KINETIC THEORY OF GASES

📇Assumptions :

- The gases are atoms/molecules that do not have volumes/cross-sectional areas
- The gas molecules are moving at random and in straight lines
- The gas molecules do not interact with each other except in collisions – elastic

📊Pressure vs speed

- Pressure of a gas is the outcome of the elastic collision of molecules against the wall of the container.

Speed of a molecule of gas, v :
- related to its component velocities in the x, y, and z directions – v_x, v_y, v_z

$$v^2 = v_x{}^2 + v_y{}^2 + v_z{}^2$$

or $v = (v_x{}^2 + v_y{}^2 + v_z{}^2)^{1/2}$

Average speed :

$$v^2 = v_x{}^2 + v_y{}^2 + v_z{}^2 = \frac{v_i{}^2}{N}$$

N = no. of molecules
Assumming $v_x{}^2 = v_y{}^2 = v_z{}^2$

$$v^2 = 3v_x{}^2 \qquad v_x{}^2 = 1/3 \ v^2$$

Derivation for pressure :

Assuming a gas molecule with mass m, moving in a cube with velocity v_x along the x axis. The molecule hits the wall and bounces with a velocity - v_x.

Change in momentum for one collision :

$$mv_x - (-mv_x) = 2 \ mv_x$$

and according to 2nd Newton law :

F = $\dfrac{\text{Change in momentum}}{\text{Time}}$

$= \dfrac{2\ mv_x}{t}$

$= \dfrac{2\ mv_x^2}{2l}$

$= \dfrac{mv_x^2}{l}$

$P = \dfrac{F}{A} = \dfrac{mv_x^2}{l^3} = \dfrac{mv_x^2}{V}$

Assuming the cube has N molecules of gas and collisions are with an average velocity v_x, v_z, v_z along the respective axes,

$P_x = \dfrac{Nmv_x^2}{V}$; $P_y = \dfrac{Nmv_y^2}{V}$; $P_z = \dfrac{Nmv_z^2}{V}$

Since $v_x^2 = v_y^2 = v_z^2 = 1/3\ v^2$
and $P_x = P_y = P_z = P$

$P = \underline{Nmv^2}$

$$PV = \frac{1}{3}Nmv^2$$

or $PV = \frac{1}{3}nMv^2$

where $n = N/N_A$ and $M = mN_A =$ molar mass.

Average kinetic energy

For 1 molecule : $e_k = \frac{1}{2}mv^2$

For N molecule : $E_k = \frac{1}{2}Nmv^2$

For N_A molecule : $E_k = \frac{1}{2}N_A mv^2 = \frac{1}{2}Mv^2$

Pressure vs kinetic energy
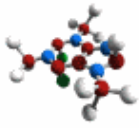
$$PV = \frac{1}{3}Nmv^2$$

$$= \frac{2}{3} \quad \frac{1}{2}Nmv^2$$

$$PV = \frac{2}{3}E_k$$

For an ideal gas, $PV = nRT$

$$nRT = \frac{2}{3}E_k$$

$$\text{or } E_k = \frac{3}{2}nRT$$

MAXWELL DISTRIBUTION OF SPEEDS

With increasing energy E, it is progressively less likely that any given particle will attain that energy, so more particles will be found with lower energies. It is assumed that an unlimited number of particles can occupy any energy state.

The probability that a particle will have energy E

$$f(E) = \frac{1}{Ae^{E/kT}}$$

Maxwell-Boltzmann

Normalization constant A

The probability for occupying a given energy state decreases exponentially with energy

Boltzmann's constant k times the absolute temperature T. The implication of this term is that for a higher temperature, it is more probable that a given particle can be found with energy E.

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The Maxwell-Boltzmann distribution of molecular velocities :

$$f(v_x) = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-\frac{mv_x^2}{2kT}}$$

The probability density for the velocity vector is the product of the probability densities in the three directions :

$$f(v_x, v_y, v_z) = f(v_x)f(v_y)f(v_z) = f(v)$$

The probability F(v)dv that a molecule has a speed between v and v + dv is given by the probable no. of points in a spherical shell of thickness dv and is given by :

$$F(v)\,dv = 4\pi v^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mv^2}{2kT}\right) dv$$

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where $F(v)dv = \dfrac{dN}{N}$

The probability density f(v) for Maxwell distribution of speeds is :

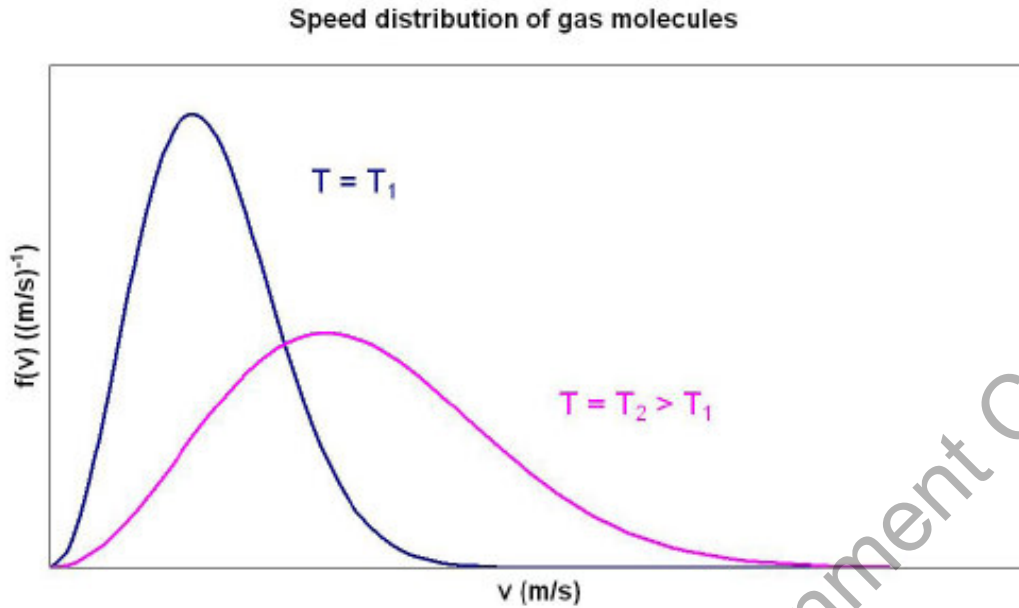$$F(v)dv = 4\pi v^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mv^2}{2kT}\right) dv$$

$$F(v)dv = 4\pi v^2 \left(\frac{M}{2\pi RT}\right)^{3/2} \exp\left(-\frac{Mv^2}{2RT}\right) dv$$

where $f(v) = \dfrac{dN/N}{dv}$

m is mass of 1 molecule ($m = M/N_A$),
k = Botlzmann constant = 1.381×10^{-23} J K^{-1}
or $k = R/N_A$

Speed distribution of gas molecules

- F(v) increases with speed up to a max. then declines.
- The probability that a molecule has a speed between any two values is given by the area under the curve.
- Very few molecules have very high or very low speeds.
- The most probable speed increases with temperature and decrease in molar mass- the curve gets wider.
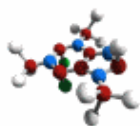
TYPES OF AVERAGE SPEEDS

- The **most probable speed**, v_{mp} is the speed at the maximum of f(v).

Setting $\dfrac{dF(v)}{dv} = 0$

$$v_{mp} = \left(\frac{2RT}{M}\right)^{1/2} = \left(\frac{2kT}{m}\right)^{1/2}$$

The **mean speed,** v is calculated as the average of v using the probability distribution f(v):
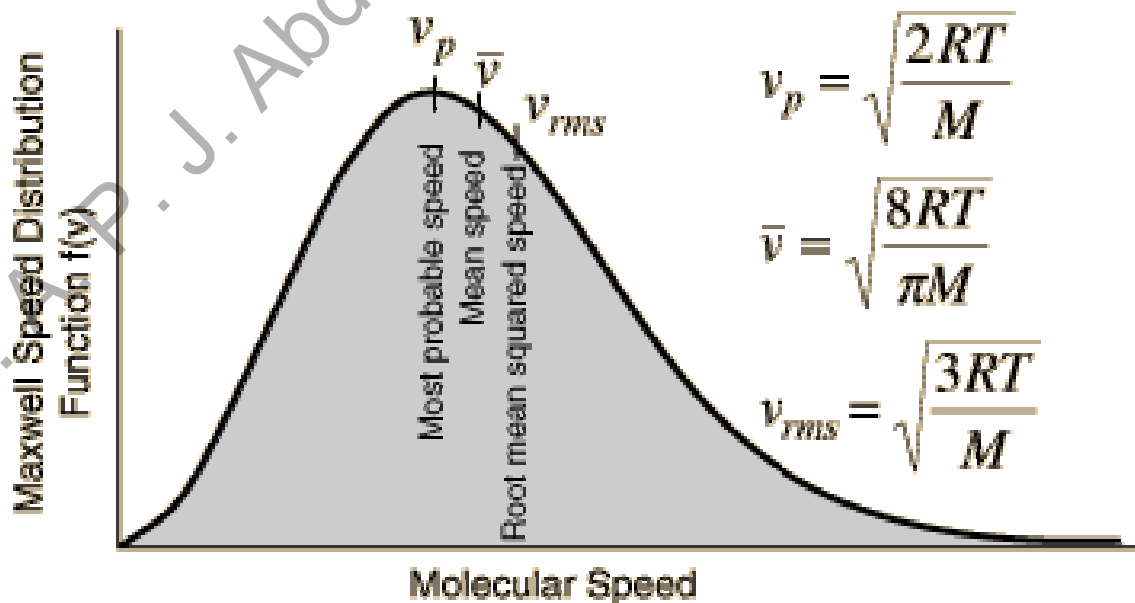
$$\overline{v} = \int_0^\infty v\, F(v)\, dv$$

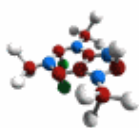$$\bar{v} = \left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}} = \left(\frac{8kT}{\pi m}\right)^{\frac{1}{2}}$$

The **root-mean-square speed**, $(v^2)^{1/2}$ is the square root of (v^2)

$$(v^2)^{\frac{1}{2}} = \left[\int_0^{\infty} v^2 F(v) dv\right]^{\frac{1}{2}}$$

$$v_{rms} = (v^2)^{\frac{1}{2}} = \left(\frac{3RT}{M}\right)^{\frac{1}{2}} = \left(\frac{3kT}{m}\right)^{\frac{1}{2}}$$

$$f(v) = 4\pi \left[\frac{M}{2\pi RT}\right]^{\frac{3}{2}} v^2 \exp\left[\frac{-Mv^2}{2RT}\right]$$

$$v_p = \sqrt{\frac{2RT}{M}}$$

$$\bar{v} = \sqrt{\frac{8RT}{\pi M}}$$

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

Maxwell Speed Distribution Function f(v)

Most probable speed v_p
Mean speed $\bar{v}$
Root mean squared speed v_{rms}
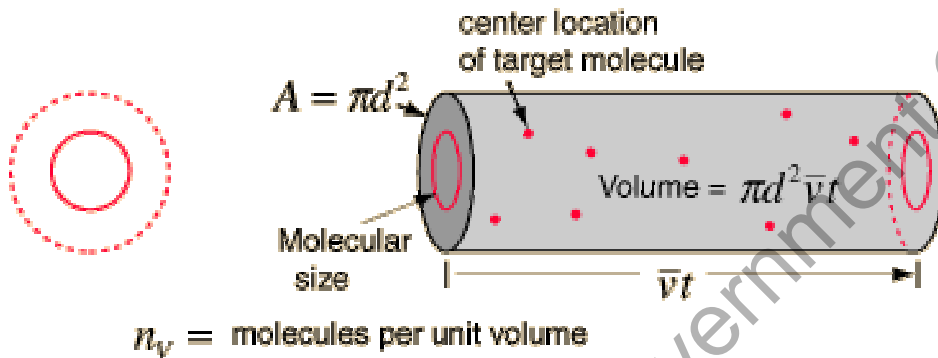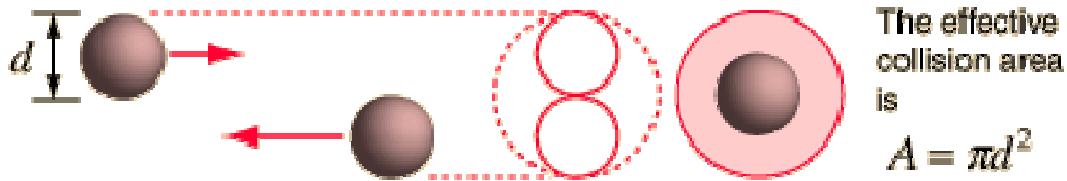
Molecular Speed

COLLISION FREQUENCY OF GASES

- Relates the kinetic behaviour of gases, e.g. flux, diffusion rate, viscosity
- Formulation of collision theories of chemical reactions

Assumptions :
- Hard spheres
- Molecules collide – centers within distance d equal to their diameters if the molecules are alike or $d_{12} = \frac{1}{2}(d_1 + d_2)$ if they are different.

d = collision diameter.

The effective collision area is
$$A = \pi d^2$$

$A = \pi d^2$

center location of target molecule

Volume $= \pi d^2 \bar{v} t$

Molecular size

$\bar{v} t$

n_v = molecules per unit volume

Case 1

• Unimolecule collision

Collision frequency = no. of collision per unit time

= no. of molecules in cylinder

= volume of cylinder x molecule density

where volume of cylinder = $\pi d_1 v_1 \Delta t$

molecule density ρ = N/V

In 1 second,

no. of molecules in cylinder = $\pi d_1 v_1 \rho$

no. of molecules in cylinder = $\pi d_1^2 \ 2 v_1 \rho$

Collision frequency $z_1 = \ 2 \pi d_1^2 v_1 \rho$

$$\rho = \frac{N}{V} = \frac{nN_A}{V} = \frac{PN_A}{RT} = \frac{P}{kT}$$

$$\bar{v} = \left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}} = \left(\frac{8kT}{\pi m}\right)^{\frac{1}{2}}$$

Mean free path, λ

- the average distance travelled between collisions is given by :

$$\frac{\text{average distance travelled per unit time}}{\text{collision frequency}}$$

$$= \frac{v_1}{z_1}$$

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$$= \frac{1}{2\,\pi {d_1}^2\,\mathrm{v}_1\,\rho}$$

$$= \frac{kT}{2\,\pi {d_1}^2\,\rho}$$

Case 2

• Bimolecular collision

- Asumming all molecules are moving
- Rate of collisions of molecules type 1 with molecules type 1, Z_{11}.
- No. of collisions per unit time per unit volume.

$$Z_{11} = \frac{1}{2} z_1 \, \rho$$

$$= \frac{1}{2} (\, 2 \, \pi d_1^{\,2} \, v_1 \, \rho) \, \rho$$

$$= \frac{2}{2} (\pi d_1^{\,2} \, v_1 \, \rho^2)$$

$$= \frac{1}{2} (\pi d_1^{\,2} \, v_1 \, \rho^2)$$

Case 3

- Bimolecular collisions between two gas type 1 and gas type 2

- $d_{12} = ½(d_1 + d_2)$

- $v_{12} = (v_1^{\,2} + v_2^{\,2})^{\,½}$

$$= \left(\frac{8RT}{\pi M_1} + \frac{8RT}{\pi M_2} \right)^{½}$$

$$= \frac{8RT}{\pi} \left(\frac{1}{M_1} + \frac{1}{M_2} \right)^{1/2}$$

$$= \frac{8RT}{\pi} \left(\frac{M_1 + M_2}{M_1 M_2} \right)^{1/2}$$
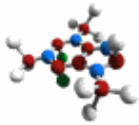
Assumming that only 1 molecule is moving (type 1 or type 2), collision frequency is given by :

$$z_{1(2)} = \pi d_{12}^2 \, v_{12} \, \rho_2$$

$$z_{2(1)} = \pi d_{12}^2 \, v_{12} \, \rho_1$$

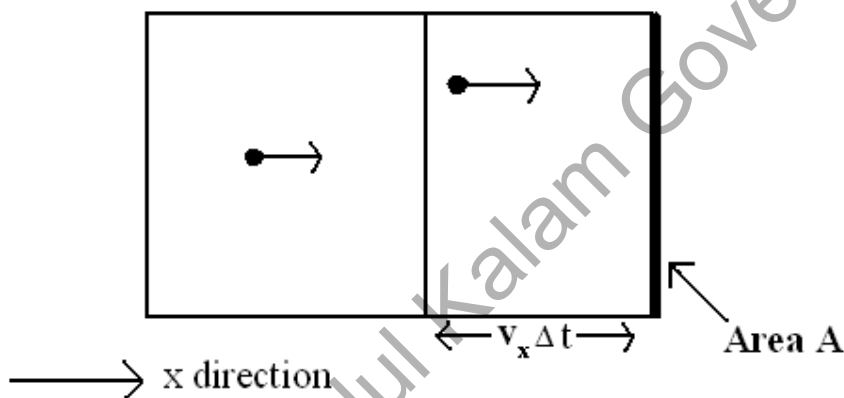Collision density between molecule 1 and 2 :

$$Z_{12} = \pi d_{12}^2 \, v_{12} \, \rho_1 \, \rho_2$$

COLLISIONS WITH A SURFACE AND EFFUSION

- relates the no. of collisions with the wall or the no. of molecules passing through a small opening.

Collisions with a surface

Total number of collisions against the wall :
= volume x molecule dencity

$A_{v_x}\Delta T$ x ρ

Taking into account the presence of a range of velocities in the sample

No. of collisions = $\rho A \Delta T \int_o v_x f(v_x) d_x$

Collision flux, $J_N \rightarrow$ no. of collisions per unit area per unit time $\therefore$

$$J_N = \rho \int_0 v_x \, f(v_x) d_x$$

$$= \rho \left(\frac{kT}{2\pi m} \right)^{1/2}$$

in terms of mean velocity :

$$J_N = \frac{\rho v}{4}$$

- replaced by P from $P = \rho kT$

$$J_N = \frac{P}{(2\pi mkT)^{1/2}}$$

- the basis of the Knudsen method for measuring vapour pressure of a solid or liquid.(placed in a container with a small hole)

- The loss in mass Δw of the container and sample is measured after time t.

$$J_N = \frac{\Delta w}{mtA}$$

$$J_N = m^{-2}\ s^{-1}$$

where A = area of the hole

$$J_N = \frac{\Delta w}{mtA} = \frac{P}{(2\pi mkT)^{1/2}}$$

Effusion

$$J_N A = \text{effusion rate} = \frac{PA}{(2\pi mkT)^{1/2}}$$

e.g. At P and T – molecules separated from a vacuum by a small hole :

rate of escape of its molecules = rate of striking the area of the hole

Gas Properties Relating to the Kinetic-Molecular Theory

Diffusion is the migration of molecules as a result of random molecular motion. The diffusion of two or more gases results in an intermingling of the molecules and, in a closed container, soon produces a homogeneous mixture.
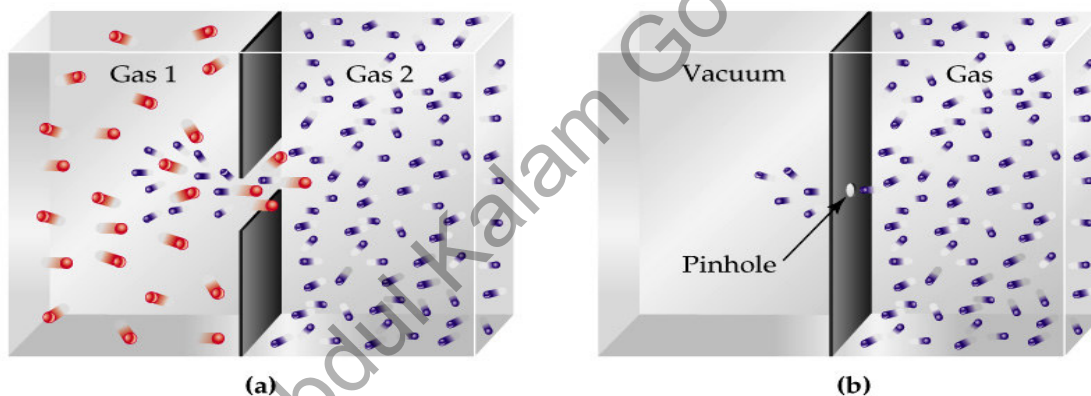
Effusion is the escape of gas molecules from their container through a tiny orifice or pinhole. The rate at which effusion occur is directly proportional to molecular speeds.

When comparing the effusion of two gases at the same condition

$$\frac{\text{rate of effusion A}}{\text{rate of effusion B}} = \sqrt{\frac{(v_{rms})_A}{(v_{rms})_B}} = \sqrt{\frac{3RT/M_A}{3RT/M_B}} = \sqrt{\frac{M_B}{M_A}}$$
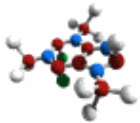
Graham's Law: the rates of effusion of two difference gases are inversely proportional to the square roots of their molar masses.

This means that molecules with a smaller mass (m) have a higher speed.

a ratio of
(1) molecular speeds
(2) effusion rates
(3) effusion times
(4) distance traveled by molecules
(5) amount of gas effusion

$= \sqrt{\text{ratio of two molar mass}}$

TRANSPORT PHENOMENA IN GASES

The rate of migration of a property such as mass and energy is measured by its Flux, J_N, the quantity of that property passing through a given area in a time interval.

- Gas not uniform with respect to composition, temperature and velocity.
- Rate of flow is proportional to the rate of change with distance.

Diffusion

Transport of matter

The flux of component i in the z direction due to diffusion is proportional to the conc. gradient, $d\rho_i/d_z$, according to Fick's law :

Flux $J_{iz} = - D(d\rho_i/d_z)$
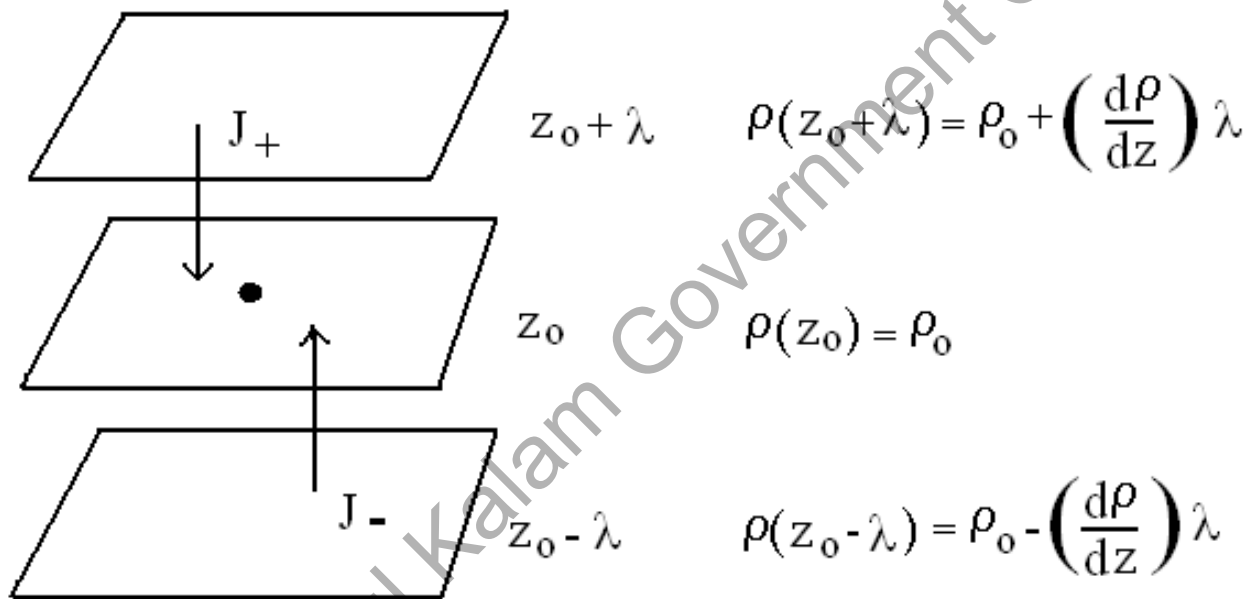
where D = diffusion coefficient ($m^2 s^{-1}$)
J_{iz} = molecule $m^{-2} s^{-1}$
$d\rho_i/d_z$ = molecule m^{-4}

Difussion

- Molecule that crosses the plane undergoes collision at two parallel planes

λ = average distance travelled between collision

$$z_0 + \lambda \qquad \rho(z_0 + \lambda) = \rho_0 + \left(\frac{d\rho}{dz}\right)\lambda$$

$$z_0 \qquad \rho(z_0) = \rho_0$$

$$z_0 - \lambda \qquad \rho(z_0 - \lambda) = \rho_0 - \left(\frac{d\rho}{dz}\right)\lambda$$

$J_N = \frac{1}{4}\,\rho\,\bar{v}$

From above : $J_+ = \frac{1}{4}\,\rho\bar{v}(z_0 + \lambda) = \frac{1}{4}\bar{v}\left[\rho_0 + \left(\frac{d\rho}{dz}\right)\lambda\right]$

From below : $J_- = \frac{1}{4}\,\rho\bar{v}(z_0 - \lambda) = \frac{1}{4}\bar{v}\left[\rho_0 - \left(\frac{d\rho}{dz}\right)\lambda\right]$

Net flux : $J - J_+ = -\frac{1}{2}\bar{v}\lambda\left(\frac{d\rho}{dz}\right)$

Fick's law : $= - D \left(\dfrac{d\rho}{dz} \right); D = \frac{1}{2} \overline{v} \lambda \ (\frac{2}{3})$

Slightly more elaborate derivation which averages more carefully gives :

$$D = \frac{1}{3} \overline{v} \lambda$$

- λ decreases with increasing P, D decreases with increasing P
- λ increases with decreasing d, small molecules diffuse faster D decreases with increasing ρ
- D proportional to $T^{3/2}$, diffusion increases with T

Thermal conduction

- Due to hotter atoms jumping into colder region & vise versa

Flux of energy q_z in the z direction due to the temperature gradient is given by :

$$q_z = -\kappa \, dT/dz$$

κ = thermal conductivity ($J \, m^{-1} \, s^{-1} \, K^{-1}$)

$q_z = J \, m^{-2} \, s^{-1}$

$dT/dz = K \, m^{-1}$

$$\kappa = \tfrac{1}{3} \rho \bar{v} \, C_v \, \lambda$$

🧪 <u>Viscosity</u>

- a measure of the resistance that a fluid offers to an applied shearing force.

Viscosity η is defined by the following equation :

$$F = - \eta \, dv_y/dz$$

F = force per unit area (kg m s^{-2}/m^2)
(momentum $m^{-2} s^{-1}$)

$\eta = $ kg m^{-1} s^{-1} (Pa s)

$dv_y/dz = $ m s^{-1}/m

$$F_{net} = -\tfrac{1}{3}\rho \bar{v} \, m\lambda \left(\frac{dv_y}{dz} \right)$$

$$= \eta = \frac{5\pi}{16} \left(\frac{kT}{\pi m} \right)^{\frac{1}{2}} \frac{m}{\pi d^2}$$

Transport Properties	Type of flux	Unit
Diffusion	Matter	Molekul $m^{-2}s^{-1}$
Thermal conductivity	Thermal energy or heat	J $m^{-2}s^{-1}$
Viscosity	Momentum	Momentum $m^{-2}s^{-1}$