Chapter 21

Concept of Ensembles and Postulates

Abstract The followed strategy in order to introduce statistical thermodynamics into the classical one is the one devised by Gibbs. It is based on the consideration of ensembles of systems. It entails the adoption of two postulates permitting to relate the average in time of a mechanical variable to the average of the same variable calculated over one ensemble of systems.

According to:

- The first postulate, the value of the mechanical property in the thermodynamic system under study is equal to its average over the ensemble of the systems, when the number of systems $\rightarrow \infty$.
- The second postulate, in a representative ensemble ($\aleph \rightarrow \infty$) of an isolated system, the systems are uniformly distributed, and, hence, they have the same probability of existence.

The energy levels of the systems are given by the Schrödinger's equation.

Keywords Ensemble • System • Mechanical variable • Closed system • Stationary energy state • Quantum mechanics • Quanto-energetic state • Schrödinger's equation • Wave function • Isolated system • Open system • Ergodic theory of matter • Thermodynamic system

The methods of thermodynamics are fully independent of the notions of atomic and molecular structures as they also are of the notions of reaction mechanisms. The results to which thermodynamics leads do not bring any direct piece of information concerning these aspects of chemistry. Actually, thermodynamics only permits to predict some relations and interconnections between variables describing macroscopic systems which can be directly observed or which can be deduced from quantities which themselves are experimentally directly accessible.

The object of statistical thermodynamics is to provide classical thermodynamics with a theoretical justification founded on the study of phenomena evolving at the molecular level.

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21.1 Strategy: Ensembles and Postulates

The goal consists in finding the expressions of thermodynamics describing the behavior of macroscopic systems at equilibrium by starting from atomic and molecular properties of matter.

Solving this problem is tremendously difficult: it is to deduce these relations by starting from the properties of a huge number of particles, of the order of 10^{20}, at least! As an example of the difficulty, let us regard the case of the pressure. In principle, if we want to calculate the pressure of a system through purely molecular considerations, we must calculate the force exerted *per* area unit upon the partitions of the system. The force is calculated according to the laws of classical or quantum mechanics (viz. next paragraph) . Given the huge number of particles constituting the system, it is absolutely unthinkable to perform the calculation by following this way. This is all the more inconceivable as the system evolves at every moment, because all the particles are in interactions. Hence, in addition to the huge number of particles, calculations should be performed by taking into account the incessant changes with time of the state of the system.

However, one characteristic of the problem simplifies the matter. It is the fact that given the inconceivably large number of particles, it is legitimate to admit that the average values of some physical quantities of the systems are perfectly representative of its (classical) thermodynamic properties.

The followed strategy in order to introduce statistical thermodynamics into the classical one is the one devised by Gibbs. It is based on the consideration of *ensembles of systems*. It entails the adoption of two postulates permitting to relate the average in time of a *mechanical* variable to the average of the same variable calculated over one ensemble of systems (viz. paragraph 3).

21.2 Quantum Mechanics: Schrödinger's Equation—Quanto-Energetic States

The goal of statistical thermodynamics being to calculate the properties of macroscopic systems by starting from those of the particles constituting them, it is an evidence that the latter must be known, including the nature of their interactions. In principle, they are obtained by applying the principles of quantum mechanics.

For our purpose, we must take into consideration the fact that these particles and the *s macroscopic systems putting them together* can only take some discrete energetic levels of values $E_0, E_1, E_2, \ldots, E_j$, often called stationary quanto-energetic states. Theoretically, they are obtained by resolution of the Schrödinger's equation corresponding to the system which applies to the particles and to the macroscopic systems as well.

Let us consider a particle i (molecule, atom) present in a container. Its mass is m_i, its cartesian coordinates x_i, y_i, and z_i, and its momenta are p_{xi}, p_{yi}, and p_{zi}. From the standpoint of quantum mechanics, the system is described by a function Ψ, called *wave function*, possessing the following property: the probability that the particle possesses its coordinates located in the intervals $x_i + dx_i$, $y_i + dy_i$, and $z_i + dz_i$ is given by the expression

$$\Psi^2 dx_i dy_i dz_i$$

In other words, Ψ^2 plays the part of a probability density. Let us suppose that the particle is in a state which is independent of time (it is often the case in chemistry, the species being, most of the time, stable in time) and that it moves in a force field, described by a potential energy E_p, function of the coordinates x_i, y_i, and z_i. The function Ψ is a solution of Schrödinger's equation taking into account these conditions. It is

$$1/m_i\left(\partial^2\Psi/\partial x_i{}^2 + \partial^2\Psi/\partial y_i{}^2 + \partial^2\Psi/\partial z_i{}^2\right) + \left(8\pi^2/h^2\right)\left(E - E_p\right)\Psi = 0$$

where h is the Planck's constant and E the total energy of the particle. The function Ψ, of course, must satisfy some conditions because of the fact that it must describe a probability. It must, indeed, only possess one value, and be finished and continuous in the domain of changes of the coordinates of the system. It must be null at the outside of this domain. Let us notice, from the pure mathematical standpoint, that the expression just above is a differential (with partial derivatives) equation of order 2 and of first degree.

For a macroscopic system containing n particles, the corresponding Schrödinger's equation is

$$\sum_i 1/m_i\left(\partial^2\Psi/\partial x_i{}^2 + \partial^2\Psi/\partial y_i{}^2 + \partial^2\Psi/\partial z_i{}^2\right) + \left(8\pi^2/h^2\right)\left(E - E_p\right)\Psi = 0$$

where x_i, y_i, and z_i are the coordinates of each particle i and E and E_p the total and potential energies of the macroscopic system, the sum being calculated over the total number n of particles.

The equation remains of the same kind as the previous one, but extremely more complicated. Complications are due to the huge number of coordinates to consider. It is important, indeed, to highlight the phenomenal and even unappreciable difficulty that the resolution of Schrödinger's equation relative to 10^{20} molecules must show and this, after having admitted that it is possible to modelize the interactions between them from the mathematical viewpoint and, moreover, that Schrödinger's equation admits analytical solutions! Actually, it is quasi-never the case, even for very simple systems. Notably, let us only think of the time one should spend, in order to write the Hamiltonian operator of such a system!

Within the framework of this brief recall, let us also mention that the general principles of quantum mechanics entail the existence of the quantification of some physical quantities when and only when there is imposition of some conditions to the studied system, such as the occurrence of a finite volume of the system and that of a finite number of particles. This property is very important in the realm of statistical mechanics.

21.3 The Concept of Ensemble of Systems

An ensemble is simply a mental collection of a very great number ℵ of systems, each being supposed to be a replicate of the thermodynamic system under study (Fig. 21.1):

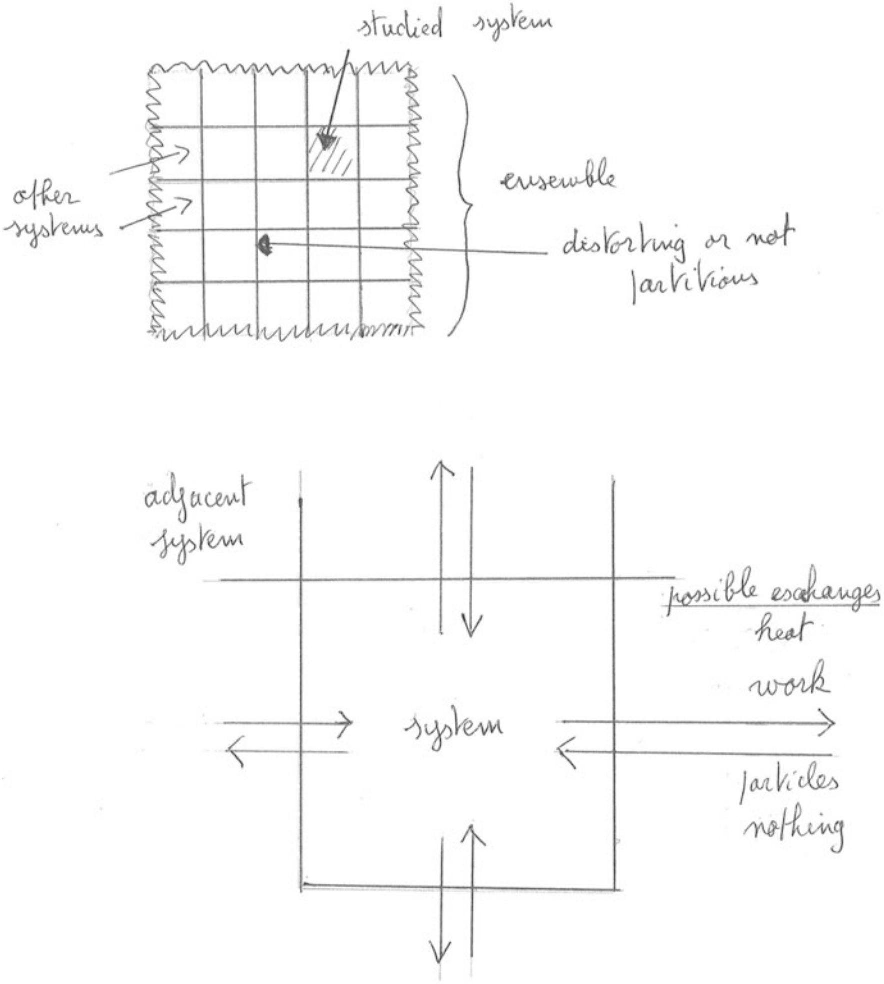

Fig. 21.1 Ensemble and systems

Let us suppose that the system possesses the volume V and contains N molecules of a component and that it is immerged in a very big heat bath at temperature T (it is the case of the canonical ensemble—see just below). The knowledge of N, V, and T is usually sufficient in order to determine the thermodynamic state of the system. The ensemble is constituted by a very large number $\aleph$ of these systems possessing the same *macroscopic* thermodynamic properties (N, V, T). Although they exhibit the same macroscopic properties, they are not similar to the molecular scale, since there exists an extremely important number of quantum states for the same set of values N, V, and T (quantum state signifying, here, *stationary energy state*). For example, in the case of pressure, there exist numerous such states. The average of the pressures of the ensemble is the average over the separated values of the pressures in each system, by giving the same weight to each system in order to perform the calculation. It is the same for each mechanical property.

Among the most important systems encountered in thermodynamics, let us mention the following:

- The *isolated system* defined in classical thermodynamics by the parameters N, V, and E, the replication of which constituting the *microcanonical ensemble*. (E is the symbol of internal energy. We are continuing to use it, as it is often the case in the literature devoted to statistical thermodynamics, although IUPAC recommends the symbol U.)
- The *closed isothermal system* defined by the parameters N, V, and T, the replication of which constitutes the *canonical ensemble*.
- The open isothermal system defined by the parameters μ, V, and T where μ is the chemical potential of the component. Its replication constitutes the grand canonical ensemble (or grand ensemble). Of course, these systems may be constituted of compounds labelized 1, 2, etc., the numbers of moles of which are N_1, N_2, etc. and the chemical potentials are μ_1, μ_2, etc. In this case, the system is defined in thermodynamics by the parameters μ_1, μ_2, V, and T (see later).

As we have just said, a system of an ensemble may or may not, according to its kind, exchange heat, work, particles, and even nothing with its neighbors (viz. Fig. 21.1).

21.4 Postulates

- First postulate: The value of the mechanical property M in the thermodynamic system under study is equal to its average over the ensemble of the systems, when $\aleph \to \infty$.
- Second postulate: In a representative ensemble ($\aleph \to \infty$) of an isolated system, the energy of which is constant, the systems are uniformly distributed, that is to say, they have the same probability of existence. This hypothesis of equiprobability is founded on the fact that each system of the ensemble does

possess the same internal energy. Thus, it seems to match the physical intuition which tends to say that two states of the same energy are equiprobable.

In any case, its consequences do not lead to results in contradistinction with experiments. This postulate constitutes the *ergodic* theory of matter.