Statistical Mechanics
Lecture 8

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Maxwell-Boltzmann Statistics:

The Maxwell- Boltzmann statistics giving the distribution function is applicable to an ensemble of particles forming a dilute gas. It may be applied to free electron in the conduction band of a semiconductor at ordinary temperature and for not too high doping.

From distribution function the number of particles N_i occupying the g_i state is given by

$$N_i = g_i \,.\, f(E_i) \rightarrow (i)$$

If the energy levels are very closely spaced then g_i may be replaced $g(E)dE$ where $g(E)$ is the density of state and N_i by $N(E)dE$, the number of particles with energies between $E \; and \; E + dE$.

Hence

$$N(E)d.E = f(E).g(E).dE \rightarrow (ii)$$

This equation (ii) is perfectly general and holds for any form of distribution function and the density of state. We shall consider an electron gas system obeying the Maxwell-Boltzmann statistics. Since there are two allowed momentum states for the two spin orientation of the electron then

$$g(E).dE = \frac{g\sqrt{2\pi}.V.m^{3/2}}{h^3}\ E^2.dE \rightarrow (iii)$$

Using Maxwell-Boltzmann form of distribution function and substituting $\beta = -\frac{1}{K_B T}$ we obtain

$$N(E)d.E = e^{\alpha}.e^{-E/K_{\beta}T}.g(E)d.E \rightarrow (iv)$$

The constant α is to be determined from the total number of particles N we have

$$N = \int_0^{\infty} N(E)\,dE = e^{\alpha}\int_0^{\infty} g(E)\,e^{-E/K_{\beta}T}dE \rightarrow (v)$$

So that

$$e^{\alpha} = \frac{N}{\int_0^{\infty} g(E).e^{-E/k_{\beta}T}.dE} \rightarrow (vi)$$

$$e^{\alpha} = \frac{Nh^3 \Big/ 8\sqrt{2\pi}.V.m^{3/2}}{\int_0^{\infty} E^{1/2}.e^{-E/K_{\beta}T}.dE} \rightarrow (vii)$$

To evaluate the integral we introduced a dimensionless variable $x = \frac{E}{K_{\beta}T}$ then we can write

$$\int_0^{\infty} E^{1/2}.e^{-E/K_{\beta}T}.dE = \left(K_{\beta}T\right)^{3/2}.\int_0^{\infty} x^{1/2}e^{-x}dx \rightarrow (viii)$$

$$\int_0^\infty E^{1/2} e^{-E/K_\beta T} dE = \left(K_\beta T\right)^{3/2} \frac{\sqrt{\pi}}{2} \rightarrow (ix)$$

Therefore

$$e^\alpha = \frac{N}{2V}\left(\frac{h^2}{2\pi m K_\beta T}\right)^{3/2} \rightarrow (x)$$

Finally for Maxwell-Boltzmann distribution function for the system is

$$f(E) = e^{\alpha} e^{-E/K_\beta T} = \frac{N}{2V}\left(\frac{h^2}{2\pi K_\beta T}\right)^{3/2} e^{-E/K_\beta T} \rightarrow (xi)$$

The distribution function is sometimes expressed in the form of

$$f(E) = \frac{N}{F(E)} e^{-E/K_\beta T} \rightarrow (xii)$$

Where

$$F(E) = \frac{2V}{h^3}\left(2\pi m K_\beta T\right)^{3/2}$$

$$F(E) = \int_0^\infty g(E) e^{-E/K_\beta T} dE \rightarrow (xiii)$$

For discrete energy state

$$F = \sum_i g_i e^{-E_i/K_\beta T} \rightarrow (xiv)$$

Where summation replaced the integration. The quantity F represents the sum of Boltzmann Factor $e^{-E/K_\beta T}$, over all the accessible state and called Partition Function. The importance of the Partition Function is that it determines the distribution function are all linked with the Partition Function. The distribution function proportional to Boltzmann Factor $e^{-E/K_\beta T}$ is known as canonical distribution.

Another Method:

In classical limit the N particles are distinguible there are no symmetry restrictions on φ and any combination of the φ such as

$$\varphi(1,2,3 \ldots\ldots N) = \varphi_a(q_1)\varphi_b(q_2) \ldots\ldots \varphi_z(q_N)$$

Is a possible state. The intangibility of particles means that any interchange of particles among occupied space φ_a, φ_b … lead to a new state for the system without a change in total system energy.

To include degeneracy we divide φ into group of $1, 2, \ldots i \ldots k$ with respective energy$\epsilon_1 .. \epsilon_2 \ldots \epsilon_i \ldots \epsilon_k$ so that the energy eigen values for all the φ in the group of lie between

$$\epsilon_i \; and \; \epsilon_i + d\epsilon_i$$

Let us assume that the number of φ's is δ_i . Each δ_i is assumed to be large but the exact value is unimportant. For a particular macroscopic state or microstate $\{n_i\}$ the number of microscopic state or microstate is

$$\Omega\{n_i\} = \frac{N!}{\sum_{i=1}^{k} n_i \, !}$$

This number is obtained by counting the different possible ways of arranging N distinguiable objects so that there are n_1 in first group, n_2 in second group and so on .

We can arrange N object in $N!$ Different ways. However permutation of N_1 Object among themselves in group 1 e.t.c. will not alter the grouping. To calculate the number of φ corresponding to their distribution. Let us denote this number by $\Omega(g_i, n_i)$. The number of φ or state is g_i in the i-th group. Among the n_i particles in this group, the first one can occupy these states g_i ways. The second one and the subsequent one can occupy a given φ in which n_i particles can occupy g_i states. This gives for the k possible group of eigen state

$$\Omega(g_i, n_i) = N! \prod_{i=1}^{k} \left[\frac{(g_i)^{n_i}}{n_i!} \right]$$

Where $n_1 + n_{2_.} \ldots. + n_k = N$ which is a constant number