Study Material – Sem. 3 – C6T –

Kinetic Theory of Gases – Dr. T. Kar –

Class 3

Mean Free Path

Even at ordinary temperature, gas molecules move with very large velocities. Opponents of the Kinetic Theory at one time, therefore, argued that such large rectilinear velocities are incompatible with many physical observations e.g., gaseous mass in a vessel would disappear in no time.

The situation however was saved by Clausius who explained that the difficulty is resolved if the molecules are attributed a finite, though small volume. Then as a molecule moves, it "collides" with another and its velocity and direction of motion get changed. But as the molecules, except in a collision, do not approach close enough, the mutual force-action is negligible. The path traversed by a molecule between two successive collisions is called free path, which will be a straight line. Thus the path of a single particle will consist of a series of short zig-zag paths as illustrated in fig. 1, as it moves and undergoes a

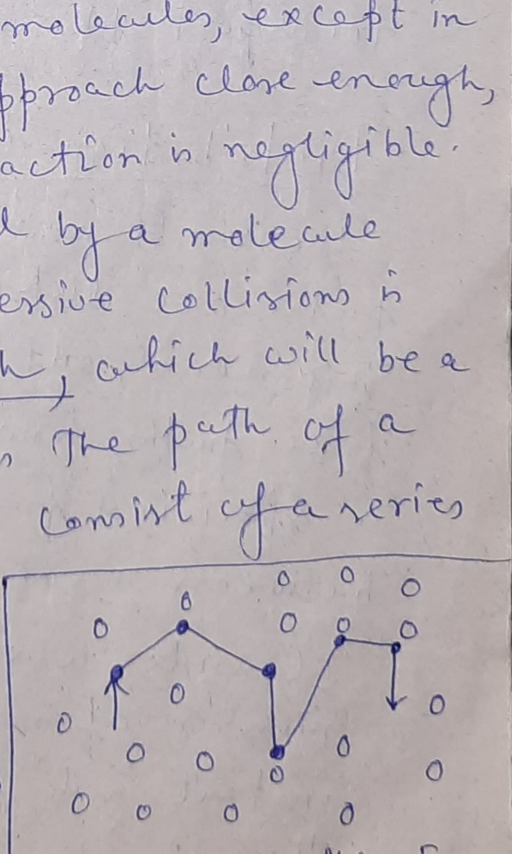

Fig. 1. Molecular Mean Free Path

number of collisions.

Plainly, some of these free paths will be relatively long and others short. We can, therefore, speak of a mean value – the mean free path – by adding the lengths of a large number of free paths and dividing it by the total number of paths. Thus, the mean free path, λ of a molecule is the average distance traversed by it between two successive collisions. It is an important quantity to study a class of phenomena called transport phenomena.

Distribution of free paths

We shall now derive how the free paths are distributed among the molecules. This means, out of a large number of free paths, how many molecules have a specified free path length, say between x and $x+dx$.

Consider a system having a large number of molecules, N_0 at a given instant and follow the group as the molecules collide. Each collision knocks out the molecules from the group. Let N be the number of molecules remaining in the group after a distance x, as measured along the free path of each, has been travelled by the group. N molecules thus have not yet made any collision. In the next additional short distance dx, some of N, say dN will again be removed from the group by way of collision. This dN will be proportional to N, the number in the group and also to dx.

$$\therefore dN = -P N dx \longrightarrow ①$$

where P is the constant of proportionality. It depends on the physical conditions of the gas but neither on N nor on x. The negative sign indicates that a collision removes a molecule from the group and thus decreases N.

From ①, $\frac{dN}{N} = -P dx \longrightarrow ②$

Integrating, we have, $\ln N = -Px + A$

At $x=0$, $N = N_0$, Therefore, $A = \ln N_0$

$$\therefore \ln\left(\frac{N}{N_0}\right) = -Px \text{ or } \boxed{N = N_0 e^{-Px}} \longrightarrow ③$$

Thus, the number remaining in the group

falls off exponentially with free path length x.

Now, From ①, we get,

$$dN = -P N_0 e^{-Px} dx \rightarrow ④$$

Thus $|dN|$ gives The number of molecules with free path lengths between x and x+dx. Now,

$$\text{Mean free path, } \lambda = \frac{x_1 dN_1 + x_2 dN_2 + \cdots}{dN_1 + dN_2 + \cdots}$$

$$= \frac{\int x\, dN}{\int dN} = \frac{1}{N_0} \int x\, dN$$

$$= \frac{1}{N_0} \int_0^\infty x P N_0 e^{-Px} dx$$

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

Let $Px = z$

$\therefore dx = \frac{dz}{P}$

& $x = \frac{z}{P}$

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

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

$\Gamma(1) = 1$

$$= P \int_0^\infty \left(\frac{z}{P}\right) e^{-z} \left(\frac{dz}{P}\right) = \frac{1}{P} \int_0^\infty z^{2-1} e^{-z} dz$$

$$= \frac{1}{P} \Gamma(2) = \frac{1}{P}$$

$$\therefore \boxed{P = \frac{1}{\lambda}} \rightarrow ⑤$$

From ③, we get, $\boxed{N = N_0 e^{-x/\lambda}} \rightarrow ⑥$

Equation ⑥ is known as The survival equation. It gives The number of molecules N (out of No) having free paths greater than x, i.e, molecules that survived over a path length x.

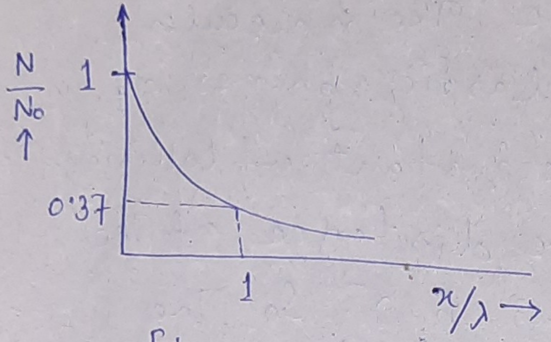

fig. 1. Plot of The survival equation

Fig. 1 shows the plot of $\frac{N}{N_0}$ against $\frac{x}{\lambda}$. The ordinate of the curve gives the fractional number of molecules with free paths greater than any fraction of the mean free path λ. Note that the number with free paths longer than λ is $\frac{1}{e}$ or 37%, while the number with free paths short than λ is 63%.

The distribution of free paths gives the probability that a molecule may describe a distance x without suffering a collision.

Expression for mean free path: An elementary treatment

Imagine that at a certain instant all the molecules of a gas assembly, except one, are at rest. The moving molecule moves among the 'frozen' ones with a velocity $\bar{c}$, the average velocity. We assume the molecules to be perfecly 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 is $\pi\sigma^2$. In an interval, t, the mobile molecule traverses

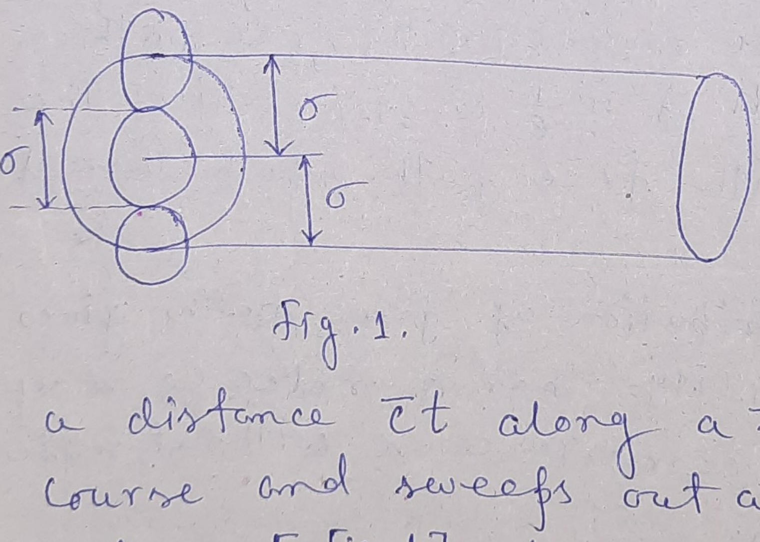

fig. 1.

a distance $\bar{c}t$ along a zig-zag course and sweeps out a cylindrical volume [fig. 1] of cross-section $\pi\sigma^2$ and length $\bar{c}t$. Plainly, it would collide in time t with all molecules having their centres within this volume. The number of such molecules is $\pi\sigma^2\bar{c}tn$, n being the molecular density.

$\therefore$ Number of collisions in time is $\pi\sigma^2\bar{c}tn$.

$\therefore$ Mean free path, $\lambda = \dfrac{\text{Distance covered in time } t}{\text{number of collisions in time } t}$

$$= \frac{\bar{c}t}{\pi\sigma^2\bar{c}tn} = \frac{1}{n\pi\sigma^2} \rightarrow ①$$

The above elementary treatment is only an appoximate method. It does not look into the actual state of affairs of the molecules. No molecule is at rest, all are in motion. So, the assumption of one mobile molecule only while others are stationary is far from the truth. The first attempt was made by Clausius and further improvements in the calculation were made by Maxwell and Tait.

The first effort to correct the expression $\lambda = \frac{1}{n\pi\sigma^2}$ was made by Clausius. He argued that all molecules are moving and therefore, the approximate value of λ must be corrected. He introduced the concept of relative velocity to make a correction to the expression ①. He argued that if the relative velocity of one molecule w.r.t others could be found, then essentially this molecule alone would move (with relative velocity) while others would be at rest. The Clausius expression for mean free path is given by → $\lambda = \frac{3}{4 n \pi \sigma^2}$ → ②

Although This is a step better Than The previous one, it is also open to criticism. The velocities are really distributed according to Maxwell's velocity distribution law. Maxwell's expression for The mean free path of The molecules is given by —

$\lambda = \frac{1}{\sqrt{2} n \pi \sigma^2}$ → ③

Transport Phenomenon In Ideal Gases

All That we have discussed so far is true only when The gas attains equilibrium condition. But before equilibrium, Three phenomena occur jointly or separately leading The system to The equilibrium stage. These phenomena are classified as-

(i) Viscosity: This phenomenon takes place when The velocity varies from layer to layer. In This case, momentum is transferre from one layer to the other, thus, giving rise to the kinetic interpretation of viscosity in gases.

(ii) Thermal Conductivity: In case the temperature varies from layer to layer, the thermal energy transfer takes place, leading to the temperature equilibrium of the gaseous system.

(iii) Diffusion: If the molecular mass/density is varying, transport of mass is involved giving rise to the phenomenon of diffusion.

Let us now discuss these phenomena elaborately.

General Method of Treating Viscosity & Conductivity Phenomena from Kinetic Theory

In the three phenomena, either momentum is transferred or the thermal energy is transferred or the mass transfer is involved. Let the physical entity (i.e., momentum, thermal energy or mass) which has different values in different layer be denoted by H.

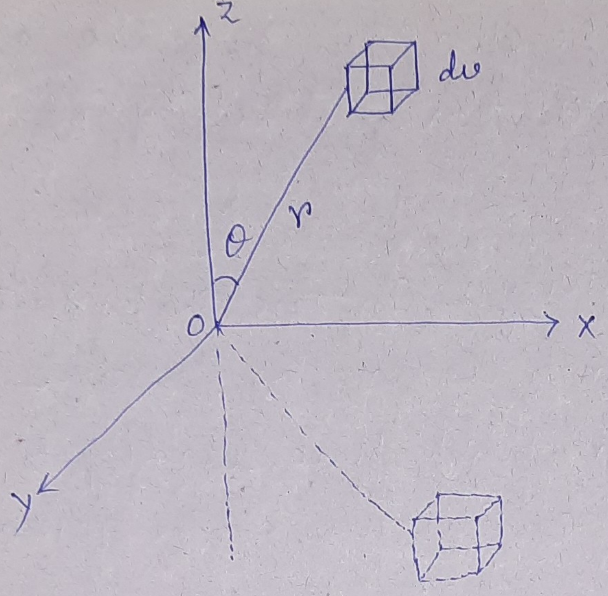

Fig. 1.

Let us consider an elementary volume dv at (r, θ) with respect to origin O (fig. 1). The layer which contains the elementary volume is at a vertical height $z = r\cos\theta$

Then if the physical entity has the value 'H' on the xy plane at the origin, Then at the layer under consideration it has the value $\left[H + \frac{dH}{dz} r\cos\theta\right]$ and at an identical layer below the reference plane its value is $\left[H - \frac{dH}{dz} r\cos\theta\right]$, assuming that the physical entity increases upward.

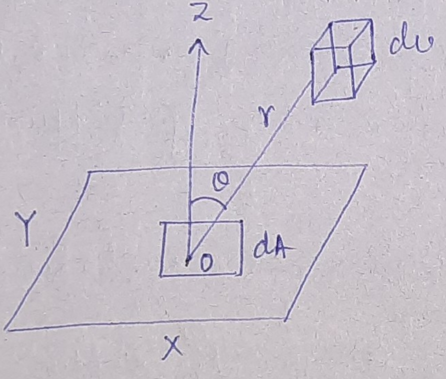

Fig. 2.

The elementary volume contains molecules moving with all possible velocities. They collide with each other and come out of the elementary volume in all possible directions

Out of these emerging molecules, some molecules determined by the solid angle subtended by the area dA at the volume will head along the direction of the area, but all these molecules will not be able to reach the area because of collision and cosequent wiping out molecules in their travel towards the area. We can find out the number reaching the area with the help of the survival equation.

The number of molecules having velocities between c and $c+dc$ contained within the volume dv is $dn_c dv$.

Now, if P_c denotes the collision probability or collision rate, then the number of collisions suffered by these molecules in time dt is $Z_c = \frac{1}{2} P_c dn_c dv dt$, the factor $\frac{1}{2}$ is there, because the collision between two molecules 1 and 2 designated as $Z_{1\to2}$ and $Z_{2\to1}$ is but one collision. But P_c includes both of them and so, actual collisions per sec is $\frac{1}{2} P_c$. Now, each collision results in two new paths along which the two molecules travel.

∴ The number of new paths emanating or the number of molecules coming out of the volume dv in time dt as a result of collision is,

$$2\times\frac{1}{2}P_c\,dn_c\,dv\,dt = P_c\,dn_c\,dv\,dt$$

The molecules come out in all possible directions and contained within a solid angle equal to 4π. from The elementary volume dv. How many of Them will be heading towards The area dA of The reference plane will be determined by The solid angle subtended by dA at The elementary volume. This solid angle is obviously $\frac{dA\cos\theta}{r^2}$.

The number of molecules heading towards The area dA is given by —

$$\frac{dA\cos\theta}{4\pi r^2}\,P_c\,dn_c\,dv\,dt$$

Out of Them some will suffer collisions in Their journey to The destination and will be wiped out.

The number of molecules which come out of The volume dv as a result of collision in time dt and reach The area dA is —

$$\frac{dA\cos\theta}{4\pi r^2}\,P_c\,dn_c\,dv\,dt\,e^{-r/\lambda}$$

$$= \frac{dA\cos\theta}{4\pi r^2}\left(\frac{c}{\lambda}\right)dn_c\,r^2dr\sin\theta\,d\theta\,d\phi\,dt\,e^{-r/\lambda}$$

$\hookrightarrow$ ①

where, $P_c = \frac{c}{\lambda}$, $c \rightarrow$ velocity of molecules
$\lambda \rightarrow$ mean free path of molecules

$dv = r^2\, dr \sin\theta\, d\theta\, d\phi$

From ①, $\frac{dA\, dt}{4\pi}\, c\, dn_c\, \frac{e^{-r/\lambda}}{\lambda}\, dr \cos\theta \sin\theta\, d\theta\, d\phi$

∴ Transport of the physical entity H downward (assuming that the molecules from a certain layer carry with them the entity characteristic of the layer) through dA in time dt is given by —

$$T\downarrow = \frac{dA\, dt}{4\pi} \int_{c=0}^{\infty} \int_{\theta=0}^{\pi/2} \int_{\phi=0}^{2\pi} \int_{r=0}^{\infty} c\, dn_c \cos\theta \sin\theta\, d\theta\, d\phi\, \frac{e^{-r/\lambda}}{\lambda} \left[H + \frac{dH}{dz} r\cos\theta\right] dr$$

Similarly, the transport of H through dA upward in time dt is

$$T\uparrow = \frac{dA\, dt}{4\pi} \int_{c=0}^{\infty} \int_{\theta=0}^{\pi/2} \int_{\phi=0}^{2\pi} \int_{r=0}^{\infty} c\, dn_c \cos\theta \sin\theta\, d\theta\, d\phi\, \frac{e^{-r/\lambda}}{\lambda} \left[H - \frac{dH}{dz} r\cos\theta\right] dr$$

∴ Net transfer of H to the reference plane through an area dA in time dt is

$$F = T\downarrow - T\uparrow$$

$$= 2\,\frac{dA\, dt}{4\pi}\left(\frac{dH}{dz}\right) \int_{c=0}^{\infty} c\, dn_c \int_{\theta=0}^{\pi/2} \cos^2\theta \sin\theta\, d\theta \int_{\phi=0}^{2\pi} d\phi \int_{r=0}^{\infty} \frac{e^{-r/\lambda}}{\lambda}\, r\, dr \quad \longrightarrow ②$$

Now,

$$\int_0^{\pi/2} \cos^2\theta \sin\theta \, d\theta$$

$$= -\int_1^0 p^2 \, dp = \int_0^1 p^2 \, dp$$

$$= \left[\frac{p^3}{3}\right]_0^1 = \frac{1}{3}$$

Let, $\cos\theta = p$

$\therefore -\sin\theta \, d\theta = dp$

If $\theta = 0 \rightarrow p = 1$

$\theta = \pi/2 \rightarrow p = 0$

$$\int_0^\infty \frac{r e^{-r/\lambda}}{\lambda} \, dr$$

$$= \int_0^\infty \frac{\lambda z \, e^{-z} \, \lambda \, dz}{\lambda}$$

$$= \lambda \int_0^\infty z^{2-1} e^{-z} \, dz = \lambda \Gamma(2) = \lambda$$

Let $r/\lambda = z$

$\therefore dr = \lambda \, dz$

$\therefore r = \lambda z$

If $r = \infty \rightarrow z = \infty$

$r = 0 \rightarrow z = 0$

From ②,

$$F = \frac{dA \, dt}{2\pi} \left(\frac{dH}{dz}\right) \int_{c=0}^\infty c \, dn_c \left(\frac{1}{3}\right)(2\pi)\lambda$$

$$= \left(\frac{1}{3}\right) dA \, dt \left(\frac{dH}{dz}\right) \lambda \int_0^\infty c \, dn_c$$

$$= \frac{1}{3} dA \, dt \left(\frac{dH}{dz}\right) \lambda n \bar{c} \longrightarrow ③$$

We shall now identify momentum and thermal energy with H in turn and obtain expressions for viscosity and conductivity gases respectively.

<u>Viscosity</u>: Here H = momentum = mu

$$\therefore \frac{dH}{dz} = m\frac{du}{dz}$$

From ③, $F = \frac{1}{3}\, dA\, dt \left(m\frac{du}{dz}\right) \lambda n \bar{c}$

$$= \frac{1}{3}\, dA\, dt\, \rho \bar{c} \lambda \left(\frac{du}{dz}\right) \quad \left[\because mn = \rho = \text{density of molecules}\right]$$

$\hookrightarrow$ ④

If two layers of a fluid (liquid or gas) are in relative motion, an internal force of friction comes into play That acts tangentially to The surface of contact and causes The slower moving layer to speed up and The faster moving layer to get retarded. This internal force of friction is called viscous force and The phenomenon The viscosity. If dA be The area of contact, dz be The separation between The layers moving with velocities u and u+du, The viscous force $F_{vis} \propto dA$

$\propto \frac{du}{dz}$, velocity gradient.

$$\therefore F_{vis} = \eta\, dA \frac{du}{dz}$$ where η = constant of proportionality called coefficient of viscosity.

$\hookrightarrow$ ⑤

From ④, F-value per unit time,

$$F' = \frac{1}{3}\, dA\, \rho \bar{c} \lambda \left(\frac{du}{dz}\right)$$

$$\therefore \eta\, dA \left(\frac{du}{dz}\right) = \frac{1}{3}\, dA\, \rho \bar{c} \lambda \left(\frac{du}{dz}\right)$$

$$\therefore \boxed{\eta = \frac{1}{3}\rho\bar{c}\lambda} \longrightarrow ⑥$$

Thermal Conductivity: Here, Let H = Thermal energy = E, Therefore, $\frac{dH}{dz} = \frac{dE}{dz}$

$\therefore F'' =$ Thermal energy flowing per unit time

$$= \frac{1}{3}\, dA\, \bar{c}\lambda n\left(\frac{dE}{dz}\right)$$

From the law of heat conduction, the quantity of heat flowing per unit time across the area dA is given by —

$K dA \frac{dT}{dz}$ where, K → Thermal conductivity

$\frac{dT}{dz}$ → Temperature gradient

$$\therefore K\, dA\left(\frac{dT}{dz}\right) = \frac{1}{3}\, dA\, n\bar{c}\lambda\left(\frac{dE}{dz}\right)$$

$$\Rightarrow K = \frac{1}{3} n\bar{c}\lambda\left(\frac{dE}{dT}\right)$$

If m be the mass, C_v be the specific heat at constant volume and T be the temperature of the material, Then,

$$E = m C_v T$$

$$\therefore \frac{dE}{dT} = m C_v$$

$$\therefore K = \frac{1}{3} n\bar{c}\lambda m C_v = \frac{1}{3}\rho\bar{c}\lambda C_v = \eta C_v$$

$\therefore \boxed{K = \eta C_v} \longrightarrow$ ⑦

Eqations ⑥ & ⑦ are expressions for viscosity and thermal conductivity as obtained from the molecular viewpoint of kinetic theory.