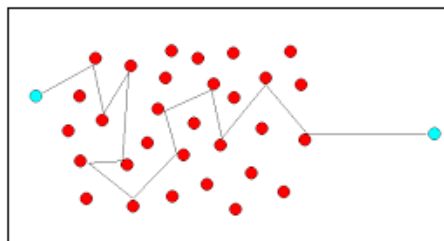## Estimation of Mean Free Path:

We have already mention in our previous discussion that during Brownian motion of the gas molecules, the straight line path traversed by the molecule in between two successive collision is the free path of that molecule and in that case , on the average, the path traversed by the molecule per collision is called mean free path.

There are three ways to estimate such mean free path of the gas molecule theoretically and these ways are i) Classical Method ii) Clausius Method and iii) Maxwell's Method . Among of all these methods, the best method is Maxwell's method by which we get very accurate estimation of mean free path which is in agreement with experimental observation. We will now discuss these methods one after another.
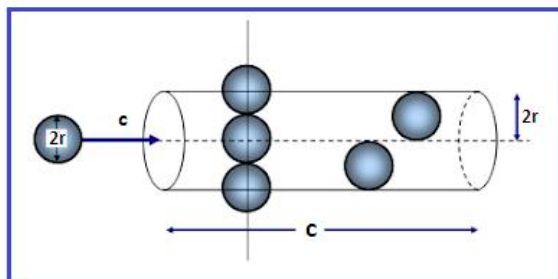
I) Classical Method:

If we consider each gas molecule to be rigid spherical then for radius r of each spherical gas molecule, when two gas molecule collides with each other then the distance between their centre will be $2r = \sigma$ and it is then called collision diameter.
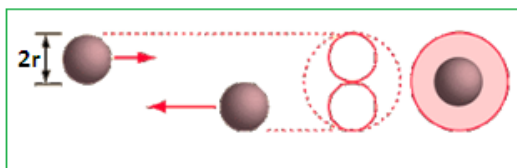
In this method we imagine that at a certain instant all the molecules of a gas, except one, are at rest. The moving molecule moves among the 'frozen' ones with a velocity c. We have already assumed that the molecules to be perfectly elastic spheres of diameter σ. At the instant of collision, the centre-to-centre distance of the colliding molecules is σ.

So, the effective cross-sectional area of the mobile molecule, i.e. collision cross-section ρ, is $\rho = \pi\sigma^2$. More clearly we now take a cylindrical region of length c and radius σ such that for the molecular concentration n, the number of molecules present in that imaginary cylindrical zone will be $N = n\pi\sigma^2 c$.

Thus if we allow that mobile molecule to move through that cylindrical region, it must suffer the no of collision $n\pi\sigma^2 c$ while traversing through the distance c in unit time.

Hence, the mean free path for the moving gas molecule will be
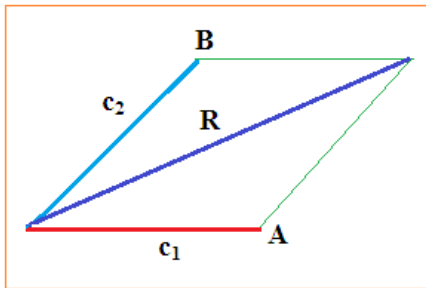
$$\lambda = \frac{\text{distane covered}}{\text{no. collisions occured}} = \frac{c}{n\pi\sigma^2 c} = \frac{1}{\pi\sigma^2 n}$$

This classical treatment is only an approximate method of estimation of mean free path. The assumption that only one molecule is moving and all others are 'frozen' in position is too idealized. More complete calculation for mean free path must take into account the motion of all the molecules of the gas, the fact that all molecules are not moving with the same speed and also other factors.

This was done, as we shall presently see, by Clausius and more so by Maxwell. But the only change that resulted in the final expression for λ is to alter the numerical coefficient of Clausius' Expression.

II) Clausius' Treatment to find Mean Free Path of the Gas Molecule:

In classical analysis of finding mean free path of the gas molecule, we have considered

only one molecule was moving; the rest were 'frozen'. This assumption is not valid in real case and then Clausius considered that all molecules within the container are moving with same magnitude of velocity equal to their relative velocity for their random motion, Clausius introduced the concept of relative velocity to make a correction to the previously obtained expression. He argued that if the relative velocity of one molecule with respect to others could be found, then essentially this molecule alone would move (with relative velocity) while others would be at rest.

Let two molecules A and B move with velocity c_1 and c_2. B moving at an angle θ with A.

Then the relative velocity of A with respect to B is $R = \sqrt{(c_1^2 + c_2^2 - 2c_1 c_2 \cos \theta)}$

To find the mean relative velocity of A with respect to all others, let $dN_{\theta,\phi}$ be the number of molecules moving between θ and $\theta + d\theta$, and ϕ and $\phi + d\phi$.

Then the mean relative velocity $\overline{R}$ of A with respect to B-type molecules in space is $\overline{R} = \frac{\int R dN_{\theta,\phi}}{\int dN_{\theta,\phi}}$. But we have $dN_{\theta,\phi} = \frac{N}{4\pi} 2\pi \sin \theta \, d\theta = \frac{N}{2} \sin \theta \, d\theta$ where N is the molecular density.

So we get $\overline{R} = \frac{\frac{N}{2} \int_0^\pi (c_1^2 + c_2^2 - 2c_1 c_2 \cos \theta)^{1/2} \sin \theta d\theta}{\frac{N}{2} \int_0^\pi \sin \theta d\theta} = \frac{1}{2} \int_0^\pi (c_1^2 + c_2^2 - 2c_1 c_2 \cos \theta)^{1/2} \sin \theta \, d\theta$

Substituting $c_1^2 + c_2^2 - 2c_1 c_2 \cos \theta = z \Rightarrow 2c_1 c_2 \sin \theta \, d\theta = dz$. we get

$$\overline{R} = \frac{1}{2} \cdot \frac{1}{2c_1 c_2} \int_{(c_1 \sim c_2)^2}^{(c_1 + c_2)^2} z^{1/2} dz = \frac{1}{2} \cdot \frac{1}{3c_1 c_2} [(c_1 + c_2)^3 - (c_1 \sim c_2)^3]$$

Since Clausius assumed that $c_1 = c_2 = \bar{c}$ that is, all molecules move with the same average velocity $\bar{c}$ we get $\bar{R} = \frac{1}{6\bar{c}^2} \cdot 8\bar{c}^3 = \frac{4}{3}\bar{c}$.

So by following the classical concept, since in moving over a distance $\bar{c}$, the number of collisions made by the moving molecule moving with a relative velocity $\bar{R}$ is $\pi\sigma^2\bar{R}n$,

We get mean free path $\lambda = \frac{\bar{c}}{\pi\sigma^2 n\bar{R}} = \frac{3}{4\pi\sigma^2 n} \longrightarrow$ This is the Clausius' expression for the mean free path.

III) Maxwell's Method for determination of Mean Free Path of the Gas Molecule:

Maxwell modified Clausius treatment of determination of mean free path and it find it, Maxwell uses the distribution rule of molecular velocity. Maxwell basically follows the average velocity technique of Clausius, but at first he determines the average of the relative velocity of **A** type molecule moving with velocity c_1 with respect to **B** type molecule having velocity c_2 for all values of c_2 obeying Maxwell's velocity distribution. After that he takes average of previous averaged relative velocity for all possible values of c_1 by obeying distribution law of velocity.

We have from Clausius treatment of mean free path the mean relative velocity $\bar{R}$ of **A** with respect to **B**-type molecules in space is $\bar{R} = \frac{1}{6c_1c_2}\left[(c_1 + c_2)^3 - (c_1 \sim c_2)^3\right]$.

Since in Maxwell's treatment $c_1 \neq c_2$ we have $\bar{R} = \frac{3c_1^2 + c_2^2}{3c_1}$ for $c_1 > c_2$ and $\bar{R} = \frac{3c_2^2 + c_1^2}{3c_2}$ for $c_1 < c_2$, we have in this treatment, the mean relative velocity of **A** type molecule with respect to all other molecules

$$r_1 = \frac{\int_{c_2=0}^{\infty} \bar{R}dn_{c_2}}{\int_{c_2=0}^{\infty} dn_{c_2}} = \frac{1}{n}\int_{c_2=0}^{\infty} \bar{R} \cdot 4\pi n a^3 e^{-bc_2^2} c_2^2 dc_2$$

$$= 4\pi a^3 \left\{ \int_{c_2=0}^{c_1} \bar{R} \cdot e^{-bc_2^2} c_2^2 dc_2 + \int_{c_2=c_1}^{\infty} \bar{R} \cdot e^{-bc_2^2} c_2^2 dc_2 \right\}$$

Thus we get $r_1 = 4\pi a^3 \left\{ \int_{c_2=0}^{c_1} \frac{3c_1^2 + c_2^2}{3c_1} \cdot e^{-bc_2^2} c_2^2 dc_2 + \int_{c_2=c_1}^{\infty} \frac{3c_2^2 + c_1^2}{3c_2} \cdot e^{-bc_2^2} c_2^2 dc_2 \right\}$ ------- (1)

where $a = \sqrt{\frac{b}{\pi}} = \sqrt{\frac{m}{2\pi kT}}$ and $b = \frac{m}{2kT}$

Again since the molecule **A** can move with any velocity c_1 ranging from **0** to ∞, the average relative velocity of any one molecule with respect to all other molecules moving in all possible direction is

$$r_2 = \frac{\int_{c_1=0}^{\infty} r_1 dn_{c_1}}{\int_{c_1=0}^{\infty} dn_{c_1}} =$$

$$\frac{1}{n} \cdot \int_{c_1=0}^{\infty} \left[4\pi a^3 \left\{ \int_{c_2=0}^{c_1} \frac{3c_1^2 + c_2^2}{3c_1} \cdot e^{-bc_2^2} c_2^2 dc_2 + \int_{c_2=c_1}^{\infty} \frac{3c_2^2 + c_1^2}{3c_2} \cdot e^{-bc_2^2} c_2^2 dc_2 \right\} \right] dn_{c_1}$$

So we get

$$r_2 = (4\pi a^3)^2 \int_{c_1=0}^{\infty} \left[\left\{ \int_{c_2=0}^{c_1} \frac{3c_1^2 + c_2^2}{3c_1} \cdot e^{-bc_2^2} c_2^2 dc_2 \right. \right.$$

$$\left. \left. + \int_{c_2=c_1}^{\infty} \frac{3c_2^2 + c_1^2}{3c_2} \cdot e^{-bc_2^2} c_2^2 dc_2 \right\} \right] e^{-bc_1^2} c_1^2 dc_1$$

and then

$$r_2 = (4\pi a^3)^2 \left\{ \int_{c_1=0}^{\infty} \int_{c_2=0}^{c_1} \frac{3c_1^2 + c_2^2}{3c_1} \cdot e^{-bc_2^2} c_2^2 dc_2 \cdot e^{-bc_1^2} c_1^2 dc_1 + \int_{c_1=0}^{\infty} \int_{c_2=c_1}^{\infty} \frac{3c_2^2 + c_1^2}{3c_2} \cdot e^{-bc_2^2} c_2^2 dc_2 \, e^{-bc_1^2} c_1^2 dc_1 \right\}$$

And finally we get

$$r_2 = (4\pi a^3)^2 \left\{ \int_{c_1=0}^{\infty} e^{-bc_1^2} c_1^3 dc_1 \int_{c_2=0}^{c_1} e^{-bc_2^2} c_2^2 dc_2 \right.$$

$$+ \frac{1}{3} \int_{c_1=0}^{\infty} e^{-bc_1^2} c_1 dc_1 \int_{c_2=0}^{c_1} e^{-bc_2^2} c_2^4 dc_2 \}$$

$$+ \{ \int_{c_1=0}^{\infty} e^{-bc_1^2} c_1^2 dc_1 \int_{c_2=c_1}^{\infty} e^{-bc_2^2} c_2^3 dc_2$$

$$\left. + \frac{1}{3} \int_{c_1=0}^{\infty} e^{-bc_1^2} c_1^4 dc_1 \int_{c_2=c_1}^{\infty} e^{-bc_2^2} c_2 dc_2 \right\} = (4\pi a^3)^2 \{ I_1 + I_2 \}$$

where $\quad I_1 = \int_{c_1=0}^{\infty} e^{-bc_1^2} c_1^3 dc_1 \int_{c_2=0}^{c_1} e^{-bc_2^2} c_2^2 dc_2 + \frac{1}{3} \int_{c_1=0}^{\infty} e^{-bc_1^2} c_1 dc_1 \int_{c_2=0}^{c_1} e^{-bc_2^2} c_2^4 dc_2$

and $\quad I_2 = \int_{c_1=0}^{\infty} e^{-bc_1^2} c_1^2 dc_1 \int_{c_2=c_1}^{\infty} e^{-bc_2^2} c_2^3 dc_2 + \frac{1}{3} \int_{c_1=0}^{\infty} e^{-bc_1^2} c_1^4 dc_1 \int_{c_2=c_1}^{\infty} e^{-bc_2^2} c_2 dc_2$

It can be shown that $\quad I_1 = I_2$. **New we have**

$$I_2 = \int_{c_1=0}^{\infty} e^{-bc_1^2} c_1^2 dc_1 \int_{c_2=c_1}^{\infty} e^{-bc_2^2} c_2^3 dc_2 + \frac{1}{3} \int_{c_1=0}^{\infty} e^{-bc_1^2} c_1^4 dc_1 \int_{c_2=c_1}^{\infty} e^{-bc_2^2} c_2 dc_2 =$$

$$\frac{1}{2} \cdot \frac{1}{b^{3/2}} \int_{c_1=0}^{\infty} [e^{-bc_1^2} (bc_1^2)^{\frac{1}{2}} d(bc_1^2) \cdot \frac{1}{2b^2} \int_{c_2=c_1}^{\infty} e^{-bc_2^2} (bc_2^2) d(bc_2^2)] +$$

$$\frac{1}{3} \frac{1}{2b^{5/2}} \int_{c_1=0}^{\infty} e^{-bc_1^2} (bc_1^2)^{\frac{3}{2}} d(bc_1^2) \cdot \frac{1}{2b} [\int_{c_2=c_1}^{\infty} e^{-bc_2^2} (bc_2^2)^{1-1} d(bc_2^2)]$$

But we have $\quad \int e^{-x} x \, dx = -x \, e^{-x} - e^{-x} = -e^{-x}(x + 1)$ **and also** $\quad \int e^{-x} dx = -e^{-x}$

So we can write $\int_{c_2=c_1}^{\infty} e^{-bc_2^2}(bc_2^2)d(bc_2^2) = [-e^{-bc_2^2}(bc_2^2+1)]_{c_2=c_1}^{\infty} = e^{-bc_1^2}(bc_1^2+1)$

And $\int_{c_2=c_1}^{\infty} e^{-bc_2^2}(bc_2^2)^{1-1}d(bc_2^2) = \int_{c_2=c_1}^{\infty} e^{-bc_2^2}d(bc_2^2) = [-e^{-bc_2^2}]_{c_2=c_1}^{\infty} = e^{-bc_1^2}$

So finally we get

$$I_2 = \frac{1}{2}\cdot\frac{1}{b^{3/2}}\int_{c_1=0}^{\infty}[e^{-bc_1^2}(bc_1^2)^{\frac{1}{2}}d(bc_1^2)\cdot\frac{1}{2b^2}\cdot\{e^{-bc_1^2}(bc_1^2+1)\}] + \frac{1}{3}\frac{1}{2b^{5/2}}\int_{c_1=0}^{\infty}e^{-bc_1^2}(bc_1^2)^{\frac{3}{2}}d(bc_1^2)\cdot\frac{1}{2b}[e^{-bc_1^2}]$$

Finally

$$I_2 = \frac{1}{2}\cdot\frac{1}{b^{3/2}}\frac{1}{2b^2}\int_{c_1=0}^{\infty}e^{-2bc_1^2}(bc_1^2)^{\frac{3}{2}}d(bc_1^2) + \frac{1}{2}\cdot\frac{1}{b^{3/2}}$$
$$\frac{1}{2b^2}\int_{c_1=0}^{\infty}e^{-2bc_1^2}(bc_1^2)^{\frac{1}{2}}d(bc_1^2) + \frac{1}{3}\frac{1}{2b^{5/2}}\frac{1}{2b}\int_{c_1=0}^{\infty}e^{-2bc_1^2}(bc_1^2)^{\frac{3}{2}}d(bc_1^2)$$

$$= \frac{1}{2}\cdot\frac{1}{b^{3/2}}\frac{1}{2b^2}\cdot\frac{1}{2^{5/2}}\cdot\Gamma\left(\frac{5}{2}\right) + \frac{1}{2}\cdot\frac{1}{b^{3/2}}\cdot\frac{1}{2b^2}\cdot\frac{1}{2^{3/2}}\Gamma\left(\frac{3}{2}\right) + \frac{1}{3}\frac{1}{2b^{5/2}}\frac{1}{2b}\cdot\frac{1}{2^{5/2}}\Gamma\left(\frac{5}{2}\right)$$

$$= \frac{1}{b^{7/2}}\cdot\left\{\frac{1}{2^{\frac{9}{2}}}\cdot\frac{3}{2}\cdot\frac{1}{2}\cdot\sqrt{\pi} + \frac{1}{2^{\frac{7}{2}}}\cdot\frac{1}{2}\cdot\sqrt{\pi} + \frac{1}{3}\cdot\frac{1}{2^{\frac{9}{2}}}\frac{3}{2}\cdot\frac{1}{2}\cdot\sqrt{\pi}\right\} = \frac{1}{b^{7/2}}\cdot\frac{1}{2^{\frac{9}{2}}}\cdot\sqrt{\pi}\cdot\left\{\frac{3}{4} + 1 + \frac{1}{4}\right\} = \frac{1}{b^{7/2}}\cdot\frac{1}{2^{\frac{7}{2}}}\cdot\sqrt{\pi} =$$
$$\frac{1}{(2b)^{7/2}}\cdot\sqrt{\pi}$$

Since $I_1 = I_2 = \frac{1}{(2b)^{7/2}}\cdot\sqrt{\pi}$

Finally we get $r_2 = (4\pi a^3)^2 2I_1 = (4\pi a^3)^2\cdot\frac{2}{(2b)^{7/2}}\cdot\sqrt{\pi} = 32\pi^2 a^6\frac{1}{(2b)^{7/2}}\cdot\sqrt{\pi}$

But $a = \sqrt{\frac{b}{\pi}} = \sqrt{\frac{m}{2\pi kT}}$ **Thus we get** $r_2 = 32\pi^2\frac{b^3}{\pi^3}\cdot\frac{1}{(2b)^{7/2}}\cdot\sqrt{\pi} = 4\cdot\frac{1}{\sqrt{2}}\cdot\frac{1}{\sqrt{b\pi}} = 2\sqrt{2}\cdot\sqrt{\frac{2kT}{\pi m}}$

Hence at the end we get $r_2 = \sqrt{2}\cdot\sqrt{\frac{8kT}{\pi m}} = \sqrt{2}\bar{c}$

So by following the classical concept, since in moving over a distance $\bar{c}$, the number of collisions made by the moving molecule moving with a relative velocity r_2 is $\pi\sigma^2 r_2 n$,

we get mean free path $\lambda = \frac{\bar{c}}{\pi\sigma^2 n r_2} = \frac{1}{\sqrt{2}\pi\sigma^2 n} \rightarrow$ **This is the Maxwell's expression for the mean free path.**