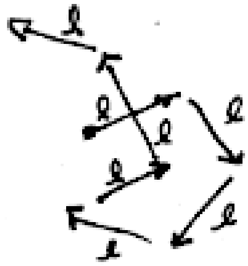


$$\langle \vec{d} \rangle = \frac{\sum d_i}{\#\ \text{paths}} = 0$$

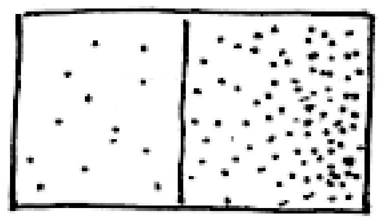
$$\langle d^2 \rangle = N l^2$$

$$\sqrt{\langle d^2 \rangle} = \sqrt{N}\, l$$

Diffusion Coeff & Fick's 1st Law

$$\text{Flux} = J_x = -D\left(\frac{dc}{dx}\right)$$

↳ Net solute passing per unit area per unit time



x →

← Higher probability

Lower Probability →

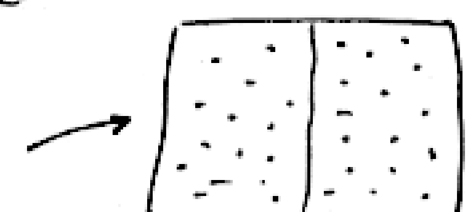
Intuitive!

Similarities to Le Chatelier... (can you see them?)

D = diffusion coefficient

At equilibrium,

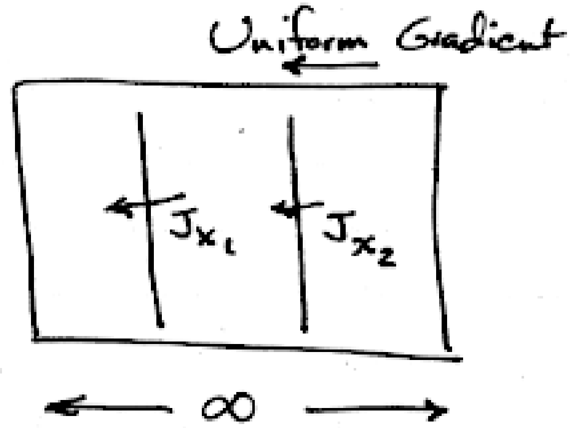
$\frac{dc}{dx} = 0$ $\quad J_x = 0$



Fick's 2ND Law

$$\left(\frac{dc}{dt}\right)_x = D\left(\frac{d^2c}{dx^2}\right)_t$$

↑ how conc changes with time

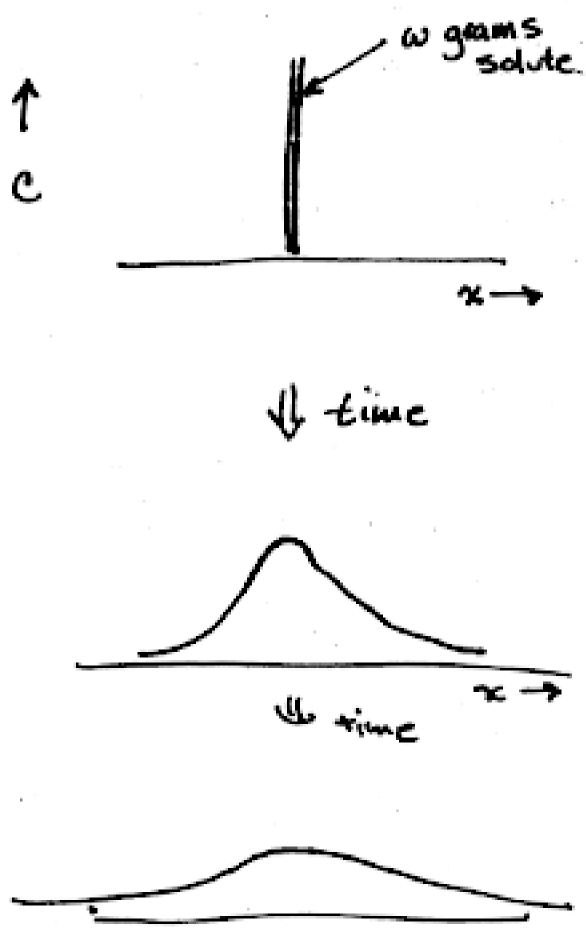


If $\frac{dc}{dx}$ is same at all x, then $J_{x_1} = J_{x_2}$

$\frac{d^2c}{dx^2} = 0$

∴ Net in = Net out

∴ No change in conc (for now)



$$\underset{g/cm^3}{C} = \frac{\omega}{(4\pi D t)^{1/2}} e^{-x^2/4Dt}$$

(from Fick's 2ND)

How does D relate to physical parameters?

Viscosity leads to opposing friction

Opposing ‖ Force

$$F_{friction} = -f u$$

friction coeff

$$D = \frac{kT}{f}$$

Part of Einstein PhD thesis

$$f = 6\pi \eta r$$

viscosity Coefficient

radius of a spherical molecule

$$\therefore \quad D = \frac{kT}{6\pi \eta r}$$

See example 6.5

For a characterized solvent (we know η), we can measure D, to determine r (assumes a spherical molecule)

Complications

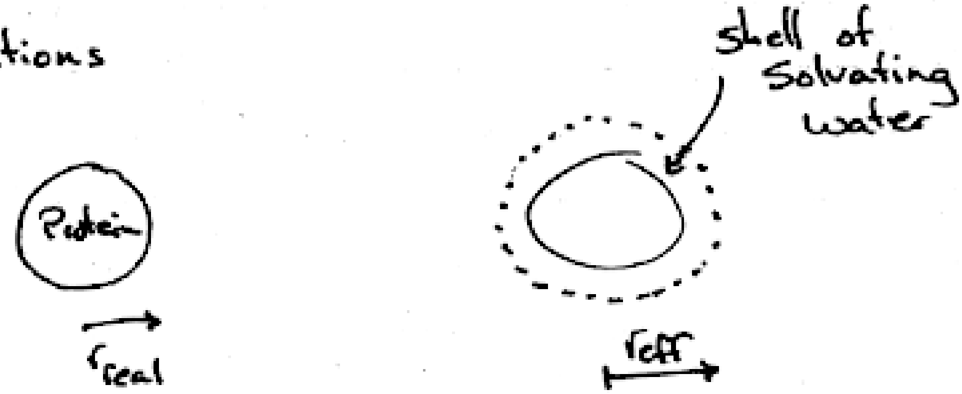


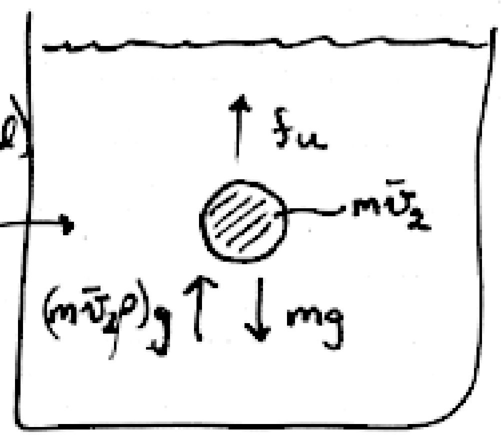
Fig 6.8 (p 278) shows that
non-spherical shapes show
that f can be different (larger)
than that for an ideal sphere

Look at various ellipsoid shapes

Sedimentation — Measurement (!)

$\bar{v}_2$ = partial specific volume
(volume ~~solute~~ particle / g ~~solute~~ particle added)

ρ = density of medium
(g solvent / volume solv)



$m\bar{v}_2$ = volume medium displaced

$\rho(m\bar{v}_2)$ = mass medium displaced

$[\rho(m\bar{v}_2)]g$ = Force to displace it.

Particle accelerates down (if more dense than medium)
until

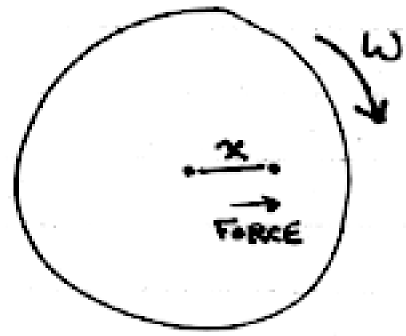
$$m(1-\bar{v}_2\rho)g = fu$$

NO NET FORCE

$$U_t = \text{terminal velocity} = \frac{m(1-\bar{v}_2\rho)}{f}\, g \qquad \text{GRAVITY}$$

$$= \frac{m(1-\bar{v}_2\rho)}{f}\, \omega^2 x \qquad \text{CENTRIFUGE}$$

ω = angular velocity (radians/sec)



Define:

$$S = \frac{U_t}{\omega^2 x} = \frac{m(1-\bar{v}_2\rho)}{f} \qquad \text{(Svedberg)}$$

$\frac{\text{velocity}}{\text{acceleration}}$

UNITS = sec

Property of a specific particle in a specific medium!

Properties in

Particle: m = mass
$\bar{v}_2$ = partial specific volume

Medium: ρ = density of medium

Both: $f = 6\pi\eta r$ (η: medium; r: particle) per molecule $\qquad\qquad$ per mole

$$s = \frac{m(1-\bar{v}_2\rho)}{kT/D} = \frac{M(1-\bar{v}_2\rho)}{RT}D$$

per molecule $\qquad\qquad$ per mole

measure $\qquad$ measure

$$M = \frac{RTs}{D(1-\bar{v}_2\rho)} = \text{Molecular Weight!}$$

measure $\qquad$ measure $\qquad$ measure

Practical Aside:

"Standard" $s \Rightarrow s_{20,w}$ $\qquad$ "standard" Conditions

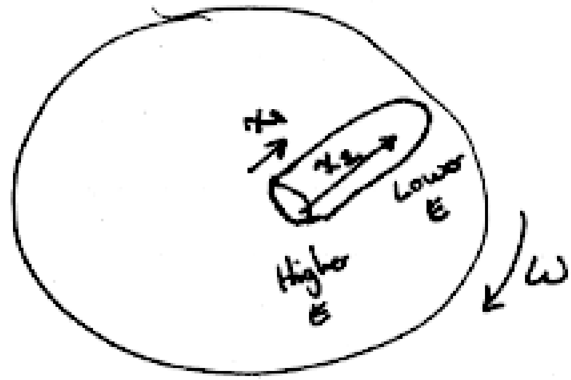
$$s_{20,w} = \left[\left(\frac{\eta}{\eta_{20,w}}\right)\frac{(1-\bar{v}_2\rho)_{20,w}}{(1-\bar{v}_2\rho)}\right]s$$

20°C $\qquad$ water $\qquad\qquad$ other temp other medium

Sedimentation Equilibrium

$$E_1 = \underbrace{M(1-\bar{v}_2\rho)}_{m} \cdot g \, x_1 \quad (\cdot\, g \cdot h)$$

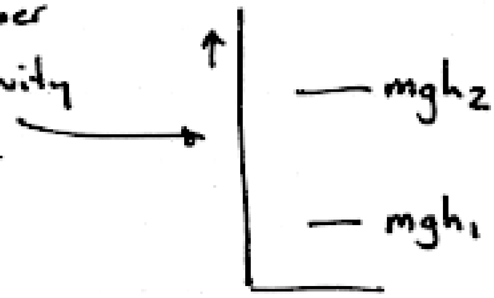
per mole   grams per mole



Boltzmann says

AT EQUILIBRIUM

Remember Gravity



$$\frac{C_j}{C_i} = e^{-(E_j - E_i)/RT}$$

$$\frac{C_2}{C_1} = e^{-\frac{M(1-\bar{v}_2\rho)(x_2 - x_1)g}{RT}} \qquad \text{GRAVITY}$$

$$= \cancel{e^{-\frac{M(1-\bar{v}_2\rho)(x_2\omega^2 x_2 - x_1\omega^2 x_1)}{RT}}}$$

(look at def of x)

In a centrifuge: $E_1 = -\frac{M(1-\bar{v}_2\rho)(\omega^2 x_1)x_1}{2}$

$\therefore$

$$\frac{C_2}{C_1} = e^{-\left[-\frac{M(1-\bar{v}_2\rho)\omega^2(x_2^2 - x_1^2)}{2RT}\right]}$$

$$\ln\frac{C_2}{C_1} = \frac{M(1-\bar{v}_2\rho)\,\omega^2(x_2^2 - x_1^2)}{2RT}$$

Plot $\ln C$ vs x^2 gives
straight line
with slope $= \dfrac{M(1-\bar{v}_2\rho)\omega^2}{2RT}$

$$\therefore \quad M = \frac{2RT}{M(1-\bar{v}_2\rho)\,\omega^2}\,(\text{slope})$$

Good way for accurately determining molecular weight in the native state.

Very often used to assess dimerization, etc.