)$$

where  $\lambda$  is a scalar. From the differential of  $E$ ,

$$dE = T dS - P dV + \mu dN, \quad (2)$$

one gets the differential of  $S$ ,

$$dS = dE/T + (P/T) dV - (\mu/T) dN \quad (3)$$

( $T$  is temperature,  $P$  the pressure and  $\mu$  the chemical potential). One sees that the temperature is given by

$$(\partial S/\partial E)_{V,N} = 1/T. \quad (4)$$

The function of state  $P(V, T, N)$  is deduced from  $T(E, V, N)$  and  $P(E, V, N) = T(\partial S/\partial V)_{E,N}$  and eliminating  $E$  from them.

## 2. The Helmholtz free energy as a potential

The second case corresponds to the system in thermal contact with a reservoir which defines the temperature of the system with volume  $V$  and number of particles  $N$ . It is supposed that: a) The ensemble reservoir with the system constitutes a closed system, b) The reservoir is much larger than the system. The thermodynamic potential is the Helmholtz free energy, which is also a minimum when  $T$ ,  $V$  and  $N$  are kept constant. Its definition is

$$F(T, V, N) = E - TS, \quad (5)$$

and the differential of  $F$  is

$$dF = dE - d(TS) = T dS - P dV + \mu dN - T dS - S dT$$

or

$$dF = -S dT - P dV + \mu dN. \quad (6)$$

One gets the entropy

$$S(T, V, N) = -(\partial F / \partial T)_{V, N} \quad (7)$$

and the energy

$$E(T, V, N) = F - T(\partial F / \partial T)_{V, N}. \quad (8)$$

The function of state here is merely  $P(T, V, N) = -(\partial F / \partial V)_{T, N}$ .

In the case of magnetic material one has to take into account the magnetization of the material under application of a magnetic field. The magnetization  $M$  is the number of effective magnetic dipoles and the contribution to the energy is  $HdM$ . The differential of  $E$  is now

$$dE = T dS - P dV + \mu dN + H dM, \quad (9)$$

since  $E$  is a function of the extensive quantities as  $M$  is. The free energy is  $F_M = E - TS - MH$ , such that its differential is

$$dF_M = -S dT - P dV + \mu dN - M dH. \quad (10)$$

In other words  $F_M$  is a function of  $T, V, N$  and  $H$ . The magnetization is obtained from  $F_M$  through its derivative relative to  $H$ ,  $M = -(\partial F_M / \partial H)_{T, V, N}$ .

## 3. The grand potential

In the third case, the system is in thermal contact with a reservoir made of the same kind of particles. But now it is enclosed in a cell of volume  $V$  with walls permeable to the particles. The variables which characterize the system are the volume  $V$ , the temperature  $T$  (imposed by the reservoir) and the chemical potential  $\mu$  which is the same for the system and the reservoir. If one particle crosses the walls from the reservoir to the system when nothing else is changed, the energy of the reservoir decreases by an amount equal to  $-\mu_R$  (chemical potential of the reservoir) when the energy of the system increases by  $\mu_S$  (chemical potential of the system). Since the total energy has not changed (the reservoir with the system constitutes a closed system), it results in the equality of the chemical potentials.

In the present case the thermodynamic potential is the grand potential

$$\Psi(T, V, \mu) = E - TS - \mu N. \quad (11)$$

From the fundamental equality of thermodynamics,  $E = TS - PV + \mu N$  one gets  $\Psi = -PV$ . The differential of  $\Psi$  is  $d\Psi = dE - d(TS) - d(\mu N)$ , or

$$d\Psi = -S dT - P dV - N d\mu. \quad (12)$$

Thus, one has

$$S = -(\partial\Psi/\partial T)_{V,\mu}, \quad (13)$$

$$P = -(\partial\Psi/\partial V)_{T,\mu}, \quad (14)$$

$$N = -(\partial\Psi/\partial\mu)_{T,V}. \quad (15)$$

The energy is given by

$$E = \Psi + TS + \mu N = \Psi - T(\partial\Psi/\partial T)_{V,\mu} - \mu(\partial\Psi/\partial\mu)_{T,V}. \quad (16)$$

In the first case, the temperature and the pressure are not controlled by some external influence and one considers the system as a closed system. In the second case, the macroscopic energy is the mean value of the energy of the system. It can fluctuate since only the temperature is imposed by the external reservoir. But it is a fundamental hypothesis that the macroscopic energy that can be measured is the mean value and that the fluctuations around the mean value

are negligible when the number of particles is very large. It is not always the case but the study of such situations is beyond the framework of this book. And in the third case, the macroscopic energy is the mean energy, and the macroscopic density corresponds to the mean value of  $N$ . Since the walls are permeable to the particles, their number in the volume  $V$  of the system can vary. If we suppose that the fluctuations are negligible, the three cases give same results and one can use the standard thermodynamics formulas.

The fundamental goal of statistical mechanics is to determine the thermodynamic potentials  $S, F$  and  $\Psi$  from the knowledge of the microscopic properties of the particles. It is the subject of the two following chapters.