Kinetic theory

In developing the Kinetic theory of gases, the idealized assumptions made are:

① A gas consists of a large number of identical molecules which are like minute hard spheres randomly moving in all possible directions with different velocities in a random manner.

② During the motion, the molecules collide with each other and simultaneously also collide with the wall of the container. These collisions are perfectly elastic, so there is no loss of Kinetic energy while collisions occur. Collisions do not effect the molecular density.

③ During collisions, there is no force of attraction or repulsion between molecules. These molecules moves in straightlines with uniform velocity between two successive collisions.

④ The collisions are instantaneous i.e. collision time is very small compared with the time between collisions.

⑤ Molecules are like geometrical mass-points, the actual volume occupied by them is negligible compared to the total volume of the gas i.e. in which container gas is kept.

Deduction of perfect gas equation:-

We consider a perfect gas enclosed in a container such that one of its surface is perpendicular to the X-axis. BAE represents this surface

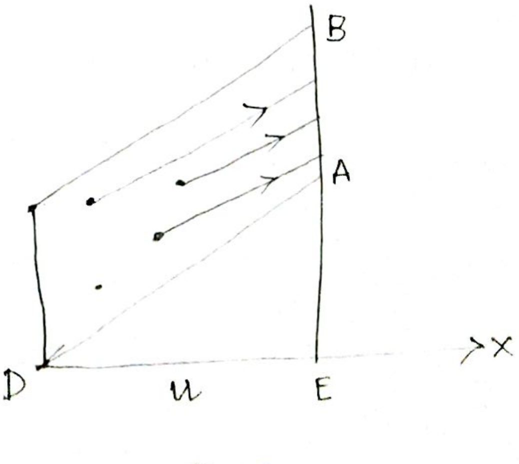


Fig. (1)

Now, any velocity c of a particle in space can be resolved into three different components u, v, w along three axes X, Y and Z respectively, So that

$$c^2 = u^2 + v^2 + w^2 \quad \cdots \quad (1)$$

the limits of u, v and w from $-\infty$ to $+\infty$, those of c are from 0 to ∞.

Now, u suffers a change in direction on reflection from the wall BAE, the other two components v and w remain unchanged by this type of reflection. The change in momentum per reflection of a molecule is

$$mu - (-mu) = 2mu$$

If n_u be the number of molecules per unit volume moving with velocity u, the number striking unit area of the wall in time dt would be contained in a cylinder of cross-Sectional area unity and vertical height udt

$\therefore$ Volume of the cylinder $= u\,dt$

Number of molecules in this cylinder $= n_u u\,dt$

The change in momentum/area suffered by the above molecules in time dt is

$$2mu \times n_u u\,dt$$

$\therefore$ The above quantity for all the molecules moving in the +ve X-direction i.e, total change in momentum/area is

$$2m \sum_{0}^{\infty} n_u u^2 dt$$

If the above change in momentum results in an average force $\delta\vec{F}$, then

$$\delta\vec{F}\,dt = 2m \sum_{0}^{\infty} n_u u^2 dt$$

$$\text{or, } \delta\vec{F} = 2m \sum_{0}^{\infty} n_u u^2$$

So the pressure $P_x = 2m \sum_{0}^{\infty} n_u u^2 \quad \cdots \quad (2)$

Let $\overline{u^2}$ be the mean squre velocity along x, so that we may write

$$\overline{u^2} = \frac{n_1 u_1^2 + n_2 u_2^2 + \cdots + n_m u_m^2}{n_1 + n_2 + \cdots + n_m} = \frac{\sum n_i u_i^2}{\sum n_i} = \frac{\sum n_i u_i^2}{\frac{n}{2}}$$

The factor $\frac{1}{2}$ appeared here due to the particle only moving +x direction.

Therefore $\sum n_i u_i^2 = \sum n_u u^2 = \frac{1}{2} n \overline{u^2}$

where 'n' total number of molecules per unit volume

$$\therefore p_x = 2m \times \frac{1}{2} n \overline{u^2} = mn\overline{u^2}$$

Similarly, $p_y = mn\overline{v^2}$, and $p_z = mn\overline{w^2}$

$\therefore$ The expression for the pressure is

$$p = p_x = p_y = p_z = mn\overline{u^2} = mn\overline{v^2} = mn\overline{w^2}$$

But $\overline{u^2} = \overline{v^2} = \overline{w^2} = \frac{1}{3}\overline{c^2}$, where $\overline{c^2}$ is the mean squre velocity

$$\therefore p = \frac{1}{3} mn\overline{c^2} = \frac{1}{3} mn C_{rms}^2 \quad \left[\overline{c^2} = C_{rms}^2\right] \quad \ldots (3)$$

Above equation also may written as

$$p = \frac{1}{3} \rho C_{rms}^2 \quad \ldots (4)$$

where $\rho = mn =$ density of the gas.

Deductions from pressure expression:-

1. RMS velocity:- The pressure p is given by

$$p = \frac{1}{3}\rho C_{rms}^2 \Rightarrow C_{rms} = \sqrt{\frac{3p}{\rho}} \quad \ldots (5)$$

Which gives the root mean squre velocity of the gas.

Let us consider one mole of the gas. Then $\rho = \frac{M}{V}$ where M is the molecular weight and V the volume occupied by one mole of gas.

$$\therefore p = \frac{1}{3}\frac{M}{V} C_{rms}^2$$

$$\text{or, } pV = \frac{1}{3} M C_{rms}^2 = RT \qquad \text{Since } pV = RT$$

$$\therefore C_{rms} = \sqrt{\frac{3RT}{M}} \quad \ldots (6)$$

mean squre velocity.

2. Pressure and Kinetic energy:-

$$p = \frac{1}{3}\rho C_{rms}^2 = \frac{2}{3} \times \frac{1}{2}\rho C_{rms}^2$$

$$\boxed{p = \frac{2}{3}E_m} \quad \dots (7)$$

where $E_m = \frac{1}{2}\rho C_{rms}^2$ = mean kinetic energy of gas molecules per unit volume.

The pressure of a gas is, therefore, equal to two-thirds of the mean kinetic energy of translation per unit volume.

3. Boyle's Law:- From the pressure equation, we get

$$p = \frac{1}{3}\rho C_{rms}^2$$

If M' be the mass of a gas that occupies a volume V,

$\rho = \frac{M'}{V}$.

$$\therefore \; p = \frac{1}{3}\frac{M'}{V}C_{rms}^2$$

$$\text{or, } \; pV = \frac{1}{3}M' C_{rms}^2$$

At fixed temperature T, C_{rms}^2 is also fixed. So

$$\boxed{pV = \text{Constant}} \quad \dots (8)$$

Which is Boyle's law. This is the equation of an isotherm. We have

4. Charle's Law:- From the above equation

$$pV = \frac{1}{3}M' C_{rms}^2$$

$$\text{or, } \; pV \propto C_{rms}^2 \qquad \text{but } C_{rms}^2 \propto T$$

Therefor $\quad pV \propto T \Rightarrow \boxed{\frac{V}{T} = \text{Const}}$ at constant p $\quad \dots (9)$

This is an equation of an isobar.

5. Dalton's law of partial pressures:- Let $m_1, m_2, m_3 \dots$ be the molecular masses of different gases 1, 2, 3 ... and $n_1, n_2, n_3 \dots$ their respective number of molecules per unit volume. Total pressure will be due to all the different types of molecules per unit volume. The total pressure

$$p = \frac{1}{3}m_1 n_1 C_1^2 + \frac{1}{3}m_2 n_2 C_2^2 + \frac{1}{3}m_3 n_3 C_3^2 \dots$$

But $\frac{1}{3}m_1 n_1 C_1^2 = p_1$, partial pressure of gas 1

$\frac{1}{3}m_2 n_2 C_2^2 = p_2$ " " gas 2 and so on

$$\therefore \; \boxed{p = p_1 + p_2 + \dots = \sum p_i} \quad \dots (10)$$

which is Dalton's law of partial pressures, i.e. the pressure of mixture of gases equal the sum of the partial pressures of its components.

6. Avagadro hypothesis :- Let us have two gases contained in separate enclosures each of volume V. Let n_1, m_1, c_1 be the number of molecules, molecular mass and r.m.s velocity respectively of gas 1; let n_2, m_2, c_2 corresponding quantities of gas 2.

when the pressure is the same, we have

$$\frac{1}{3} m_1 \frac{n_1}{V} c_1^2 = \frac{1}{3} m_2 \frac{n_2}{V} c_2^2$$

$$\text{a. } \frac{1}{3} m_1 n_1 c_1^2 = \frac{1}{3} m_2 n_2 c_2^2 \quad \ldots \quad (11)$$

Since temperature is same, so

$$\frac{1}{2} m_1 c_1^2 = \frac{1}{2} m_2 c_2^2$$

So, from eqn (11) we have

$$\boxed{n_1 = n_2} \quad \ldots \quad (12)$$

So, equal volumes of all gases under same pressure and ~~sam~~ temperature, Contain equal number of molecules.

7. ~~Clayp~~ Clapeyron's equation :- We have, pressure

$$p = \frac{1}{3} m n C_{rms}^2 = \frac{1}{3} \frac{n}{N_A} m N_A C_{rms}^2 \quad [N_A \text{ Avogadro number}]$$

$$= \frac{1}{3} \frac{n}{N_A} M C_{rms}^2$$

$$= \frac{n}{N_A} pV = \frac{n}{N_A} RT$$

$$\boxed{p = nKT} \quad \ldots \quad (13) \qquad \left[\frac{R}{N_A} = K = \text{Boltzmann Const.}\right]$$

This is clayperon's equation

Computation of various constants :-

① Avogadro Number (N_A) :- If 'm' be the mass of a molecule, then $m N_A = M$, the molecular weight.

$$\therefore N_A = \frac{M}{m} = \frac{2}{3.32 \times 10^{-24} \text{kg}} \quad (\text{taking } H_2 \text{ gas})$$

$$= 6.023 \times 10^{23} \text{ per mole}$$

$$= 6.023 \times 10^{26} \text{ per Kilo mole.}$$

② Universal gas Constant :- (R). From the relation $pV = RT$

$$R = \frac{pV}{T} = \frac{76 \times 13.6 \times 981 \times 22.4 \times 10^3}{273} \text{ erg/mole/K}$$

$$R = 8.31 \cdot J/mole/K$$

$$= \frac{8.31\times10^{7}}{4.18\times10^{7}} = 1.99\ cal/mole/K$$

③ Boltzmann Constant (k) :—

$$K = \frac{R}{N_A}$$

$$= \frac{8.31\times10^{7}}{6.023\times10^{23}}$$

$$= 1.38\times10^{-16}\ erg/K$$

$$\boxed{k = 1.38\times10^{-23}\ J/K}$$

Maxwell's Velocity distribution law:—

Let us represent all the molecules in a velocity diagram (velocity space). Let OX, OY, OZ be the axes of a rectangular system of co-ordinates with O as origin and u, v, w be the components of any velocity c, along three axes.

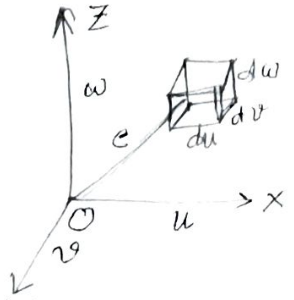


Fig (2)

$$\therefore\ c^2 = u^2 + v^2 + w^2 \quad \dots (1)$$

Differentiating equation (1), we have

$$u\,du + v\,dv + w\,dw = 0 \quad \dots (2)$$

Equation (2) is a condition equation that shows that du, dv, dw are not independent to each other.

Now the probability that a molecule has a velocity between u and u+du is f(u)du. Similarly, the probabilities that a molecule has velocity components lying between v and v+dv and w and w+dw are f(v)dv and f(w)dw respectively.

∴ The probability that a molecule has component velocities between u and u+du, v and v+dv, w and w+dw is the product of the individual probabilities, i.e.

$$f(u)\,f(v)\,f(w)\,du\,dv\,dw$$

If N be the total number of molecules in the gas ensemble and dN° the number having the specified range of velocities, then

$$dN^{\circ} = N f(u)\,f(v)\,f(w)\,du\,dv\,dw \quad —③$$

or $\frac{dN^*}{N\,du\,dv\,dw} = N f(u) f(v) f(w)$

or $\rho = N f(u) f(v) f(w)$ . . . (4)

'ρ' is the number of molecules of the specified type per unit volume of the velocity space.

Since the gas is in a steady state, the molecular density in any direction is constant, that is $d\rho = 0$.

$$\therefore \; d\left[f(u) f(v) f(w) \right] = 0$$

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

Dividing by $f(u) f(v) f(w)$,

$$\frac{f'(u)}{f(u)}\,du + \frac{f'(v)}{f(v)}\,dv + \frac{f'(w)}{f(w)}\,dw = 0 \quad \text{—— (5)}$$

Since du, dv, dw are not independent, so we cannot equate the coefficients of each of the differentials to zero. However, we can multiplying eqn (2) by 'α' and adding with eqn (5), we get

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

Now du, dv, dw are in effect independent. So

$$\left.\begin{aligned} &\frac{f'(u)}{f(u)} + \alpha u = 0 \\ &\frac{f'(v)}{f(v)} + \alpha v = 0 \\ \text{and } &\frac{f'(w)}{f(w)} + \alpha w = 0 \end{aligned}\right\} \quad . . . . (6)$$

Integrating each of the equations of Set eqn (6) above.

$$f(u) = A e^{-\frac{\alpha u^2}{2}}; \quad f(v) = A e^{-\frac{\alpha v^2}{2}}; \quad f(w) = A e^{-\frac{\alpha w^2}{2}}$$

From eqn (3) $\quad dN = N A^3 e^{-\frac{\alpha}{2}(u^2+v^2+w^2)}\,du\,dv\,dw$

or $\frac{dN}{du\,dv\,dw} = \rho = N A^3 e^{-\frac{\alpha}{2}(u^2+v^2+w^2)}$ . . . ~~(7)~~

$$\boxed{\rho = N A^3 e^{-bc^2}} \quad . . . (7)$$

where $\quad b = \frac{\alpha}{2}$ and $u^2+v^2+w^2 = c^2$

Eqn (7) shows that the molecular density is a function of c only.

Evaluation of A:- Since the total number of molecules in the gas assembly is N.

$$\iiint_{-\alpha}^{+\alpha} N A^3 e^{-b(u^2+v^2+w^2)}\, du\, dv\, dw = N$$

$$\Rightarrow \frac{1}{A^3} = \iiint_{-\alpha}^{+\alpha} e^{-b(u^2+v^2+w^2)}\, du\, dv\, dw$$

Now let. $I = \int_{-\alpha}^{+\alpha} e^{-bu^2} du = \int_{-\alpha}^{+\alpha} e^{-bv^2} dv = \int_{-\alpha}^{+\alpha} e^{-bw^2} dw$

$\therefore I^3 = \frac{1}{A^3}$, Hence $I = \frac{1}{A}$.

But $I = \int_{-\alpha}^{+\alpha} e^{-bu^2} du = \sqrt{\frac{\pi}{b}} = \frac{1}{A}$

$$\therefore \boxed{A = \sqrt{\frac{b}{\pi}}} \quad \text{——} \quad (8)$$

Evaluation of b:- The pressure p of the gas is

$$p = 2m \sum_0^{\alpha} n_u u^2$$

where n_u = number of molecules per unit volume with velocities between u and $u+du$ = $n\, f(u)\, du$

where n is the number of molecules per unit volume.

$$\therefore p = 2mn\int_0^{\alpha} f(u)\, u^2\, du$$

$$= 2mnA \int_0^{\alpha} u^2 e^{-bu^2} du$$

$$= 2mn \times \sqrt{\frac{b}{\pi}} \times \sqrt{\frac{\pi}{b^3}} \times \frac{1}{4}$$

$$= \frac{\cancel{8}mn}{2b}$$

$$\therefore b = \frac{mn}{2p} = \frac{mn}{2 \times \cancel{n}KT} \qquad [p = nKT]$$

$$\therefore \boxed{b = \frac{m}{2KT}} \quad \text{——} \quad (9)$$

and $\boxed{A = \sqrt{\frac{m}{2\pi KT}}}$

So, finally we have,

$$f = N\left(\frac{m}{2\pi KT}\right)^3 e^{-\frac{m}{2KT}c^2} \quad \text{——} (10)$$

The left hand side of the eqn (10) is the number of specified molecules per unit volume. So the number of molecules dN_c having velocity lying between c and c+dc is f times the volume between the two spheres of radius c and c+dc. The volume of the spherical shell is $4\pi c^2 dc$

$$\therefore dN_c = f\, 4\pi c^2 dc$$

$$= 4\pi N \sqrt[3]{\frac{m}{2\pi KT}}\, e^{-bc^2} c^2 dc$$

$$\boxed{dN_c = 4\pi N \left(\frac{m}{2\pi KT}\right)^{3/2} e^{-\frac{mc^2}{2KT}} c^2 dc} \quad \ldots (11)$$

This is the well known Maxwell's Velocity distribution law.

From eqn (11) we have $\frac{dN_c}{N} = 4\pi \left(\frac{m}{2\pi KT}\right)^{3/2} e^{-\frac{mc^2}{2KT}} c^2 dc = F dc$

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

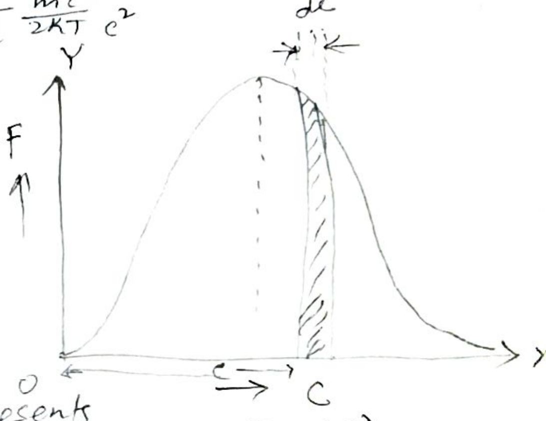


Fig (3)

A plot of function F against c gives the distribution curve of molecular velocity in fig(3).

If at a distance c from the origin, a thin strip of thickness dc is taken, then the area of the strip Fdc represents the fraction of the total number of molecules with velocity lying between c and c+dc. i.e. $\frac{dN_c}{N}$

From Maxwell's eqn, $dN_c = 0$, when $c = 0$ and $c = \infty$. This is also confirmed by the nature of the curve. It means that the number of molecules having velocities tending to zero and also tending to infinity is quite small. Between these two extremes there is a value of 'c' for which F is maximum. Maximum number of molecules will possess this velocity is called the most probable velocity.

Average or mean speed:- Let n_1 molecules have speed c_1, n_2 have speed c_2 and so on. So by definition, the average or mean speed $\bar{c}$ is given by

$$\bar{c} = \frac{n_1 c_1 + n_2 c_2 + \ldots}{n_1 + n_2 + \ldots} = \frac{\sum n_i c_i}{\sum n_i}$$

$$= \frac{1}{N}\int_0^\infty c\, dN_c \qquad [\because \sum n_i = N]$$

Now $dN_c = 4\pi N A^3 e^{-bc^2} c^2 dc$

$$\therefore \bar{c} = \frac{4\pi N A^3}{N}\int_0^\infty c^3 e^{-bc^2} dc \quad \text{———} \quad (1)$$

$$= 4\pi A^3 \int_0^\infty c^3 e^{-bc^2} dc$$

But $\int_0^\infty e^{-bc^2} c^3 dc = \frac{1}{2b^2}\int_0^\infty e^{-z} z\, dz$ Let $bc^2 = z$.

$$= \frac{1}{2b^2}\Gamma(2)$$

$$= \frac{1}{2b^2}$$ As $\Gamma(2) = \Gamma(1+1) = 1 \cdot \Gamma(1) = 1$.

Therefore $\bar{c} = \frac{4\pi A^3}{2b^2} = \frac{2\pi \times \left(\frac{m}{2\pi KT}\right)^{3/2}}{\left(\frac{m}{2KT}\right)^2}$

$$\boxed{\bar{c} = \sqrt{\frac{8KT}{m\pi}}} \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

<u>RMS Speed:-</u> By definition, the r.m.s or the root mean squre speed c is defined as

$$C = \sqrt{\overline{c^2}}, \quad \text{Where } \overline{c^2} = \text{Mean squre velocity}$$

$$\overline{c^2} = \frac{n_1 c_1^2 + n_2 c_2^2 + n_3 c_3^2 + \cdots}{n_1 + n_2 + n_3 + \cdots} = \frac{\sum n_i c_i^2}{\sum n_i}$$

where n_1 molecules have speed c_1, n_2 molecules have speed c_2 and so on.

$$\therefore \overline{c^2} = \frac{1}{N}\int_0^\infty c^2 dN_c$$

$$= \frac{4\pi N A^3}{N}\int_0^\infty c^2 e^{-bc^2} c^2 dc$$

$$= 4\pi A^3 \int_0^\infty c^4 e^{-bc^2} dc$$

$$= 4\pi A^3 \cdot \frac{1}{2b^{5/2}}\Gamma(5/2) \qquad \left[\because \int_0^\infty c^4 e^{-bc^2} dc = \frac{1}{2b^{5/2}}\Gamma(5/2)\right]$$

$$= 4\pi \times \left(\frac{m}{2\pi KT}\right)^{3/2} \times \frac{1}{2 \times \left(\frac{m}{2KT}\right)^{5/2}} \cdot \frac{3}{2} \cdot \frac{1}{2} \cdot \sqrt{\pi}$$

$$= \frac{3 \times 2KT}{2 \times m}$$

$$= \frac{3KT}{m}$$

Therefore $\boxed{C_{rms} = \sqrt{\overline{c^2}} = \sqrt{\frac{3KT}{m}}} \quad \cdot \quad \cdot \quad \cdot \quad (3)$

<u>Most Probable Speed:-</u> From Maxwell's velocity distribution law, we have

$$F = 4\pi A^3 c^2 e^{-bc^2} \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

The value of c for which F is maximum is the most probable velocity, C_m

Differentiating equation(4), we have

$$\frac{dF}{dc} = 4\pi A^3 \left[2c e^{-bc^2} - 2bc^3 e^{-bc^2}\right]$$

For C_m, $\frac{dF}{dc} = 0$, $b = \frac{1}{C_m^2}$

$$\text{or, } \boxed{C_m = \sqrt{\frac{1}{b}} = \sqrt{\frac{2KT}{m}}} \quad \cdot \quad \cdot \quad \cdot \quad (5)$$

Ratio of the three speeds:-

The ratio of the average, rms and most probable velocities at a given temperature is, therefore,

$$\bar{c} : c_{rms} : c_m = \sqrt{\frac{8KT}{m\pi}} : \sqrt{\frac{3KT}{m}} : \sqrt{\frac{2KT}{m}}$$

$$= \sqrt{\frac{8}{\pi}} : \sqrt{3} : \sqrt{2}$$

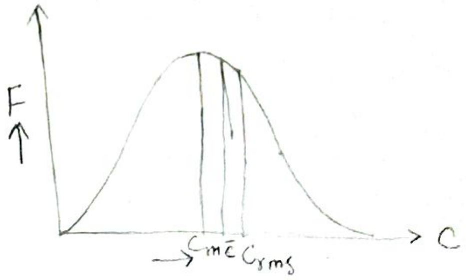


Fig.(4)

So, $\frac{\bar{c}}{c_{rms}} = \sqrt{\frac{8}{3\pi}} = 0.921$

$\frac{c_m}{c_{rms}} = \sqrt{\frac{2}{3}} = 0.817$

Thus, the ratio of the speeds in the ascending order is

$$c_m : \bar{c} : c_{rms} = 1 : 1.128 : 1.224$$

Velocity distribution: Temperature dependence :-

If we integrate the expression for the fraction of molecules having a specified velocity between c and c + dc, i.e.,

$$\frac{dN_c}{N} = 4\pi A^3 e^{-bc^2} c^2 dc$$

w.r.to c for all the possible values of it, we should get 1.

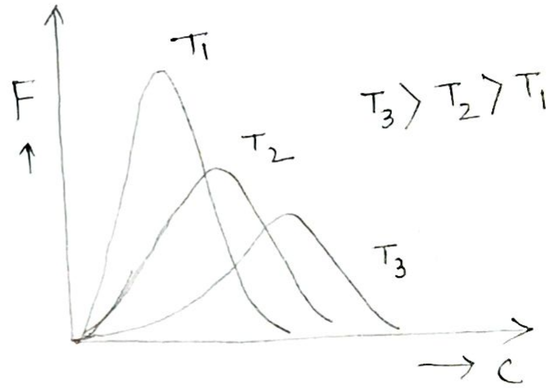


Fig.(5)

$$\therefore \int_0^\infty 4\pi \left(\frac{m}{2\pi KT}\right)^{3/2} e^{-\frac{mc^2}{2KT}} c^2 dc = 1$$

This implies that the integral

$$\int_0^\infty F\, dc = 1$$

This means that the area under the distribution curve of molecular velocity i.e., F vs. c plot is unity.

But we have seen that the maximum of the F-c curve occurs at $c = c_m = \sqrt{\frac{2KT}{m}}$.

So when the temperature increases, the peak of the curve should get itself shifted to a higher c-value. But since, the area is fixed, the curve would get broadened with increase in temperature.

Experimental verification of Maxwell's law:-

① **Eastermann, Simpson and Stern's method:-** The experimental arrangement is shown diagramatically in fig (6). O is electrical oven from which emerges a molecular beam of caesium. The beam passes through the collimating slit S and impinges upon the hot tungsten wire D. The pressure of residual gas in the apparatus is very low, 10^{-8} mm of Hg. The caesium atoms, on striking the tungsten wire, ionise, re-evaporate and are collected in a negatively charged cylinder surrounding the wire. The ions constitute an ion-current to the collector, the current directly gives the number of atoms hitting the wire per second.

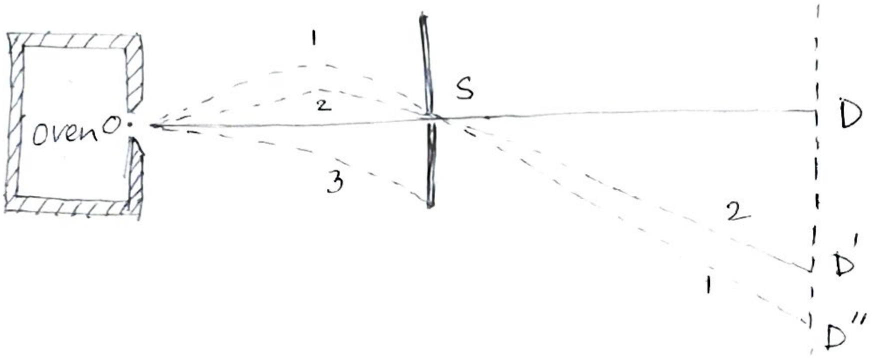


Fig.(6)

In the absence of gravitational field, only the atoms emerging horizontally would pass through S and strike D irrespetive of velocities. In fact the path of an atom is parabolic and an atom emerging from slit O in a horizontal direction (path 3) would not pass through S. Only approximately directed molecules (marked 2, 1) would pass through S and hit D at points D', D'' respectively. The molecules of path 2 move slower than those of path 1. The measurement of ion current, which is a function of vertical height from the point D measured downwards, then gives the velocity distribution.

Fig. (7) shows both the theoretical and experimental distributions — dotted curve experimental, continuous curve theoretical. The ordinate of the curve is the intensity which is proportional to the ion current and abscissa represents the vertical height S of the ion collector.

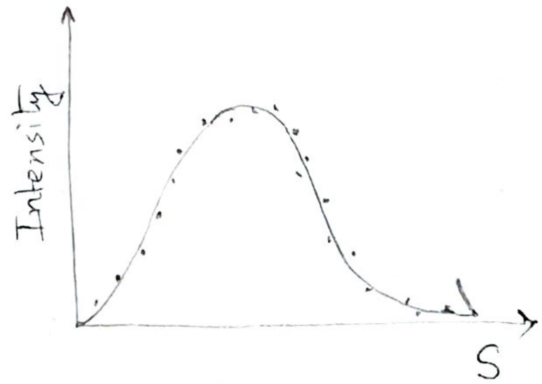


Fig. 6(7)

Degrees of freedom of a dynamical System :-

If a particle moves along a straight line, say along x-axis, its position is completely specified by one co-ordinate (x) only. The particle possess one degrees of freedom. If the particle moves over a plane, say the xy plane, then to specify its position completely, two co-ordinates (x, y) are needed. The particle is now said to have two degrees of freedom. Similarly, to completely specify the position of a particle in space, three co-ordinates (x, y, z) are required. The particle has now three degrees of freedom. So the degrees of freedom we mean the number of independent co-ordinates necessary to specify the position or configuration of a dynamical System.

Again, the Kinetic energy of the particle in the first instance is given by $\frac{1}{2}m\dot{x}^2$, that in the second by $\frac{1}{2}m(\dot{x}^2+\dot{y}^2)$ and in the third by $\frac{1}{2}m(\dot{x}^2+\dot{y}^2+\dot{z}^2)$. So we can define the degrees of freedom as also the number of squrred terms occuring in the expression for the Kinetic energy of the System

If there is a material system consisting N partides (x_1, y_1, z_1), (x_2, y_2, z_2), --- (x_N, y_N, Z_n), subjected to smooth constraints represented analytically by m equations.

$$F_j(x_1, y_1, z_1, \ldots x_N, y_N, z_N) = 0 \quad \text{where } j = 1, 2, 3 \cdots m$$

then if $m < 3N$, the number of degrees of freedom f of the system is given by

$$\boxed{f = 3N - m}$$

Equipartion energy:- Maxwell showed that, if the molecule in their motion obey the laws of mechanics, the equipartition principles states that the mean kinetic energy of a dynamical system in thermal equilibrium is equally partitioned i.e. divided amon its different degrees of freedom and for each degrees of fre it is equal to $\frac{1}{2}KT$, Where T is the equilibrium temperat in absolute scale, K is the Boltzmann constant.

Degrees of freedom and ratio of heat capacities :-

Let a system consist of only free particles having f degrees of freedom. Since energy $\frac{1}{2}KT$ Corresponds to each degrees of freedom, the energy per mole of the system is

$$E = \frac{1}{2}KT \cdot f \cdot N_A = \frac{1}{2} f RT \qquad [R = kN_A]$$

where N_A is the Avogadro's number.

$$\therefore \text{ Molar heat capacity, } C_V = \left(\frac{dE}{dT}\right)_V$$

$$= \frac{d}{dT}\left(\frac{1}{2} f RT\right)_V$$

$$= \frac{1}{2} f R \quad \ldots \quad (1)$$

But we know, $C_P - C_V = R$

$$\therefore C_P = R + C_V$$

$$= R + \frac{1}{2} f R$$

$$= R\left(1 + \frac{f}{2}\right) \quad \ldots \quad (2)$$

$$\therefore \text{ Ratio of two specific heat, } \gamma = \frac{C_P}{C_V} = \frac{R(1+f/2)}{Rf/2}$$

$$\boxed{\gamma = 1 + \frac{2}{f}} \quad \ldots \quad (3)$$

This is an important general expression relating γ and f.

Examples :-

① Monoatomic gas :- For the gas whose molecules are mono atomic and for which the energy is totally Kinetic energy of translation, the degrees of freedom $f = 3$

$$C_V = \frac{1}{2} f R = \frac{3}{2} R$$

$$\therefore \gamma = 1 + \frac{2}{f} = 1 + \frac{2}{3} = 1.67$$

(2) Diatomic gas :- In diatomic gases, the molecules may be pictured as made up of two atoms at a certain distance from each other but joined rigidly like a dumbbell. So, there is one inter-atomic constant fixed.

$$\therefore \text{ Number of degrees of freedom} = 3.2 - 1$$

$$f = 5$$

$$\therefore \gamma = 1 + \frac{2}{f} = 1 + \frac{2}{5}$$

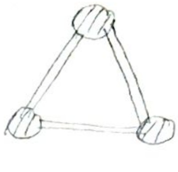
$$\boxed{\gamma = 1.4}$$

Non rigid diatomic molecules, the atoms vibrate along the line joining them and thereby introduce two vibrational degrees of freedom, since the vibrational energy is partly kinetic and ~~Kine~~ partly potential. Thus $f = 7$.

$$C_V = \frac{7}{2} R. \qquad \gamma = 1 + \frac{2}{7} = \frac{9}{7} = 1.28$$

Triatomic gas :- In triatomic non-linear molecules in which the atoms are arranged at the vertices of a triangle, the number of degrees of freedom would be 6.

$$f = 6\ 3.N - 3$$
$$= 3\cdot 3 - 3 = 6$$

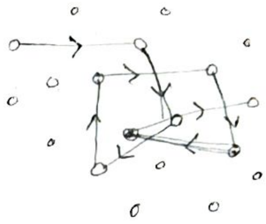


$$\therefore \quad \gamma = 1 + \frac{2}{6} = 1.33$$

If the atoms are linearly arranged ; m = 2

$$\therefore f = 3\cdot 3 - 2 = 7$$
$$\gamma = 1 + \frac{2}{7} = 1.28$$

Mean free path :- The molecules move at random and because of their finite size, in course of their movement, they collide each other. Each collision would result in a change of direction and velocity. The path traversed by a molecule between two successive collisions is called free path, which will be a straight line. Thus path of a single particle will be a zig-zag paths while it moves and undergoes a ~~non~~ number of collisions.



Fig(8)

Some of these ~~path~~ free paths will be long and others short. Therefore we can speak of a mean value - mean free path - by adding the lengths of a large number of free paths and dividing it by the total number. Thus the mean free path λ of a molecule is the average distance traversed ~~by it~~ between two successive collisions.

The distribution of free paths :-

This gives an idea how the free paths are distributed among the molecules, i.e. What is the probability that a molecule may describe a distance x without suffering collisions.

Consider a system of N_0 molecules to starts with., They move along a certain direction. Some are knocked out of the competition and let N molecules be able to cross distance x without collision, Now out of these N again, dN molecules are further thrown out as result of collisions on their onward journey through a distance dx. Then it is easy to see that

$$dN \propto N$$
$$\propto dx$$

$\therefore$ $dN = -P_c N\,dx$, (−ve sign because each collision wipes out a molecule, so dN must be −ve, P_c is const. of proportionality.

So, $\frac{dN}{N} = -P_c dx$

Integrating, $\log N = -P_c x + \text{cont.}$

At $x=0$, $N = N_0$,

Therefore const. = $\log N_0$.

$\therefore$ $\log N = -P_c x + \log N_0$

or, $\frac{N}{N_0} = e^{-P_c x}$

or $\boxed{N = N_0 e^{-P_c x}}$ . . . . (1)

Differentiating eqn (1), we have

$$dN = -N_0 P_c e^{-P_c x} dx \quad \text{. . . (2)}$$

From eqn (2), taking the magnitude, we get the number of molecules which have free paths equal to x

$$\therefore \lambda = \frac{x_1 dN_1 + x_2 dN_2 + \cdots}{N_0}$$

$$= \frac{\int_0^\infty x\,dN}{N_0}$$

$$= \int_0^\infty \frac{N_0 P_c e^{-P_c x}}{N_0} dx \cdot x$$

$$= P_c \int_0^\infty x e^{-P_c x} dx$$

$$= P_c \times \frac{1}{P_c^2} = \frac{1}{P_c}$$

or $\boxed{P_c = \frac{1}{\lambda}}$ . . . (3)

From (1), $\boxed{N = N_0 e^{-\frac{x}{\lambda}}}$ . . . . (4)

This is well known survival equation

It shows that the molecules falls off exponentially with the distance x. Plotting N/N_0 against $\frac{x}{\lambda}$, we get the curve as shown in fig. (9).

From the eqn (4), the probability of a free path equal to P_x is given by

$$\boxed{\frac{N}{N_0} = P_x = \bar{e}^{x/\lambda}}$$

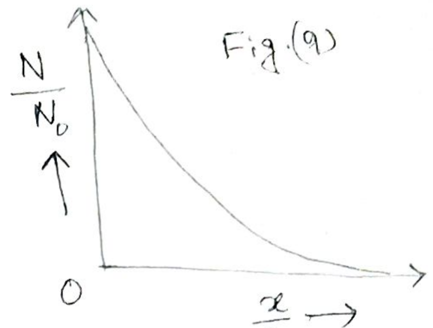


Fig. (9)

Expression for mean free path :-

An elementary treatment

Imagine that at certain instant all the molecules of a gas, except one are at rest. The moving molecules moves among the 'frozen' ones with a velocity $\bar{c}$, the average velocity. We assume the molecules to be perfectly elasti spheres of diameter σ. At the instant of collision, the centre to centre distance of the colliding molecules is σ in fig. (10).

The centre-to-centre distance would thus be the same if the radius of the moving molecule were increased to σ and the molecules at rest were all shrunk to more geometrical points.

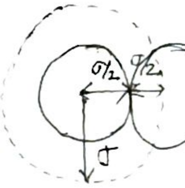


Fig. (10)

So, the effective cross-sectional area of the molecule, i.e. collision cross section ρ, is

$$\rho = \pi\sigma^2$$

In an interval t, the mobile molecule traverses a distance $\bar{c}t$ along a zigzag course and sweeps out a cylindrical volume (Fig-11) of cross section ρ and length $\bar{c}t$.

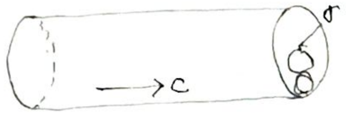


Fig. (11)

Plainly, it would collide in time t with all molecules having their centres within this volume. The number of such molecules is obviously $\rho n\bar{c}t$, n being the molecular density.

$\therefore$ Number of collisions in time t = $\rho n\bar{c}t$

$\therefore$ Collision frequency, $z = \rho n\bar{c}$ which is simply the number of collisions per unit time.

$$\therefore \text{Mean free path, } \lambda = \frac{\text{distance traversed in time 't'}}{\text{no. of collisions in 't'}}$$

$$= \frac{\bar{c}t}{\rho n\bar{c}t}$$

$$= \frac{1}{\rho n}$$

$$\boxed{\lambda = \frac{1}{n\pi\sigma^2}} \quad \ldots \quad (1)$$

Clausius method:- In the previous section we consider only one molecule was moving, the rest were frozen. This assumption is not valid and if the target molecules move, the collision probability goes up. ~~Clausius~~ Clausius introduced the concept of relative velocity to make correction appropriately. 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 angle θ with A. Then the relative velocity of A with respect to B is

$$R = \sqrt{(c_1^2 + c_2^2 - 2c_1c_2\cos\theta)} \quad \ldots (2)$$

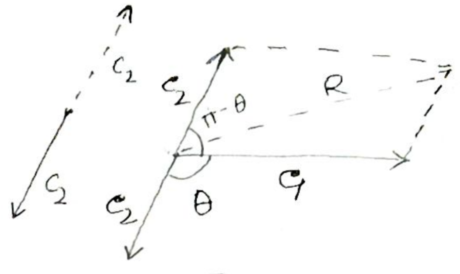


Fig (12)

To find the mean relative velocity of A w.r.to all others, let $dN_{\theta,\phi}$ be the molecules moving between θ and $\theta + d\theta$, ~~ϕ~~ and ϕ and $\phi + d\phi$. Then the mean relative velocity $\overline{R}$ of A w.r.to B types molecules is

$$\overline{R} = \frac{\int R\, dN_{\theta,\phi}}{\int dN_{\theta,\phi}} \quad \ldots (3)$$

But we have $dN_{\theta,\phi} = \frac{N}{4\pi r^2} r^2 \sin\theta\, d\theta\, d\phi \quad \ldots (4)$

where N is the molecular density.

$$\therefore \overline{R} = \frac{\frac{N}{4\pi}\int_0^{\pi}(c_1^2 + c_2^2 - 2c_1c_2\cos\theta)^{1/2}\sin\theta\, d\theta \int_0^{2\pi} d\phi}{\frac{N}{4\pi}\int_0^{\pi}\sin\theta\, d\theta \int_0^{2\pi} d\phi}$$

$$= \frac{1}{2}\int_0^{\pi}(c_1^2 + c_2^2 - 2c_1c_2\cos\theta)^{1/2}\sin\theta\, d\theta$$

Substituting, $c_1^2 + c_2^2 - 2c_1c_2\cos\theta = z$, we get $2c_1c_2\sin\theta\, d\theta = dz$

$$\therefore \overline{R} = \frac{1}{2}\cdot\frac{1}{2c_1c_2}\int_{(c_1 \sim c_2)^2}^{(c_1+c_2)^2} z^{1/2}\, dz$$

$$= \frac{1}{6c_1c_2}\left[(c_1 + c_2)^3 - (c_1 \sim c_2)^3\right] \quad \ldots (5)$$

Clausius assumed that $c_1 = c_2 = \bar{c}$, i.e. all molecules move with the same average velocity $\bar{c}$.

$$\therefore \overline{R} = \frac{1}{6\bar{c}^2} \times 8\bar{c}^3 =$$ [illegible]

$$= \frac{4}{3}\bar{c}$$

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

$$\therefore \text{Mean free path, } \lambda = \frac{\bar{c}}{\pi\sigma^2\overline{R}n} = \frac{3}{4\pi n\sigma^2}$$

This is the Clausius expression for the mean free path.

Maxwell's method:- Maxwell also followed the relative velocity technique introduced by Clausius. He first found the relative velocity of the molecules A moving with velocity c_1 w.r.to B type molecules moving with velocity c_2 and then averaging for all possible values of c_2. He next multiplied this mean value of relative velocity by the number of molecules moving with velocity c_1 and averaging over all possible values c_1 from 0 to ∞. Thus the mean relative velocity of any molecule with respect to all others in space was obtained.

From eqn (5), the mean relative velocity of a molecule with velocity c_1 w.r.to molecules having velocity c_2 is

$$\bar{R} = \frac{1}{6c_1c_2}\left[(c_1+c_2)^3 - (c_1\sim c_2)^3\right]$$

$$= \frac{3c_1^2+c_2^2}{3c_1} \quad \text{when } c_1>c_2 \quad \cdots (6)$$

or,

$$= \frac{3c_2^2+c_1^2}{3c_2} \quad \text{when } c_1<c_2 \quad \cdots (7)$$

The mean relative velocity of a A-type molecule w.r.to all other molecules is

$$r_1 = \frac{\int \bar{R}\, dn_{c_2}}{\int dn_{c_2}} = \frac{\int_0^\infty \bar{R}\; 4\pi n\left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mc_2^2}{2kT}\right) c_2^2\, dc_2}{\int_0^\infty 4\pi n\left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mc_2^2}{2kT}\right) c_2^2\, dc_2}$$

$$= \int_0^\infty 4\pi\bar{R}\left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-mc_2^2/2kT\right) c_2^2\, dc_2$$

Since the integral in the denominator gives n

$$= \int_0^{c_1} 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} \cdot \frac{3c_1^2+c_2^2}{3c_1} \exp\left(-\frac{mc_2^2}{2kT}\right) c_2^2\, dc_2$$

$$+ \int_{c_1}^\infty 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} \frac{3c_2^2+c_1^2}{3c_2} \exp\left(-\frac{mc_2^2}{2kT}\right) c_2^2\, dc_2 \quad \cdots (8)$$

with appropriate values for $\bar{R}$ in appropriate ranges.

Now, the molecule A again may move with all possible values of c_1 ranging from 0 to ∞. So the mean relative velocity of any one molecule w.r.to all others moving in all possible manner is

$$\bar{r} = \frac{\int_0^\infty r_1\, dn_{c_1}}{\int_0^\infty dn_{c_1}} = \frac{1}{n}\int_0^\infty r_1\, dn_{c_1}$$

$$= \frac{1}{n}\int_0^\infty 4\pi n\left(\frac{m}{2\pi kT}\right)^{3/2} r_1 e^{-\frac{mc_1^2}{2kT}} c_1^2\, dc_1$$

$$= \int_0^\infty 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} r_1 e^{-\frac{mc_1^2}{2kT}} c_1^2\, dc_1 \quad \cdots (9)$$

Substituting value of r_1 in eqn (9), we have

$$\bar{r} = 16\pi^2\left(\frac{m}{2\pi kT}\right)^3\left[\int_0^\infty c_1^2 e^{-\frac{mc_1^2}{2kT}} dc_1 \int_0^{c_1} \frac{3c_1^2+c_2^2}{3c_1} e^{-\frac{mc_2^2}{2kT}} c_2^2\, dc_2\right] \rightarrow I_1$$

$$+16\pi^2\left(\frac{m}{2\pi kT}\right)^3\left[\int_0^\infty c_1^2 e^{-\frac{mc_1^2}{2kT}} dc_1 \int_{c_1}^\infty \frac{3c_2^2+c_1^2}{3c_2} e^{-\frac{mc_2^2}{2kT}} c_2^2\, dc_2\right] \rightarrow I_2 \quad \cdots (10)$$

Let us denote the term in the first [ ] by I_1 and in the second [ ] above by I_2.

$$\therefore \quad I_2 = \int_0^\infty q^2 e^{-\frac{mq^2}{2kT}} dq \int_q^\infty \frac{3c_2^2+q^2}{3c_2} e^{-\frac{bc_2^2}{2kT}} c_2^2 dc_2$$

Now,
$$\int_q^\infty \frac{3c_2^2+q^2}{3c_2} \times c_2^2 dc_2 \, e^{-bc_2^2}$$

$$= \int_q^\alpha c_2^3 dc_2 e^{-bc_2^2} + \frac{q^2}{3}\int_q^\infty c_2 dc_2 \, e^{-bc_2^2}$$

$$= \frac{1}{2b}\int_q^\alpha c_2^2 e^{-bc_2^2} d(bc_2^2) + \frac{q^2}{6b}\int_q^\infty e^{-bc_2^2} d(bc_2^2)$$

$$= \frac{1}{2b^2}\int_{bq^2}^\infty z e^{-z} dz + \frac{q^2}{6b}\left[-e^{-bc_2^2}\right]_q^\infty, \quad \text{putting } bc_2^2 = z$$

$$= \frac{1}{2b^2}\left[-ze^{-z} - e^{-z}\right]_{bq^2}^\infty + \frac{q^2}{6b}\left[-e^{-bc_2^2}\right]_q^\infty$$

$$= \frac{1}{2b^2}\left(bq^2 e^{-bq^2} + e^{-bq^2}\right) + \frac{q^2}{6b} e^{-bq^2}$$

$$\therefore \; I_2 = \frac{1}{2b}\int_0^\infty q^4 e^{-bq^2} dq + \frac{1}{2b^2}\int_0^\infty q^2 e^{-bq^2} dq + \frac{1}{6b}\int_0^\infty q^4 e^{-2bq^2} dq$$

$$= \frac{1}{2b} \times \frac{3}{8}\sqrt{\frac{\pi}{(2b)^5}} + \frac{1}{2b^2}\cdot\frac{1}{4}\sqrt{\frac{\pi}{(2b)^3}} + \frac{1}{6b}\cdot\frac{3}{8}\sqrt{\frac{\pi}{(2b)^5}}$$

$$= \frac{1}{8\sqrt{2}}\sqrt{\frac{\pi}{b^7}}$$

It can be shown that the term I_1 is also equal to I_2.

$$\therefore \quad \bar{r} = 16\pi^2\left(\frac{m}{2\pi kT}\right)^3\left[\frac{1}{8\sqrt{2}}\sqrt{\frac{\pi}{b^7}} + \frac{1}{8\sqrt{2}}\sqrt{\frac{\pi}{b^7}}\right]$$

$$= 16\pi^2\left(\frac{b}{\pi}\right)^3 \cdot \frac{1}{4\sqrt{2}} \times \sqrt{\frac{\pi}{b^7}}$$

$$= \frac{2\sqrt{2}}{\sqrt{\pi b}} = 2\sqrt{2}\cdot\frac{1}{\sqrt{m\pi/2kT}}$$

$$= \sqrt{2}\sqrt{\frac{8kT}{m\pi}} = \sqrt{2}\,\bar{c}$$

$\therefore$ Mean free path, $\lambda = \dfrac{\bar{c}}{n\pi\sigma^2\sqrt{2}\,\bar{c}}$

$$\boxed{\lambda = \frac{1}{\sqrt{2}\, n\pi\sigma^2}}$$

This is the Maxwell's expression for the mean free path of the molecules.