Transport – Lecture 3
molecular version

Suppose I take N steps, of length δ, one step per τ time.

How far will I get after $N\tau$?

N total steps

$n_\ell + n_r = N$

$n_\ell - n_r = n$ distance $n\delta = x$

$$P(n) = \frac{1}{2^N}\binom{N}{n_\ell} = \frac{1}{2^N}\frac{N!}{\left(\frac{N+n}{2}\right)!\left(\frac{N-n}{2}\right)!}$$

Example $N = 3$

$N! \approx (2\pi N)^{1/2} N^N e^{-N}$ stirling's approx.

$\ln N! \approx N \ln N - N$

$$P(n) = \left(\frac{2}{\pi N}\right)^{1/2} e^{-n^2/2N}$$

$n = \frac{x}{\delta}$ $N = \frac{t}{\tau}$

$$P(x,t) = \left(\frac{2\tau}{\pi t}\right)^{1/2} e^{-x^2\tau/2\delta^2 t}$$

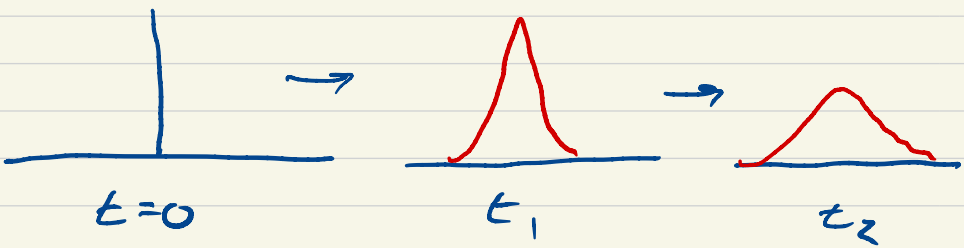
$$\langle x^2 \rangle = \frac{\delta^2}{\tau} t \qquad \boxed{D = \frac{\delta^2}{2\tau}}$$

Einstein-Smoluchowski eq

$$\rightarrow \quad P(x,t) = \frac{1}{2\sqrt{\pi D t}} e^{-x^2/4Dt}$$

Gaussian, $\langle x \rangle = 0$ $\langle x^2 \rangle = 2Dt$

Spreads in $\sqrt{t}$



Can be thought of as comparing one walker many times, or many identical walkers @ once.

Diffusion can be thought of as a random walk of steps δ in time τ

Ideal gas $\delta \sim \lambda$

$\tau \sim \lambda / \langle v \rangle$

$D = \frac{1}{2} \lambda \langle v \rangle$ in 1-D

$D = \frac{1}{3} \lambda \langle v \rangle$ in 3-D

eg N_2, 298 K, $\langle v \rangle \sim 475$ m/s

$\lambda \sim 68$ nm

$D \sim 1 \times 10^{-5}$ m^2/s

In 3-D, becomes $\langle r^2 \rangle = 6Dt$

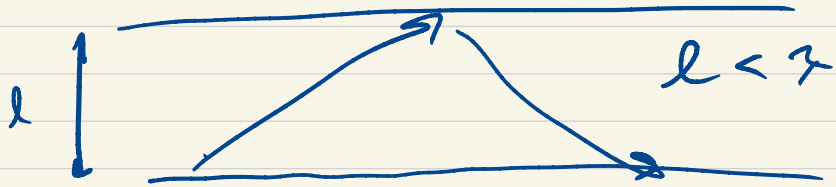
ex N_2, 298 K, $D = 1.1 \times 10^{-5}$ m^2/s

t	$\langle r^2 \rangle^{1/2}$
1 s	8×10^{-3} m
100 s	8×10^{-2}
10^5 s	0.8

Long tails though

Very μscopic view of diffusion

Knudsen diffusion in a pore

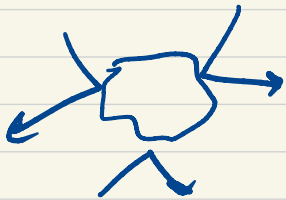


$$D = \frac{1}{2} L \langle v \rangle$$

Brownian motion

Can see grains of dust hopping around on surface of a liquid. Why?

Einstein reasoned that any object that is thermally agitated, eg by being "kicked" by molecules, would appear to diffuse



$$D \sim \underbrace{k_B T}_{\text{"kick"}} \cdot \underbrace{\mu}_{\text{"mobility"}} \qquad \mu = \left(\frac{\text{dist}}{\text{momentum}}\right)$$

If grains are spherical + uniform

$$\mu = \frac{1}{6\pi r} \cdot \frac{1}{\eta} \qquad \eta : \text{viscosity}$$

$$\boxed{D = \frac{k_B T}{6\pi \eta r}}$$

Stokes-Einstein eq

This model correctly predicts motion of Brownian particles

- final proof of kinetic theory
- route to measure N_{av}

$$D = \frac{RT}{6\pi\eta \cdot r} \cdot \left(\frac{1}{N_{AV}}\right)$$

One of four contributions in Einstein's Annus Mirablis (1905)

Stick ~~Slip~~ boundary

$$D = \frac{k_B T}{6\pi\eta r}$$

~~Stick~~ slip boundary

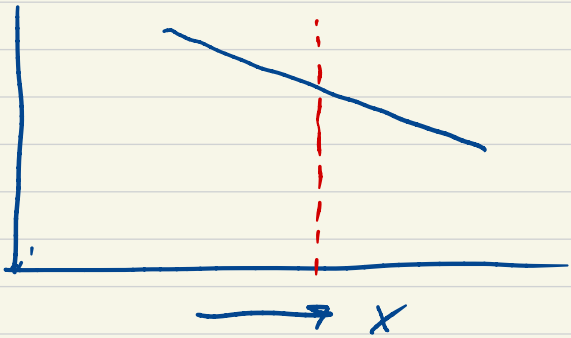
$$\frac{k_B T}{4\pi\eta r}$$

appropriate to things of size comparable to liquid

continuum approach

diffusion

$\frac{N}{V} = c$



suppose concentration changes w/ position.

Variation will be linear over short distances, say $\sim \lambda$.

Imagine a dividing wall, do balance on molecules moving from left to right & vice versa.

$$Z_{w\,\text{right}} = \frac{1}{4}\langle v\rangle\left(c_0 - \lambda\left(\frac{dc}{dx}\right)\right)$$

$$Z_{w\,\text{left}} = \frac{1}{4}\langle v\rangle\left(c_0 + \lambda\left(\frac{dc}{dx}\right)\right)$$

$$J = Z_w^r - Z_w^l = -\frac{1}{2}\lambda\langle v\rangle\frac{dc}{dx}$$

$\frac{\text{net \#}}{\text{time}\cdot\text{area}}$

Fick's first law

Net flux is linear in concentration gradient.

Call that proportionality the diffusion constant.

$$D = \frac{1}{2}\lambda\langle v\rangle$$

dist · velocity
$\propto T^{1/2}$

In 3-D, becomes

$$\vec{J} = -D\nabla c$$

$$\boxed{D = \frac{1}{3}\lambda\langle v\rangle}$$

How might we know? Fick's second law

$$\frac{dc(\vec{r},t)}{dt} = -\nabla \cdot \vec{J}$$

conc change

change in fluxes in - out

general continuity with no advection or accumulation

$$\boxed{\frac{dc}{dt} = D \nabla^2 c}$$

In 1-D $\Rightarrow$ $\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$

Ex in 1-D

δ function

$$c(x, t=0) = \begin{cases} c_0, & x=0 \\ 0, & x=0 \end{cases}$$

"label" all molecules an origin

Separate variables : $c(x,t) = X(x)\,T(t)$

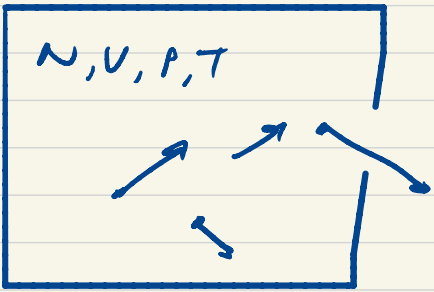
$$X(x) \frac{dT}{dt} = T(t) \frac{d^2X}{dx} \cdot D$$

$$\frac{1}{T} \frac{dT}{dt} = \frac{D}{X} \frac{d^2X}{dx^2} = \text{CONSTANT}$$

$$\rightarrow \quad c(x,t) = \frac{1}{2\sqrt{\pi D t}} e^{-x^2/4Dt}$$

Right back to where we were!

effusion



vacuum

mass balance on system

$$\frac{dN}{dt} = \cancel{in}^{\,0} - out + \cancel{generation}$$

$$= -out = -J_w \cdot A$$

If hole is small so that inside box stays in quasi-equilibrium,

$$\frac{dN}{dt} = -A \cdot \left(\frac{1}{4}\right)\left(\frac{N}{V}\right)\langle v \rangle$$

$$\frac{dN}{N} = -\underbrace{\left(\frac{A}{V}\right)\left(\frac{1}{4}\right)\langle v \rangle}_{1/\tau} dt$$

characteristic time

Integrate

$$\int_{N_0}^{N} \frac{dN}{N} = -\frac{1}{\tau}\int_0^t dt$$

$$N = N_0 e^{-t/\tau}$$ N decays exponentially

$$P = N\left(\frac{RT}{V}\right) \rightarrow P \propto N$$

$$P = P_0 e^{-t/\tau}$$ Graham's law of effusion

$$\tau \propto \frac{1}{\langle v \rangle} \propto \frac{1}{m^{1/2}}$$

A way to get at relative MW of gases, by measuring relative τ.

$$\frac{\tau_1}{\tau_2} \propto \left(\frac{MW_2}{MW_1}\right)^{1/2}$$

Transport

Consequences of kinetic theory for moving stuff around?

- energy/heat : thermal conductivity
- momentum : viscosity
- matter : diffusion

$$\kappa = \frac{1}{3} \langle v \rangle \lambda \cdot c_v$$

$$\eta = \frac{1}{3} \langle v \rangle \lambda \cdot m$$

laminar