Study Material - Sem. 3 - C6T -
Kinetic Theory of Gases - Dr. T. Kar
- Class 1

Maxwell-Boltzmann Velocity Distribution Law

From kinetic Theory of gases, we know That The gas molecules are in random motion and Their velocities are changed both in direction and magnitude due to collision. Yet we can speak of a steady state when The number of molecules n_c having velocity c is not changed by collision. The law which expresses n_c as a function of c is known as velocity distribution law and was first derived by Maxwell from kinetic Theory of gases.

Let n_u be The no. of molecules/cc having velocity u.

$\therefore$ no. of molecules/cc having velocity between u and $u+du$ becomes $n_u du$.

We express The probability of a molecule to have velocity u as a function of u i.e,

$f(u) = \frac{n_u}{n}$, when n is The total no of molecules/cc.

$\therefore$ no. of molecules/cc having velocity between u and $u+du$ becomes $n_u du = n f(u) du$

Similarly, no. of molecules/cc having velocity component between v and $v+dv$ is $nf(v)dv$. for component w, it is $nf(w)dw$.

Again, The probability of that a molecule will have simultaneously velocity components u, v and w is $f(u)\,f(v)\,f(w)$.

$\therefore$ Probability of having velocity component u and $u+du$, v and $v+dv$ and w and $w+dw$ becomes $f(u)\,f(v)\,f(w)\,dw\,du\,dv$

$\therefore$ The no. of molecules/cc having velocity components in the above range is $n\,f(u)\,f(v)\,f(w)\,du\,dv\,dw$.

Now, as $c^2 = u^2+v^2+w^2$, The above no. of molecules/cc will have resultant velocities between c and $c+dc$.

Also no. of molecules/cc having velocity c is $nF(c)$.

We get, $n\,f(u)\,f(v)\,f(w) = nF(c)$

$$= n\,\phi\,(u^2+v^2+w^2)$$

$$= n\,\phi\,(c^2)$$

For a particular velocity, $c =$ constant

$\therefore \phi(c^2) =$ constant

$\therefore d\,[\phi(c^2)] = 0$

or, $d\,[f(u)\,f(v)\,f(w)] = 0$

or, $f'(u)\,du\,f(v)\,f(w) + f'(v)\,dv\,f(u)\,f(w)$
$+ f'(w)\,dw\,f(u)\,f(v) = 0$

Dividing by $f(u)\,f(v)\,f(w)$, we get

$$\frac{f'(u)\,du}{f(u)} + \frac{f'(v)\,dv}{f(v)} + \frac{f'(w)\,dw}{f(w)} = 0$$

Also, $c^2 = u^2 + v^2 + w^2 =$ constant

Differentiating, we get, $u\,du + v\,dv + w\,dw = 0$

Using Lagrange's method of undetermined multipliers, we get,

$$\left[\frac{f'(u)}{f(u)} + \beta u\right] du + \left[\frac{f'(v)}{f(v)} + \beta v\right] dv + \left[\frac{f'(w)}{f(w)} + \beta w\right] dw = 0$$

As, w, u, v are independent of each other, we have the above terms to be separately zero. i.e,

$\frac{f'(u)}{f(u)} du = -\beta u\,du$ and so on

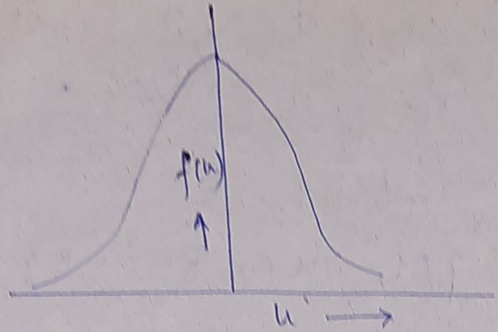
or, $\frac{f'(u)}{f(u)} du = -\beta u\,du$

Integrating, $\log_e f(u) = -\beta \frac{u^2}{2} + \log_e a$

or, $\log_e \left[\frac{f(u)}{a}\right] = -\beta \frac{u^2}{2}$

or, $f(u) = a e^{-\beta \frac{u^2}{2}}$

or, $f(u) = a e^{-bu^2}$ where $b = \frac{\beta}{2}$



We have total no. of molecules/cc to be,

$$n\left\{\int f(u)\,du \int f(v)\,dv \int f(w)\,dw\right\} = n$$

or, $$\iiint f(u)\, f(v)\, f(w)\, du\, dv\, dw = 1$$

or, $$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} a^3 e^{-b(u^2+v^2+w^2)}\, du\, dv\, dw = 1 \longrightarrow (1)$$

Now, $$\int_{-\infty}^{\infty} e^{-bu^2}\, du$$

$$= 2\int_0^{\infty} e^{-bu^2}\, du$$

$$= 2\int_0^{\infty} e^{-x}\, \frac{dx}{2bu}$$

$$= \int_0^{\infty} e^{-x}\, dx \left[\frac{b\sqrt{x}}{\sqrt{b}}\right]^{-1}$$

$$= \int_0^{\infty} e^{-x}\, \frac{x^{-1/2}}{b^{1/2}}\, dx$$

$$= \frac{1}{\sqrt{b}} \int_0^{\infty} e^{-x}\, x^{\frac{1}{2}-1}\, dx = \frac{1}{\sqrt{b}}\, \Gamma\left(\frac{1}{2}\right) = \sqrt{\frac{\pi}{b}}$$

Let,

$bu^2 = x$ or, $u = \sqrt{\frac{x}{b}}$

$\therefore 2bu\, du = dx$

or, $du = \frac{dx}{2bu}$

$$\Gamma(n) = \int_0^{\infty} e^{-x} x^{n-1}\, dx$$

$$\Gamma(n+1) = n\,\Gamma(n)$$

$$\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}$$

$n - 1 = \frac{-1}{2}$

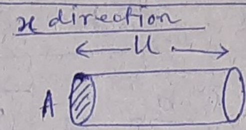
or, $n = \frac{1}{2}$

From (1), we get,

$$a^3\left(\frac{\pi}{b}\right)^{3/2} = 1 \quad \text{or}, \quad a^3 = \left(\frac{b}{\pi}\right)^{3/2} \quad \text{or}, \quad a = \sqrt{\frac{b}{\pi}}$$

From Kinetic Theory,

Pressure exerted by a perfect gas is given by $p = 2m \sum_{0}^{\infty} n_u u^2$



no. of molecules in the cylinder $= n_u A u$

Change in momentum/collision $= 2mu$

Pressure $= \frac{2mu\, n_u A u}{A} = 2mu^2 n_u$

Again number of molecules/cc having velocity u is —

$$n_u = n a e^{-bu^2}$$

$$= n\sqrt{\frac{b}{\pi}}\, e^{-bu^2}$$

$\therefore$ Pressure $p = 2mn \int_0^{\infty} \sqrt{\frac{b}{\pi}}\, u^2 e^{-bu^2}\, du$

$$= 2mn\sqrt{\frac{b}{\pi}} \int_0^{\infty} u^2 e^{-bu^2}\, du \longrightarrow (2)$$

Let $bu^2 = x$ or, $u = \sqrt{\frac{x}{b}}$

$\therefore 2bu\, du = dx$ or, $u\, du = \frac{dx}{2b}$

$$\therefore p = 2mn\sqrt{\frac{b}{\pi}} \int_0^{\infty} e^{-x} \frac{\sqrt{x}}{\sqrt{b}} \frac{dx}{2b}$$

$$= \frac{2mn}{2b^{3/2}}\sqrt{\frac{b}{\pi}} \int_0^{\infty} e^{-x} x^{\frac{3}{2}-1}\, dx$$

$$= \frac{mn}{b^{3/2}}\sqrt{\frac{b}{\pi}}\, \Gamma\left(\frac{3}{2}\right) = \frac{mn}{b^{3/2}}\sqrt{\frac{b}{\pi}}\, \Gamma\left(1+\frac{1}{2}\right)$$

$$= \frac{mn}{b^{3/2}}\sqrt{\frac{b}{\pi}}\, \frac{1}{2}\Gamma\left(\frac{1}{2}\right) = \frac{mn}{2b^{3/2}} \frac{b^{1/2}}{\sqrt{\pi}} \sqrt{\pi} = \frac{mn}{2b} \quad (3)$$

Again, $p = nkT$

Then, from (3), we get,

$$nkT = \frac{mn}{2b} \quad ; \quad \boxed{b = \frac{m}{2KT}}$$

$$\boxed{a = \sqrt{\frac{b}{\pi}} = \sqrt{\frac{m}{2\pi KT}}}$$

So, we get the number of molecules/cc having velocity components between u and $u+du$, v and $v+dv$, w and $w+dw$

to be —

$$dn = n a^3 e^{-b(u^2+v^2+w^2)} du\, dv\, dw$$

$$= n\left(\frac{m}{2\pi KT}\right)^{3/2} e^{-\frac{m}{2KT}(u^2+v^2+w^2)} du\, dv\, dw \quad (4)$$

Again, the above no. of molecules/cc have resultant velocities between c and $c+dc$. To expain the no. of molecules in terms of resultant velocity c, we consider a spherical space.

The molecules having velocity components between u and $u+du$, v and $v+dv$, w and $w+dw$ lie in an element of velocity space of volume $du\, dv\, dw$.

In spherical space, these molecules will lie between two concentric spheres of radii c and $c+dc$, having volume $= 4\pi c^2 dc$

~~By~~ Replacing $(u^2+v^2+w^2)$ by c^2 and $du\,dv\,dw$ by $4\pi c^2 dc$.

Therefore, no. of molecules/cc having velocity between c and $c+dc$ is

$$dn = 4\pi n a^3 e^{-bc^2} c^2 dc$$

$$= 4\pi n \left(\frac{m}{2\pi KT}\right)^{3/2} e^{-mc^2/2KT} c^2 dc \longrightarrow (5)$$

Equation (5) is the Maxwell's law of velocity distribution ~~of~~ for the molecules in the state of gaseous assembly.

$$\frac{dn}{n} = 4\pi \left(\frac{m}{2\pi KT}\right)^{3/2} e^{-\frac{mc^2}{2KT}} c^2 dc = F\,dc$$

If the function F is plotted against c, we get distribution curve (Fig. 1).

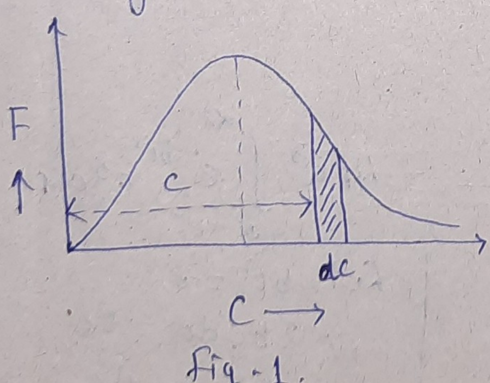


Fig. 1.

If at a distance c from the origin, we take a thin strip of thickness dc, area of the strip will be $F\,dc$, which represents the fraction of the total no. of molecules i.e, $\frac{dn}{n}$. From the molecular distribution law, we see that for $c=0$ or ∞, $dn=0$, which is also confirmed by the nature of the curve. So in between these limiting values, there is a value of c for which F is maximum. So maximum number of molecules will possess this velocity, called the most probable velocity.