STATISTICAL THERMODYNAMICS

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Statistical thermodynamics or statistical mechanics provides a link between quantum mechanics (or wave mechanics) and classical thermodynamics. Classical thermodynamics deals with *macroscopic* properties of matter and describes the behaviour of large number of molecules in terms of properties such as pressure, volume, temperature, composition, etc. Quantum mechanics, on the other hand, deals almost exclusively with matter at the microscopic level. It tells us that each microscopic system can be described by a wave function. However, it does not indicate which wave function of a molecule will represent the state of the system at a given instant. Neither classical thermodynamics nor quantum mechanics is able to calculate the macroscopic properties of matter from the microscopic structures of individual molecules.

Since any observed equilibrium property of matter must be some kind of an average of a large number of molecules, it is evident that we must use statistical methods to determine this property. *The discipline which deals with the computation of the macroscopic properties of matter from the data on the microscopic properties of individual atoms (or molecules)* is called **statistical mechanics** or **statistical thermodynamics.**

Fundamental contributions to the subject were made by J.C. Maxwell, L. Boltzmann and J. Willard Gibbs and several other scientists such as M. Planck, A. Einstein, S.N. Bose, E. Fermi, P.A.M. Dirac, R.C. Tolman, R.H. Fowler, E.A. Guggenheim, M. Born, P. Debye, L. Onsager, L.D. Landau, N. Bogoliubov, J.G. Kirkwood, I. Prigogine, A. Khinchin, N. Wiener, J.E. Mayer, K.G. Wilson, A. Sommerfeld and R. Kubo. The 1983 Physics Nobel Laureate, S. Chandrasekhar (1910-1995) was the first to apply quantum statistics to stellar dynamics—in particular, to white dwarfs.

Statistical mechanics can be applied easily to simple ideal systems such as monoatomic and diatomic gases. For application to interacting systems such as liquids (where strong intermolecular forces exist), the details of the intermolecular potential energy, which is not always known accurately, have also to be taken into account. That is why statistical mechanics of liquids is a difficult but fascinating subject. Gases under high pressures, too, are difficult to treat statistically since they deviate strongly from ideality. In recent years statistical methods have been applied successfully to simple liquids and dense gases. Progress in this area has been made possible by the application of both the advanced mathematical methods and high-speed computers which can numerically solve the otherwise highly intractable differential and integro-differential equations involved in advanced theoretical treatments.

Types of Statistics. Different physical situations encountered in nature are described by three types of statistics, *viz.*, the *Maxwell-Boltzmann* (or M-B) *statistics, the Bose-Einstein* (or B-E) *statistics and the Fermi-Dirac* (or F-D) *statistics*. The M-B statistics, developed long before the advent of quantum mechanics, is also called **classical statistics** whereas the Bose-Einstein statistics and the Fermi-Dirac statistics are collectively called **quantum statistics.** The characteristics of the three types of statistics are summed up as follows :

1. In **M-B statistics,** the particles are assumed to be *distinguishable* and any number of particles may occupy the same energy level. Particles obeying M-B statistics are called **boltzons** or **maxwellons.**

2. In **B–E statistics,** the particles are *indistinguishable* and any number of particles may occupy a given energy level. This statistics is obeyed by particles having integral spin, such as hydrogen (H_2) deuterium (D_2), nitrogen (N_2), helium-4 (^4He) and photons. Particles obeying B-E statistics are called **bosons**.

3. In **F–D statistics,** the particles are *indistinguishable* but only one particle may occupy a given energy level. This statistics is obeyed by particles having half-integral spin, *e.g.*, the protons, electrons, helium-3 (^3He) and nitric oxide (NO). Particles obeying F–D statistics are called **fermions**.

We will mention here, without proof, another equivalent definition of fermions and bosons. **Fermions** are those species whose wave functions are *antisymmetric* with respect to the exchange of particles whereas **bosons** are those species whose wave functions are *symmetric* with respect to the exchange of particles. These ideas on quantum statistics are discussed in Chapter 27.

The three types of statistics are described here.

1. Maxwell–Boltzmann Statistics. Consider a system of *N distinguishable* particles occupying energy levels ε_0, ε_1, ε_2, etc. The total number of arrangements for placing n_0 particles in the ground state energy level ε_0, n_1 particles in the first excited state energy level ε_1, n_2 particles in the second excited state energy level ε_2, and so on, is known as the **thermodynamic probability, *W*,** of the given macrostate. It is, in general, a very large number. Our problem is to determine *W*, *i.e.*, to determine how many *microstates* correspond to a given *macrostate*. It can be shown that *W* is given by

$$W = \frac{N!}{n_1!\,n_2!\,n_3!\cdots\cdots n_j!} = \frac{N!}{\Pi n_i!} \qquad \ldots(1)$$

where $N = \Sigma n_i$.

In Eq. 1, *N* is the total number of particles and the summation is over all the energy levels. It is possible to realize a given energy level in more than one way, *i.e.*, more than one quantum state has the same energy. When this happens, the energy level is said to be **degenerate,** Let g_i be the **degeneracy** (or **multiplicity**) of the energy level ε_i. This means that if there is one particle in the *i*th energy level, there are g_i ways of distributing it. For two particles in the *i*th energy level, there are g_i^2 possible distributions. Thus, for n_i particles in the *i*th energy level, there are $g_i^{n_i}$ possible distributions. Hence, the thermodynamic probability for the system of *N* particles is given by

$$W = N!\prod_i \frac{g_i^{n_i}}{n_i!} \times \text{constant} \qquad \ldots(2)$$

It is well known that the entropy *S* and probability *W* of a given state of a system are related by the Boltzmann equation, the most famous equation in statistical mechanics, *viz.*,

$$S = k \ln W \qquad \ldots(3)$$

The probability must be a maximum for an equilibrium state so that at equilibrium

$$S = k \ln W_{max} \qquad \ldots(4)$$

We are thus interested in finding a distribution that will make *W* a maximum. It is more convenient, however, to maximize the logarithm of *W*. It is known from calculus that at the maximum, the derivative of a function vanishes. Hence, at equilibrium,

$$d \ln W = \frac{\partial \ln W}{\partial n_1} dn_1 + \frac{\partial \ln W}{\partial n_2} dn_2 + \cdots\cdots \frac{\partial \ln W}{\partial n_3} dn_3 + \cdots\cdots$$

$$= \sum_i \frac{\partial \ln W}{\partial n_i} dn_i = 0 \qquad \ldots(5)$$

If we confine our investigation to a *closed system of independent particles*, it would meet the following two requirements :

(i) The total number of particles is *constant, i.e.,*

$$N = \sum_i n_i = \text{constant} \qquad ...(6)$$

(ii) The total energy, U, of the system is *constant, i.e.,*

$$U = \sum n_i \varepsilon_i = \text{constant} \qquad ...(7)$$

The constancy of the total number of particles implies that

$$dN = \sum dn_i = 0 \qquad ...(8)$$

and the constancy of the total energy implies that

$$dU = \sum \varepsilon_i \, dn_i = 0 \qquad ...(9)$$

From Eq. 2, taking logarithms of both sides, we get

$$\ln W = \ln N! + \sum_i n_i \ln g_i - \sum_i \ln n_i! + \text{constant} \qquad ...(10)$$

Here we invoke the **Stirling approximation** according to which, for large x,

$$\ln x! = x \ln x - x \qquad ...(11)$$

Using this approximation for $\ln n_i!$, Eq. 10 becomes

$$\begin{aligned} \ln W &= \ln N! + \sum_i n_i \ln g_i - \sum_i n_i \ln n_i + \sum_i n_i + \text{constant} \\ &= (N \ln N - N) + \sum_i n_i \ln g_i - \sum_i n_i \ln n_i + N + \text{constant} \\ &= N \ln N + \sum_i n_i \ln g_i - \sum_i n_i \ln n_i + \text{constant} \end{aligned} \qquad ...(12)$$

Differentiating and bearing in mind that N and g_i are constants, we get

$$d \ln W = \sum_i \ln g_i \, dn_i - \sum_i \ln n_i \, dn_i - \sum n_i \, d \ln n_i \qquad ...(13)$$

Now,

$$\sum_i n_i \, d \ln n_i = \sum_i n_i \frac{dn_i}{n_i} = \sum_i dn_i = 0 \qquad ...(14)$$

Hence, at equilibrium,

$$d \ln W = \sum \ln g_i \, dn_i - \sum \ln n_i \, dn_i = 0 \qquad ...(15)$$

Eq. 15 gives *the change in* ln *W which results when the number of particles in each energy level is varied.*

If our system is *open,* then n_i would vary without restriction and the variations would be *independent* of one another. It would then be possible to solve Eq. 15 by setting each of the coefficients of the dn_i terms in Eq. 15 equal to zero. However, our system is not open but closed and since N is constant, the values of dn_i are not independent of one another, as is seen from Eq. 14. Again, the energy of the system is constant, too. How, then, can we solve Eq. 15 subject to the constraints of Eqs. 6 and 7 ?

The desired solution is obtained by applying the method of **Lagrange's undetermined multipliers.** Rewriting Eq. 15, we have

$$\sum_i \ln \frac{g_i}{n_i} dn_i = 0 \qquad ...(16)$$

Multiplying Eqs. 8 and 9 by the arbitrary constants α and β (known as Lagrange's undetermined multipliers) and subtracting from Eq. 16, we get

$$\sum_i \left[\ln \frac{g_i}{n_i} - \alpha - \beta \varepsilon_i \right] dn_i = 0 \qquad ...(17)$$

We can now select values of α and β in such a manner that one of the terms in the summation (say, $i = 1$) is zero, the value of dn_i being immaterial. The remaining dn_i terms then become independent of one another since dn_i can be obtained from these dn_i terms (Eq. 8). We are now in a position to set each of the coefficients of dn_i in Eq. 17 equal to zero. Thus,

$$\ln (g_i/n_i) - \alpha - \beta\varepsilon_i = 0 \quad \text{or} \quad \ln g_i/n_i = \alpha + \beta\varepsilon_i \quad \text{or} \quad \ln n_i = \ln g_i - \alpha - \beta\varepsilon_i$$

or

$$n_i = g_i e^{-\alpha - \beta\varepsilon_i} \qquad ...(18)$$

Eq. 18 which is one form of the **Boltzmann distribution law,** gives the **most probable distribution for a macrostate,** *i.e.*, it gives the occupation numbers of the molecular energy levels for the most probable distribution in terms of the energies ε_i, the degeneracy g_i and the undetermined multiplies α and β.

2. Bose–Einstein Statistics. Consider a system of N *indistinguishable* particles such that n_i particles are in the ith energy level with degeneracy g_i. The n_i particles have to be distributed among g_i states. For the sake of simplicity, imagine that the ith energy level has $g_i - 1$ partitions which are sufficient to separate the energy level into g_i intervals. Now the possible number of distributions of n_i particles among the g_i states may be determined by permuting the array of partitions and particles. The total number of permutations of n_i particles and $(g_i - 1)$ partitions is $(n_i + g_i - 1)!$. However, *the partitions and the particles are indistinguishable*. This implies that interchanging two partitions does not alter an arrangement ; also interchanging two particles does not alter an arrangement. Hence, we must divide $(n_i + g_i - 1)!$ by the number of permutations of the $g_i - 1$ partitions, *viz.*, $(g_i - 1)!$ and the number of permutations of n_i particles, *viz.*, $n_i\,!$ to obtain the number of possible arrangements of the n_i particles in the energy level ε_1. Thus,

$$\text{The number of arrangements} = \frac{(n_i + g_i - 1)!}{n_i\,!(g_i - 1)!} \qquad ...(19)$$

As in the case of Maxwell–Boltzmann statistics, we assume that in the present case also the total number of particles is constant and the total energy of the system is also constant, *i.e.*,

$$N = \sum_i n_i = \text{constant} \qquad \text{(Eq. 6)}$$

$$U = \sum n_i \varepsilon_i = \text{constant} \qquad \text{(Eq. 7)}$$

Thus, the thermodynamic probability W for the system of N particles (*i.e.*, the number of ways of distributing N particles among the various energy levels) is given by

$$W = \prod_i \frac{(n_i + g_i - 1)!}{n_i\,!\,(g_i - 1)!} \times \text{constant} \qquad ...(20)$$

Taking logarithms of both sides of Eq. 20, we get

$$\ln W = \sum_i [\ln (n_i + g_i - 1)! - \ln n_i\,! - \ln (g_i - 1)!] + \text{constant} \qquad ...(21)$$

Here, too, since n_i and g_i are very large numbers, we can invoke Stirling's approximation, *viz.*, $\ln x\,! = x \ln x - x$, to obtain

$$\ln W = \sum_i [(n_i + g_i) \ln (n_i + g_i) - n_i \ln n_i - g_i \ln g_i] + \text{constant} \qquad ...(22)$$

where we have set $n_i + g_i - 1 = n_i + g_i$ and $g_i - 1 = g_i$. Since, n_i is very large, it can be treated as a *continuous variable*. Differentiation of Eq. 22 with respect to n_i and setting the differential equal to zero gives for the most probable thermodynamic state of the system,

$$\delta \ln W = \sum [\ln n_i - \ln (n_i + g_i)]\, \delta n_i = 0 \quad \text{or} \quad \sum_i \left[\ln \frac{n_i}{(n_i + g_i)} \right] \delta n_1 = 0 \qquad ...(23)$$

From Eqs. 6 and 7, $\delta N = \sum_i \delta n_i = 0$ ...(24)

$$\delta U = \sum_i \varepsilon_i \, dn_i = 0 \qquad \text{...(25)}$$

Applying the method of Lagrange's undetermined multipliers to Eqs. 23, 24 and 25, we get

$$\sum_i \left[\ln \frac{n_i}{(n_i + g_i)} + \alpha + \beta \varepsilon_i \right] \delta n_i = 0 \qquad \text{...(26)}$$

Since the variations δn_i are independent of one another, hence

$$\ln \frac{n_i}{(n_i + g_i)} + \alpha + \beta \varepsilon_i = 0 \qquad \text{...(27)}$$

whence

$$\ln \left[\frac{g_i}{n_i} + 1 \right] = \alpha + \beta \varepsilon_i \quad \text{or} \quad \frac{g_i}{n_i} + 1 = e^{\alpha} + \beta \varepsilon_i \qquad \text{...(28)}$$

$$n_i = g_i / [\exp(\alpha + \beta \varepsilon_i) - 1] \qquad \text{...(29)}$$

Eq. 29 *is the expression for the most probable distribution of N particles among the various energy levels according to the Bose–Einstein statistics.*

3. **Fermi-Dirac Statistics.** Consider that the n_i particles are distributed among the g_i states ($n_i < g_i$) where g_i , as before, is the degeneracy of the ith energy level. Imagine that the particles are *distinguishable*. This implies that the first particle may be placed in any one of the g_i states and for each one of these choices, the second particle may be placed in any one of the remaining $g_i - 1$ states, and so on. Thus, the number of arrangements is given by the expression $g_i!/(g_i - n_i)!$.

Since, however, the particles are *indistinguishable,* the above expression has to be divided by the possible number of permutations of n_i particles, *viz.*, $n_i!$. Hence, the number of arrangements of n_i particles in the ith energy level is given by the expression $g_i!/(n_i!\,(g_i - n_i)!)$.

Thus, the thermodynamic probability W for the system of N particles (*i.e.*, the number of ways of distributing N particles among the various energy levels) is given by

$$W = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!} \times \text{constant} \qquad \text{...(30)}$$

Taking logarithms of both sides of Eq. 30, we have

$$\ln W = \sum_i [\ln g_i! - \ln n_i! - \ln (g_i - n_i)!] + \text{constant} \qquad \text{...(31)}$$

Assuming that n_i, g_i and $g_i - n_i$ are very large, we can apply Stirling's approximation, obtaining

$$\ln W = \sum_i [(n_i - g_i)\ln(g_i - n_i) - n_i \ln n_i + g_i \ln g_i] + \text{constant} \qquad \text{...(32)}$$

Thus, for the most probable state,

$$\delta \ln W = \sum_i [\ln n_i - \ln(g_i - n_i)]\delta n_i = 0 \quad \text{or} \quad \sum_i [\ln n_i/(g_i - n_i)]\,\delta n_i = 0 \qquad \text{...(33)}$$

Since

$$N = \sum_i n_i = \text{constant} \quad \text{and} \quad U = \sum_i n_i \varepsilon_i = \text{constant},$$

hence,

$$\delta N = \sum_i \delta n_i \quad \text{and} \quad \delta U = \sum_i \varepsilon_i dn_i = 0 \qquad \text{...(34)}$$

Applying Lagrange's method of undetermined multipliers, we obtain

$$\sum_i [\ln n_i/(g_i - n_i) + \alpha + \beta \varepsilon_i]\,\delta n_i = 0 \qquad \text{...(35)}$$

Since the variations δn_i are independent of one another, hence.

$$\ln n_i/(g_i - n_i) + \alpha + \beta \varepsilon_i = 0 \quad \text{or} \quad \ln[(g_i/n_i) - 1] = \alpha + \beta \varepsilon_i \quad \text{or} \quad (g_i/n_i) - 1 = e^{\alpha + \beta \varepsilon_i} \qquad \text{...(36)}$$

$$\therefore \qquad n_i = g_i/[\exp(\alpha + \beta\varepsilon_i) + 1] \qquad ...(37)$$

Eq. 37 is *the expression for the most probable distribution of N particles among the energy levels according to the Fermi-Dirac statistics.*

Evaluation of Lagrange's Undetermined Multipliers. We now proceed to determine α and β. Since $N = \sum_i n_i$, hence from Eq. 18,

$$\sum_i g_i e^{-\alpha-\beta\varepsilon_i} = N \quad \text{or} \quad e^{-\alpha} = N/\sum_i g_i e^{-\beta\varepsilon_i} \qquad ...(38)$$

Defining a quantity q, called the **molecular partition function,** as

$$q = \sum_i g_i e^{-\beta\varepsilon_i} \qquad ...(39)$$

we obtain $\qquad e^{-\alpha} = N/q \qquad ...(40)$

Accordingly, the Boltzmann distribution law equation (*viz.*, Eq. 18), becomes

$$n_i = N g_i e^{-\beta\varepsilon_i}/q \qquad ...(41)$$

The partition function, q, is a quantity of immense importance in statistical thermodynamics. We shall see presently that by evaluating the partition function for a system we can calculate the value of any thermodynamic function for that system.

However, before we proceed with the task of evaluating the partition function, let us determine the constant β. Taking logs of Eq. 2 and applying Stirling's approximation to $\ln N!$ and $\ln n_i!$, we have

$$\ln W = \ln N! + \Sigma(n_i \ln g_i - \ln n_i!) \qquad ...(42)$$

$$= N\ln N - N + \sum_i(n_i \ln g_i - n_i \ln n_i + n_i) = N\ln N + \sum_i n_i \ln g_i - \sum_i n_i \ln n_i \qquad ...(43)$$

Taking logs of Eq. 41, we have

$$\ln n_i = \ln N - \ln q + \ln g_i - \beta\varepsilon_i \qquad ...(44)$$

Substituting in Eq. 43, we get

$$\ln W = N\ln N + \sum_i n_i \ln g_i \sum_i n_i(\ln N - \ln q + \ln g_i - \beta\varepsilon_i)$$

$$= N\ln N + \sum_i n_i \ln g_i - N\ln N + N\ln q - \sum_i n_i \ln g_i + \beta\sum_i n_i \varepsilon_i \qquad ...(45)$$

$$= N\ln q + \beta U$$

Substituting this result into the Boltzmann equation (*viz.*, Eq. 3), we have

$$S = k\ln W = Nk\ln q + k\beta U \qquad ...(46)$$

From the combined statement of the First and the Second laws of thermodynamics, we know that for a simple system,

$$dU = TdS - PdV \qquad ...(47)$$

At constant volume (V = constant ; $dV = 0$), $dU = TdS \qquad ...(48)$

$$\therefore \qquad (\partial S/\partial U)_V = 1/T \qquad ...(49)$$

Differentiating Eq. 46 with respect to U at constant V, we get

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{Nk}{q}\left(\frac{\partial q}{\partial U}\right)_V + k\beta + kU\left(\frac{\partial \beta}{\partial U}\right)_V = \frac{Nk}{q}\frac{dq}{d\beta}\left(\frac{\partial \beta}{\partial U}\right)_V + k\beta + kU\left(\frac{\partial \beta}{\partial U}\right)_V \qquad ...(50)$$

Also, from Eq. 39, $dq/d\beta = -Uq/N$ ...(51)

Substitution of Eq. 51 in Eq. 50 results in cancellation of the first and the last terms, giving

$$(\partial S/dU)_V = k\beta \qquad \text{...(52)}$$

Comparing Eqs. 49 and 52, we find that

$$\beta = 1/kT \qquad \text{...(53)}$$

Hence, from Eq. 39, the molecular partition function q becomes

$$q = \sum_i g_i e^{-\varepsilon_i/kT} \qquad \text{...(54)}$$

and the Maxwell-Boltzmann distribution equation (Eq. 41) becomes

$$n_i = (N g_i e^{-\varepsilon_i/kT})/q \qquad \text{...(55)}$$

From Eq. 55 we can easily obtain the ratio of the populations, *i.e.*, the number of particles in any two energy levels ε_i and ε_j. Thus,

$$\frac{n_i}{n_j} = \frac{g_i}{g_j} e^{-(\varepsilon_i - \varepsilon_j)/kT} \qquad \text{...(56)}$$