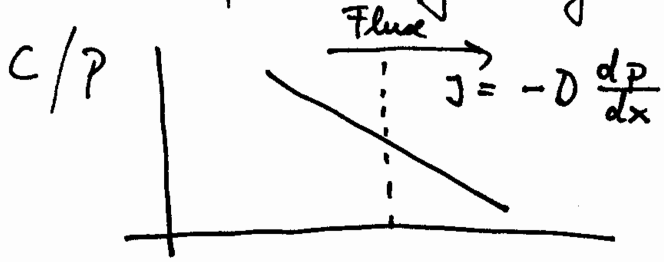
Free Diffusion

- Molecules diffuse from regions of high concentration, i.e. probability to regions of low conc./prob.



$$J(x) = -D \frac{dp}{dx}(x) \qquad \underline{\text{Fick's law}}$$

$$J = -D \nabla p$$

- If the flux is not uniform, then the concentration will change

$$\frac{\partial p}{\partial t}(x,t) = -\frac{\partial J}{\partial x}(x,t)$$

(Consequences: no conc. change in time $\frac{dp}{dt} = 0$ $\Leftrightarrow$ Flux same in space $\frac{dJ}{dx} = 0$

- Inserting into Fick's law gives <u>diffusion equation</u>

$$\frac{\partial p}{\partial t}(x,t) = D \frac{\partial^2 p}{\partial x^2}(x,t) \qquad \frac{\partial p}{\partial t} = D \nabla^2 p$$

~~Solution for free~~

Reformulate for spherically symmetric systems

$$J_r = -D \frac{\partial p}{\partial r}$$

$$\frac{\partial p}{\partial t} = D \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial p}{\partial r}\right)$$

see Arfken for coordinate transforms

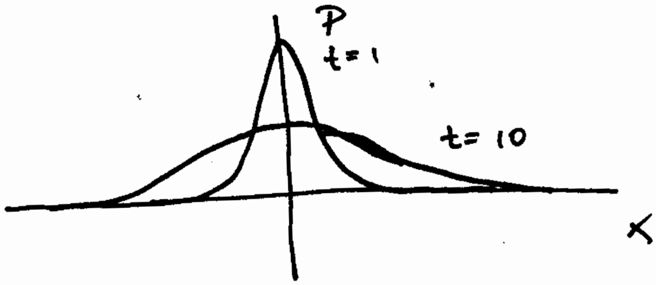
Free 1D diffusion from a point source

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

This is a Gaussian

$$\left(p(k) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-k^2/2\sigma^2} \right)$$

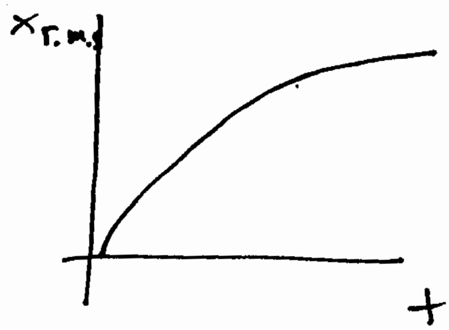
with $\sigma = \sqrt{2Dt}$



=> Root-mean-Square displacement $(= \sigma)$

$x_{rms} \propto \sqrt{t} = \sqrt{2Dt}$

Remember $x \propto t$ for linear motion at constant velocity



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

(Boltzmann law for viscous drag)

	r	η	D	time for 1 μm	100 μm
K^+	0.1 nm		2000 μm²/s	0.25 ms	2.5 s
Protein	3 nm	0.89 mPa/s	100 μm²/s	5 ms	50 s
Organelle	500 nm	0.89 mPa/s	0.5 μm²/s	1 s	10^4 s

First - mean passage time

How long does it take, on average, for a molecule to diffuse a certain distance?

aka mean time to capture

$$t_0 = \frac{x_0^2}{2D} \quad \text{for free diffusion}$$

Derivation

Flux Eq. with external forces

$$-D \frac{dp}{dx}(x) + \frac{F(x)}{\gamma} p(x) = j(x)$$

In equilibrium, $j(x) \equiv j_0 = \text{const}$

(think of river flowing)

Consider

$$-D \frac{d}{dx}\left\{p(x)\, e^{\frac{U(x)}{D\gamma}}\right\} = j_0\, e^{\frac{U(x)}{D\gamma}} \qquad (*)$$

Eq. $(*)$ is equivalent to flux eq.

→ take derivative

$$-D \frac{dp}{dx} \cancel{e^{U(x)/D\gamma}} - D p(x) \cancel{e}^{U(x)/D\gamma} \frac{1}{D\gamma}\frac{dU}{dx} = j_0\, e^{U(x)/D\gamma}$$

$$-D \frac{dp}{dx} + \frac{F(x)}{\gamma} p(x) = j_0 \qquad \text{if } F(x) = -\frac{dU}{dx}$$

It follows from $(*)$

$$p(x)\, e^{U(x)/D\gamma} = A - \frac{j_0}{D} B(x)$$

$A = \text{const}$

$$\frac{dB}{dx} = e^{U(x)/D\gamma}$$

Hence,

$$p(x) = \left[A - \frac{\gamma_0}{D} B(x) \right] e^{-U(x)/D\gamma} .$$

This needs to agree with Boltzmann's law

$$\Rightarrow A = \frac{1}{Z} \qquad D\gamma = kT$$

so as to make

$$p(x) = \frac{1}{Z} e^{-U(x)/k_B T}$$

(assuming flux $= 0$)

First - mean passage time system

$\leftarrow$ absorbing wall : removes particles i.e. $p(x_0) = 0$

Start from $(*)$, integrate from x to x_0

$$p(x) e^{U(x)/D\gamma} \Big|_x^{x_0} = p(x_0) e^{U(x_0)/D\gamma} - p(x) e^{U(x)/D\gamma}$$

$$\overset{p(x_0)=0}{=} - p(x) e^{U(x)/D\gamma} = -p(x) e^{U(x)/k_B T}$$

$$= -\frac{\gamma_0}{D} \int_x^{x_0} e^{U(x)/k_B T} dx$$

Multiplying with $-e^{-U(x)/k_B T}$ and integrating from 0 to x_0 gives

$$\int_0^{x_0} p(x) = 1 = \frac{\gamma_0}{D} \int_0^{x_0} e^{-U(x)/k_B T} \left\{ \int_x^{x_0} e^{U(y)/k_B T} dy \right\} dx$$