Q. 4.13. (*a*) Derive Maxwell Boltzmann relation $n_i = \frac{g_i}{e^{\alpha + \beta u_i}}$ for the energy distribution of an ideal gas in equilibrium. (*K. U.* 2002)

(*b*) Show that the probability of a molecule to have its velocity component between

$$v_x \text{ and } v_x + dv_x;\ P(v_x)\, dv_x = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{\frac{-mv_x^2}{2kT}}\, dv_x$$ (*A. U.*, 1993)

Ans. (*a*) Maxwell-Boltzmann relation. To prove Maxwell Boltzmann relation

$$n_i = e^{\frac{g_i}{\alpha + \beta u_i}}$$ See Q. 4.10 Eq. (*vii*) (*a*)

(*b*) Probability for *x*-component of velocity. To calculate the number of molecules having *x*-component of velocity between v_x and $(v_x + dv_x)$ we consider the number of molecules in the momentum interval p and $p + dp$. It is given by

$$n(p)\,dp = g(p)\,e^{-\alpha}\,e^{-\beta p^2/2m}\,dp \qquad ...(i)$$

where α and β are arbitrary constants and $g(p)\,dp$ is the number of cells in the phase space corresponding to the momentum interval between p and $p + dp$

[For proof see equation (*ix*) Q. 4.10]

Now $p^2 = p_x^2 + p_y^2 + p_z^2$ where p_x, p_y and p_z are the components of p

and $$g(p)\,dp = \frac{V}{h^3}\iiint dp_x\,dp_y\,dp_z$$ [See Eq. (*ix a*) Q. 4.10]

Substituting this value of $g(p)\,dp$ in Eq. (*i*) we have

$$n(p)\,dp = \frac{V}{h^3}\iiint e^{-\alpha}\,e^{-\beta\frac{(p_x^2+p_y^2+p_z^2)}{2m}}\,dp_x\,dp_y\,dp_z$$

The integration extends from $-\infty$ to $+\infty$ for each variable.

∴ Total number of molecules $n = \int_{-\infty}^{+\infty} n(p)\,dp$

$$= \frac{V}{h^3}e^{-\alpha}\int_{-\infty}^{+\infty} e^{\frac{-\beta}{2m}p_x^2}\,dp_x \int_{-\infty}^{+\infty} e^{\frac{-\beta}{2m}p_y^2}\,dp_y \int_{-\infty}^{+\infty} e^{\frac{-\beta}{2m}p_z^2}\,dp_z$$

Applying the standard integral $\int_{-\infty}^{+\infty} e^{-ax^2}dx = \sqrt{\frac{\pi}{a}}$, we have

$$\int_{-\infty}^{+\infty} e^{\frac{-\beta}{2m}p_x^2}\,dp_x = \int_{-\infty}^{+\infty} e^{\frac{-\beta}{2m}p_y^2}\,dp_y = \int_{-\infty}^{+\infty} e^{\frac{-\beta}{2m}p_z^2}\,dp_z = \sqrt{\frac{2\pi m}{\beta}} \qquad ...(ii)$$

$$\therefore \quad n = \frac{V}{h^3}e^{-\alpha}\left(\frac{2\pi m}{\beta}\right)^{3/2} \quad \text{or} \quad e^{-\alpha} = \frac{nh^3}{V}\left(\frac{\beta}{2\pi m}\right)^{3/2} \qquad ...(iii)$$

To find the number of molecules whose *x*-component of momentum lies between p_x and $(p_x + dp_x)$, we have

$$n(p_x)\,dp_x = \frac{V}{h^3}e^{-\alpha}\,e^{\frac{-\beta}{2m}p_x^2}\,dp_x \int_{-\infty}^{+\infty} e^{\frac{-\beta}{2m}p_y^2}\,dp_y \int_{-\infty}^{+\infty} e^{\frac{-\beta}{2m}p_z^2}\,dp_z$$

Substituting the value of $e^{-\alpha}$ from Eq. (*iii*) and $\int_{-\infty}^{+\infty} e^{\frac{-\beta}{2m}p_y^2}\,dp_y$ and $\int_{-\infty}^{+\infty} e^{\frac{-\beta}{2m}p_z^2}\,dp_z$ from Eq. (*ii*), we have

$$n(p_x)\,dp_x = \frac{V}{h^3}\frac{nh^3}{V}\left(\frac{\beta}{2\pi m}\right)^{3/2} e^{\frac{-\beta}{2m}p_x^2}\,dp_x\left(\frac{2\pi m}{\beta}\right)^{1/2}\left(\frac{2\pi m}{\beta}\right)^{1/2} = n\left(\frac{\beta}{2\pi m}\right)^{1/2} e^{\frac{-\beta}{2m}p_x^2}\,dp_x$$

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

$$\therefore \quad n(p_x)\,dp_x = \frac{n}{\sqrt{2\pi mkT}}\,e^{\frac{-p_x^2}{2mkT}}\,dp_x \qquad ...(iv)$$

To find the number of molecules having their *x-component of velocity* between v_x and $(v_x + dv_x)$, we put $p_x = mv_x$ and $dp_x = m dv_x$ in Eq (*iv*) and get

$$n(v_x)\, dv_x = \frac{n}{\sqrt{2\pi mkT}}\, e^{\frac{-m^2 v_x^2}{2mkT}}\, m\, dv_x = \frac{n}{\sqrt{2\pi mkT}}\, e^{\frac{-mv_x^2}{2kT}}\, m\, dv_x = n\sqrt{\frac{m}{2\pi kT}}\, e^{\frac{-mv_x^2}{2kT}}\, dv_x$$

Probability. The probability that a molecule may have its *x*-velocity component lying between v_x and $(v_x + dv_x)$ is given by

$$P(v_x)\, dv_x = \frac{n(v_x)\, dv_x}{n} = \sqrt{\frac{m}{2\pi kT}}\, e^{\frac{-mv_x^2}{2kT}}\, dv_x = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT}\, dv_x$$

Q. 4.14. Discuss Maxwell-Boltzmann's law of distribution of velocities (speeds) for gas molecules. How can it be represented graphically? (*H.P.U.*, 2003; *K.U.* 2001, 2000; *G.N.D.U.* 2001; *P.U.* 2001, 1995; *M.D.U.* 2006, 2000; *Luck. U.* 2001; *Gharwal. U.* 2000)

Ans. Maxwell-Boltzmann's law. Maxwell-Boltzmann's law of distribution of velocities among the molecules of an ideal gas is derived on the basis of classical statistics assuming the molecules to be distinguishable. According to this law

$$n(v)\, dv = 4\pi n \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{m}{2kT}v^2}\, v^2\, dv \qquad \ldots(i)$$

where $n(v)\, dv$ denotes the number of gas molecules possessing velocities between v and $(v + dv)$, n the total number of molecules, m the mass per molecule, k the Boltzmann gas constant and T the absolute temperature. Therefore the fraction y or the probability $P(v)\, dv$ of the molecules having velocities lying between v and $(v + dv)$ is given by

$$P(v)\, dv = y = \frac{n(v)\, dv}{n} = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{m}{2kT}v^2}\, v^2\, dv \qquad \ldots(ii)$$

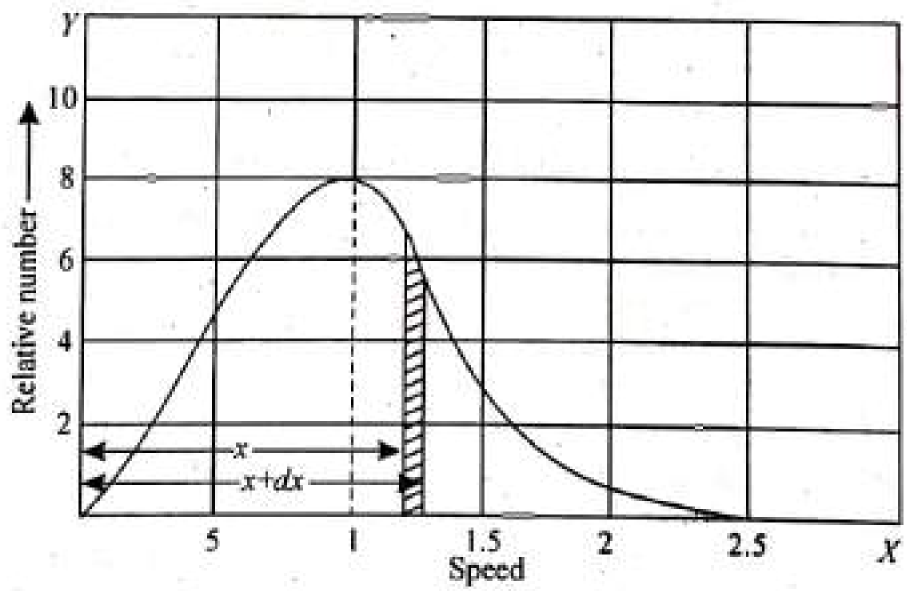

Fig. 4.4

Graphical representation

To represent the law graphically let $\sqrt{\frac{m}{2kT}}\, v = x$, then $\sqrt{\frac{m}{2kT}}\, dv = dx$

$$\therefore \quad y = \frac{n(v)\, dv}{n} = \frac{4\pi}{\pi^{3/2}}\, \frac{m}{2kT}\, v^2\, e^{-\frac{m}{2kT}v^2} \sqrt{\frac{m}{2kT}}\, dv \quad \text{or} \quad y = \frac{4}{\sqrt{\pi}}\, x^2\, e^{-x^2}\, dx$$

Plotting $\left(y = 4\pi^{-\frac{1}{2}} e^{-x^2} x^2\right)$ against x, a curve of the form shown in Fig. 4.4 is obtained. The number of molecules the velocities of which lie between the values given by x and $x + dx$ is proportional to the shaded area while the total area between the curve and the X-axis gives the total number of molecules n having velocities between zero and a maximum value.

The ordinate y corresponding to any value of x gives the number of molecules having a velocity represented by that value of x. We find that the most probable value of velocity corresponds to $x = 1$ which gives $v_{mp} = \sqrt{\frac{2kT}{m}}$

The Maxwell's law of distribution of velocities establishes that in a steady state the number of molecules with a given velocity remains constant. It does not, however, mean that it is always the same molecules which are moving with a given velocity. It only means that if some molecules change their velocities due to collision etc. an equal number of other molecules acquire the original velocity of the molecules that have undergone a change thereby, keeping the overall position the same.

Equation (*ii*) can be put in the form

$$P(v) = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} e^{\frac{-m}{2kT}v^2} v^2 \qquad ...(iii)$$

It is clear from Eq. (*iii*) that the function $P(v) = 0$ for $v = 0$

Hence the probability of a molecule to have zero velocity (speed) is nil.

Evidence in favour. For a long time the evidence in favour of Maxwell-Boltzmann law of distribution of velocities of gas molecules was of an indirect nature but it conclusively established the truth of the law. The most important indirect evidence is the finite width of spectral lines. Theoretically every monochromatic beam of light should be represented by geometrical line *i.e.*, a line, without width but in actual practice every spectral line has some finite breadth extending over some range of wavelength (or frequency) on either side of the mean position. This is because all the molecules of the source are moving with all possible velocities and due to Doppler effect the frequency of light emitted is given by the relation $\nu_0 \pm \frac{v}{c} \nu_0$ where ν_0 is the frequency if the molecule is at rest and v the velocity of the molecule in the direction of the observer. The positive sign is used if the velocity is towards and the negative sign if the velocity is away from the observer. Thus the intensity of the line from its mean position varies according to the number of molecules having the velocity causing the necessary displacement. A micro photometric study of the variation of the intensity of the spectral line with distance from the centre shows that it obeys the same law as Maxwell's law of distribution of velocities.