Average Energy of the Particle

Consider a system of "n" number of particles. The total energy of an isolated system is given by

$$E = \sum_i n_i E_i = n_1 E_1 + n_2 E_2 + n_3 E_3 + ...$$

$$\Rightarrow E = g_1 e^{-\alpha-\beta E_1} E_1 + g_2 e^{-\alpha-\beta E_2} E_2 + g_3 e^{-\alpha-\beta E_3} E_3 + ...$$

$$\Rightarrow E = e^{-\alpha} \sum_i^N g_i e^{-\beta E_i} E_i = \frac{N}{Z} \sum_i^N g_i e^{-\beta E_i} E_i \qquad \textbf{(1)}$$

We know, $$Z = \sum_i^N g_i e^{-\beta E_i} \Rightarrow \frac{dZ}{d\beta} = \frac{d}{d\beta} \sum_i^N g_i e^{-\beta E_i} = -\sum_i^N g_i e^{-\beta E_i} E_i$$

From (1) $$\Rightarrow E = -\frac{N}{Z}\frac{dZ}{d\beta} = -N \frac{d}{d\beta}[\log Z]$$

The average energy of a particle is given by,

$$\Rightarrow E_{av} = \frac{E}{N} = -\frac{d}{d\beta}[\log Z] \qquad \textbf{(2)}$$

This shows that for a given system, the total energy *E*, the partition function *Z*, and the average energy of the particle E_{av} depends on the parameter β. Therefore, β may be taken to characterize the internal energy of the system. So, it is customary to represent parameter β as follows:

$$\beta = \frac{1}{kT}$$

***k*: Boltzmann constant**
***T*: Temperature**

M-B distribution law in terms of temperature $\mathrm{n_i} = \frac{N}{Z}\left[g_i e^{-E_i/kT}\right]$

$$\beta = \frac{1}{kT} = d\beta = -\frac{dT}{kT^2}$$

Energy of the particle: $E = (NkT^2)\frac{d}{dT}\left[\log Z\right]$ **(3)**

Average energy of the particle: $E_{av} = (kT^2)\frac{d}{dT}\left[\log Z\right]$ **(4)**

Thus the temperature of a system can be regarded as the average energy of the particle of the system.

Partition function

The probability of finding the system in one particular state of energy E_i is given by:

$$p_i = \frac{g_i e^{-E_i/kT}}{\sum_i^N g_i e^{-E_i/kT}}$$

The sum in the denominator: $$Z = \sum_i^N g_i e^{-E_i/kT}$$

is called the partition function or "sum-over states". The partition function depends on the temperature T and on the parameters that determine the energy levels.

Importance: Although the partition function itself is not a measurable quantity, it however does form an important bridge between the statistical expressions for the state of a system and the corresponding thermodynamic functions. For example: physical quantities like mean energy, entropy etc or even dispersion can be immediately obtained by taking suitable derivatives of logZ. Thus by the partition function it can be evaluated the macroscopic properties easily in statistical mechanics.

Derive the Maxwell-Boltzmann Distribution in the form:

$$\mathrm{n}(E)\mathrm{d}E = \frac{2\pi N}{(\pi kT)^{3/2}}\sqrt{E}e^{-E/kT}dE$$

Consider an ideal gas of N identical non-interacting point particles, each of mass m, confined in a volume V at absolute temperature T. The M-B distribution law is given by,

$$\mathrm{n_i} = \mathrm{g_i}e^{-\alpha-\beta \mathrm{E_i}} \qquad \textbf{(1)}$$

If the gas has a continuous distribution of molecular energies instead of the discrete sets E_1, E_2, E_3,…., the eq(1) becomes

$$\mathrm{n(E)dE} = \mathrm{g(E)}e^{-\alpha-\beta \mathrm{E}}\mathrm{dE} \qquad \textbf{(2)}$$

Here, n(E)dE represents the number of molecules having energies between E and E+dE and g(E)dE represents the number of states having energies between E and E+dE.

Let us first find g(E)dE. A molecule of energy E has a momentum whose magnitude is given by,

$$p = \sqrt{2mE} = \sqrt{p_x^2 + p_y^2 + p_z^2}$$

Each set of momentum components p_x, p_y, p_z specifies a different state of motion. Let us imagine a momentum space whose coordinate axes are p_x, p_y, p_z. The available number of momentum states of particles between p and p+dp is proportional to the volume of a spherical shell in momentum space of radius p and thickness dp. Volume of this spherical shell is $4\pi p^2 dp$. Hence,

$$g(p)dp = Bp^2 dp \qquad (3)$$

where B is constant.

Again $$p^2 = 2mE \Rightarrow 2p = 2m\frac{dE}{dp} \Rightarrow dp = \frac{mdE}{\sqrt{2mE}}$$

From Eq. (3) $$g(E)dE = \sqrt{2}m^{2/3}B\sqrt{E}dE \qquad (4)$$

Substituting eq(4) into eq (2)

$$\mathrm{n(E)dE} = C\sqrt{E}e^{-\beta \mathrm{E}}\mathrm{dE} \qquad \textbf{(5)}$$

Where C is constant. $\mathrm{C} = \sqrt{2}\mathrm{m}^{2/3}\mathrm{B}\sqrt{\mathrm{E}}\ \mathrm{e}^{-\alpha}$

To find the value of C, normalization condition is used where the total number of molecules is N.

$$\mathrm{N} = \int_0^\infty \mathrm{n(E)dE} = C\int_0^\infty \sqrt{E}e^{-\beta \mathrm{E}}\mathrm{dE} = C\frac{1}{2\beta}\sqrt{\frac{\pi}{\beta}} = C\frac{\sqrt{\pi}}{2}(kT)^{3/2} \qquad \textbf{(6)}$$

Where used the integration rule: $\int_0^\infty \sqrt{x}e^{-ax}\mathrm{dx} = \frac{1}{2\mathrm{a}}\sqrt{\frac{\pi}{a}}$

Use eq (6) $\mathrm{C} = \frac{2\pi N}{(\pi kT)^{3/2}}$

Use eq (5) $$\mathrm{n(E)dE} = \frac{2\pi N}{(\pi kT)^{3/2}}\sqrt{E}e^{-E/kT}dE \qquad \textbf{(7)}$$

The total internal energy of the system is:

$$\mathrm{E} = \int_0^\infty \mathrm{E}\, \mathrm{n(E)dE} = \frac{2\pi N}{(\pi kT)^{3/2}} \int_0^\infty E^{2/3} e^{-E/kT}\, dE$$

$$= \frac{2\pi N}{(\pi kT)^{3/2}} \frac{3}{4} (kT)^2 \sqrt{2\pi T} = \frac{3}{2} NkT \qquad \textbf{(8)}$$

The average energy of an ideal gas molecule

$$\mathrm{E}_{\mathrm{av}} = \frac{E}{N} = \frac{3}{2} kT$$

M-B Velocity Distribution Law: The number of molecules with speeds between v and v+dv in an assembly of ideal gas containing N molecules at absolute temperature T can be found by substituting E=1/2 mv^2 and dE=mvdv in eq(7). We get

$$\mathrm{n(v)dv} = \frac{\sqrt{2} N m^{3/2}}{(\pi kT)^{3/2}} \mathrm{v}^2 e^{-mv^2/2kT}\, \mathrm{dv} \qquad \textbf{(9)}$$