

Chapter 23

Thermodynamic Quantities Within the Framework of the Canonical Ensemble

Abstract The chapter describes the handling of the mathematical relations previously found within the framework of the canonical ensemble through the partition function in order to assimilate them to the expressions of classical thermodynamic functions. Concerning now the introduction of the nonmechanical functions such as the entropy and the temperature into the realm of statistical thermodynamics, the strategy consists in comparing the expressions concerning the mechanical quantities obtained (thanks to the theory of the canonical ensemble) and those stemming from classical thermodynamics. Therefore, the statistical expressions of internal energy, entropy, pressure, and chemical potential are obtained. Some of these functions are calculated with the aid of the characteristic function of the canonical function which spontaneously introduces itself into the calculations.

Keywords Thermodynamic quantities • Entropy • Enthalpy • Partition function • System • Quantum mechanics • Statistical analogues of classical thermodynamic functions • Boltzmann's constant • Characteristic functions • Canonical function • Closed system • Chemical potential • Characteristic function • Nonmechanical properties • Internal energy • Gibbs and Helmholtz energies

The theoretical handling of some ensembles throws some light, in terms of molecular parameters, on the deep significance of some thermodynamic quantities, among them, notably, the Gibbs energy from which are following the concepts of fugacity and of activity.

In this chapter, as a first example, we handle the mathematical relations previously found within the framework of the canonical ensemble.

In order to introduce the nonmechanical functions such as the entropy and the temperature into the realm of statistical thermodynamics, the strategy consists in comparing the expressions concerning the mechanical quantities obtained thanks to the theory of the canonical ensemble and those stemming from classical thermodynamics.

23.1 Association Average Energy \bar{E} and Internal Energy

According to the expressions (22.6) and (22.7) of the previous chapter

$$\bar{E} = \sum_j E_j e^{-\beta E_j} / \sum_j e^{-\beta E_j} \quad (\text{relation 6 - previous chapter})$$

$$P_j = e^{-\beta E_j} / \sum_i e^{-\beta E_i} \quad (\text{relation 7 - previous chapter})$$

we obtain

$$\bar{E} = \sum_j P_j E_j$$

or in differentials

$$d\bar{E} = \sum_j E_j dP_j + \sum_j P_j dE_j \quad (23.1)$$

The first term of the right member of (23.1) represents the energy change due to the variation of the probability P_j for a system being in the energy state E_j which does not vary during the process. This entails that there is no change in the volume of the system, i.e., there is no work done on the system or performed by it. Hence, this term represents an energy change of the system without the fact that a work would be involved. According to the first principle, it follows that the first term of the right member represents a heat exchange. A consideration of the fundamental postulates shows that a heat absorption by a system must be associated with the probability that a system of the ensemble does possess the (authorized) energy E_j . Hence, we can set up the correspondence:

$$dq \leftrightarrow \sum_j E_j dP_j$$

According to the algebraic formulation of the first principle, the second term of the right member of (23.1) must be identified to the work done on the system, whence

$$dw \leftrightarrow \sum_j P_j dE_j$$

Finally, we can set up the correspondence:

$$\bar{E} \leftrightarrow \text{internal energy}$$

23.2 Statistical Expression of the Entropy

From relation (23.7) of the preceding chapter

$$P_j = e^{-\beta E_j} / \sum_i e^{-\beta E_i} \quad (\text{relation 7 - preceding chapter})$$

we deduce

$$E_j = -1/\beta (\ln P_j + \ln Q) \quad \text{with} \quad Q = \sum_j e^{-\beta E_j} \quad (23.2)$$

whence, according to (23.1) and the just preceding considerations,

$$d\bar{E} = -1/\beta \sum_j (\ln P_j + \ln Q) dP_j + \sum_j P_j dE_j \quad (23.3)$$

Moreover, according to the expression of the total differential, we can write

$$dE_j = (\partial E_j / \partial V)_N dV + (\partial E_j / \partial N)_V dN$$

Since, according to the conditions prevailing to the canonical ensemble, the number of the particles of the system is constant, $dN = 0$, and

$$dE_j = (\partial E_j / \partial V)_N dV$$

Relation (23.3) becomes

$$d\bar{E} = -1/\beta \sum_j (\ln P_j + \ln Q) dP_j + \sum_j P_j (\partial E_j / \partial V)_N dV$$

and since $dV = 0$

$$d\bar{E} = -1/\beta \sum_j (\ln P_j + \ln Q) dP_j$$

From another standpoint

$$\sum_j P_j = 1 \quad \text{whence} \quad \sum_j dP_j = 0$$

we obtain

$$d\bar{E} = -1/\beta \sum_j \ln P_j dP_j$$

This relation can be transformed into another one, more general. The transformation is done in the following manner. Already, let us mention that this transformation leads to the notion of *statistical entropy*. Let us consider the function $\sum_j P_j \ln P_j$. In differential writing, it gives

$$\begin{aligned} d\left(\sum_j P_j \ln P_j\right) &= \sum_j \ln P_j dP_j + \sum_j P_j d \ln P_j \\ d\left(\sum_j P_j \ln P_j\right) &= \sum_j \ln P_j dP_j + \sum_j P_j dP_j/P_j \\ d\left(\sum_j P_j \ln P_j\right) &= \sum_j \ln P_j dP_j \quad \text{since} \quad \sum_j dP_j = 0 \end{aligned}$$

As a result

$$d\bar{E} = -1/\beta d\left(\sum_j P_j \ln P_j\right)$$

Let us compare this relation with that purely thermodynamic governing the internal energy change of a system during a reversible heat exchange, without any production of work:

$$dE = TdS$$

Let us make the association:

$$TdS \leftrightarrow -1/\beta d\left(\sum_j P_j \ln P_j\right)$$

whence

$$dS = (-1/\beta T) d\left(\sum_j P_j \ln P_j\right)$$

dS being an exact differential, the ratio $1/\beta T$ cannot be anything else than a constant. It is called Boltzmann's constant: symbol k . Its unity is the joule by kelvin J K^{-1} . Let us notice that we again find the fact that the ensemble is isothermal, condition of the study with the canonical ensemble. Therefore

$$dS = -k d\left(\sum_j P_j \ln P_j\right)$$

To sum up, by regarding these two first analogies: in a closed, isothermal, system (ensemble N, V, T):

- The probability for the system to be in the state of energy E_j , entailed by the composition N and the volume V (condition coming from the principles of quantum mechanics), is given by the expression

$$P_j(N, V, T) = e^{-E_j(N, V) / kT} / Q(N, V, T) \quad (23.4)$$

where $Q(N, V, T) = \sum_j e^{-E_j(N, V) / kT}$ is the partition function of the canonical ensemble. (Let us recall that the symbolism N is general and can mean that there is only one or several components with a constant number of moles, as well.)

- The entropy is given by the expression

$$S(N, V, T) = -k \sum_j P_j \ln P_j \quad (23.5)$$

where P_j is given by relation (23.4). It clearly appears that entropy is a statistic quantity.

23.3 The Characteristic Function of the Canonical Ensemble

As we shall see it, firstly in the case of the canonical ensemble and later in that of other ensembles, there exists a characteristic function of each ensemble. It is a function different from the *partition function* of the same ensemble, even if both are mathematically related to each other.

The characteristic function appears naturally in thermodynamics, but statistical thermodynamics permits to relate it, mathematically, to the corresponding partition function. Once known, the characteristic function permits to calculate all the other thermodynamic functions. We know, indeed, that to some thermodynamic functions, i.e., the internal energy, the Gibbs and Helmholtz energies, and the enthalpy, corresponds a set of independent variables for each of them, called their natural variables (viz. Chap. 4). These sets (defining the system) permit to immediately calculate all the other quantities of the system. For example, for the Gibbs energy, they are the pressure, volume, and numbers of moles of every component. They are the same variables than those which define the corresponding ensembles in statistical thermodynamics.

The characteristic function of the canonical ensemble is obtained as follows. Let us introduce the expression of P_j into that of entropy (given just above); we obtain, after having taken into account the relation (23.6) of the preceding chapter and since

$$\bar{E} = \frac{\sum_j E_j e^{-\beta E_j}}{\sum_j e^{-\beta E_j}}$$

$$S = \bar{E}/T + k \ln Q$$

By assimilating this expression of S to that of purely thermodynamic origin

$$S = E/T - A/T$$

where A is the Helmholtz energy, it comes to light the following meaning of the latter in statistical thermodynamics:

$$A(N, V, T) \leftrightarrow -kT \ln Q(N, V, T)$$

The function A is the characteristic function of the canonical ensemble defined by the parameters N , V , and T since, once it is known, it permits, as we shall see, to calculate the entropy, pressure, internal energy, and chemical potentials of the components.

23.4 Calculation of the Thermodynamic Functions by Starting from the Characteristic Function of the Canonical Ensemble

This kind of calculation is particularly important. It is the one which is practiced, notably in the statistical part of this book, for the calculation of the changes of the thermodynamic quantities and for obtaining the energy levels E_j . Analogous calculations, of course, are also performed by starting from partition functions of other ensembles.

Let us consider the following relation from purely thermodynamic origin by noticing that it contains the three variables defining the canonical system (T , V , n_k , or N):

$$dA = -SdT - p dV + \sum_k \mu_k dn_k \quad (23.6)$$

(k index of the component the number of moles of which is n_k)

and also from the expression of the total differential

$$dA = (\partial A/\partial T)_{V, n_k} dT - (\partial A/\partial V)_{T, n_k} dV + \sum_k (\partial A/\partial n_k)_{T, V, n_j} dn_k \quad (n_i \neq n_k)$$

By replacing $A(N, V, T)$ by the characteristic function $kT \ln Q(N, V, T)$, by operating the calculations of partial derivation on the characteristic function and by identifying with the corresponding elements of the relation (23.6), some very interesting results are obtained. Concerning:

23.4.1 The Entropy

Since $S = -(\partial A / \partial T)_{V, N}$ (dA exact total differential)

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

As a result

$$S = kT(\partial \ln Q / \partial T)_{V, N} + k \ln Q \quad (23.7)$$

23.4.2 The Pressure

Since $p = -(\partial A / \partial V)_{T, N}$, we obtain

$$p = kT(\partial \ln Q / \partial V)_{T, N} \quad (23.8)$$

23.4.3 The Internal Energy

Since $E = -T^2 (\partial A / T / \partial T)_{V, N}$

$$U = kT^2(\partial \ln Q / \partial T)_{V, N} \quad (23.9)$$

23.4.4 The Chemical Potential

Even if the canonical ensemble is a closed system, its component(s) possess(es) a well-determined chemical potential, of course in the state of the system. It can also be calculated from the characteristic function. According to relation (23.6), we immediately obtain

$$\begin{aligned} \mu_k &= (\partial A / \partial N_k)_{T, V, N, k \neq i} \\ \mu_k &= -kT(\partial \ln Q / \partial N_k)_{T, V, N, k \neq i} \end{aligned} \quad (23.10)$$

23.5 Degenerated Energy States E_j and Energy Levels

For numerous applications or to tackle new problems, it is interesting to group all the energetic states of the same level E_j . Let $\Omega_i(N, V)$ be the number of states of the energy level $E_i(N, V)$, i.e., in the listing of the possible states E_j , the same value E_i exists Ω_i times. $\Omega_i(N, V)$ is the degeneracy. As a result, the partition function which was

$$Q(N, V, T) = \sum_j e^{-E_j(N, V)/kT}$$

becomes

$$Q(N, V, T) = \sum_i \Omega_i(N, V) e^{-E_i(N, V)/kT} \quad (23.11)$$

where, this time, the sum is calculated on the energy levels, whereas before it was calculated on all the states, included those of the same energy.