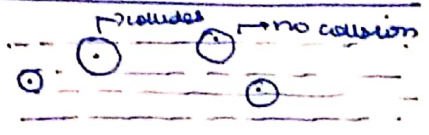## Mean free path

↳ mean distance travelled by a molecule b/w two successive collisions.

$$\lambda = \frac{\lambda_1 + \lambda_2 + \cdots + \lambda_N}{N} = \frac{\text{Total distance travelled}}{\text{Total no. of collisions}}$$

or $$\boxed{\lambda = \frac{vt}{N}}$$

Zeroth order Approximation


Collision of two molecules of radii r.

Each molecule of gas having mass m and diameter $d (= 2r)$. In zeroth order approximation, we assume that a single molecule moves with velocity v and all others are at rest. The collision is possible when (centre to centre distance b/w 2 molecules is $2r$. It can also be seen as the moving molecule growing to be a molecule of $2r$ radius and other shrinking to a point size. Now, while moving, it will cover a cylinder of radius $2r$, area πd^2 and length vt. During time 't' it will collide with all molecules who centre will lie within this cylinder. If there are n molecules per m^3, then the total no. of colliding molecules will be $n\pi d^2 vt$. ∴ mean free path:

$$\lambda = \frac{vt}{n\pi d^2 vt} = \frac{1}{n\pi d^2} = \frac{1}{n\sigma} \quad \text{where } \sigma: \text{microscopic collision (cross section)}$$

First order Approximation

In this we consider that all the molecules are moving with an average velocity $\bar{v}$. The no. of collisions now can be calculated by calculating average relative velocity of the molecules.
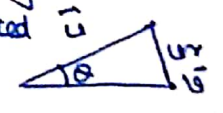
If θ is the angle of inclination, then

$$v_r = [\bar{v}^2 + \bar{v}^2 - 2(\bar{v}^2)\cos\theta]^{1/2}$$

$$= [2(1-\cos\theta)\bar{v}^2]$$

$$= 2\sin\frac{\theta}{2}\bar{v}$$

All directions of the velocity are equally probable, so, we must average v_r over the solid angle.

$$\bar{v}_r = \int \frac{d\Omega}{4\pi} v_r$$

$$= \int \frac{2\pi\sin\theta d\theta}{4\pi} \cdot 2 \cdot \sin\frac{\theta}{2}\bar{v}$$

$$= \int \sin\theta \cdot \sin\frac{\theta}{2}\bar{v}\, d\theta$$

$$\therefore \quad \bar{v}_r = 2\bar{v} \int_0^{\frac{\pi}{2}} \sin\frac{\theta}{2}\cos\frac{\theta}{2} \, d\theta \qquad , \quad \text{taking } \sin\frac{\theta}{2} = t$$

$$\frac{1}{2}\cos\frac{\theta}{2} \, d\theta = dt$$

$$= 4\bar{v} \int_0^1 2x^2 \, dx$$

$$= \frac{4}{3}\bar{v} .$$

$$\therefore \quad \lambda = \frac{\bar{v}t}{\pi d^2 \eta \, \bar{v}_r t} = \frac{3}{4\pi d^2 \eta} .$$

Assuming Maxwellian distribution, $\lambda = \frac{1}{\sqrt{2}\pi d^2 \eta}$

[See derivation : book appendix II if time permits.

So, $\lambda = \frac{1}{\sqrt{2}\pi d^2 \eta}$

$$= \frac{1}{\sqrt{2}\pi d^2} \frac{k_B T}{p} \qquad (\eta = p/k_B T.)$$

$$\boxed{\begin{array}{l} \therefore \; \lambda \propto T \\ \quad \propto \frac{1}{p} \end{array}}$$
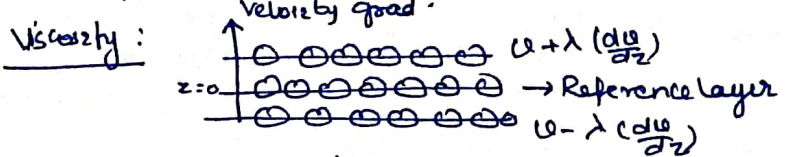
1 Litro = $10^{-3} m^3$.

Transport phenomenon : Transports are measured per unit area per unit time per gradient

Viscosity — transfer of momentum → mech e/m
Conduction — " " energy → Thermal "
diffusion — " " mass . → chemical "

$D = \dfrac{\text{no. of particles energy / area / time}}{\text{conc. grad}}$

~~Diffusion~~
~~Viscosity : Transport of~~ ~~molecules~~ ~~mass~~

$= \dfrac{(dN/dt)}{A (dn/dz)}$

Viscosity :

Velocity grad.

$z=0$ → Reference Layer

$u + \lambda \left(\dfrac{du}{dz}\right)$

$u - \lambda \left(\dfrac{du}{dz}\right)$

average momentum : $\vec{p} = m\vec{u}$

Velocity and its gradient are $\perp$.

λ: MFP

- There is a relative motion b/w layers.
  Δp when a single layer molecule crosses upwards as downwards $= 2\lambda m \left(\dfrac{\partial v}{\partial z}\right)$
  $n = \dfrac{N}{V}$: molecule per unit volume is known.

- No. of molecules per unit area per unit time :

$$\dfrac{N}{A dt} = \dfrac{N}{A dx} \cdot \left(\dfrac{dx}{dt}\right) = \dfrac{N}{V}\left(\dfrac{dx}{dt}\right) = \dfrac{N}{V}\vec{u} = n\vec{u}$$

- In $\perp$ particles direction, no. of particles crossing per unit area per unit ~~volume~~ time, $= \dfrac{n\vec{u}}{3}$

Using a
~~This result uses~~ statistical result which can be calculate as the avg. distance 'd' below the reference plane where molecules make its last collision. It comes out to be $2\lambda/3$.

No. of particles crossing upwards = downwards $= \dfrac{n\vec{u}}{6}$

change in momentum per unit area per unit time when a molecule crosses either upwards or downwards $= \left(\dfrac{n\vec{u}}{6}\right) \times 2\lambda m \left(\dfrac{du}{dz}\right)$

$= \dfrac{1}{3} mn \vec{u}\lambda \left(\dfrac{du}{dz}\right)$

Now, $\dfrac{\left(\dfrac{F}{A}\right)}{\left(\dfrac{du}{dz}\right)} = \eta = \dfrac{1}{3} mn \vec{u}\lambda$.

$n = P/k_B T$, $\lambda = \dfrac{1}{\sqrt{2}\pi d^2 n}$.

$\therefore \boxed{\eta = \dfrac{1}{3} \dfrac{m\vec{u}}{\sqrt{2}\pi d^2}}$ $\vec{u} = \sqrt{\dfrac{8k_B T}{\pi m}}$ $\left[\begin{array}{l}\text{for gases } \eta \propto \sqrt{T} \\ \text{liquid } \eta \propto \dfrac{1}{T}\end{array}\right]$

$\eta \sim f(P)$ only at very high and very low pressure. as at very high pressure $\lambda \approx$ ~~dimension of~~ diameter of molecule and at low pressure $\lambda \propto$ dimension of apparatus.

ΔN net per unit area / time $= 2 \cdot \dfrac{dn}{dz} \cdot \lambda \cdot \dfrac{\bar{v}}{6}$.

$$\therefore \quad \dfrac{\left(\dfrac{\Delta N}{\Delta t}\right)}{A \left(\dfrac{dn}{dz}\right)} = \boxed{\dfrac{1}{3} \bar{v} \lambda = D}.$$

Now, $\bar{v} \propto T^{1/2}$

$\lambda \propto T/P_1$

$\therefore \quad D \propto T^{3/2} P^{-1}$

Vander waals equation

1. Gas molecules ≡ finite size and can't be treated as point masses.

2. Molecules attract one another with a weak force which depends upon distance b/w them only.

3. No. of collisions with walls of container are exactly same for point & finite size molecules.

4. Molecular density is small.

A. Corrections for finite size : If the molecules have finite size, then the volume available for each molecule for free movement will be less compared to the volume available in the absence of this finite size. Let this red^n in V to be b, so, (called covolume) we can write:

$$p(V-b) = RT.$$

The magnitude of b is 4 times the total molecular volume of 1 mole of a v.d.w. gas.

Proof:
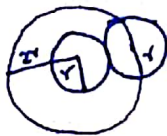
 collision of 2 molecules of radii r.

Let r = radius of 1 molecule. At any instant of collisions, centre to centre distance is d = 2r, i.e around any molecule, a spherical volume of $4/3 \pi d^3 = 8 V_m$ is denied to other molecule.

$(V_m = 4/3 \pi r^3)$;

Volume available to 1st molecule = V

"   "   " 2nd " $= V - 8 V_m = V - V_s$

"   "   " 3rd " $= V - (8+1) V_s$

$\therefore$ "   "   " Nth " $= V - (N-1) V_s$

$\therefore$ average volume available $= \dfrac{\sum\limits_{i=1}^{N} V - (i-1) V_s}{N}$

$= V - \dfrac{\sum\limits_{i=1}^{N} (i-1) V_s}{N}$

$= V - \dfrac{N(N-1)}{2} V_s$

or $\quad = V - \dfrac{NV_s}{2} = V - 4VmN$

$$\therefore \boxed{b = 4V_m N}$$

ⓑ **Correction for intermolecular attraction**

🔹 -a molecule in the interior of the gas is on the average, attracted equally in all directions so that there is no resultant force on it. This is not true for a molecule in a outermost layer close to the surface. Since the molecules is only on one side, there will be a net inward force. So, whenever a molecule strikes the wall of the container, the momentum communicated will be less than that for an ideal gas. ∴ Intermolecular force cause a ↓ in pressure and this drop is known as cohesive pressure.

This cohesive pressure will be proportional to the no. of molecules/volume in the surface layer and layer just below it.

$$\therefore \Delta p \propto \left(\frac{N}{V}\right)^2$$

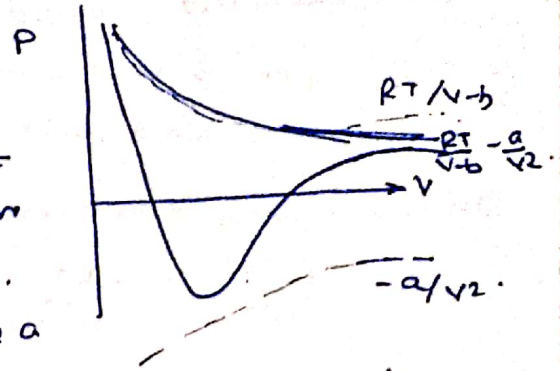$$\text{or} \quad \Delta p = \frac{a'N}{V^2} = \frac{a}{V^2}.$$

$$\therefore \text{total pressure} : p + \Delta p = \left(p + \frac{a}{V^2}\right).$$

∴ our equation of state for an ideal gas modifies to :

$$\boxed{\left(p + \frac{a}{V^2}\right)(V - b) = RT.} \quad \text{vander waals eqn of state}$$

For n moles, $V = V/n$.

$$\therefore \boxed{\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT}$$

Discussion

$$p = \frac{RT}{V-b} - \frac{a}{V^2}.$$

$$\Rightarrow pV^3 - (Pb + RT)V^2 + a(V-b) = 0$$

① The above eqn is cubic in V. For a given P, T; V will have 3 solns, all real or 1 real, 2 imag; at low temp. 3 real roots, as temp ↑, they approach each other and @ T = T_c, they become equal. Above T_c only 1 real root exists meaning no condensation.

② $V \to \infty$, $p \to 0$ & as $V \to b$, $p \to \infty$ ⇒ continuity.