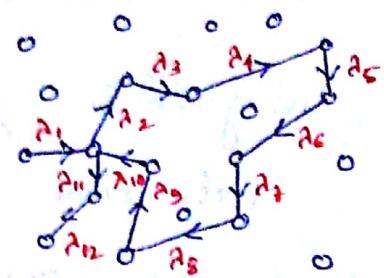


Mean free path We calculated that K.T. gives  $\sim 1 \text{ km/s}$  velocity for molecular movement. But we see clouds suspended in air holds together for hours. So there must be some factors that prevent the free escape of atoms.

Clausius showed that such discrepancy goes away if we take small & finite volume for atoms & they change velocity & direction of motion in the process of collision, zigzag path (discrete)

In between two successive collision, the traversed path is free path ( $\lambda_1, \lambda_2, \dots, \lambda_n$ ).

$$\text{Mean free path} = \frac{\lambda_1 + \lambda_2 + \lambda_3 + \dots + \lambda_N}{\text{Number of collision}}$$



### Collision probability

Suppose collision rate is  $P$ , average velocity of an atom is  $\bar{c}$  & in time  $t$ , distance covered =  $\bar{c}t$  & number of collisions suffered is  $N$ . Then  $N = \frac{\bar{c}t}{P} = \frac{\bar{c}}{P} t$ .

Before we calculate "A", let's compute the distribution of  $A$ , meaning probability of an atom moving a distance  $x$  without collision, say  $f(x)$ . This means that  $f(x+dx)$  is the probability that atom traverses  $x+dx$  length without collision.

If  $P$  is collision probability per unit time, then for  $N$  atoms number of collisions in time  $t = \frac{1}{2} N P t$ . ( $\frac{1}{2}$  because each collision between 2 atoms is counted twice).

Probability that after traversing  $x$ , an atom will suffer a collision within  $dx$  in time  $dt = P dt = P \frac{dx}{c} = \frac{dx}{\lambda}$  where  $\lambda = \frac{c}{P}$  is the free path for atoms with velocity  $c$ .

$\therefore$  As total probability = 1, probability of no collision in distance  $dx = (1 - \frac{dx}{\lambda})$ .

As successive collisions are independent, therefore the joint probability of no collision at  $x+dx$  is  $f(x) \times (1 - \frac{dx}{\lambda})$

$$\therefore f(x+dx) = f(x) \left(1 - \frac{dx}{\lambda}\right).$$

Expand LHS using Taylor's theorem.

$$f(x) + f'(x)dx + \frac{1}{2} f''(x)(dx)^2 + \dots = f(x) \left(1 - \frac{dx}{\lambda}\right) \quad [\lim_{dx \rightarrow 0}]$$

$$\therefore f'(x) = -f(x)/\lambda. \quad \text{or} \quad \frac{f'(x)}{f(x)} = -\frac{1}{\lambda}. \quad -\frac{x}{\lambda}$$

$$\text{Integrating, } \ln f(x) = -\frac{x}{\lambda} + \ln C \Rightarrow f(x) = Ce^{-x/\lambda}$$

note that when  $x=0$ ,  $f(x)=1$ .  $\therefore C=1$ .

$$\therefore f(x) = e^{-x/\lambda}. \quad \Rightarrow \text{law of distribution of free paths}$$

### Method 2

Let, out of  $N$  atoms,  $N'$  atoms cross  $x$  without collision. If after that in  $dx$  distance,  $dN'$  atoms are thrown out due to collision. Then  $\frac{dN'}{dx} \propto N'$  or  $\frac{dN'}{dx} = -pN'dx$  (-ive for decrease)

$$\therefore \frac{dN'}{N'} = -pdx$$

$$\text{Integrating, } \ln N' = -px + \ln C$$

$$\text{or } N' = Ce^{-px}. \quad \text{Now put boundary condition at } x=0, N'=N.$$

$$\therefore C=N. \quad \therefore N' = Ne^{-px}$$

thrown out molecules are  $dN' = +pNe^{-px}dx$  (+ive number)

$$\lambda = \frac{x_1 dN'_1 + x_2 dN'_2 + \dots}{N} = \frac{1}{N} \int_0^\infty x dN'$$

$$= \frac{1}{N} \int_0^\infty x pNe^{-px} dx = p \int_0^\infty e^{-px} x dx$$

$$= p \frac{1}{p^2} \int_0^\infty e^{-x^2} x dx = \frac{1}{p} \Gamma(2) = \frac{1}{p}.$$

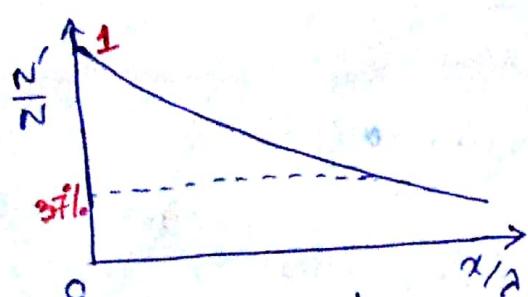
put  $px=2$   
 $pdx=dz$

$$\therefore N' = Ne^{-x^2/2}$$

$$\therefore f(x) = e^{-x^2/\lambda}$$

This is the "survival equation."

$$dN' = \frac{N}{\lambda} e^{-x/\lambda} dx \quad \Rightarrow \quad \frac{dN'}{dx} = \frac{N}{\lambda} e^{-x/\lambda}$$

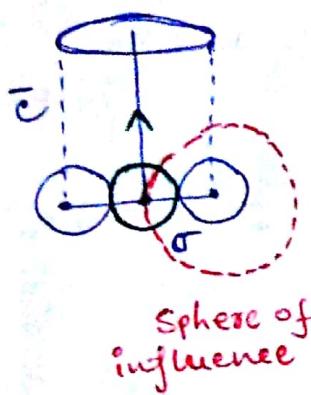


$$\text{Number} > \lambda \text{ is } e^{-1} \sim 37\% \\ < \lambda \text{ is } 1 - 37\% = 63\%$$

(a)  $P \propto 1/\lambda \Rightarrow$  collision probability is reciprocal of free path.

(b) Intensity of atomic beam & number of atoms.  $\therefore I' = I e^{-x/\lambda}$ .  
Initial intensity  
↓  
Final intensity.

### Calculation of $\lambda$



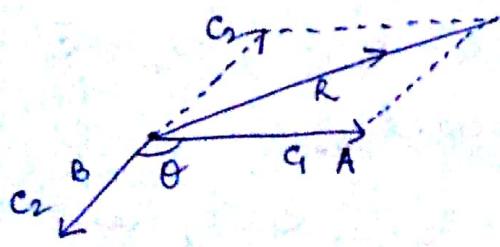
Suppose all atoms are rest but only one moves with velocity  $c$ . Rigid spherical shape with diameter  $r$ . It can only collide when they touch & can reach distance  $c$ , so it collides with  $\pi r^2 c n$  many atoms. This is also number of collisions per second.

$$\therefore \text{Mean free path } \lambda = \frac{c}{\pi r^2 c n} = \frac{1}{n \pi r^2}$$

This is approximate & Clausius did the first correction followed by Maxwell-Tait.

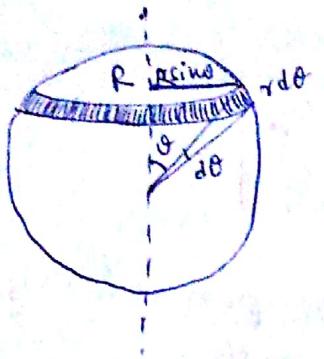
### Clausius correction

as all atoms are in motion.



Consider A & B atom moves with velocity  $c_1$  &  $c_2$  & angle  $\theta$ . Making atom B observer (meaning applying equal & opposite velocity  $c_2$  to B), B is in rest & relative to that A moves with relative velocity

$$R = \sqrt{c_1^2 + c_2^2 - 2c_1 c_2 \cos \theta}$$



Now we have to find mean relative velocity of atom A with respect to all others. If  $dN_{\theta,\phi}$  is the number of atoms moving between  $\theta \text{ & } \theta + d\theta, \phi \text{ & } \phi + d\phi$  then

$$dN_{\theta,\phi} = \frac{N}{4\pi R^2} R^2 \sin\theta d\theta d\phi = \frac{N \sin\theta d\theta d\phi}{4\pi}$$

$$\text{and } \bar{R} = \frac{\int R dN_{\theta,\phi}}{\int dN_{\theta,\phi}} = \frac{\int_0^\pi \int_{\phi=0}^{2\pi} \frac{\sqrt{c_1^2 + c_2^2 - 2c_1 c_2 \cos\theta}}{4\pi} \frac{N \sin\theta d\theta d\phi}{4\pi}}{\int_0^\pi \int_{\phi=0}^{2\pi} \frac{N \sin\theta d\theta d\phi}{4\pi}}$$

$$= \frac{N}{4\pi} \cancel{\int_{\theta=0}^\pi} \int_{\phi=0}^{2\pi} \frac{\sqrt{c_1^2 + c_2^2 - 2c_1 c_2 \cos\theta} \sin\theta d\theta}{\frac{N}{4\pi} \cancel{\int_{\theta=0}^\pi}} / \frac{N}{4\pi} \cancel{\int_{\phi=0}^{2\pi}}$$

substitute  $c_1^2 + c_2^2 - 2c_1 c_2 \cos\theta = z^2$  or  $2c_1 c_2 \sin\theta d\theta = dz$

$$\int z^2 \frac{1}{2c_1 c_2} dz = \frac{1}{2c_1 c_2} \int_{(c_1 - c_2)^2}^{(c_1 + c_2)^2} z^2 dz = \frac{1}{2c_1 c_2} \left[ \frac{z^3}{3/2} \right]_{(c_1 - c_2)^2}^{(c_1 + c_2)^2}$$

$$= \frac{1}{3c_1 c_2} [(c_1 + c_2)^3 - (c_1 - c_2)^3]$$

$$\therefore \bar{R} = \frac{1}{6c_1 c_2} [(c_1 + c_2)^3 - (c_1 - c_2)^3].$$

According to Clausius's assumption  $c_1 = c_2 = \bar{c}$

$$\therefore \bar{R} = \frac{1}{6\bar{c}^2} 8\bar{c}^3 = \frac{4}{3}\bar{c}$$
, meaning in traveling a distance

$\bar{R}$  is  $\pi \sigma^2 \bar{R} n$  & therefore  $A_{Cl} = \frac{\bar{c}}{\pi \sigma^2 n \bar{R}} = \frac{3}{4} \frac{1}{n \pi \sigma^2}$ .

### Maxwell's correction

Clausius took  $c_1 = c_2 = \dots = c_N = \bar{c}$

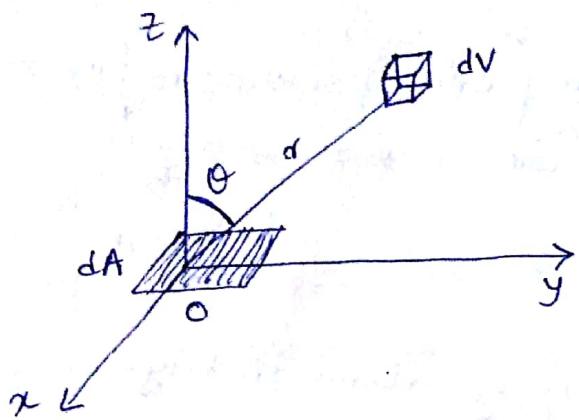
but they're Maxwellian distributed in reality!

Maxwell corrected by considering both  $c_1 > c_2$  &  $c_1 < c_2$  case  
with  $dN_{c_2} = 4\pi N \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mc_2^2/2k_B T} c_2^2 dc_2$

to obtain  $\bar{R} = \sqrt{2} \bar{c}$  (see AB Gupta § 2.21.2 for derivation)

$$\therefore \lambda_{\text{Maxwell}} = \frac{\bar{c}}{\sqrt{2\pi}\sigma^2 n \bar{c}} = \frac{1}{\sqrt{2\pi}\sigma^2 n}$$

Pressure of a gas using mean free path



Once again, we want to compute atoms within volume  $dV$  at distance  $r$  with inclination  $\theta$  to a surface  $dA$  at origin that reach  $dA$  after collision with other atoms, using survival equation.

Number of molecules between  $c$  &  $c+dc$  in volume  $dV$  is  $dn_c dV$ .

If  $\lambda$  is mean free path of the gas atoms then ~~no~~ number of collision suffered by one atom per unit time =  $\frac{c}{\lambda}$ .

As  $1 \rightarrow 2$  &  $2 \rightarrow 1$  collision is counted twice, so the number of collisions suffered by  $dn_c dV$  number of atoms in unit time is  $\frac{1}{2} \frac{c}{\lambda} dn_c dV$ . But each collision results to two new paths along which atoms travel.

∴ The number of new paths or number of atoms emanating from  $dV$  per unit time =  $\frac{1}{2} \frac{c}{\lambda} dn_c dV \times 2$  & that are pointed towards the area  $dA$  is the solid angle subtended by  $dA$  at  $dV$  =  $\frac{dA \cos \theta / r^2}{4\pi}$  ( $4\pi$  = all molecules contained)

∴ That exit from  $dV$  pointing to  $dA$ , that number is

$$N_0 = \frac{c}{\lambda} dn_c dV \frac{dA \cos \theta}{4\pi r^2} \quad (\text{per unit time})$$

In  $N_0$ , only those atoms with  $\lambda \gg r$  can reach  $dA$ , which is

$$N = N_0 e^{-\frac{r}{\lambda}} = \frac{c}{\lambda} dn_c dV \frac{dA \cos \theta}{4\pi r^2} e^{-\frac{r}{\lambda}}$$

$$\begin{aligned}
 &= \frac{cdn_c dA \cos\theta \sqrt{2} \sin\theta d\theta d\phi dr}{\lambda^4 4\pi r^2} e^{-r/\lambda} \\
 &= \frac{dA}{\lambda} \times \frac{cdn_c \sin\theta \cos\theta d\theta d\phi}{4\pi} \times \frac{e^{-r/\lambda}}{\lambda} dr \\
 \therefore \text{No. of atoms striking } dA &= \frac{dA}{4\pi} \int_{c=0}^{\infty} \int_{\theta=0}^{\pi/2} \int_{\phi=0}^{2\pi} \int_{r=0}^{r/\lambda} e^{-r/\lambda} dr \times \\
 &= \frac{dA}{4\pi} n \bar{c} \frac{1}{2} 2\pi \times 1 = \frac{dA}{4} n \bar{c}
 \end{aligned}$$

So per unit area per unit time, number of atoms striking

$$\therefore \boxed{\frac{n \bar{c}}{4}}$$

Again, we know one atom suffers momentum change =  $2mc \cos\theta$

So change of momentum for all atom are

$$\frac{dA}{4\pi} \int_{c=0}^{\infty} \int_{\theta=0}^{\pi/2} \int_{\phi=0}^{2\pi} \int_{r=0}^{r/\lambda} e^{-r/\lambda} d(r/\lambda) \cdot$$

$$df = \frac{mdA}{2\pi} \bar{c}_{rms}^2 \frac{1}{3} 2\pi = \frac{1}{3} m n \bar{c}_{rms}^2 dA$$

$$\therefore \rho = \frac{df}{dA} = \boxed{\frac{1}{3} m n \bar{c}_{rms}^2}$$

$$\left[ \bar{c}_{rms}^2 = \frac{1}{n} \int_{c=0}^{\infty} c^2 dn_c \right]$$

### Mean free path of a mixture of a gas

If we consider two different molecule with diameter  $\sigma_1, \sigma_2$  then  $\sigma_1$  diameter molecule will collide with all molecule that are  $\frac{\sigma_1 + \sigma_2}{2}$  distance apart from  $\sigma_1$  molecule. Hence  $\lambda$  will be  $1/n\pi\sigma_a^2$  where  $\sigma_a = \frac{\sigma_1 + \sigma_2}{2}$  &  $n$  = number of molecules per unit volume of  $\sigma_2$  type. But  $\sigma_2$  molecules are not at rest then if  $\sigma_1$  type moves with  $\bar{c}_1$  &  $\sigma_2$  type moves with  $\bar{c}_2$  & if the molecules of  $\sigma_2$  move perpendicular to  $\sigma_1$  then

relative velocity  $R = \sqrt{\bar{c}_1^2 + \bar{c}_2^2}$  & therefore  $\frac{R}{\bar{c}_1} = \frac{\sqrt{\bar{c}_1^2 + \bar{c}_2^2}}{\bar{c}_1}$

So  $\lambda_1$  of  $\sigma_1$  type of molecules within  $\sigma_2$  type molecules are

$$\lambda_1 = \frac{1}{n\pi\sigma_a^2 \sqrt{\bar{c}_1^2 + \bar{c}_2^2}}$$

Similarly,  $\lambda_2$  of  $\sigma_2$  type of molecules

$$\text{within } \sigma_1 \text{ type molecules are } \lambda_2 = \frac{1}{n\pi\sigma_a^2 \sqrt{\bar{c}_1^2 + \bar{c}_2^2}}.$$

perpendicular directionality assumption gives

Maxwell's distribution with relative velocity  $R$ , & if we had assumed

$\bar{c}_1 = \bar{c}_2$  & then we could get back Maxwell's expression of free path.

If we now consider  $n_1$  molecule of  $\sigma_1$  type with  $\bar{c}_1$  &  $n_2$  molecule of  $\sigma_2$  type with  $\bar{c}_2$  avg. velocity then no. of impact/sec by  $\sigma_1$

$$\Gamma_1 = \underbrace{\sqrt{2}\bar{c}_1 n_1 \pi \sigma_1^2}_{\sigma_1 \text{ with } \sigma_1} \left( = \frac{\bar{c}_1}{\lambda_{11}} \right) + \underbrace{n_2 \pi \sigma_a^2 \bar{c}_1 \sqrt{\bar{c}_1^2 + \bar{c}_2^2}}_{\sigma_1 \text{ with } \sigma_2} \left( = \frac{\bar{c}_1}{\lambda_{12}} \right)$$

$\therefore$  Mean free path of  $\sigma_1$  type molecules in the gas mixture

$$\lambda_1 = \frac{\bar{c}_1}{\Gamma_1} = \frac{\bar{c}_1}{\sqrt{2}\pi n_1 \bar{c}_1 \sigma_1^2 + \pi \sigma_a^2 n_2 \sqrt{\bar{c}_1^2 + \bar{c}_2^2}} \text{ & Mean free path for the other}$$

$$\lambda_2 = \frac{\bar{c}_2}{\Gamma_2} = \frac{\bar{c}_2}{\sqrt{2}\pi n_2 \bar{c}_2 \sigma_2^2 + \pi \sigma_a^2 n_1 \sqrt{\bar{c}_1^2 + \bar{c}_2^2}}$$

HW 1. Estimate the size of a He atom, assuming its mean free path

is  $28.5 \times 10^{-6}$  cm at N.T.P. & density is 0.178 gm/litre at N.T.P.

& the mass of He atom is  $6 \times 10^{-24}$  gm.

2. The diameter of a gas molecule is  $3 \times 10^{-8}$  cm. Calculate the mean free path at N.T.P. Given  $K_B = 1.38 \times 10^{-16}$  ergs/ $^\circ$ C.

3. Find the diameter of a molecule of Benzene if its mean free path is  $2.2 \times 10^{-8}$  m & the number of Benzene molecules/unit volume is  $2.79 \times 10^{25}$  molecules/m<sup>3</sup>.

## (Nonequilibrium) Transport Phenomena in Gases

(ii) Viscosity: velocity varies from layer to layer & momentum is transferred from layer to layer leading to kinetic interpretation of viscosity in gases. In 1860, Maxwell interpreted that if two layers have relative velocity, viscous force acts along the surface of contact retarding the faster moving layer & making the slower moving layer to move faster. Retarding force is proportional to area of contact & velocity gradient.

$$F \propto A \quad \text{or} \quad F = \eta A \frac{dv}{dz} \quad \text{or} \quad \sigma = \eta \dot{\gamma} \rightarrow \text{strain rate}$$

$\downarrow$  stress       $\downarrow$  coeff. of viscosity

Newton's law of viscosity

(iii) Thermal conductivity: Taken a solid rod & heated in one end, after sufficiently long time when measured temperature at different distances then amount of heat conducted  $\propto$  (rate) is proportional to temperature gradient, area of face of slab.

$$Q \propto A \quad \text{or} \quad Q = KA \frac{dT}{dz}$$

$\downarrow$  thermal conductivity

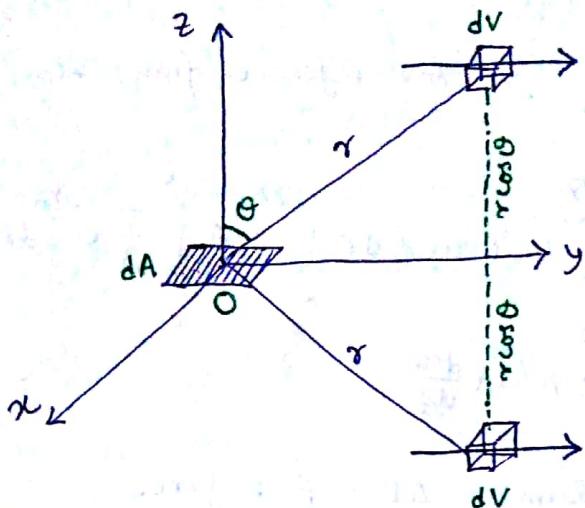
Fourier's law of heat conduction

(iv) Diffusion: Whenever there is difference in concentration, mass transfer results to an equilibrium distribution of concentration. In monodisperse system, diffusion to concentration gradient is called self-diffusion & if two gases diffuse into each other, called inter-diffusion. Number of molecules crossing is proportional to

$$N \propto A \frac{du}{dz} \quad \text{or} \quad N = DA \frac{du}{dz}$$

Fick's law of diffusion

## General method for obtaining coefficient of viscosity & conduction



In a reference frame, consider an elementary volume  $dV$  at coordinate  $(r, \theta)$ . The layer that contains  $dV$  is at a vertical height  $r \cos \theta$  from XY plane at origin O. If the physical entity has a value  $f_0$  (energy, momentum etc) on the XY plane at origin, then the

value at the upper layer is  $f_0 + r \cos \theta \frac{df_0}{dz}$ . For an identical layer beneath at same distance, the value is  $f_0 - r \cos \theta \frac{df_0}{dz}$

The number of molecules within  $c$  &  $c+dc$  in  $dV$  is  $d n_c dV$ . If  $\lambda$  is the mean free path, then the number of collision suffered in unit time is  $\frac{c}{\lambda} \frac{1}{2} d n_c dV$ . Factor  $\frac{1}{2}$  is because collision between two molecules are identical & counted twice. But each collision results in 2 paths. So the number of molecule coming out of  $dV$  in all possible direction is  $2 \times \frac{1}{2} \frac{c}{\lambda} d n_c dV$ .

Number of molecules which are headed towards area  $dA$  at origin is  $\frac{dA \cos \theta}{4\pi r^2} \frac{c}{\lambda} d n_c dV$ . Due to collision some of them cannot reach  $dA$  & the number that reaches  $dA$  in unit time is

$$\frac{dA \cos \theta}{4\pi r^2} \frac{c}{\lambda} d n_c dV e^{-\frac{r}{\lambda}} = \frac{dA \cos \theta}{4\pi r^2} \frac{c}{\lambda} d n_c r^2 \sin \theta d\theta d\phi dr e^{-\frac{r}{\lambda}}$$

If the molecule carry the physical entity characteristic of the layer when they last suffered collision then the transport of physical entity downwards through area  $dA$  per unit time is

$$L_J = \frac{dA}{4\pi} \int_{c=0}^{\infty} \int_{r=0}^{\infty} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} c d n_c \sin \theta \cos \theta d\theta d\phi e^{-\frac{r}{\lambda}} \frac{dr}{\lambda} (r \lambda + r \cos \theta \frac{df_0}{dz})$$

Considering an identical volume below the reference frame, the transport of physical entity upwards is

$$L \uparrow = \frac{dA}{4\pi} \int_{r=0}^{\infty} \int_{\theta=0}^{\pi/2} \int_{\phi=0}^{2\pi} c d n_c \sin \theta \cos \theta d\theta d\phi e^{-\frac{r}{\lambda}} \frac{dr}{\lambda} (g - r \cos \theta \frac{d\theta}{dz})$$

$\therefore$  The net transfer of physical entity to the reference frame via area  $dA$  in unit time is

$$\Delta L = L \downarrow - L \uparrow = \frac{dA}{4\pi} \frac{d\theta}{dz} \int_{r=0}^{\infty} c d n_c \int_0^{\pi/2} \cos \theta \sin \theta d\theta \int_0^{2\pi} d\phi \int_0^{\infty} \frac{r}{\lambda} e^{-\frac{r}{\lambda}} dr$$

$$= dA \frac{d\theta}{dz} \frac{1}{3} \lambda \int_0^{\infty} c d n_c = \frac{1}{3} n \bar{c} \lambda dA \frac{d\theta}{dz}$$

(i) Viscosity:  $g_c = m v = \text{momentum}$ ,  $\Delta L = F = \text{force}$

$$\therefore F = \frac{1}{3} n \bar{c} \lambda dA \frac{m dv}{dz} = \eta dA \frac{dv}{dz}$$

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

(ii) Thermal conductivity:  $\mathcal{E} = E = \text{thermal energy}$ ,  $\Delta L = Q = \text{heat}$

$$\therefore Q = \frac{1}{3} n \bar{c} \lambda dA \frac{dE}{dz} = \frac{1}{3} n \bar{c} \lambda dA \frac{dE}{dT} \frac{dT}{dz} = K dA \frac{dT}{dz}$$

$$\therefore K = \frac{1}{3} n \bar{c} \lambda \frac{dE}{dT}$$

If  $c_v$  = specific heat of molecules,  $E = m c_v T \Rightarrow \frac{dE}{dT} = m c_v$

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

Variation of  $K/\eta c_v$  with the atomicity of molecules

$K/\eta c_v = 1$  was not matching with experiments, because many factors are omitted to reach the expression. In general  $K/\eta c_v = \epsilon = [1, 2.5]$

for a polyatomic molecule, the energy transfer is not only translational but also internal energy (rotational, vibrational etc). In rigorous calculation, Chapman found total energy transferred per unit time is  $\frac{1}{3} n \bar{c} \lambda dA \left( \frac{5}{2} \frac{dE_T}{dT} + \frac{dE_R}{dT} \right)$ .  $E_T$  = Translational energy &  $E_R$  = Rotational energy.

$$K dA \frac{dT}{dz} = \frac{1}{3} n \bar{c} A dA \frac{dT}{dz} \left\{ \frac{5}{2} \frac{dE_T}{dT} + \frac{dE_R}{dT} \right\}$$

$$\text{or } K = \frac{\eta}{m} \left( \frac{5}{2} \frac{dE_T}{dT} + \frac{dE_R}{dT} \right) \quad \dots \quad (1)$$

From the principle of equipartition of energy, total energy associated with 1 gm molecule of gas is  $\frac{3+\beta}{2} RT$ ,  $\beta = \# \text{ of d.o.f. for rotational motion}$ .  $\therefore$  Molar specific heat  $c_V = \frac{dE}{dT} = \frac{3+\beta}{2} R$ .

$$\text{Using } c_p - c_v = R, \quad c_p = \frac{5+\beta}{2} R$$

$$\text{or } \gamma = \frac{c_p}{c_v} = \frac{5+\beta}{3+\beta} = 1 + \frac{2}{3+\beta}. \quad \dots \quad (2) \quad \text{or } \beta = \frac{2}{\gamma-1} - 3$$

$$\text{But } E_T = \frac{3}{2} K_B T, \quad E_R = \frac{\beta}{2} K_B T \quad \Rightarrow \quad \frac{dE_T}{dT} = \frac{3}{2} K_B, \quad \frac{dE_R}{dT} = \frac{\beta}{2} K_B$$

$$\text{putting in (1), } K = \frac{\eta}{m} \left( \frac{15}{4} + \frac{\beta K_B}{2} \right)$$

$$\text{But } c_v = \frac{3+\beta}{2} \frac{K_B}{m} \quad (\text{molecular specific heat})$$

$$= \frac{K_B}{m(\gamma-1)} \quad [\text{using (2)}] \quad \text{or } K_B = m(\gamma-1)c_v$$

$$\therefore K = \frac{\eta}{m} m(\gamma-1) c_v \left( \frac{15+2\beta}{4} \right) = \eta c_v (\gamma-1) \left( \frac{15}{4} + \frac{\beta}{2} \right)$$

$$= \eta c_v (\gamma-1) \left[ \frac{15}{4} + \frac{1}{\gamma-1} - \frac{3}{2} \right] = \eta c_v (\gamma-1) \left( \frac{9}{4} + \frac{1}{\gamma-1} \right)$$

$$= \eta c_v \left( \frac{9\gamma-5}{4} \right). \quad \therefore \epsilon = \frac{9\gamma-5}{4}$$

monatomic gas  $\gamma = 1.66, \epsilon = 2.5$

diatomic gas  $\gamma = 1.4, \epsilon = 1.9$

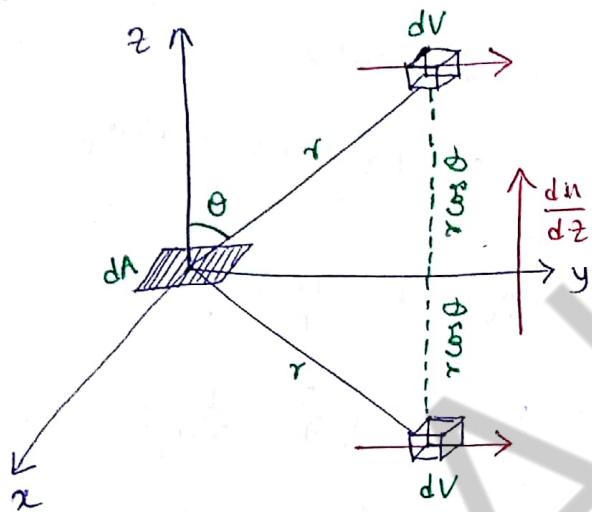
### Variation of $\eta$ with temperature & pressure

$$\eta = \frac{1}{3} m \bar{c} \lambda = \frac{1}{3} m \bar{c} \frac{1}{\sqrt{2\pi\sigma^2 N}} = \frac{1}{3} \frac{m \bar{c}}{\sqrt{2\pi\sigma^2}}$$

$\eta$  is independent of concentration, that Maxwell found at moderate pressure. At very high pressure,  $\eta$  increases & at low pressure,  $\eta$  decreases with pressure. At very high pressure, mean free path of molecules are comparable to the molecular dimension. Hence  $\eta \propto p$ . On  $\lambda = \text{constant}$  At low pressure, mean free path is comparable to the dimension of the container.

$f$  again is constant. So reducing pressure  $n$  decreases  $f$  hence  $\eta$ .  
as  $\bar{c} = \sqrt{\frac{8K_B T}{m\pi}}$ , so  $\eta \propto \sqrt{T}$  but in reality  $\eta$  varies more rapidly.  
This is because in K.T. molecular interaction is not taken care of.  
The molecular force field in K.T. is zero but in reality increase  
in temperature impinges the molecules to penetrate into each other  
so the effective size of molecule decreases or increases in  $\eta$ .  
Sutherland found that  $\eta = \frac{A\sqrt{T}}{1 + b/T}$  holds for hydrogen, helium,  
argon etc.

### General Method for obtaining Diffusivity



If there is a concentration gradient  $\frac{dn}{dz}$  along  $z$ -direction, then the number of molecules that flows through  $dA$  per unit time is  $N = DdA \frac{dn}{dz}$   
Let the concentration in XY plane is  $n$  & concentration gradient increases in  $z$  direction,

No. of molecules within  $c$  &  $c+dc$  contained at  $dV$  located at  $(r, \theta)$

$$\approx 4\pi A^3 e^{-bc^2} c^2 dc \left( n + r \cos\theta \frac{dn}{dz} \right) dV, \quad A = \sqrt{\frac{m}{2\pi K_B T}}, \quad b = \frac{m}{2K_B T}$$

Due to collision, number of new paths emanating in unit time is  $2 \times \frac{1}{2} \frac{c}{\lambda} \left( n + r \cos\theta \frac{dn}{dz} \right) 4\pi A^3 e^{-bc^2} c^2 dc dV$  & out of them, the number that will head towards  $dA$  is

$$\frac{dA \cos\theta}{4\pi r^2} \frac{c}{\lambda} \left( n + r \cos\theta \frac{dn}{dz} \right) 4\pi A^3 e^{-bc^2} c^2 dc dV (= \cancel{\pi \sin\theta d\theta d\phi})$$

Taking collision into account, total number of molecules crossing area  $dA$  in downward direction

$$N \downarrow = A^3 dA \int_{c=0}^{\infty} \int_{r=0}^{\infty} \int_{\theta=0}^{\pi/2} \int_{\phi=0}^{2\pi} \left( n + r \cos\theta \frac{dn}{dz} \right) \cos\theta \sin\theta d\theta d\phi dr \frac{e^{-\frac{bc^2}{\lambda}}}{\lambda} c^3 e^{-bc^2} dc$$

Similarly the number of molecules crossing  $dA$  in upward direction

$$N\uparrow = A^3 dA \int_{c=0}^{\infty} \int_{r=0}^{\infty} \int_{\theta=0}^{\pi/2} \int_{\phi=0}^{2\pi} (n - r \cos\theta \frac{dn}{dz}) \sin\theta \cos\theta dr d\phi d\theta dz e^{-r/\lambda} c^3 e^{-bc^2} dc$$

$\therefore$  Net number of molecules moving through  $dA$  in unit time

$$\Delta N = N\downarrow - N\uparrow = 2A^3 dA \int_0^{\infty} c^3 e^{-bc^2} dc \int_0^{\infty} r e^{-r/\lambda} dr \int_0^{\pi/2} \cos^2\theta \sin\theta d\theta \times \int_0^{2\pi} d\phi \times \frac{du}{dz}$$
$$= \frac{2\pi}{3} \lambda dA \frac{du}{dz} A^3 / b^2 = \frac{1}{3} dA \lambda \frac{du}{dz} \sqrt{\frac{8KT}{m\pi}} = \frac{1}{3} \lambda \bar{c} dA \frac{du}{dz}$$

From Fick's law,  $\Delta N = D dA \frac{du}{dz}$

$$\therefore D = \frac{1}{3} \lambda \bar{c} = \frac{n}{\rho}$$

$$= \frac{1}{3} \sqrt{\frac{1}{2\pi} \sigma^2 n} \sqrt{\frac{8KT}{m\pi}}$$

$$\therefore D \propto \frac{1}{n} \propto \frac{T}{P}$$

$\propto \frac{1}{\sqrt{m}}$  (Graham's law)

### Brownian motion

first observed by R. Brown in 1827 on suspended pollen grains on water. Perpetual, random motion of big solute particle in solvent is the Brownian motion.

Features: (i) Motion of Brownian particle is completely irregular.

No two particle execute the same motion.

(ii) Motion is continuous & based on discrete collisional steps.

(iii) Smaller particles are more agitated than larger particles, but motion is independent of the nature of suspended particles. Two particles of same weight & size move equally fast at same temperature.

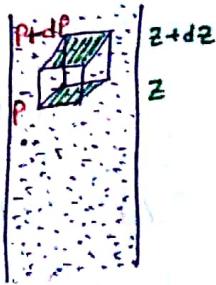
(iv) The motion is vigorous with increasing temperature, & in lower viscosity.

(v) Motion is not modified due to shaking of container.

Basis fluctuation + dissipation

### Law of Atmosphere

Brownian particles form a gas in equilibrium under the gravitational force. Consider a vertical cylinder of unit cross-section in a gas having end face at  $z$  &  $z+dz$  & corresponding pressure  $P$  &  $P+dp$  then



Force of gravity in layer vertically downward =  $1 \times dz \times \rho g = \rho g dz$

As cylinder is in equilibrium, net force on layer = 0.

$$(P+dp) - P + \rho g dz = 0$$

$$\therefore dp = -\rho g dz \quad \text{---(1)} \quad (\text{-ive sign means } P \text{ decreases with } z)$$

$m$  = mass of single molecule,  $n$  = average number of molecules per unit volume.

$$\rho = mn.$$

Using Clapeyron's equation  $P = n k_B T$ ,  $dp = dn k_B \Delta T$ . ---(2)

Equating (1) & (2),  $dn k_B \Delta T = -mn g dz$

$$\therefore \frac{dn}{n} = -\frac{mg}{k_B T} dz = -\frac{mgn}{RT} dz \quad (k_B = \frac{R}{N})$$

$$\text{Integrating: } \ln n = -\frac{mgn}{RT} z + \ln C$$

$$\text{at } z = z_0, n = n_0 \quad \ln n_0 = -\frac{mgn}{RT} z_0 + \ln C$$

$$\therefore \ln n = -\frac{mgn}{RT} z + \ln n_0 + \frac{mgn}{RT} z_0$$

$$\therefore \ln \frac{n}{n_0} = -\frac{mgn}{RT} (z - z_0)$$

$$\therefore n = n_0 e^{-\frac{mgn}{RT} (z - z_0)}$$

Exponential decrease of no. density of Brownian particles with height.

for colloidal solution, particles have downward force due to gravity & upward force due to the buoyancy of liquid. If  $\rho'$  is the density of particle then effective mass of particle  $m = \frac{4}{3} \pi r^3 (\rho' - \rho)$

$$\therefore \ln \frac{n}{n_0} = - \frac{4\pi r^3 (\rho' - \rho) g N}{3 RT} (z - z_0)$$

$$\therefore N = \frac{3RT}{4\pi r^3 (\rho' - \rho) g (z - z_0)} \ln \frac{n_0}{n}$$

Thus Avogadro number can be calculated if  $r, \rho'$  are known.

### Langevin equation of Brownian motion

Equation of motion  $m \frac{d\vec{v}}{dt} = -\vec{F}_V + \vec{F}_B(t)$

$\downarrow$  Viscous       $\downarrow$  Brownian

Time average over sufficiently long time  $t \gg \tau$ ,  $m \frac{d\langle \vec{v} \rangle}{dt} = \langle \vec{F}_B \rangle$

for colloidal fluid  $m \frac{d\vec{v}}{dt} = -\alpha \vec{v} + \vec{F}_B(t)$

from hydrodynamics, Stokes calculated that  $\alpha = 6\pi\eta a$  for a spherical object of size  $a$  moving at velocity  $v$  through a liquid with viscosity  $\eta$ . This is known as Stokes law.

Clearly,  $\langle \vec{v} \rangle = 0$  but  $\langle \vec{v}^2 \rangle \neq 0$ .  $\langle \vec{F}_B(t) \rangle = 0$

### Magnitude of fluctuations

$$m \frac{d^2\vec{v}}{dt^2} = -\alpha \frac{d\vec{v}}{dt} + \vec{F}_B(t)$$

$$\therefore m \alpha \frac{d^2\vec{v}}{dt^2} = -\alpha \alpha \frac{d\vec{v}}{dt} + \alpha \vec{F}_B(t)$$

$$\therefore m \left[ \frac{d}{dt} (\vec{v} \cdot \vec{v}) - \vec{v}^2 \right] = -\alpha \alpha \frac{d\vec{v}}{dt} + \alpha \vec{F}_B(t)$$

Now,  $\langle \vec{v} \cdot \vec{F}_B(t) \rangle = \langle \vec{v} \rangle \langle \vec{F}_B(t) \rangle = 0$  "statistical independence"

and from equipartition theorem,  $\frac{1}{2} m \langle \vec{v}^2 \rangle = \frac{1}{2} k_B T$

$$\therefore m \langle \frac{d}{dt} (\vec{v} \cdot \vec{v}) \rangle = m \langle \vec{v}^2 \rangle - \alpha \langle \vec{v} \frac{d\vec{v}}{dt} \rangle + \langle \vec{v} \cdot \vec{F}_B(t) \rangle$$

$$\text{or } m \frac{d}{dt} \langle x\dot{x} \rangle = k_B T - \alpha \langle x\dot{x} \rangle$$

$$\text{or } \frac{d \langle x\dot{x} \rangle}{dt} + \frac{\alpha}{m} \langle x\dot{x} \rangle = \frac{k_B T}{m}$$

$$\begin{aligned}\text{integrating factor} &= e^{+\alpha_m t} \\ \text{particular integral} &= e^{-\alpha_m t} \int e^{\alpha_m t'} \frac{k_B T}{m} dt' \\ &= e^{-\alpha_m t} \frac{k_B T}{m} \left( \frac{m}{\alpha} e^{\alpha_m t} + c' \right) \\ \langle x\dot{x} \rangle &= \frac{k_B T}{\alpha} + c e^{-\alpha_m t}\end{aligned}$$

$$\text{at } t=0, \langle x\dot{x} \rangle = \langle x \rangle \langle \dot{x} \rangle = 0 \therefore c + \frac{k_B T}{\alpha} = 0$$

$$\therefore \langle x\dot{x} \rangle = \frac{k_B T}{\alpha} (1 - e^{-\alpha_m t})$$

$$\text{or } \frac{1}{2} \frac{d}{dt} \langle x^2 \rangle = \frac{k_B T}{\alpha} (1 - e^{-\alpha_m t})$$

$$\text{or } \boxed{\langle x^2 \rangle = \frac{2k_B T}{\alpha} \left[ t - \frac{m}{\alpha} (1 - e^{-\alpha_m t}) \right]}$$

$$\underline{\text{Case I}} \quad \frac{m}{\alpha} \gg t, \quad e^{-\alpha_m t} \approx 1 - \frac{\alpha}{m} t + \frac{1}{2} \frac{\alpha^2}{m^2} t^2 - \dots$$

$\therefore \langle x^2 \rangle = \frac{k_B T}{m} t^2$ . Therefore for a short time interval

the particle moves ballistically with constant velocity  $v = \sqrt{\frac{k_B T}{m}}$

$$\underline{\text{Case II}} \quad \frac{m}{\alpha} \ll t, \quad e^{-\alpha_m t} \approx 0, \quad t - \frac{m}{\alpha} \gg 0 \approx t.$$

$\langle x^2 \rangle = \frac{2k_B T}{\alpha} t$ . Therefore the Brownian particle diffuses

$$\text{as } \langle x^2 \rangle = 2Dt = \frac{2k_B T}{\alpha} t = \frac{k_B T}{3\pi N \eta a} t = \frac{RT}{3\pi N \eta a} t$$

$$\boxed{D = \frac{RT}{6\pi N \eta a}}$$

$D \propto \frac{1}{a}$  but independent of mass.

## Einstein's argument

$\tau$  = time interval << observation time scale  
 >> large enough than individual collision  
 that two consecutive intervals of  $\tau$  are mutually independent.  
 For  $N$  solute (Brownian) particle in time interval  $\tau$ ,  $x$  coordinate increase by  $\Delta$  (both +ive) due to thermal motion, no. of solute particles that are between  $\Delta$  &  $\Delta+d\Delta$  is

$$dN = N \phi(\Delta) d\Delta \text{ with the property } \phi(\Delta) = \phi(-\Delta) \text{ &} \\ \int_{-\infty}^{\infty} \phi(\Delta) d\Delta = 1. \text{ (normalized)}$$

If  $f(x, t)$  is the no. of particles at time  $t$  at position  $x$

$$\text{Then } f(x, t+\tau) dx = dx \int_{-\infty}^{\infty} f(x+\Delta, t) \phi(\Delta) d\Delta$$

Kramers - Moyal Expansion:  $f(x+\Delta, t) = f(x, t) + \Delta \frac{\partial f(x, t)}{\partial x} + \frac{\Delta^2}{2} \frac{\partial^2 f(x, t)}{\partial x^2} + \dots$

$$f(x, t+\tau) = f(x, t) + \tau \frac{\partial f(x, t)}{\partial t} \quad \text{as } \tau \text{ is short.}$$

$$\therefore f + \tau \frac{\partial f}{\partial t} = f \int_{-\infty}^{\infty} \phi(\Delta) d\Delta + \frac{\partial f}{\partial x} \int_{-\infty}^{\infty} \Delta \phi(\Delta) d\Delta + \frac{\partial^2 f}{\partial x^2} \int_{-\infty}^{\infty} \frac{\Delta^2}{2} \phi(\Delta) d\Delta + \dots$$

~~odd function~~

Equating  $\frac{\partial f}{\partial t} = \frac{1}{\tau} \int_{-\infty}^{\infty} \frac{\Delta^2}{2} \phi(\Delta) d\Delta \quad \frac{\partial^2 f}{\partial x^2} = D \frac{\partial^2 f}{\partial x^2}$

So  $D = \frac{1}{\tau} \int_{-\infty}^{\infty} \frac{\Delta^2}{2} \phi(\Delta) d\Delta$

$$\frac{\partial f}{\partial t} = D \frac{\partial^2 f}{\partial x^2}$$

Diffusion equation

CW observation on Brownian movement in water showed that the horizontal displacement for a test particle in 11 successive intervals of 33 secs were  $[0, 5.6, -1.7, -10.8, 6.6, -9.8, -11.2, -4.0, 15.0, 19.1, 16.0] \times 10^{-5} \text{ cm}$   
 $T = 20^\circ \text{C}$  &  $\eta_{\text{water}} = 0.01 \text{ cgs unit}$ , radius of particle  $1.15 \times 10^{-5} \text{ cm}$  &  
 $R = 8.32 \times 10^7 \text{ ergs/deg/mole}$ . Obtain  $N$ .

$$\langle x^2 \rangle = \frac{RT}{N} \frac{1}{3\pi\eta a} t$$

$$\langle x^2 \rangle = \frac{x_1^2 + x_2^2 + x_3^2 + \dots + x_{11}^2}{11} = 1.18 \times 10^{-6} \text{ cm}^2$$

$$\therefore N = \frac{RTt}{\langle x^2 \rangle 3\pi\eta a} = \frac{8.32 \times 10^7 \times 293 \times 30}{1.18 \times 10^{-6} \times 3 \times 3.14 \times 0.01 \times 1.18 \times 10^{-5}}$$
$$= 5.72 \times 10^{23}$$