Quadrant II- Transcript and Related Materials

Programme : Bachelor of Science (Third Year)

Subject : Physics

Semester : V

Paper Code : PYC 105

Paper Title : DSC: Classical Mechanics and Thermal Physics

Unit 4 : statistical distribution

Module Name : Maxwell Boltzmann Statistics

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Notes:

Maxwell Boltzmann Statistics :

Maxwell Boltzmann statistics is applied for identical distinguishable particles with any spin. For Ex. Molecules of a gas. Consider a system of N molecules . The possible energies of the molecules are $\mathrm{E}_1, \mathrm{E}_2, \mathrm{E}_3 \ldots \ldots \mathrm{E}_k$. Energies are arranged in increasing order.

The energies $\mathrm{E}_1, \mathrm{E}_2, \mathrm{E}_3 \dots \dots \mathrm{E}_k$ may be discrete energy states or may represent average energies of the intervals, in case there are energy intervals.

Let n_1 be the number of molecules with energy E_1, n_2 be the number of molecules with energy E_2 , n_i the number of molecules with energy E_i

The total energy of the system is $\mathrm{E_T}$ and the total number of particles are N.

$$\sum_i n_i = n_1 + n_2 + \mathrm{n}_3 + \cdots + \mathrm{n_k} = \mathrm{N} \dots \dots ..(1)$$

$$\sum_i n_i \mathrm{E}_i = n_1 \mathrm{E}_1 + n_2 \mathrm{E}_2 + \cdots n_k \mathrm{E}_k = \mathrm{E_T} \dots \dots ..(2)$$

We wish to find the most probable distribution of molecules among the k energies. Let g_i be the priory probability that a molecule has energy E_i . Probability W for any distribution is given

$$\mathrm{W} = g_1^{n_1} . g_2^{n_2} \dots \dots .. g_i^{n_i} \dots . g_k^{n_k} \frac{\mathrm{N}!}{n_1! \, n_2! \, n_3! \dots n_k!} \dots \dots ..(3)$$

Here W is maximum implies,

$$-\sum_i log_e n_i \ \delta \, n_i + \sum_i log_e g_i \delta n_i = 0 \dots \dots ..(4)$$

And

$$\sum_i \delta n_i = 0 \quad \dots \dots ..(5)$$

$$\sum_i \mathrm{E}_i \delta \, n_i = 0 \dots \dots \dots (6)$$

Using Lagrange's undetermined multipliers α and β both are independent of n_i . Multiplying equation (5) by $-\alpha$ and (6) by$-\beta$ and adding it to equation (4) we get

$$\sum_{i}(-log_e n_i \quad + log_e g_i - \alpha - \beta \mathrm{E_i})\delta n_i = 0$$

Since δn_i 's are all independent , the coefficient of each δn_i must be zero.

$$\sum_{i}(-log_e n_i \quad + log_e g_i - \alpha - \beta \mathrm{E_i}) = 0$$

$$log_e \frac{g_i}{n_i} - \alpha - \beta \mathrm{E_i} = 0$$

$$\frac{g_i}{n_i} = e^{\alpha + \beta \mathrm{E_i}}$$

$$n_i = g_i e^{-\alpha - \beta \mathrm{E_i}} \ldots \ldots . . (7)$$

Equation 7 is known as the Maxwell –Boltzmann distribution law of energy .

Here we wish to determine the $e^{-\alpha}$ and β. It is more convenient to consider a continuous distribution of energies rather than considering discrete energies.

For the continuous distribution of energy ,

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

Where $n(\mathrm{E})d\mathrm{E}$ gives the number of molecules lying in the range E and E+dE .

Now $\mathrm{E} = \frac{\mathrm{p}^2}{2m}$ where p is momentum of the molecule. Hence the number of molecules with momentum between p and p+dp is

$$n(p)dp = g(p)e^{-\alpha - \beta}\frac{p^2}{2m}dp$$

Here g(p) is the priori probability that a molecule has a momentum between p and p+dp.

Where $g(p)dp = \frac{4\pi p^2 V dp}{h^3}$

$$\therefore n(p)dp = \frac{4\pi p^2 V dp}{h^3} e^{-\alpha} e^{-\beta \frac{p^2}{2m}} dp \ldots \ldots . . (8)$$

Since $\int_0^\infty n(p)dp = \mathrm{N}$

$$\therefore \frac{4\pi V}{h^3} e^{-\alpha} \int_0^\infty p^2\, e^{-\beta\frac{p^2}{2m}} dp = \mathrm{N}$$

Using the relation $\int_0^\infty x^2 e^{-ax^2} dx = \frac{1}{4}\sqrt{\frac{\pi}{a^3}}$

we get $\mathrm{N} = \frac{4\pi V}{h^3} e^{-\alpha} \frac{1}{4} \sqrt{\frac{\pi}{(\frac{\beta}{2m})^3}}$

$$\therefore e^{-\alpha} = \frac{\mathrm{N}h^3}{V} (\frac{\beta}{2\pi m})^{3/2}$$

Substituting $e^{-\alpha}$ in equation (8) we get

$$\therefore n(p)dp = 4\pi \mathrm{N} (\frac{\beta}{2\pi m})^{3/2} p^2 e^{-\beta\frac{p^2}{2m}} dp \ldots\ldots\ldots (9)$$

The second multiplier β is determined by considering total energy E_T of the assembly of molecules.

We have $\mathrm{E} = \frac{p^2}{2m},$

$$\therefore p^2 = 2m\mathrm{E}$$

$$2pdp = 2md\mathrm{E}$$

$$\therefore dp = \frac{md\mathrm{E}}{p} = \frac{md\mathrm{E}}{\sqrt{2m\mathrm{E}}}$$

Substituting dp in equation (9) we get ,

$$\therefore n(E)dE = 4\pi \mathrm{N} (\frac{\beta}{2\pi m})^{3/2} 2m\mathrm{E} e^{-\beta \mathrm{E}} (\frac{md\mathrm{E}}{\sqrt{2m\mathrm{E}}})$$

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

The total energy is $\mathrm{E}_T = \int_0^\infty E n(\mathrm{E}) d\mathrm{E}$

$$\mathrm{E_T} = 2\mathrm{N}\frac{\beta^{3/2}}{\sqrt{\pi}}\int_0^\infty \mathrm{E}^{3/2}e^{-\beta\mathrm{E}}d\mathrm{E}\text{..........}(10)$$

Making use of the relation $\int_0^\infty x^{3/2}\, e^{-ax}dx = \frac{3}{4a^2}\sqrt{\frac{\pi}{a}}$

We get $$\int_0^\infty \mathrm{E}^{3/2}e^{-\beta\mathrm{E}}d\mathrm{E} = \frac{3}{4\beta^2}\sqrt{\frac{\pi}{\beta}} \dots\dots\dots (11)$$

Substituting equation (11) in the equation (10) we get

$$\mathrm{E_T} = 2\mathrm{N}\frac{\beta^{3/2}\frac{3}{4\beta^2}\sqrt{\frac{\pi}{\beta}}}{\sqrt{\pi}}$$

$$\therefore \mathrm{E_T} = \frac{3}{2}\frac{\mathrm{N}}{\beta}\dots\dots..(12)$$

But this total energy $\mathrm{E_T}$ of N molecules of an ideal gas at the absolute temperature T is, $\mathrm{E}_T = \frac{3\mathrm{NkT}}{2}\dots\dots.(13)$

Where k is Boltzmann constant . From equation (12) and (13) we get

$$\frac{3\mathrm{NkT}}{2} = \frac{3}{2}\frac{\mathrm{N}}{\beta}$$

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

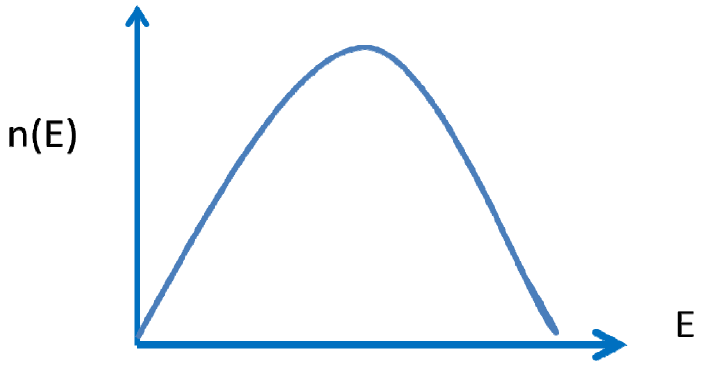
Hence equation (I) becomes,

$$n(E)dE = \frac{2\pi\mathrm{N}}{(\pi kT)^{3/2}}\sqrt{\mathrm{E}}e^{-\mathrm{E}/kT}d\mathrm{E}\dots\dots..(14)$$

This is known as **Boltzmann distribution of energies**. This gives the number of molecules of an ideal gas with energies between E and E+dE in a sample containing N molecules in thermal equilibrium at absolute temperature T.

We have Total energy $E_T = \frac{3NkT}{2}$

Therefore the average energy $\overline{E} = \frac{E_T}{N} = \frac{3kT}{2}$



Boltzmann Energy distribution curve .