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Molecular Collisions:

Mean Free Path.

At ordinary temperature, in an ideal gas, the constituent particles or molecules move randomly at all directions with all possible velocities. So large number of collisions occure. The path traversed by a molecule between two successive collisions is called Free Path, which is a straight line. Thus the path of a single particle will consists of a series of short zig-zag paths, some of these free paths will be relatively long and others short. I we speak the 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 i.e. the mean free path λ of a molecule is the average distance traversed by it between two successive collisions.

The distribution function of freepath

To estimate this free path and mean free path, we have to calculate the satistical distribution function of this mean free path among the molecule. We have to estimate how the freepaths are distributed among the molecule. large number of molecules.

So we have to deduce, out of a large number of freepaths, how many molecules have a specified freepaths length say x and $x + dx$.

Let us consider a large number of molecules at a given instant t. Let N be the number of molecules which has free path x, some molecules dN among the N group has travel the short distance dx. This dN number of molecules will be removed from the group of N and will travel dx distance and it directly proportional to N.

$$dN \propto N\,dx.$$

$$dN = -P_c N\,dx \longrightarrow (1).$$

The proportionality constant P_c is known as collision probability. It depends on the physical conditions in the gas but neither on x nor on N. The $-ve$ sign indicates that a collision removes a molecule from the group and thus decreases N. From equ(1).

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

Integrating $\ln N = -P_c x + \text{Constant}$.

At $x=0$, $N=N_0$, So integration constant is $\ln N_0$. So.

$$\ln N = -P_c x + \ln N_0.$$

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

$$\text{or, } \boxed{N = N_0 e^{-P_c x}} \Longrightarrow (2).$$

Substituting the value of N from equ(2) in equ(1) we get.

$$dN = -P_c N_0 e^{-P_c x} \longrightarrow ③.$$

Thus $|dN|$ gives the number of molecules with freepath lengths between x and $x+dx$. Then mean free path λ can thus be obtained as

$$\lambda = \frac{x_1 dN_1 + x dN_2 + \cdots\cdots}{dN_1 + dN_2 + \cdots\cdots} = \frac{\int x\,dN}{\int dN}$$

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

$$= \frac{1}{N_0}\int_0^{\infty} P_c N_0 x e^{-P_c x}\,dx \quad \text{using equ(3)}$$

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

$$= \frac{P_c}{P_c^2}\Gamma(2)$$

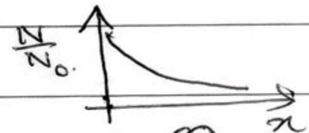
$$= \frac{1}{P_c}$$

$$\therefore \boxed{P_c = \lambda^{-1}} \Longrightarrow (4)$$

The collision probability P_c is equal to the reciprocal of the molecular mean free path λ.

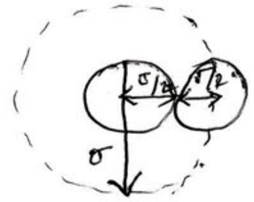
The collision probability P_c is equal to the reciprocal of the molecular mean free path λ. The number remaining in the group ~~[illegible]~~ after a distance x.

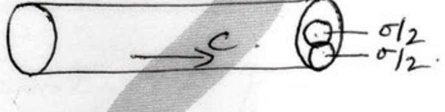
$$N = N_0 e^{-P_c x}.$$



or, $N = N_0 e^{-x/\lambda}$. ⟹ ⑤

This eqn (5) is known as the survival equation. The moving molecules have a velocity $\bar{c}$, the average velocity. One can assume 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.





|| Collision of two molecules
Centre-to-centre distance ||

The effective cross-sectional area of the moving. molecule i.e. collision cross section $P = \pi\sigma^2$.

In an interval t, the molecule traverses a distance $\bar{c}t$ along a zig-zag course and sweeps out a cylindrical volume of cross-section ρ and length $\bar{c}t$. It would collide in time t with all molecules having their centres within this volume. So the number of such molecules is $\rho n\bar{c}t$, where n is the molecular density.

So number of collisions in time $t = \rho n\bar{c}t$.

$$\therefore \text{Mean Free Path } \lambda = \frac{\text{distance covered in time } t}{\text{number of collision in time } t}.$$

$$\lambda = \frac{\bar{c}t}{\rho n\bar{c}t} = \frac{1}{\rho n}.$$

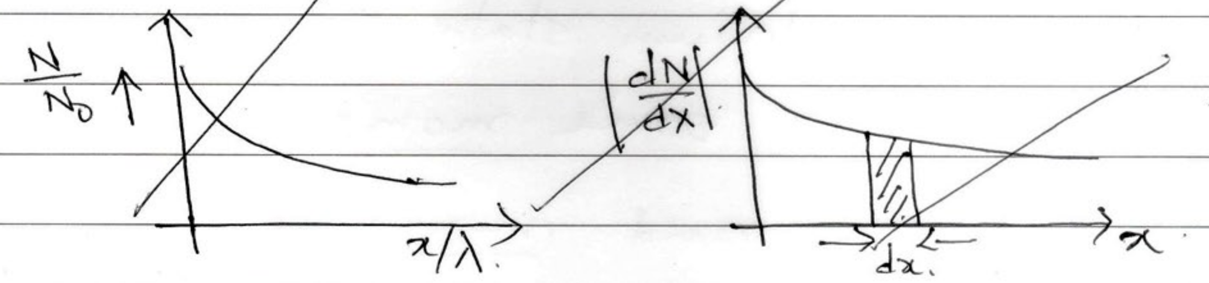
$$\boxed{\lambda = \frac{1}{\pi\sigma^2 n}}$$

This elementary treatment is only an approximate method.

According to Clausius' expression where relative velocity of the molecules are considered, the mean free path $\Rightarrow \lambda = \frac{3}{4\pi\sigma^2 n}$

Again $N = N_0 e^{-x/\lambda} \Longrightarrow ⑤$

i.e. $|dN| = \frac{N_0}{\lambda} e^{-x/\lambda} dx$



Transport Phenomena in Ideal Gases.

So far we considered gases in equilibrium only, so that none of the parameters are time dependent. The collisions between constituent molecules does not distrub the equilibrium of the state. So the pressure, volume, temperature are time independent i.e. steady state. Now if we consider the gas is not in equilibrium but in steady state, i.e system parameters pressure, volume, temperature are time independent. Then to restore the equilibrium state the system transports some momentums, thermal energies and masses from one position to other position within the system. This phenomena is known as Transport Phenomena.

Transport phenomena is involving the movement of various entities such as mass, momentum or energy through a medium by virtue of nonuniform condition of the gas. We have already saw that the macroscopic pressure is related to the molecular motion in case of perfect gases. There are three types of Transport phenomena.

(i) Diffusion ⇒ molecular transport due to concentration gradients.

(ii) Thermal Conduction ⇒ Transport of energy.

(iii) Viscosity ⇒ Transport of momentum.

They are described by their corresponding coefficients.

(i) D for diffusion.

(ii) K for thermal conduction.

(iii) η for viscosity.

Diffusion.

Let the equilibrium of a gas is disturbed by adding a small amount of the same gas or different gas to a gas system filling a certain volume. So with identical pressure and temperature throughout the concentration is disturbed, one part is greater than in others. i.e. equilibrium is disturbed. After certain time the added gas gets distributed throughout the entire volume and the concentration becomes uniform. So equilibrium is restored. And this restoration work is done due to the motion of the molecules from regions of higher concentration to those of lower ones. Molecules at the same time move by collision to regions of higher concentration, so that the pressure of the gas remains constant. This is the phenomenon of diffusion.

Diffusions are two types :(a) Self-diffusion and (b) inter-diffusion.

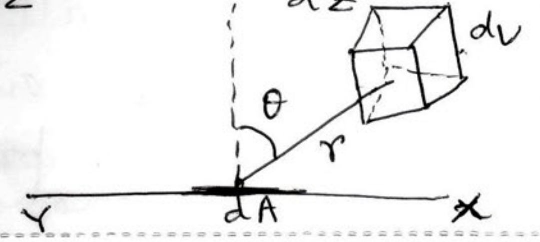
Now if we consider with a concentration gradient it should be clear that molecules will move from the more concentrated area to the less concentrated area via a process of collision due to random movement of molecules. This is diffusion process. If over distance dx concentration change is dn, then the concentration ~~change is dn, then~~ gradient is $\frac{dn}{dx}$, The number of molecules crossing area A normal to gradient per second can be written as

$$\frac{dN}{dt} = -D\frac{dn}{dx}A$$

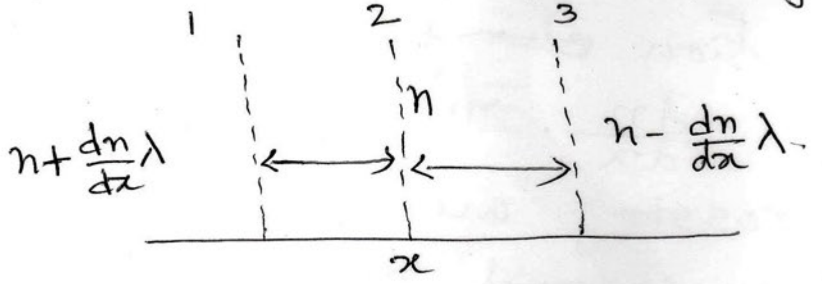
$$\frac{1}{A}\frac{dN}{dt} = -D\frac{dn}{dx}.$$

where D is called the coefficient of self-diffusion and the negative sign implies flow in the direction of smaller concentration.

Let n be the concentration on the reference plane xy and let the concentrations above and below xy plane be $n + \frac{dn}{dz}$ and $n - \frac{dn}{dz}$ respectively. $\frac{dn}{dz}$ is the concentration gradient. Consider a volume element dV at (r, θ) from an area dA of the reference plane.



Consider the following situation



We would then have the number of molecules per second crossing from 1.

$$= \frac{1}{6}\left(n + \frac{dn}{dx}\lambda\right)\bar{v}A.$$

and from . 3 $= \frac{1}{6}\left(n - \frac{dn}{dx}\lambda\right)\bar{v}A$

There will also be molecules leaving on each side of 2 of a number $= \frac{1}{6} n \bar{v} A$
So the net transfer is then

$$-\frac{1}{6}\left(n + \frac{dn}{dx}\lambda\right)\bar{v}A + \frac{1}{6}\left(n - \frac{dn}{dx}\lambda\right)\bar{v}A - \frac{1}{6}n\bar{v}A + \frac{1}{6}n\bar{v}A$$

$$= -\frac{1}{3}\frac{dn}{dx}\lambda\bar{v}A = -D\frac{dn}{dx}A.$$

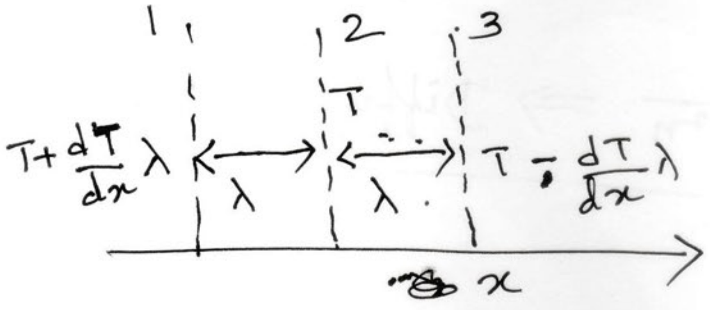
where $D = \frac{\lambda\bar{v}}{3}$; Again $\bar{v} = \left(\frac{8kT}{\pi m}\right)^{1/2}$.

and $\lambda = \frac{1}{\pi\sigma^2 n}$

So, $\boxed{D = \frac{v}{3\pi\sigma^2 n} \Rightarrow \text{Diffusion Coefficient.}}$

Thermal Conductivity.

If the equilibrium of a gas is disturbed by heating a part of it, then temperature-inequality occures among the parts. But after some time, it is found that the thermal equilibrium is restored. It is occured due to continuous motion of the molecules, which is responsible to restore the thermal inequality. There is a transport of thermal energy from regions of higher temperature to the region of lower ones.



Total heat quantity

$$Q = -KA\frac{dT}{dx}$$

where K is the thermal conductivity.

Now the rate of transport, this time of thermal energy ($dQ = C_v dT$) is from 1.

$$\frac{n\bar{v}A}{6}c_v\left(T+\frac{dT}{dx}\lambda\right).$$

from 3

$$\frac{n\bar{v}A}{6}c_v\left(T-\frac{dT}{dx}\lambda\right).$$

So the net transfer at 2 is $\frac{n\bar{v}A}{3}c_v\frac{dT}{dx}\lambda$

Hence $Q = -\frac{n\bar{v}A}{3}c_v\left(\lambda\frac{dT}{dx}\right).$

$$= K\lambda\frac{dT}{dx}.$$

where $K = \frac{n\bar{v}A}{3}c_v.$

So, coefficient of thermal conductivity

$$\boxed{K = \frac{n\bar{v}\lambda}{3}c_v.}$$

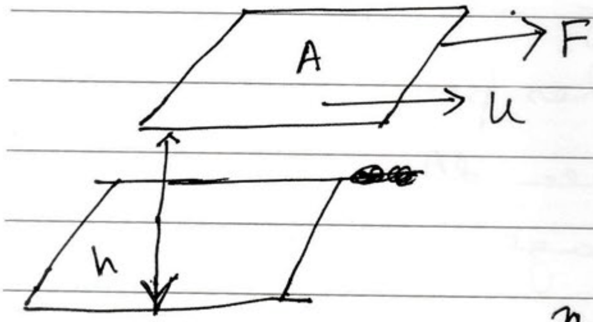
where $\bar{v} = \left(\frac{8k_BT}{\pi m}\right)^{1/2}.$

= average Thermal velocity.

Viscosity

If the equilibrium state of an ideal gas is disturbed by a flow velocity i.e. mass motion, being ~~imp~~ imparted to one of its parts that differs from the flow velocity of ~~adv~~ adjacent parts. So there would be relative motion of the gas. If the disturbed gas is left to itself, equilibrium is restored after some time. It is ~~due to~~ the thermal motion of the gas molecules that level out the ~~f~~ flow velocity by transport of momentum from the faster moving parts to the slower moving parts. This gives rise to the phenomenon of internal friction or viscosity.

The force F must be applied to maintain constant flow. Here this force is viscous force (rate of change of momentum) and it is proportional to A and u/h

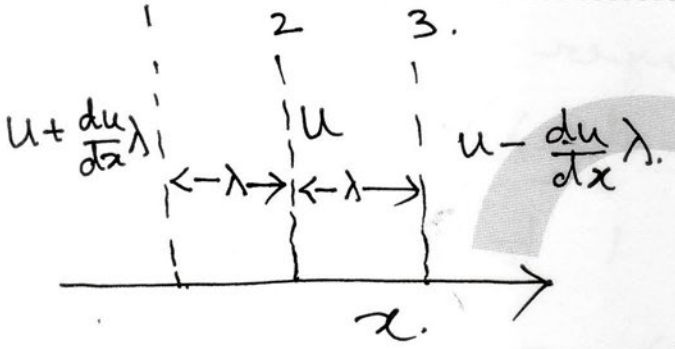


The force is F where.

$$F = \eta A \frac{du}{dx}.$$

η is constant and it is known as coefficient of viscosity.

1, 2, 3 represent three layers, 2 lying between 1 and 3 and separated from others by a distance λ, the mean free path of the gas. If n be the number of molecules per unit volume, then approximately $\frac{1}{3}n$ molecules per unit volume move along



each directions x, y, and z. On the average $\frac{1}{6}n$ molecules per unit volume move along +ve x direction

∴ Number of molecules per unit volume crossing an area dA of the layer A, is on the average $\frac{1}{6}n\bar{v}\,dA$

where $\bar{v}$ = averager thermal velocity.

We assume that $u \ll v$.

The number of molecules crossing from layer 3, this moleculas bring to ~~layer~~ 2 layer net horizontal moment $m\left(u - \frac{du}{dx}\lambda\right) n \frac{\bar{v}}{6} A$.

Similarly from 1 to 2 thus

$$m\left(u + \frac{du}{dx}\lambda\right) \frac{n\bar{v}}{6} A.$$

But layer 2 sends $\frac{1}{6}mvA$ molecules both ways.

Thus the total momentum transfer per seconds i.e. force is

$$F = \frac{m\lambda n\bar{v}}{3} A \frac{du}{dx}.$$

$$\therefore \quad \eta = \frac{1}{3} m\lambda n\bar{v} = \text{Coefficient of Viscosity.}$$

Brownian Motion

The Brownian motion is named after a British Botanist Robert Brown, who first observed this movement.

He observed that when pollen grains are suspended in water and viewed under a high power microscope, they show a continuous, random, erratic motion, consisting of translations and rotations. This type of chaotic ~~motion~~ and random motion of the particles suspended in a liquid or a gas is termed Brownian Motion after Robert Brown.

3.8.1 Salient features of Brownian motion

The following salient features of Brownian motion are the outcome of special investigations carried out painstakingly by a number of workers over a number of years.

(a) The motion is *continuous, eternal, irregular* and *random.* No two particles in close vicinity move in the same direction at the same time. This shows that the cause does not lie in eddies, convection or streaming motion of the fluid.

(b) The motion is *independent* of the mechanical vibration, say the shaking of the container.

(c) The *smaller* the particle *size, greater* is the *motion.*

(d) The *lower* the *viscosity* of the liquid (or gas), *greater* is the *motion* and conversely.

(e) The *higher* the *temperature, greater* is the *motion* and conversely. Two particles of the same size move equally fast at the same temperature.

3.9 Vertical distribution of Brownian particles

Brownian particles constitute a gas which is in equilibrium under the action of gravitational force-field. We shall now derive the *law of distribution* in an *isothermal vertical column* of the Brownian gas.

Consider a column of the gas bounded by surfaces at heights z and $z + dz$ (z-axis is vertically upward) where the pressures are p and $p + dp$ respectively (Fig. 3.10). Let T be its uniform temperature. If ρ be the density of the gas at the height z, the force due to gravity on this layer of unit cross-section is $g\rho dz$. The net force on the layer is therefore given by

$$p + dp - p + g\rho dz$$

which, for equilibrium of the layer, must vanish. We must therefore have

$$p + dp - p + g\rho dz = 0.$$

$$\therefore \ dp = -g\rho dz \tag{3.9.1}$$

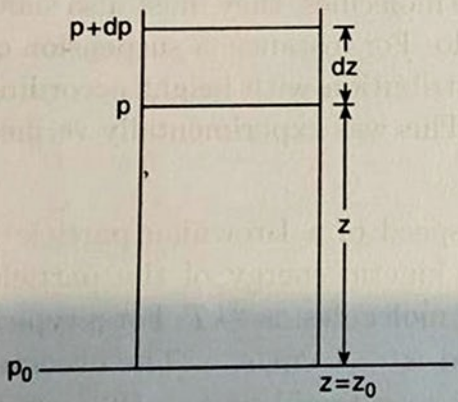


Fig. 3.10 Vertical distribution of Brownian particles

For an ideal gas, $\rho = Mp/RT$ where M is the mass of 1 mole of the gas, R the gas constant.

$\therefore$ From equation (3.9.1), we obtain by substituting for ρ,

$$\frac{dp}{p} = -\frac{Mg}{RT}dz \tag{3.9.2}$$

Integrating (3.9.2), with proper limits,

$$\int_{p_0}^{p} \frac{dp}{p} = -\frac{Mg}{RT}\int_{z_0}^{z} dz$$

where p_0 is the pressure at the height $z = z_0$.

$$\therefore \ \ln\frac{p}{p_0} = -\frac{Mg}{RT}(z - z_0)$$

$$\Rightarrow \ \boxed{p = p_0 e^{-Mg(z-z_0)/RT}}$$

which is the ***law of atmosphere*** or the ***barometric equation***.

The Brownian particles thus *obey the law of atmosphere* or the barometric equation.

Since for an ideal gas, $p = nkT$ where n is number of particles per unit volume at a height z, we have

$$n = n_0 e^{-Mg(z-z_0)/RT} \tag{3.9.3}$$

n_0 being the number of particles per unit volume at the height z_0.

Introducing the mass m of the particle by $m = M/N_A$ where N_A is Avogadro number, we obtain

$$\boxed{n = n_0 e^{-N_A mg(z-z_0)/RT}} \tag{3.9.4}$$

Perrin used (3.9.4) for a precisional determination of Avogadro number N_A in 1909.

The effective mass of the suspended particle (assumed spherical) is $\frac{4}{3}\pi r^3(d - d')$ where r is the radius of the particle, d and d' the densities of the particle and the inter-granular liquid respectively. Therefore from equation (3.9.4), we get

$$\boxed{N_A = \frac{3RT}{4\pi r^3(d-d')g(z-z_0)} \ln \frac{n_0}{n}} \tag{3.9.5}$$

which is the most convenient form for and evaluation of N_A.