In fancy jargon, we might say that an <u>entropic force</u> is driving the flux, i.e., entropy is moving the particles.

How is $N(x)$ changing with time? The flux j at $x-\frac{L}{2}$ increases $N(x)$ (if $j(x-\frac{L}{2})>0$), and the flux j at $x+\frac{L}{2}$ decreases it if $j(x+\frac{L}{2})>0$). So in fact

$$\frac{dN(x)}{dt} = YZ\,j(x-\tfrac{L}{2}) - YZ\,j(x+\tfrac{L}{2})$$

or since $c(x) = N/(LYZ)$,

$$\frac{dc(x)}{dt} = \frac{1}{L}\left(j(x-\tfrac{L}{2}) - j(x+\tfrac{L}{2})\right) = -\frac{dj(x)}{dx}$$

as $L \to 0$.

This result

$$\frac{dc}{dt} = -\frac{dj}{dx}$$

is a continuity equation; we derived it by assuming that the particles are conserved — they don't pop in or out of existence.

If we combine the last two differential equations $j = -D\frac{dc}{dx}$ and $\frac{dc}{dt} = -\frac{dj}{dx}$, then we find

$$\frac{dc}{dt} = -\frac{dj}{dx} = -\frac{d}{dx}\left(-D\frac{dc}{dx}\right) = D\frac{d^2c}{dx^2} \quad (4.20)$$

since D is a constant. This is the <u>diffusion equation</u>.

This diffusion equation often is written as

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

in which the ∂'s mean that one variable x or t is held constant while the other is varied.

Although the walk of each particle is random, the evolution in time of the concentration $c(x,t)$ obeys the diffusion equation, which is deterministic — we can compute $c(x,t)$ in terms of $c(x,0)$ for $t > 0$. But the diffusion equation is true only in the limit of infinitely many particles.

One consequence of the diffusion equation is that a uniform distribution of particles does not change with time. If $c(x,t)$ is uniform, then it does not depend upon x, and so

$$\frac{dc}{dt} = D\,\frac{d^2c}{dx^2} = 0.$$

So a uniform concentration is constant — it is independent of both x and t. This makes sense only for infinitely many randomly walking particles.

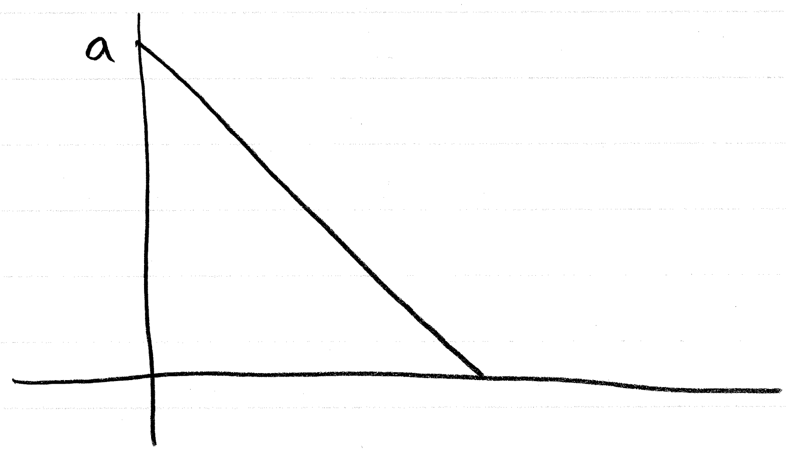
What about 10 particles? Suppose 10 particles are evenly spaced in a box and are moving randomly. Then if we wait a long time until $\frac{tL}{\Delta t}$ is much bigger than the size of the box, the chance that all 10 particles are in the left half of the box is

$$\left(\frac{1}{2}\right)^{10} = 0.000977 \approx 0.001 = 0.1\%.$$

So $c(x,t)$ obeys the diffusion equation if it represents the concentration at x and t of a swarm of infinitely many particles, but not if it describes 10 or 100 particles. Since a mole has $N_A = 6.0 \times 10^{23}$ particles, if $c(x,t)$

represents a few grams of molecules, then it obeys the diffusion equation because 6×10^{23} is huge.

Suppose $c(x,0) = a - bx$.



Then

$$\frac{dc}{dt} = D\frac{d^2c}{dx^2} = D\frac{d}{dx}\left(\frac{d}{dx}(a-bx)\right)$$

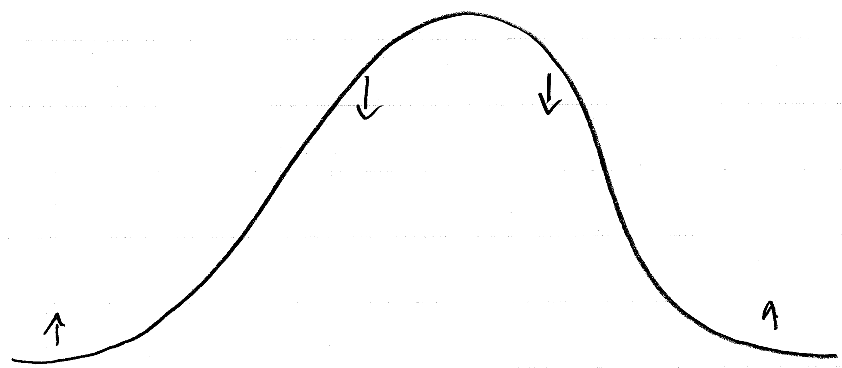
$$= D\frac{d}{dx}(-b) = 0.$$

Now the concentration $c(x,t) = c(x,0)$ is independent of the time t because the flux $j = -D\frac{dc}{dx} = bD$ is independent of x. So the particles coming in from the left make up for those leaving from the right.

Now suppose the initial concentration $C(x,0)$ is peaked at $x=0$

$$C(x,0) = C_0 e^{-\frac{x^2}{2L^2}}$$

$C(x,0)$



$x=0$

Now

$$\frac{dc}{dt} = D\frac{d^2c}{dx^2} = Dc_0\frac{d}{dx}\left(-\frac{x}{L^2}e^{-\frac{x^2}{2L^2}}\right)$$

$$= -\frac{1}{L^2}c_0 D \frac{d}{dx}\left(x e^{-x^2/L^2}\right)$$

$$= -\frac{1}{L^2}c_0 D\left(e^{-x^2/L^2} - \frac{x^2}{L^2}e^{-\frac{x^2}{L^2}}\right)$$

So

$$\frac{dC(x,0)}{dt} = -\frac{C_0 D}{L^2}\left(1-\frac{x^2}{L^2}\right)e^{-x^2/L^2},$$

So at $t = 0$, the concentration $c(x,0)$ is dropping at $x = 0$

$$\frac{dc(0,0)}{dt} = -\frac{c_0 D}{L^2}$$

and also at x that are small enough that $1 - x^2/L^2 > 0$.

That is, $c(x,0)$ is decreasing for

$$-L < x < L .$$

But for $x < -L$ and $x > L$, $c(x,0)$ is increasing. At $x = L$ and $x = -L$, $c(x,0)$ is neither increasing nor decreasing – these are <u>inflection points</u>, points where the curvature vanishes $\frac{d^2c}{dx^2} = 0$.

Look at a point $x > L$. At first, the concentration $c(x,t)$ rises because $\frac{dc}{dt} > 0$ at $x > L$ and $t = 0$. Particles are flowing to x from the region $-L < x < L$, and fewer are moving away. But this rise in $c(x,t)$ slows down as fewer particles are left between $-L$ and L. Eventually $\frac{dc(x,t)}{dt} = 0$, and x is now an inflection point. The inflection points move out as time goes by. After the inflection point has moved past x, the concentration $c(x,t)$ subsides. As $t \to \infty$, the concentration approaches a constant

$c(x,\infty)$ that is independent of x.

We will see later that the time evolution of this distribution of particles is

$$c(x,t) = \frac{c_0}{\sqrt{1+\frac{2Dt}{L^2}}}\, e^{-\frac{x^2}{2L^2\left(1+\frac{2Dt}{L^2}\right)}}.$$

So the inflection points are at

$$\pm L\sqrt{1+\frac{2Dt}{L^2}}$$

and they move out as time goes by.

To verify that $c(x,t)$ satisfies the diffusion equation

$$\frac{dc}{dt} = D\frac{d^2c}{dx^2}$$

we differentiate.

$$\frac{dc(x,t)}{dt} = D\frac{1}{L^2}\frac{1}{\left(1+\frac{2Dt}{L^2}\right)}\left[\frac{x^3}{L^2\left(1+\frac{2Dt}{L^2}\right)} - 1\right]c(x,t)$$

$$= D\,\frac{d^2c(x,t)}{dx^2}.$$

So the concentration

$$c(x,t) = \frac{C_0}{\sqrt{1+\frac{2Dt}{L^2}}}\,e^{-\frac{x^2}{2L^2\left(1+\frac{2Dt}{L^2}\right)^2}}$$

satisfies the diffusion equation

$$\frac{dc}{dt} = D\,\frac{d^2c}{dx^2}.$$

The details of the differentiations are on pages 50 & 51 of the notes.

I used the abbreviations

$$\sqrt{} = \sqrt{1+\frac{2Dt}{L^2}} \quad \text{and} \quad (\quad) = 1+\frac{2Dt}{L^2}.$$

$$c = \frac{c_0}{\sqrt{1+\frac{2Dt}{L^2}}}\, e^{-\frac{x^2}{2L^2\left(1+\frac{2Dt}{L^2}\right)}}$$

$$\frac{dc}{dx} = \frac{c_0}{\sqrt{\quad}}\left[-\frac{x}{L^2(\quad)}\, e^{-\frac{x^2}{2L^2(\quad)}}\right]$$

$$\frac{d^2c}{dx^2} = \frac{c_0}{\sqrt{\quad}}\,\frac{1}{L^2(\quad)}\left(-1 + \frac{x^2}{L^2(\quad)}\right) e^{-\frac{x^2}{2L^2(\quad)^2}}$$

$$= \left[\frac{x^2}{L^2(\quad)} - 1\right]\frac{1}{L^2(\quad)}\, c(x,t)$$

$$= \frac{1}{L^2}\,\frac{1}{\left(1+\frac{2Dt}{L^2}\right)}\left[\frac{x^2}{L^2\left(1+\frac{2Dt}{L^2}\right)} - 1\right] c(x,t)$$

The time derivative is

$$\frac{dc}{dt} = -\frac{1}{2}(\ \ )^{-3/2}\frac{2D}{L^2}c_0\, e^{-\frac{x^2}{2L^2(\ \ )}} + \frac{x^2}{2L^2(\ \ )^2}\frac{2D}{L^2}\, c(x,t)$$

$$= D\,c(x,t)\left[-\frac{1}{L^2(\ \ )} + \frac{x^2}{L^4(\ \ )^2}\right]$$

$$= D\,c(x,t)\left[-\frac{1}{L^2\left(1+\frac{2Dt}{L^2}\right)} + \frac{x^2}{L^4\left(1+\frac{2Dt}{L^2}\right)^2}\right]$$

$$= D\frac{1}{L^2\left(1+\frac{2Dt}{L^2}\right)}\left[\frac{x^2}{L^2\left(1+\frac{2Dt}{L^2}\right)} - 1\right] c(x,t)$$

$$= D\frac{d^2c}{dx^2}.$$

So

$$c(x,t) = \frac{c_0}{\sqrt{1+\frac{2Dt}{L^2}}}\, e^{-\frac{x^2}{2L^2\left(1+\frac{2Dt}{L^2}\right)}}$$

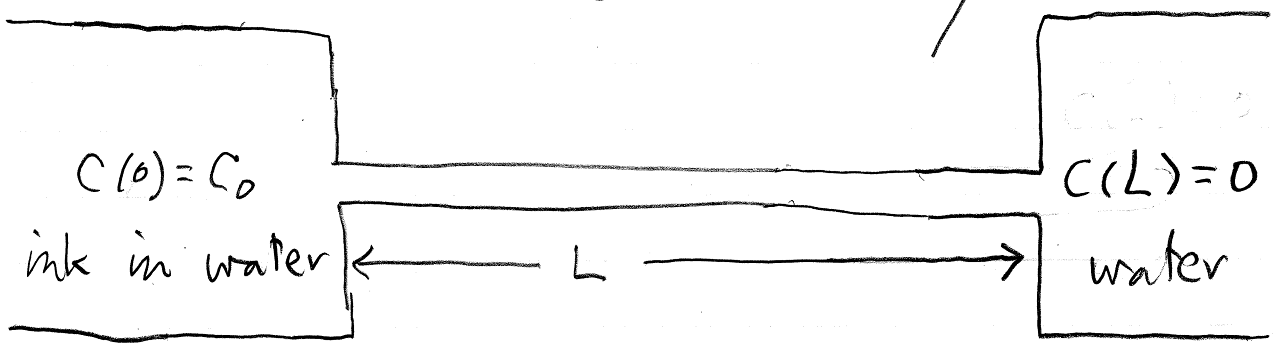
satisfies the diffusion equation.

The sketch is meant to depict a traveling wave moving in the x-direction — for instance, an intensity $\mathcal{I}(x,t)$ of the form

$$\mathcal{I}(x,t) = \mathcal{I}_0 \, e^{-\frac{(x-vt)^2}{2Dt}}$$

describes a lump of height $\mathcal{I}_0$ moving at speed v in the x-direction and spreading out.

Membrane Permeability



In the quasi-steady state

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

so c should be linear in x

$$c(x) = c_0\left(1 - \frac{x}{L}\right).$$

By Fick's law (4.19), the flux is

$$j_s = -D\frac{dc}{dx} = -Dc_0\left(-\frac{1}{L}\right) = \frac{Dc_0}{L}$$

where "s" reminds us that the diffusing particles are solute, not solvent.