

Chapter 27

Classical Statistical Mechanics, Configuration, and Classical Canonical Partition Function

Abstract To deeply grasp the physical significance of an activity, statistical thermodynamics must be considered and, in particular, it is the case of the notions of configuration of a system and of the classical canonical partition function.

Firstly, the chapter presents a definition of the configuration of a system. Secondly, the chapter is a presentation of the classical canonical partition function and of some relations stemming from it. It may be viewed as being an extension, in some definite conditions, of the canonical partition function occurring in quantum mechanics. All the mathematical terms constituting the function are presented. This is especially the case of the hamiltonian of the system. In some conditions, Hamilton's function is nothing more or less than the energy of the system. It entails the kinetic energy of the whole particles constituting the system and their mutual interacting potential energy. A simple example of its handling, concerning perfect gases, is given at the end of the chapter.

The partition function, indeed, is the most used partition function in the field of applications of statistical thermodynamics to chemistry. The function will be quasi-systematically used until the end of the book. It is a physical parameter of first importance in the grasping of the significance of an activity.

Keywords System • Stirling's approximation • System configuration • Classical statistical mechanics • Configurational partition function • Classical and quantum mechanics • Classical canonical partition function • Hamiltonian

In order to grasp the physical significance of an activity more deeply than before, we must turn ourselves toward statistical thermodynamics and especially, at the beginning, toward the notion of partition function, notion which also exists in the realm of classical statistical mechanics.

In this chapter, we present the classical canonical partition function and we mention some relations stemming from it. It may be viewed as being an extension of the canonical partition function occurring in quantum mechanics in some definite conditions. This is the standpoint we adopt here.

The canonical partition function, indeed, is the most used partition function in the field of applications of statistical thermodynamics to chemistry. We give an example of its handling with the case of perfect gases at the end of this chapter.

27.1 Classical and Quantum Mechanics

In the classical mechanics, we consider that the state of a system is defined, at any instant, by the values of its coordinates and of its momenta.

In quantum mechanics, the state of the system at any instant is defined by a probability amplitude permitting to only know the probability of occurrence of some values of its coordinates and its momenta.

In either case, there are some situations in which the theoretical treatments just above evoked are not possible. In these cases, one no longer studies a sole system but a collection (one ensemble) of several systems, each of them duplicating the one studied. This is the essence of statistical methods.

27.2 Quantum and Classical Mechanics in Statistical Thermodynamics

It is true that, in some definite conditions, the results following from quantum-mechanical arguments tend toward those obtained from classical mechanics ones. This is the case, for instance, when the quantum numbers involved in a process take high numerical values. Thus, in the quantum-mechanical canonical ensemble partition function, the terms corresponding to the higher quantum numbers make more and more important contributions to the sum constituting it as the temperature increases. Owing to the importance of the canonical partition function for our purpose, it is of great interest for us to know the classical canonical partition function.

According to the preceding example, one may prejudge that the quantum-mechanical canonical function must tend toward the classical one.

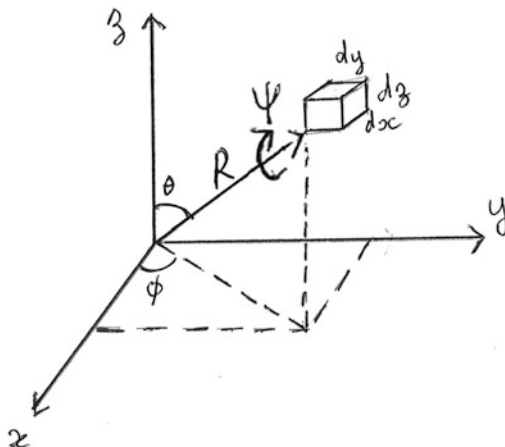
Hence, one can infer that the quantum-mechanical canonical partition function $[Q(T, V, N)]_{\text{quant}} = \sum_i \exp[-\beta E_i(N, V)]$ (viz. Chap. 23) must go over asymptotically into the corresponding classical function in the limit of large quantum numbers,

$$Q(T, V, N)_{\text{quant}}(\text{large quantum numbers}) \rightarrow Q_{\text{class}} = ?$$

The principal goal of this chapter is to express the function Q_{class} .

According to the very foundations of classical mechanics, the energy of a moving body, for instance, varies continuously. Hence, one may already infer from this observation that Q_{class} is a continuous function of energy instead of Q_{quant} which is a discrete function.

Fig. 27.1 Symbolism used to describe the configuration of a molecule



27.3 Cartesian Coordinates of a Specific Particle in a System

The locations of the centers of the molecules are often denoted in rectangular coordinates x, y, z . It is the same as to locate it at the extremity of the vector \mathbf{R} defined by its components x, y, z . Thus, the center of the molecule i is defined by the vector \mathbf{R}_i (Fig. 27.1).

For simple particles such as hard spheres (which do not actually exist although, however, argon atoms look closely like them), vectors $\mathbf{R}_i, \mathbf{R}_j, \dots$ are sufficient to describe one configuration of the system (constituted by the N particles i, j, \dots). This means that, in this case, the sole location of their centers is sufficient to describe the configuration of the system symbolized by \mathbf{R}^N . It is symbolically written:

$$\mathbf{R}^N = \mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3, \dots \mathbf{R}_N$$

The symbol \mathbf{R}^N means that the location of the centers of *all* the particles constituting the system is known through the knowledge of vectors \mathbf{R}_i . They are, of course, defined by the three components x_i, y_i , and z_i .

27.4 Configuration of a System

More generally, the description of the configuration of a molecule may necessitate to know both its location and its orientation \mathbf{X}_i . This was not the case of the preceding spherical particles having no internal structure. For a rigid nonspherical molecule i (such as water for example), its orientation, defined by the parameter Ω_i , must also be taken into account. Ω_i is given by the relation (viz. Fig. 27.1):

$$d\Omega_i = d\phi_i \sin \theta_i d\theta_i d\psi_i$$

The whole configuration of such a molecule is symbolized by \mathbf{X}_i . The vector \mathbf{X}_i is related to vectors \mathbf{R}_i and Ω_i by:

$$\mathbf{X}_i = \mathbf{R}_i \Omega_i$$

The configuration of the system is given by the relation:

$$\mathbf{X}^N = \mathbf{X}_1, \mathbf{X}_2, \dots \mathbf{X}_N$$

and the infinitesimal element of a single molecule i is given by:

$$d\mathbf{X}_i = d\mathbf{R}_i d\Omega_i$$

Vector \mathbf{X}_i is a six-dimensional $(x_i, y_i, z_i, \phi_i, \theta_i, \psi_i)$ vector (the definitions of these six variables are given in Fig. 27.1). The integration over Ω_i takes into account all the orientations of the molecule. It is represented by the expression:

$$\int d\Omega_i = \int_0^{2\pi} d\phi_i \int_0^\pi \sin \theta_i d\theta_i \int_0^{2\pi} d\psi_i$$

that is to say:

$$\int d\Omega_i = 8\pi^2$$

and

$$\mathbf{X}_i = 8\pi^2 \mathbf{R}_i$$

Remark: For nonrigid molecules, a supplementary parameter describing their internal rotations may be needed. This is the case, for example, of n-butane. It is not treated further in this book.

27.5 Spherical Coordinates ϕ, θ, r of a Particle

An infinitesimal element of volume located at the extremity of the vector \mathbf{R} is equally denoted dV , dR or $dx dy dz$ (viz. Fig. 27.1). The change of the cartesian to the spherical coordinates systems is done by using the expression:

$$d\mathbf{R}_i = dx_i dy_i dz_i = r^2 \sin \theta d\theta d\phi dr$$

where r is the radius of the studied sphere.

27.6 Classical Analogue of the Quantum-Mechanical Canonical Partition Function

Let E_i be the energy of a molecule i in a system of N simple, “indistinguishable,” in mutual interactions but for which it is unnecessary to specify their orientations. It is equal to the sum of its potential and kinetic energies U and E_k .¹ Its potential energy U depends on its proper coordinates x_i, y_i, z_i but also on those of other molecules in mutual interactions with it. These interactions, indeed, depend on the intermolecular distances. The kinetic energy of i depends on the components p_{xi}, p_{yi}, p_{zi} of its momentum \mathbf{p} . Therefore, one can write:

$$E_i = U(x_i, y_i, z_i) + E_k(p_{xi}, p_{yi}, p_{zi}) \quad i = 1 \dots N$$

The whole energy E of the system is equal to the sum of the individual energies E_i .

It is demonstrated that the classical canonical partition function of a N spherical particles system, without an internal structure, is given by the relation (for an approach of it, viz. Appendix F and the supplement one):

$$Q(N, T, V) = [1/N! h^{3N}] \times \int_{-\infty}^{+\infty} \int \exp[-H(x_1, y_1, z_1 \dots x_N y_N z_N; p_{x1}, p_{y1}, p_{z1} \dots p_{xN} p_{yN} p_{zN})] \times /kT \times dx_1, dy_1, dz_1 \dots dx_N, dy_N, dz_N \dots dp_{x1}, dp_{y1}, dp_{z1} \dots dp_{xN}, dp_{yN}, dp_{zN} \quad (27.1)$$

H is Hamilton's function involved in Lagrange's mechanics. The terms in brackets, $x_1, y_1, z_1 \dots x_N y_N z_N; p_{x1}, p_{y1}, p_{z1} \dots p_{xN} p_{yN} p_{zN}$ are the variables on which depend H . It is sufficient for our purpose to know that Hamilton's function is usually expressed in terms of generalized coordinates q and p , but in the present case, using cartesian coordinates and momenta is equivalent to the use of the generalized ones. h is Planck's constant ($h = 6.626 \times 10^{-34}$ Js) and k Boltzmann's constant ($k = 1.38 \times 10^{-23}$ JK⁻¹). T is the thermodynamic temperature.

For this kind of system, Hamilton's function is nothing more or less than the energy of the system, hence:

¹We are continuing to symbolize the potential energy, which is an energy of interaction between molecules, by U . According to IUPAC, U is, usually, the symbol of the internal energy and E_p is the potential energy.

$$H = \sum_i (1/2m)(p_{x_i}^2 + \dots p_{z_N}^2 + U(x_1, \dots, z_N)) \quad (27.2)$$

m is the molecular mass of each particle. In equation (27.1), all the summations are over the whole coordinates from $-\infty$ to $+\infty$.

The fact that equation (27.1) contains the factor $N!$ must be noticed. Its presence is for the same reason as in the analogous quantum-mechanical partition function. That is to say: particles are “indistinguishable” and the interactions between two of them must not be taken into account several times. Surprisingly, also, equation (27.1) contains Planck’s constant h which is a reminiscence of quantum mechanics. It is introduced as an integration constant in the mathematical developments devoted to the classical partition function. Its introduction is necessary since, without it, calculations performed through the classical partition function fail to provide correct values of the entropy and of other thermodynamic quantities of the system.

Relation (27.1) is by no means surprising. We can, indeed, notice the similarity:

$$\sum e^{-\text{energy}/kT} \Leftrightarrow \int \dots \int e^{-\text{energy}/kT} dx_1 \dots dz_N$$

Let us recall that the sum Σ goes over all the quantum states. Here, one again finds the pathway between quantum and classical functions and, from a strict mathematical standpoint, the fact that an integral is a sum of infinitely small quantities over an infinitely large number of them. Relation (27.1) is not surprising for a second reason. Quite evidently, $Q(N, T, V)$ is a continuous function. (This point is somewhat detailed in Appendix F).

Equation (27.1) is often written equivalently as:

$$Q(N, T, V) = [1/N!h^{3N}] \int_{-\infty}^{+\infty} \int \exp[-H/kT] d\mathbf{R}^N d\mathbf{p}^N \quad (27.3)$$

with:

$$H = H(\mathbf{p}^N, \mathbf{R}^N)$$

and more precisely:

$$H(\mathbf{p}^N, \mathbf{R}^N) = U_N(\mathbf{R}^N) + \sum_{i=1}^N (\mathbf{p}_i^2/2m) \quad (27.4)$$

where \mathbf{p}^N and \mathbf{R}^N recalls the dependence of Hamilton’s function on momenta and on the configuration.

With more complex molecules, the classical canonical partition function is:

$$Q(N, T, V) = [q^N / 8\pi^2]^N \Lambda^{3N} N! \int_{-\infty}^{+\infty} \exp[-\beta H(\mathbf{X}^N)] d\mathbf{X}^N d\mathbf{p}^N \quad (27.5)$$

$$H = \sum_{i=1}^N (\mathbf{p}_i^2 / 2m) + U_N(\mathbf{X}^N)$$

and

$$\beta = 1/kT$$

The symbol $U_N(\mathbf{X}^N)$ means the total potential energy of interaction of the system in the configuration \mathbf{X}^N . Note the use of (\mathbf{X}^N) in place of (\mathbf{R}^N) (with respect to the preceding case) in agreement with the working hypothesis.

In the relation (27.5), there exist also some supplementary terms. Let us recall that Λ is the thermal de Broglie wavelength, q is the *molecular* partition function of the species constituting the system. q takes into account the proper partition functions of translation, electronic, of vibration, of rotation, and nuclear of the species (viz. Chap. 26). For example, for most monoatomic gases: $q = 1$. (The product of electronic, nuclear, vibration, and rotation partition functions is called internal partition function.) The factor $8\pi^2$ lying in the denominator is introduced in order not to count the volume twice in the integration. The integration over $d\mathbf{R}$ amounts, indeed, to obtain the volume in a first time and, in a second one, the integration over the three angles also leads to the volume (viz. preceding paragraph):

$$\int d\Omega_i = 8\pi^2$$

27.7 Condition Required for the Applicability of the Partition Functions (27.1) and (27.3)

Partition functions (27.1) and (27.3) and those deriving from them cannot be used for all kinds of systems. Their handling is legitimate when the following condition is satisfied:

$$\Lambda^3 N / V \ll 1$$

where Λ is the thermal de Broglie wavelength of the particle defined by:

$$\Lambda = h / (2\pi m k T)^{1/2}$$

We see that the condition is satisfied when its density number N/V is small and the mass of the particle and temperature are large. Both conditions are frequently satisfied.

27.8 Some Examples of Handling of Classical Partition Functions: The Case of Perfect Gases

A gas is considered as being perfect when there exist no intermolecular forces between its particles. The mathematical counterpart of this definition is:

$$U_N(\mathbf{X}^N) = 0$$

whichever the configuration \mathbf{X}^N is.

When the gas is monoatomic and is not endowed with internal structure, the classical partition function reduces to:

$$Q(N, T, V) = [1/N!h^{3N}] \int_{-\infty \dots} \int \exp[-\beta H(\mathbf{p}^N)] d\mathbf{R}^N d\mathbf{p}^N \quad (27.6)$$

Since the potential energy does not exist, the expression of $H(\mathbf{p}^N)$ is:

$$H(\mathbf{p}^N) = \sum_{i=1}^N 1/2m(p_{x_i}^2 + \dots + p_{z_i}^2)$$

Integrations over $d\mathbf{R}^N$ and $d\mathbf{p}^N$ give:

$$Q(T, V, N) = V^N / \Lambda^{3N} N! \quad (27.7)$$

since:

- The integration over $d\mathbf{R}^N$ is immediate, because it is carried out on a cube of length unity:

$$\int d\mathbf{R}_i = \int_0^1 dx_i \int_0^1 dy_i \int_0^1 dz_i$$

and because there are N particles;

- The integration over the momenta $d\mathbf{p}^N$ is carried out, firstly, by setting up the following equality:

$$\begin{aligned}
 & h^{-3N} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \exp[-\beta(\mathbf{p}_i^2/2m)] d\mathbf{p}^N \\
 &= \left[h^{-1} \int_{-\infty}^{+\infty} \exp[-\beta p^2/2m] dp \right]^{3N}
 \end{aligned}$$

The right side of the last equality is justified by the fact that the particles are identical and by the fact that there are $3N$ variables of integration (so that $d\mathbf{p}_i = dp_i^3$ and $d\mathbf{p}_i = d\mathbf{p}_i$). The remaining integral is easily calculated by starting from the standard integral value:

$$\int_0^{\infty} \exp[-ax^2] dx = 1/2(\pi/a)^{1/2}$$

It is very interesting to notice that the equality (27.7) is equivalent to the following one:

$$\mu = kT \ln \Lambda^3 + kT \ln N/V \quad (27.8)$$

or:

$$\mu = kT \ln \Lambda^3 + kT \ln \rho$$

(27.8) is obtained from the equality (27.7) and from the general relationship (viz. Chap. 23)

$$\mu = -kT(\partial \ln Q / \partial N)_{T,V}$$

after use of Stirling's approximation. Relation (27.8) is already very interesting. It is sufficient to compare it to the following one (viz. Chap. 6)

$$\mu = \mu^\circ + RT \ln x$$

to be convinced.

- A polyatomic gas may exhibit a perfect behavior, but because it is polyatomic, it does possess an internal structure. Its molecular partition function q is no longer equal to 1 as in the monoatomic case. Of course, since by hypothesis, there exist no mutual interactions between molecules

$$U(\mathbf{X}^N) = 0$$

The knowledge of the whole coordinates \mathbf{R}^N is no longer sufficient to describe the system. The whole ensemble coordinates \mathbf{X}^N must be used. As a result, the canonical partition function is:

$$Q(N, T, V) = \left\{ q^N / \left[(8\pi^2)^N \Lambda^{3N} N! \right] \right\} \int_v \dots \int d\mathbf{X}^N$$

The limits of integration are noticed in the following relation (v means that the integration of \mathbf{R} is carried out over a cube of length unity) (see before):

$$Q(N, T, V) = \left\{ q^N / \left[(8\pi^2)^N \Lambda^{3N} N! \right] \right\} \left[\int_v d\mathbf{R} \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\psi \right]^N$$

Finally:

$$Q(N, T, V) = q^N V^N / \Lambda^{3N} N!$$