Free diffusion

$$J(x) = -D \ \frac{dP}{dx}(x) \qquad\qquad J = -D \ \nabla P$$

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

Free (1 D) 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 $\sigma = \sqrt{2Dt}$

$\Rightarrow$ R.M.S. displacement $\propto \sqrt{t}$

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

(not $x \propto t$ for const. velocity)

Spherically symmetric

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

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

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

	r	η	D	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 ~1 min
Organelle	500 nm		0.5 μm²/s	1 s	10^4 s ~3 hr

First - mean passage time

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

aka mean time to capture

$$t_0 = \frac{x_c^2}{2D} \qquad \text{for free diffusion}$$

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

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

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

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,

$$P(x) = \left[A - \frac{j_0}{D} B(x)\right] e^{-U(x)/D\gamma}$$

This needs to agree with Boltzmann's law

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

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. $P(x_0) = 0$

$x = 0$ $\qquad$ $x = x_0$

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

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

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

$$= -\frac{j_0}{D} \int_x^{x_0} e^{U(x)/k_B T} dx$$

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

$$\int_0^{x_0} P(x) = 1 = \frac{j_0}{D} \int_0^{x_0} e^{-U(x)/k_B T} \left\{ \int_x^{x_0} e^{U(y)/k_B T} dy \right\} dx$$

At steady state, flux is constant $\qquad t_0 = \frac{1}{j(x_0)}$

$$t_0 = \frac{1}{j_0} = \frac{1}{D} \int_0^{x_0} e^{-U(x)/k_BT} \left\{ \int_x^{x_0} e^{U(y)/k_BT} dy \right\} dx$$

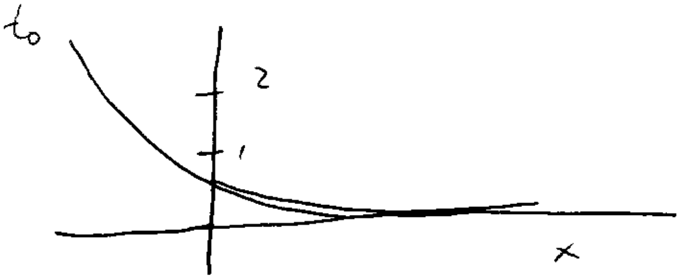
This integral needs to be solved for different choices of forces

① Free diffusion (no force) $\quad U(x)=0$

$$t_0 = \frac{1}{j_0} = \frac{1}{D}\frac{x_0^2}{2}$$

② Constant force $\quad U(x) = -Fx$

$$t_0 = 2\frac{x_0^2}{2D}\left(\frac{k_BT}{Fx_0}\right)^2 \left\{ e^{-\frac{F(x_0)}{k_BT}} + \frac{Fx_0}{k_BT} - 1 \right\}$$



'Downhill' movement $\quad x_0 \to$ large

$$t_0 \to \frac{\gamma x_0}{F} \quad \frac{x_0}{V}$$

'Uphill' movement

$$t_0 \sim e^{Fx_0/k_BT}$$

like transfer over energy barrier

③ Harmonic potential $\quad U(x) = \frac{1}{2}Kx^2$

for $U(x_0) \gg k_BT$

$$t_0 = \frac{\gamma}{K}\sqrt{\frac{\pi}{4}}\sqrt{\frac{k_BT}{U_0}}\, e^{U_0/k_BT}$$