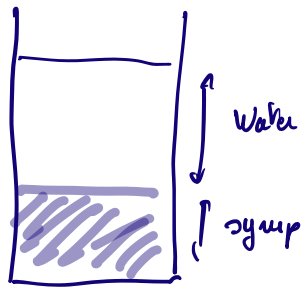
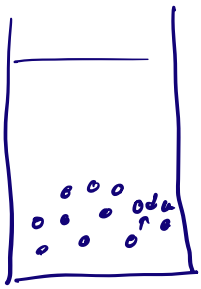
TD n°1 From Brownian motion to heat & mass transport equations

1) Syrup in a glass of water



$\hookrightarrow$



→ equilibrium configuration!

model as ideal gas

$\Rightarrow P_{os} V = N k_B T$

P_{os}: osmotic pressure; N: number of particles

$P_{os} = n k_B T$

n: particles / volume

$P_{os}(z+dz)\,S + n \frac{4}{3}\pi a^3 \Delta\rho g\, S\,dz = P_{os}(z)\,S$

$\Rightarrow \frac{dP_{os}}{dz} = -\frac{4}{3}\pi a^3 \Delta\rho g \frac{P_{os}}{k_B T}$

$\Rightarrow P_{os} = P_0 \exp(-z/\ell)$

$$\boxed{\ell = \frac{k_B T}{\frac{4}{3}\pi a^3 \Delta\rho g}}$$

$\Rightarrow n(z) = n_0 \exp(-z/\ell)$

$\int_0^\infty n(z)\,dz = n_0 \ell = n_{initial} L_{initial}$.

$n_0 = n_{init} \frac{L_{init}}{\ell}$

Numerical estimation:

$k_B T = 4.10^{-21} J$ $\quad \Delta\rho \simeq 600\ kg/m^3$ $\quad a \sim 10^{-9} m$

$\ell \simeq \frac{4.10^{-21}}{\frac{4}{3}\pi . 10^{-27} . 600 . 10} \sim 100\ m$ $\Rightarrow$ far from equilibrium

Jean Perrin ~ 1910 ⇒ atomistic theories beat N_a unknown
↳ size of atoms unknown

⇒ measure of d, knows a

⇒ measure k_B

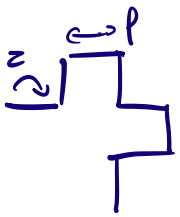
R known from $PV = nRT$

⇒ $N_a = \frac{R}{k_B}$

→ 1912 Crystal structures by X-ray diffraction

How long does it take to diffuse?

Diffusion viewed as random walk



very simplified model

$x = l \sum_{\pm 1}^{N} \delta_i$ ⇒ $\langle x \rangle = 0$

$x^2 = l^2 \left(\sum^N \delta_i^2 + \sum^{i \neq j} \delta_i \delta_j \right)$

↳ $\langle \; \rangle = 0$ δ_i non correlated to δ_j

⇒ $\langle x^2 \rangle = N l^2$

$t = N\tau$ ⇒ $\langle x^2 \rangle = \frac{l^2}{\tau} t$

↳ diffusion coefficient

dissipation for each jump:

$\underbrace{6\pi \eta a U l}$ ~ $k_B T$

↳ viscous drag

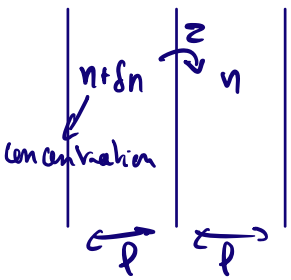
$U \sim \frac{l}{\tau}$

⇒ $\frac{l^2}{\tau} = D = \frac{k_B T}{6\pi \eta a}$

Numerical estimate: $D \simeq 2 \cdot 10^{-10} \, m^2/s$

↳ homogeneization over 10cm! $\frac{(0.1)^2}{2 \cdot 10^{-10}} = 5 \cdot 10^7 s \sim 1,5$ year!

Fick's law

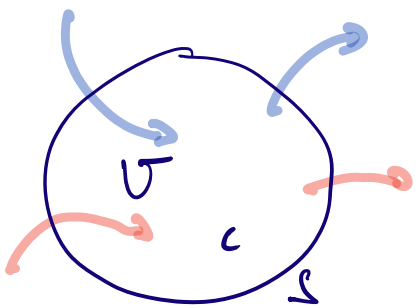


$$\delta j z = \delta n \cdot l \Rightarrow j = \frac{\delta n}{z} l$$

$$\frac{\delta n}{l} \hookrightarrow -\frac{\partial n}{\partial x} \Rightarrow j = -\frac{l^2}{z}\frac{\partial n}{\partial x} = -D\frac{\partial n}{\partial x}$$

↳ generalization $\underline{j} = -D\nabla n$

2) Adding convection



convective flux $\underline{j_c} = c\,\underline{u}$

diffusive flux $\underline{j_D} = -D\nabla c$

fixed volume V

$$n = \iiint_V c \, dv$$

↳ evolution in time: $\frac{dn}{dt} = \iiint_V \frac{\partial c}{\partial t} dv = -\oint_S (\underline{j_c} + \underline{j_D}) \cdot \underline{n} \, ds$

divergence theorem: $\oint_S \underline{A} \cdot \underline{n} \, ds = \iiint_V \nabla \cdot \underline{A} \, dv$

$$\Rightarrow \iiint_V \frac{\partial c}{\partial t} dv = -\iiint \nabla \cdot (\underline{j_c} + \underline{j_D}) \, dv$$

V arbitrary $\Rightarrow$ $\frac{\partial c}{\partial t} = -\nabla \cdot (\underline{j_c} + \underline{j_D})$

$$\frac{\partial c}{\partial t} = -\nabla \cdot (c\underline{u}) + \nabla \cdot (D \nabla c)$$

$$\frac{\partial c}{\partial t} = -c \cdot \cancel{\nabla \cdot \underline{u}} - \underline{u} \cdot \nabla c + D \Delta c + \cancel{\nabla D \cdot \nabla c}$$

incompressible flow; assume D uniform

$$\Rightarrow \boxed{\frac{\partial c}{\partial t} + \underline{u} \cdot \nabla c = D \Delta c}$$