Transport

Consequences of kinetic theory for moving stuff around?

- matter : diffusion Transport 2

* $D = \frac{1}{3}\langle v \rangle \lambda$ diffusion coefficient

speed · length

- energy/heat : thermal conductivity

$\kappa = \frac{1}{3}\langle v \rangle \lambda \cdot C_v$ heat transfer coef

speed · length · heat capacity

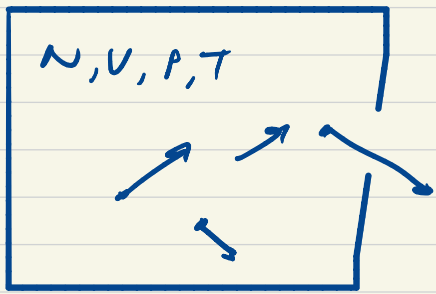
- momentum : viscosity Transport 1

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

speed · length · mass

Take a look at gas kinetic theory implications for the last.

effusion



vacuum

$$J_w = \frac{1}{4}\left(\frac{N}{V}\right)\cdot\langle v\rangle$$

$$\langle v\rangle = \left(\frac{k_B T}{2\pi m}\right)^{1/2}$$

mass balance on system

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

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

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

$$\tau = 4\left(\frac{V}{A}\right)\frac{1}{\langle v\rangle} \propto m^{1/2}$$ units of 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

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

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

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

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

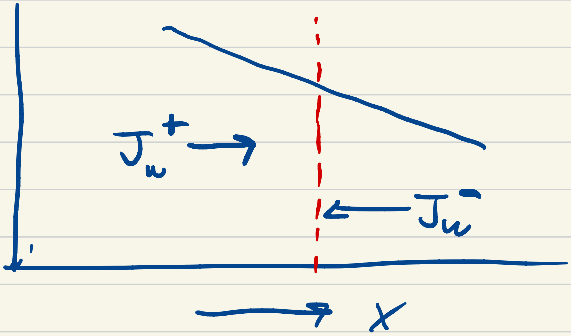
$$\frac{\tau_1}{\tau_2} \propto \left(\frac{MW_1}{MW_2}\right)^{1/2}$$

Larger τ is, slower the decay

diffusion

consider conc variations over small distances

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



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.

$$J_w^+ = \frac{1}{4}\langle v\rangle\left(\rho_0 - \lambda\left(\frac{d\rho}{dx}\right)\right)$$

$$J_w^- = \frac{1}{4}\langle v\rangle\left(\rho_0 + \lambda\left(\frac{d\rho}{dx}\right)\right)$$

$$J = J_w^+ - J_w^- = -\frac{1}{2}\lambda\langle v\rangle\frac{d\rho}{dx}$$

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

Fick's first law

Net flux is linear in concentration gradient.

Call that proportionality the diffusion constant.

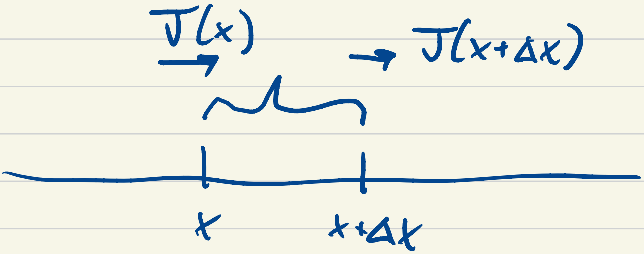
$$D = \frac{1}{2} \lambda \langle v \rangle$$ dist · velocity $\propto T^{1/2}$

In 3-D, becomes

$$\vec{J} = -D \nabla c \qquad \boxed{D = \frac{1}{3} \lambda \langle v \rangle}$$

How does density evolve with time?

consider control volume Δx



$$\frac{d}{dt}\left(\rho(x)\Delta x\right) = \text{in} - \text{out} + \cancelto{0}{\text{generation}}$$

$$= J(x) - J(x+\Delta x)$$

$$= J(x) - \left[J(x) + \frac{dJ}{dx}\Delta x\right]$$

$$= -\frac{dJ}{dx}\Delta x$$

$$\frac{d\rho}{dt} = -\frac{dJ}{dx} = D \cdot \frac{d^2\rho}{dx^2}$$

$$\boxed{\frac{d\rho}{dt} = -\nabla \cdot \vec{J} = D\nabla^2\rho}$$

Fick's second law

Ex in 1-D   δ function

$$\rho(x, t=0) = \begin{cases} \rho_0, & x=0 \\ 0, & x=0 \end{cases}$$

"label" all molecules on origin

In 1-D ⇒ $$\frac{\partial \rho}{\partial t} = D \frac{\partial^2 \rho}{\partial x^2}$$

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

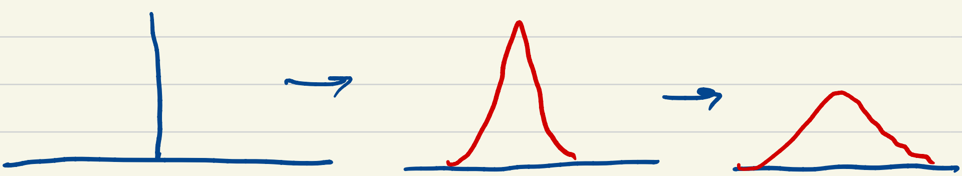
$$X(x) \frac{\partial T}{\partial t} = T(t) \frac{\partial^2 X}{\partial x^2} \cdot D$$

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

⇒ $$\boxed{\rho(x,t) = \frac{1}{2\sqrt{\pi D t}} e^{-x^2/4Dt}}$$

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

Spreads in $\sqrt{t}$



$t=0$ t_1 t_2

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

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

$\lambda \sim 68$ nm

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

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

Molecular perspective on D

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

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

N total steps

$N_l + N_r = N$

$N_l - N_r = n$ distance $n\delta = x$

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

Example $N = 3$

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

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

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

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

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

Compare to

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

$$\boxed{D = \frac{\delta^2}{2\tau}}$$

Einstein-Smoluchowski eq

Diffusion is a random walk of step size δ and step time τ!

Ideal gas $\quad \delta \sim \lambda$

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

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

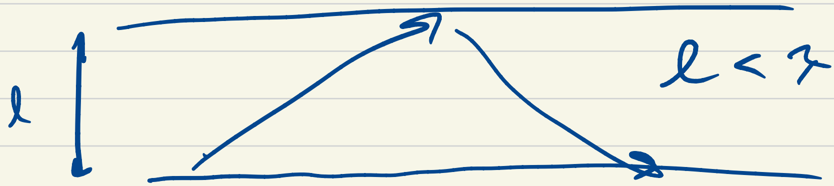
($1/3$ in 3D)

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

What if step size is controlled by wall?

$\lambda > L$

Knudsen diffusion in a pore



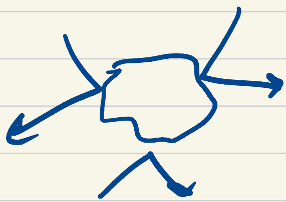
$D = \frac{1}{2} L \langle v \rangle$

Diffusion in Liquids

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



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

If grains are spherical + uniform

$\mu = \frac{1}{6\pi r} \cdot \frac{1}{\eta}$ η : 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

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

Slip ~~Stick~~ boundary

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

appropriate to things of size comparable to liquid

Note Bene

1-D Diffusion Solution

$$\frac{\partial \rho}{\partial t} = D\frac{\partial^2 \rho}{\partial x^2} \qquad \rho(x,t=0) = \begin{cases} \rho_0, & x=0 \\ 0, & x=0 \end{cases}$$

$$\int \rho(x,t)\,dx = \rho_0$$

T-part

$$\frac{1}{DT}\frac{dT}{dt} = \frac{1}{X}\frac{d^2X}{dx^2} = \text{CONSTANT} = -\lambda$$

$$\frac{1}{T}\frac{dT}{dt} = -\lambda D \Rightarrow T = \rho' e^{-\lambda D t}$$

X-part Fourier expansion

$$\frac{1}{X}\frac{d^2X}{dx^2} = -\lambda \qquad X = \int c_\alpha \sin\alpha x \, d\alpha$$

$$X' =$$

$$\frac{d^2X}{dx^2} + \lambda X = 0 \qquad X'' =$$

$$-\alpha^2 \sin\alpha x + \lambda \sin\alpha x = 0$$

$$\alpha = \sqrt{\lambda}$$