Chap. 8. Molecules in motion

Kinetic theory (model) of gas: kinetic energy and collision

Assumptions: negligible size, elastic collision (momentum conservation), non-stop motion

$$\mathbf{v} = v_x \mathbf{e_x} + v_y \mathbf{e_y} + v_z \mathbf{e_z}$$

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

$$\text{K.E.} = \frac{m}{2} v^2 = \frac{m}{2}(v_x^2 + v_y^2 + v_z^2)$$

Different molecules have different velocities

$$c = \langle v^2 \rangle^{1/2}$$

$$\langle \text{K.E.} \rangle = \frac{m}{2} c^2$$

Derivation of $pV = \frac{nMc^2}{3}$, $M = mN_A$

Pressure is caused by molecules hitting the wall and being reflected back

Assume the x component of velocity is v_x

$$\text{Number of particles colliding the wall during } \Delta t = \Delta t|v_x|A\frac{nN_A}{2V}$$

$$\text{Change of momentum} = 2m|v_x|$$

$$p = \text{Force per unit area} = \frac{\Delta t|v_x|A\frac{nN_A}{2V}\cdot 2m|v_x|}{\Delta t A} = \frac{mv_x^2 nN_A}{V}$$

Each molecule has different velocity $\longrightarrow$ $p = \frac{m\langle v_x^2\rangle nN_A}{V} = \frac{nc^2 mN_A}{3V}$

$$\langle v_x^2\rangle = \frac{1}{3}\langle v^2\rangle = \frac{c^2}{3}$$

$$c = \left(\frac{3RT}{M}\right)^{1/2}$$

515 m s^{-1} for N_2

Root-mean-square velocity based on Maxwell distribution

Probability for the molecule to have speed v

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

$$\bar{c} = \int_0^\infty dv \; v f_M(v) = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} \int_0^\infty dv \; v^3 e^{-Mv^2/2RT} = \left(\frac{8RT}{\pi M}\right)^{1/2}$$

slightly smaller than $c = \left(\frac{3RT}{M}\right)^{1/2}$

Derivation of Maxwell distribution

For a particle with $\mathbf{v} = v_x \mathbf{e_x} + v_y \mathbf{e_y} + v_z \mathbf{e_z}$ $\Rightarrow$ $E = \frac{m}{2}\left(v_x^2 + v_y^2 + v_z^2\right)$

$$f_B(v_x, v_y, v_z) = \left(\frac{m}{2k_B T}\right)^{3/2} e^{-m(v_x^2+v_y^2+v_z^2)/(2k_B T)}$$

$$1 = \int_{-\infty}^\infty dv_x \int_{-\infty}^\infty dv_y \int_{-\infty}^\infty dv_z f_B = 4\pi \int_0^\infty dv \; v^2 f_B = \int_0^\infty dv f_M$$

$$f_M(v) = 4\pi v^2 f_B(v_x, v_y, v_z), \;\; v^2 = v_x^2 + v_y^2 + v_z^2$$

Most probable speed c^*

$$\left.\frac{\partial f_M}{\partial v}\right|_{v=c^*} = 0$$

$$\frac{\partial f_M}{\partial v} = \left(\frac{m}{2k_BT}\right)^{3/2} 4\pi \left(2v - \frac{mv^3}{k_BT}\right) e^{-mv^2/2k_BT} \longrightarrow c^* = \left(\frac{2RT}{M}\right)^{1/2}$$

Consider a system of two particles (in one dimension)

$$\text{K.E.} = \frac{1}{2}\left(m_1 v_1^2 + m_2 v_2^2\right)$$

$$v_{cm} = \frac{m_1 v_1 + m_2 v_2}{m_1 + m_2}$$

$$v_{rel} = v_1 - v_2$$

$$\longrightarrow$$

$$v_1 = v_{cm} + \frac{m_2}{m_1 + m_2} v_{rel}$$

$$v_2 = v_{cm} - \frac{m_1}{m_1 + m_2} v_{rel}$$

$$K.E. = \frac{1}{2}\left\{(m_1 + m_2)v_{cm}^2 + \frac{m_1 m_2}{m_1 + m_2} v_{rel}^2\right\}$$

$$\longrightarrow \quad \bar{c}_{rel} = \left(\frac{8k_BT}{\pi\mu}\right)^{1/2}, \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

Relative motion of two particles is equivalent to the motion of one particle with reduced mass μ.

Collision frequency and mean free path

Collision cross section: $\sigma = \pi d^2$

Diameter of a molecule

The volume of a collision tube: $\sigma \bar{c}_{rel} \Delta t$

# of particles within the collision tube: $\sigma \bar{c}_{rel} \Delta t \frac{N}{V}$

Collision frequency: $$z = \frac{\#}{\Delta t} = \sigma \bar{c}_{rel} \frac{N}{V}$$

Mean free path: $$\lambda = \frac{\bar{c}}{z} = \frac{\bar{c}}{\sigma \bar{c}_{rel}} \frac{k_B T}{p} = \frac{k_B T}{\sqrt{2}\sigma p} = \frac{v_m}{\sqrt{2}\sigma}$$

$$v_m = \frac{k_B T}{p} = \frac{V}{N_A}$$

Collision flux and effusion rate

$$\#\text{ of collisions} = \frac{N}{V} A\Delta t \int_0^\infty v_x f(v_x) dv_x$$

$$f(v_x) = \sqrt{\frac{m}{2\pi k_B T}} e^{-mv_x^2/2k_B T}$$

$$Z_w = \frac{\#\text{ of collisions}}{A\Delta t} = \frac{N}{V}\sqrt{\frac{k_B T}{2\pi m}} = \frac{p}{k_B T}\sqrt{\frac{k_B T}{2\pi m}} = \frac{p}{\sqrt{2\pi m k_B T}}$$

For 1 bar and T=300 K, $Z_w \approx 3 \times 10^{23} \text{cm}^{-2}\text{s}^{-1}$

Effusion - process where individual molecules flow through a hole without collisions between molecules

$$\text{Rate of effusion through a hole of area } A_0 = Z_w A_0 = \frac{pA_0 N_A}{\sqrt{2\pi M R T}}$$

Knudsen method : Determination of the vapour pressure of liquids and solids by measuring the rate of loss of mass from a cavity with a hole

Transport properties

Flux: Quantity of certain property passing through a unit area (perpendicular to the direction of flow) per unit time.

Examples with the convention that z : direction of flow

Diffusion coefficient $\mathrm{m^2 s^{-1}}$

Matter flux: $\mathrm{m^{-2}s^{-1}}$

$$J(\text{matter}) = -D\frac{d\mathcal{N}}{dz} \leftarrow \mathrm{m^{-4}}$$

Thermal conductivity $\mathrm{JK^{-1}m^{-1}s^{-1}}$

Energy flux: $\mathrm{Jm^{-2}s^{-1}}$

$$J(\text{energy}) = -\kappa\frac{dT}{dz} \leftarrow \mathrm{Km^{-1}}$$

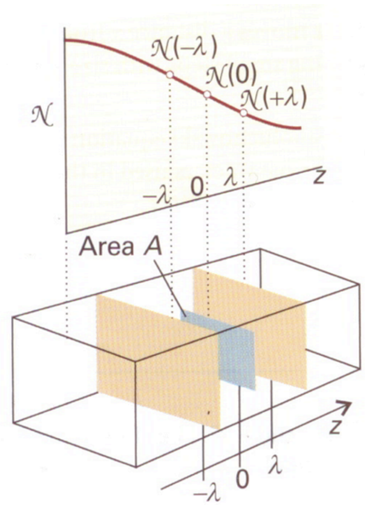
Viscosity $\mathrm{kgm^{-1}s^{-1}}$

Momentum flux: $\mathrm{kgm^{-1}s^{-2}}$

$$J(\text{x-comp momentum}) = -\eta\frac{dv_x}{dz} \leftarrow \mathrm{s^{-1}}$$

Special unit of viscosity: $1 \text{ poise (P)} = 10^{-1}\mathrm{kg\ m^{-1}\ s^{-1}}$

Derivation of $D = \frac{1}{3}\lambda\bar{c}$



number of particles/volume

$$\mathcal{N}(\pm\lambda) = \mathcal{N}(0) \pm \lambda \left(\frac{d\mathcal{N}}{dz}\right)_0$$

$$J(L \to R) = \frac{\frac{1}{4}A_0\mathcal{N}(-\lambda)\bar{c}\Delta t}{A_0\Delta t} = \frac{1}{4}\mathcal{N}(-\lambda)\bar{c}$$

$$J(R \to L) = -\frac{1}{4}\mathcal{N}(\lambda)\bar{c}$$

$$J = \frac{1}{4}\bar{c}\{\mathcal{N}(-\lambda) - \mathcal{N}(\lambda)\} = -\frac{1}{2}\bar{c}\lambda\left(\frac{d\mathcal{N}}{dz}\right)_0 \quad \longrightarrow \quad D = \frac{1}{2}\bar{c}\lambda$$

Consideration of geometric factor $\longrightarrow$ $D = \frac{1}{3}\bar{c}\lambda$

$$J(L \to R) = \frac{2\pi\int_{\pi/2}^{\pi} d\theta \sin\theta A_0 |\cos\theta| \bar{c}\Delta t \mathcal{N}(\lambda\cos\theta)}{4\pi A_0 \Delta t} = -\frac{\bar{c}}{2}\int_{-1}^{0} d\cos\theta \cos\theta \mathcal{N}(\lambda\cos\theta)$$

$$J(R \to L) = \frac{-2\pi\int_{0}^{\pi/2} d\theta \sin\theta A_0 \cos\theta \bar{c}\Delta t \mathcal{N}(\lambda\cos\theta)}{4\pi A_0 \Delta t} = -\frac{\bar{c}}{2}\int_{0}^{1} d\cos\theta \cos\theta \mathcal{N}(\lambda\cos\theta)$$

$$J = J(L \to R) + J(R \to L) = -\frac{\bar{c}}{2}\int_{-1}^{1} d\cos\theta \frac{d\mathcal{N}}{dz}\cos^2\theta\lambda = -\frac{\bar{c}}{3}\lambda\left(\frac{d\mathcal{N}}{dz}\right)_0$$

$$D = \frac{1}{3}\bar{c}\lambda = \frac{1}{3}\frac{k_B T}{\sqrt{2}\sigma p}\left(\frac{8k_B T}{\pi m}\right)^{1/2}$$

$$p \downarrow, T \uparrow, \sigma(\text{size}) \downarrow \Rightarrow \ D \uparrow$$

Energy flux

Density of (Kinetic) Energy

$$J(\text{energy}) = -\frac{1}{3}\bar{c}\lambda\frac{d}{dz}\mathcal{E} = -\frac{1}{3}\bar{c}\lambda\frac{dT}{dz}\frac{d\mathcal{E}}{dT} = -\frac{1}{3}\bar{c}\lambda\frac{n}{V}C_{V.m}\frac{dT}{dz}$$

$$\frac{d\mathcal{E}}{dT} = \frac{n}{V}\frac{d}{dT}(N_A\mathcal{E}_m) = \frac{n}{V}C_{V,m}$$

$$\kappa = \frac{1}{3}\bar{c}\lambda\frac{n}{V}C_{V,m} = \frac{1}{3}\frac{k_B T}{\sqrt{2}\sigma p}\left(\frac{8k_B T}{\pi m}\right)^{1/2}C_{V,m}\frac{n}{V} = \frac{1}{3}\frac{1}{\sqrt{2}\sigma}\left(\frac{8k_B T}{\pi m}\right)^{1/2}\frac{C_{V,m}}{N_A}$$

independent of pressure

$$T \uparrow, \sigma(\text{size}) \downarrow, C_{V,m} \uparrow \Rightarrow \ \kappa \uparrow$$

Momentum flux

$$J(\text{x-comp. of momentum}) = -\frac{1}{3}\bar{c}\lambda\frac{d}{dz}\left(mv_x\mathcal{N}\right) \approx -\frac{1}{3}\bar{c}\lambda\mathcal{N}m\frac{dv_x}{dz}$$

$$\eta = \frac{1}{3}M\lambda\bar{c}\frac{n}{V} = \frac{1}{3}M\frac{k_BT}{\sqrt{2}\sigma p}\left(\frac{8k_BT}{\pi m}\right)^{1/2}\frac{n}{V} = \frac{1}{3}\frac{M}{\sqrt{2}\sigma N_A}\left(\frac{8k_BT}{\pi m}\right)^{1/2}$$

independent of pressure $T\uparrow, \sigma(\text{size})\downarrow, M\uparrow \Rightarrow \eta\uparrow$

Mobility of ions and conductivity

$$s = uE$$

← **Electric Field**

Speed **mobility**

$$J(\text{ions}) = \frac{sA\Delta t\nu cN_A}{A\Delta t} = s\nu cN_A \rightarrow J(\text{charge}) = zeJ(\text{ion}) = zs\nu ceN_A = zs\nu cF$$

$$I = JA = G\Delta\phi = \frac{\kappa A}{l}\Delta\phi = \kappa AE$$

Conductance **Conductivity**

$$\kappa = zu\nu cF$$

Molar conductivity $\Lambda_m = zu\nu F$

Concentration gradient and thermodynamic force

Non-expansion work per mole for moving substances for a distance dx.

$$dw_e = d\mu = \left(\frac{\partial \mu}{\partial x}\right)_{p,T} dx$$

Thermodynamic force

$$\mathcal{F} = -\left(\frac{\partial \mu}{\partial x}\right)_{p,T}$$

For a solution with

$$\mu(x) = \mu^{\ominus} + RT\ln\{a(x)\}$$

$$\mathcal{F} = -RT\left(\frac{\partial \ln\{a(x)\}}{\partial x}\right)_{p,T} = -\frac{RT}{a(x)}\left(\frac{\partial a(x)}{\partial x}\right)_{p,T}$$

Relative change of activity determines the gradient of chemical potential.

For an ideal solution

$$\mathcal{F}_{ideal} = -\frac{RT}{c(x)}\left(\frac{\partial c(x)}{\partial x}\right)_{p,T}$$

Mobility in solution

When particles move with steady drift speed in solution in the presence of concentration gradient,

Thermodynamic force → $\mathcal{F} = N_A f s$ ← Drift speed

Friction coefficient

Flux is proportional to drift speed $J \propto s$

Fick's first law of diffusion: $$J = -D\frac{dc}{dx}$$

Relation of drift speed with Diffusion coefficient $$s = \frac{J}{c} = -\frac{D}{c}\frac{dc}{dx} = \frac{D\mathcal{F}}{RT}$$

Stokes-Einstein equation: $$D = \frac{RT}{N_A f} = \frac{k_B T}{f}$$

$$f = 6\pi\eta a$$ Stokes formula for friction

Mobility of ion in solution

Thermodynamic force is equal to the electric force applied to charges due to electric field

$$\mathcal{F} = N_A ezE$$

$$\rightarrow \quad s = \frac{DN_A ezE}{RT}$$

For an ion with mobility $u = \frac{s}{E}$ $\rightarrow$ $u = \frac{zFD}{RT}$

Typical values of mobility and diffusion coefficients $u \approx 5 \times 10^{-8}\ \mathrm{m^2 s^{-1} V^{-1}}$ $\quad D \approx 1 \times 10^{-9}\ \mathrm{m^2 s^{-1}}$

Limiting conductivity of unit ion $\lambda = zuF = \frac{z^2 DF^2}{RT}$

Nernst-Einstein equation: $\Lambda_m^0 = (\nu_+ z_+^2 D_+ + \nu_- z_-^2 D_-)\frac{F^2}{RT}$

Diffusion Equation

One dimensional continuity equation: $$\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x}$$

$$A\Delta x\frac{\Delta c}{\Delta t} = J(x)A - J(x+\Delta x)A = -A\frac{\partial J}{\partial x}\Delta x$$

From the definition of diffusion constant: $$J = -D\frac{\partial c}{\partial x}$$

$$\rightarrow \quad \frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \quad \rightarrow \quad c(x,t) = \frac{n_0}{A\sqrt{\pi D t}}e^{-\frac{x^2}{4Dt}}$$

In the presence of convection, $$J = -D\frac{\partial c}{\partial x} + cv$$

Convection velocity

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x}$$