Diffusion: Microscopic and Macroscopic Theory

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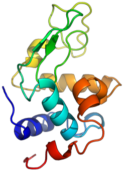
Physics/Neuro 141

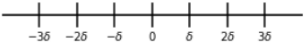
Week 5

Microscopic Theory



Lysozyme

- Mass = $m = 2.3 \times 10^{-20}$g
- $k_B T = 4 \times 10^{-14}$g cm^2/sec^2
- $\langle v_x^2 \rangle^{1/2} = 1.3 \times 10^3$cm/sec



1D random walk

- Particles start at the origin
- Step Size = δ
- Step Interval = τ
- Instantaneous velocity = δ/τ

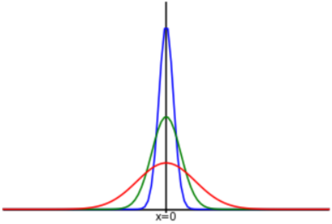
- Each particle steps to the right or to the left once every τ seconds, moving at velocity $\pm v_x$ a distance $\delta = \pm v_x \tau$.
- the position of a particle after the nth step differs from its position after the $(n-1)$th step by $\pm\delta$:

$$x_i(n) = x_i(n-1) \pm \delta$$

- The mean displacement does not change:

$$\begin{aligned} \langle x(n) \rangle &= \frac{1}{N} \sum_{i=1}^{N} [x_i(n-1) \pm \delta] \\ &= \frac{1}{N} \sum_{i=1}^{N} x_i(n-1) \\ &= \langle x(n-1) \rangle \end{aligned}$$

- If $\langle x(0) \rangle = 0$, then $\langle x(t) \rangle = 0$



- The probability of finding particles at different points at $t = 1, 4,$ and 16 sec.
- Standard deviations increase with the square root of time

Squared coordinate of each particle changes with time:

$$x_i^2(n) = x_i^2(n-1) \pm 2\delta x_i(n-1) + \delta^2$$

Mean squared coordinates of all particles grows with time:

$$\langle x^2(n) \rangle = \frac{1}{N} \sum_{i=1}^{N} x_i^2(n)$$

$$= \frac{1}{N} \sum_{i=1}^{N} \left[x_i^2(n-1) \pm 2\delta x_i(n-1) + \delta^2 \right]$$

$$= \langle x^2(n-1) \rangle + \delta^2$$

The diffusion coefficient

- Since $x_i(0) = 0$ for all particles i, $\langle x^2(0) \rangle = 0$. Thus, $\langle x^2(1) \rangle = \delta^2$, $\langle x^2(2) \rangle = 2\delta^2$, $\langle x^2(3) \rangle = 3\delta^2$, ..., and $\langle x^2(n) \rangle = n\delta^2$.
- It follows that the mean-square displacement is proportional to t, the root-mean-square displacement is proportional to the square-root of t. Note that $n = t/\tau$, so that:

$$\left\langle x^2(t) \right\rangle = (t/\tau)\delta^2 = (\delta^2/\tau)t$$

- For convenience, we define a diffusion coefficient, $D = \delta^2/2\tau$. This gives us

$$\left\langle x^2 \right\rangle = 2Dt$$

The Diffusion Coefficient

The Equations for Fluid Dynamics

- Navier-Stokes Equations

$$-\nabla p + \eta \nabla^2 \mathbf{v} = \rho \frac{\partial \mathbf{v}}{\partial t} + \rho(\mathbf{v} \cdot \nabla)\mathbf{v}$$

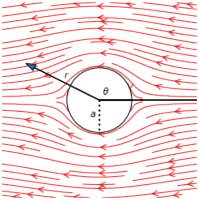
- Reynolds number

$$\Re = \frac{aV\rho}{\eta}$$

- When $\Re \ll 1$

$$-\nabla p + \eta \nabla^2 \mathbf{v} = 0$$

- Linear relationships between velocity and force at Low Reynolds numbers



Viscous flow around a sphere:

$$v_r = -V\cos\theta\left(1 - \frac{3a}{2r} + \frac{a^3}{2r^3}\right)$$

$$v_\theta = V\sin\theta\left(1 - \frac{3a}{4r} - \frac{a^3}{4r^3}\right)$$

Force on a sphere with velocity $\mathbf{V}$:

$$\mathbf{F} = 6\pi\eta a\mathbf{V}$$

Einstein-Smoluchowski: $D = k_B T / f_r$

If $\xi = \frac{dx}{dt}$ is the velocity of a particle, the average is given by equipartition:

$$m \left\langle \xi^2 \right\rangle = k_B T$$

A particle moving with respect to the fluid at the speed ξ, experiences a viscous resistance equal to $-f_r \xi$ according to Stokes' formula.

The equation of motion in the x-direction, adding a random fluctuating force owing to the surrounding molecules $X(t)$ is:

$$m \frac{d^2 x}{dt^2} = -f_r \frac{dx}{dt} + X(t)$$

$X(t)$ is indifferently positive and negative, and its magnitude is such that it maintains the agitation of the particle which the viscous resistance is constantly dissipating.

EINSTEIN-SMOLUCHOWSKI: $D = k_B T / f_r$ CONT'D

Multiplying the equation of motion by x and rewriting we have:

$$\frac{m}{2}\frac{d^2x^2}{dt^2} - m\xi^2 = -\frac{f_r}{2}\frac{dx^2}{dt} + Xx$$

Take the average of the equation of motion for a large number of particles:

- $\langle m\xi^2 \rangle = k_B T$
- $\langle Xx \rangle = 0$
- Define $\frac{d\langle x^2 \rangle}{dt} = z$

$$\frac{m}{2}\frac{dz}{dt} + \frac{f_r}{2} z = k_B T \qquad (1)$$

The general solution of Equation 1 is:

$$z = \frac{2k_B T}{f_r} + Ce^{-\frac{f_r}{m}t} \qquad (2)$$

Einstein-Smoluchowski: $D = k_B T / f_r$ cont'd

The second term in Equation 2 has a very small time constant (nanoseconds for typical small particles) and so vanishes:

$$\frac{d\left\langle x^2 \right\rangle}{dt} = \frac{2k_B T}{f_r} \tag{3}$$

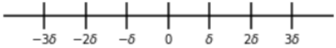
Hence, for some period of time τ:

$$\left\langle x^2 \right\rangle = 2\frac{k_B T}{f_r}\tau \tag{4}$$

The diffusion coefficient following Langevin's method is thus:

$$D = \frac{k_B T}{f_r} \tag{5}$$

PROBABILITY DISTRIBUTIONS FOR DIFFUSING PARTICLES



For a one-dimensional random walk, suppose that a particle steps to the right with a probability p and to the left with a probability q.

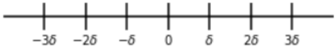
$$P(k; n, p) = \frac{n!}{k!(n-k)!} p^k q^{n-k} \tag{6}$$

The displacement of the particles in n trials, $x(n)$, is equal to the number of steps to the right minus the number of steps to the left times the step length, δ:

$$x(n) = [k - (n-k)]\,\delta = (2k - n)\delta \tag{7}$$

Since we know the distribution of k, we know the distribution of x. The two distributions have the same shape.

Diffusion follows binomial statistics cont'd



The mean displacement of the particle is:

$$\langle x(n) \rangle = (2\langle k \rangle - n)\delta \tag{8}$$

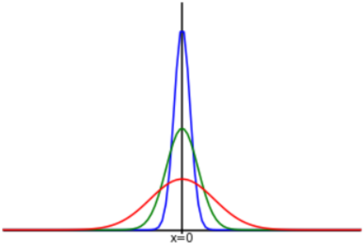
where $\langle k \rangle = np$.

The mean-square displacement is

$$\left\langle x^2(n) \right\rangle = \left\langle [2k - n)\delta]^2 \right\rangle = (4\left\langle k^2 \right\rangle - 4\langle k \rangle n + n^2)\delta^2 \tag{9}$$

where $\langle k^2 \rangle = (np)^2 + npq$

Binomial to Gaussian statistics



When n and np are both very large, the binomial distribution, $P(k; n, p)$ is equivalent to:

$$P(k)dk = \frac{1}{(2\pi\sigma^2)^{1/2}} e^{-(k-\mu)^2/2\sigma^2} dk$$

Substitute $x = (2k-n)\delta$, $dx = 2\delta dk$, $p = q = 1/2$, $t = n/\tau$, and $D = \delta^2/2\tau$,

$$P(x)dx = \frac{1}{(4\pi Dt)^{1/2}} e^{-x^2/4Dt} dx$$

- $P(x)dx$ is the probability of finding a particle between x and $x + dx$.
- The variance is $\sigma_x^2 = 2Dt$.
- The standard deviation is $\sigma_x = (2Dt)^{1/2}$.

Macroscopic Theory

Fick's First Law

1. At time t there are $N(x)$ particles at position x, $N(x+\delta)$ particles at $x+\delta$.
2. At time $t+\tau$, half of each set will have stepped left or right.
3. The net number crossing to the right will be: $-\frac{1}{2}\left[N(x+\delta)-N(x)\right]$

4. To obtain the net flux, divide by the area normal to the x axis and by τ:

$$J_x = -\frac{1}{2}\left[N(x+\delta)-N(x)\right]/A\tau \tag{10}$$

Multiplying Eq. 10 by δ^2/δ^2 and rearrange:

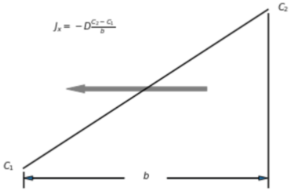
$$J_x = -\frac{\delta^2}{2\tau}\frac{1}{\delta}\left[\frac{N(x+\delta)}{A\delta}-\frac{N(x)}{A\delta}\right]$$

Define $D=\delta^2/2\tau$ to be the diffusion coefficient:

$$J_x = -D\frac{1}{\delta}\left[C(x+\delta)-C(x)\right]$$

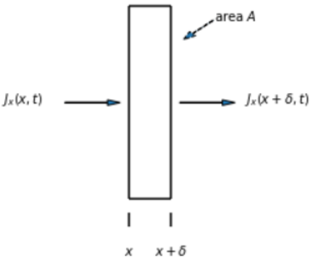
In the limit $\delta \to 0$, we get Fick's First Law:

$$J_x = -D\frac{\partial C}{\partial x}$$



The flux due to a linear concentration gradient $(C_2 - C_1)/b$. Net movement from right to left occurs because there are more particles at the right.

- **Fick's First Law** states that the net flux (at x and t) is proportional to the slope of the concentration function (at x and t). The constant of proportionality is D.
- If the particles are uniformly distributed, the slope is 0, i.e., $\partial C/\partial x = 0$ and $J_x = 0$.
- If the slope is constant, i.e., if $\partial C/\partial x$ is constant, J_x is constant. This occurs when C is a linear function of x.



Fluxes through the faces of a box. The area of each face is A. The faces are normal to the x axis. In time τ, $J_x(x)A\tau$ particles will enter from the left and $J_x(x+\delta)A\tau$ particles will leave from the right. The volume of the box is $A\delta$.

The number of particles per unit volume in the box must increase at the rate

$$\begin{aligned}\frac{1}{\tau}\left[C(t+\tau) - C(t)\right] &= \\ &= -\frac{1}{\tau}\left[J_x(x+\delta) - J_x(x)\right]\frac{A\tau}{A\delta} \\ &= -\frac{1}{\delta}\left[J_x(x+\delta) - J_x(x)\right]\end{aligned}$$

When $\tau \to 0$ and $\delta \to 0$, we get **Fick's Second Law**

$$\frac{\partial C}{\partial t} = -\frac{\partial J_x}{\partial x}$$

Fick's First Law in three dimensions

In three dimensions, we have $J_x = -D\partial C/\partial x$, $J_y = -D\partial C/\partial y$, and $J_z = -D\partial C/\partial z$. These are components of a flux vector:

$$\mathbf{J} = -D\boldsymbol{\nabla} C \tag{11}$$

Fick's Second Law in three dimensions

In three dimensions, we have $\partial C/\partial t = -\left(\partial J_x/\partial x + \partial J_y/\partial y + \partial J_z/\partial z\right)$:

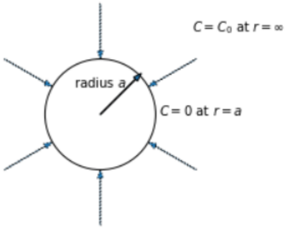
$$\frac{\partial C}{\partial t} = -\boldsymbol{\nabla} \cdot \mathbf{J} \tag{12}$$

The Diffusion Equation

Combining Eqs. 11 and 12 produces the three-dimensional diffusion equation

$$\frac{\partial C}{\partial t} = D\boldsymbol{\nabla}^2 C \tag{13}$$

Diffusion to Capture



A spherical adsorber of radius a in an infinite medium containing particles at concentration C_0 The dashed arrows are lines of flux.

If the problem is spherically symmetric, the flux is radial,

$$J_r = -D\partial C/\partial r$$

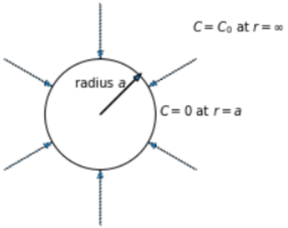
and

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

The concentration at $r = a$ is 0. The concentration at $r = \infty$ is C_0. With these boundary conditions, the diffusion equation has the solution:

$$C(r) = C_0\left(1 - \frac{a}{r}\right)$$

The spherical adsorber, cont'd



A spherical adsorber of radius a in an infinite medium containing particles at concentration C_0 The dashed arrows are lines of flux.

The flux is

$$J_r = -DC_0 \frac{a}{r^2}$$

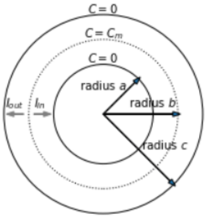
The net migration of molecules is radially inward.
The particles are adsorbed by the sphere at a rate equal to the area, $4\pi a^2$ times the inward flux $-J_r(a)$:

$$I = 4\pi D a C_0$$

This adsorption rate, I, is the diffusion current.

Probability of capture

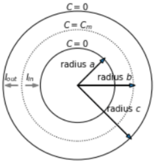
Suppose a particle is released near a spherical adsorber of radius a at a point $r = b > a$? What is the probability that the particle will be adsorbed at $r = a$ rather than wander away for good?



- A spherical shell source, radius b, between a spherical adsorber of radius a and a spherical shell adsorber of radius c.
- Particles released at $r = b$ move inward and are adsorbed at $r = a$ at rate I_{in} or move outward and are adsorbed at $r = c$ at rate I_{out}.
- Their steady-state concentration rises from 0 at $r = a$ to to C_m at $r = b$ and then falls again to 0 at $r = c$.

Probability of capture, cont'd

A boundary value problem



Steady-state diffusion equation

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C}{\partial r}\right) = 0$$

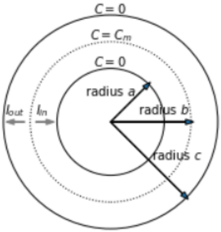
Boundary conditions

$$C(r = a) = 0$$
$$C(r = b) = C_m$$
$$C(r = c) = 0$$

The solution

$$C(r) = \begin{cases} \dfrac{C_m}{1 - a/b}\left(1 - \dfrac{a}{r}\right) & \text{if } a \le r \le b, \\ \dfrac{C_m}{c/b - 1}\left(\dfrac{c}{r} - 1\right) & \text{if } b \le r \le c \end{cases} \qquad J_r(r) = \begin{cases} \dfrac{-DC_m}{1 - a/b}\,\dfrac{a}{r^2} & \text{if } a \le r \le b, \\ \dfrac{DC_m}{c/b - 1}\,\dfrac{c}{r^2} & \text{if } b \le r \le c \end{cases}$$

Probability of capture, cont'd cont'd



- The diffusion current from the spherical shell source to the inner adsorber is

$$I_{in} = 4\pi D C_m \frac{a}{1 - a/b} \tag{14}$$

- The diffusion current from the spherical shell source to the outer adsorber is

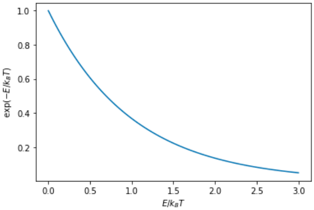
$$I_{out} = 4\pi D C_m \frac{c}{c/b - 1} \tag{15}$$

- The probability that a particle released at $r = b$ will be adsorbed at $r = a$ is the ratio:

$$\frac{I_{in}}{I_{in} + I_{out}} = \frac{a(c - b)}{b(c - a)} \tag{16}$$

- In the limit $c \to \infty$, the probability of being adsorbed is a/b.

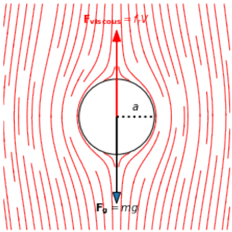
Einstein relation



The density of particles suspended in a fluid in a gravitational field is given by the Boltzmann distribution:

$$\rho(z) = \rho_0 e^{-mgz/k_BT}$$

because $E = mgz$



Each particle sediments at a velocity given by the balance between gravitational force ($\mathbf{F} = m\mathbf{g}$) and viscous force ($\mathbf{F} = -f_r\mathbf{V}$).

Upward flux due to diffusion is given by Fick's First Law

$$J_z^{diff} = D \times \frac{mg}{k_B T} \times \rho_0 e^{-\frac{mgz}{k_B T}}$$

Downward flux due to sedimentation is given by the product of velocity and particle density

$$J_z^{sed} = -\frac{mg}{f_r} \times \rho_0 e^{-\frac{mgz}{k_B T}}$$

At steady state, $J_z^{diff} + J_z^{sed} = 0$:

$$D \times \frac{mg}{k_B T} \times \rho_0 e^{-\frac{mgz}{k_B T}} - \frac{mg}{f_r} \times \rho_0 e^{-\frac{mgz}{k_B T}} = 0$$

$$\frac{D}{k_B T} - \frac{1}{f_r} = 0$$

Hence,

$$D = \frac{k_B T}{f_r}$$