We define the <u>diffusion constant</u> D

as

$$D = \frac{L^2}{2\Delta t}$$

where Δt is the time to take a step of length L. Then

$$N = \frac{t}{\Delta t}$$

and so

$$\langle x_N^2 \rangle = N L^2$$

$$= \frac{t L^2}{\Delta t}$$

$$= 2\left(\frac{L^2}{2\Delta t}\right) t$$

$$= 2 D t$$

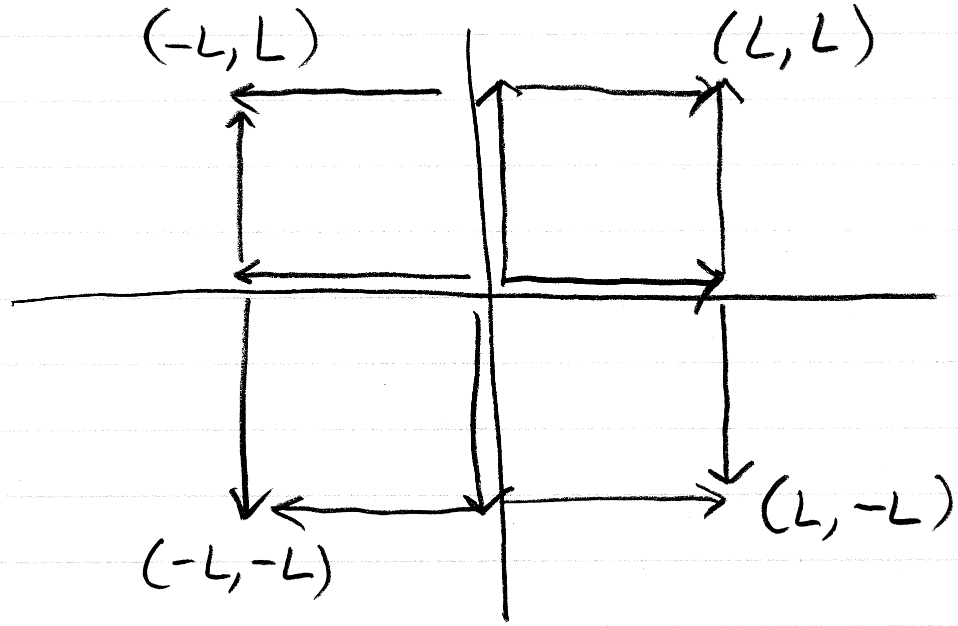
for one-dimensional random walks.

Since $\langle x_N^2 \rangle = 2Dt$, we will find big excursions to X if we wait long enough — to $t = \frac{X^2}{2D}$.

In fact, we can <u>measure</u> the diffusion constant D by measuring x_i^2 at M successive times t_i and computing the average

$$D = \frac{1}{M} \sum_{i=1}^{M} \frac{x_i^2}{2t_i} .$$

How about random walks in two dimensions? We can model these as two one-dimensional random walks.



One step walks go to (L, L), $(L, -L)$, $(-L, L)$, and $(-L, -L)$.

$$\langle x_N^2 \rangle = N L^2$$

$$\langle y_N^2 \rangle = N L^2$$

$$\begin{aligned}\langle \vec{r}_N^{\,2} \rangle &= \langle \vec{r}_N \cdot \vec{r}_N \rangle \\ &= \langle x_N^2 + y_N^2 \rangle \\ &= N L^2 + N L^2 \\ &= 2 N L^2 .\end{aligned}$$

If we say $N = t/\Delta t$ and keep $D = \dfrac{L^2}{2\Delta t}$, then for a two-dimensional random walk

$$\langle \vec{r}_N^{\,2} \rangle = 2NL^2 = 4\left(\frac{L^2}{2\Delta t}\right)t$$

$$= 4Dt.$$

Similarly, in three dimensions

$$\langle x_N^2 \rangle = NL^2$$

$$\langle y_N^2 \rangle = NL^2$$

$$\langle z_N^2 \rangle = NL^2$$

So

$$\langle \vec{r}_N^{\,2} \rangle = \langle \vec{r}_N \cdot \vec{r}_N \rangle$$

$$= \langle x_N^2 + y_N^2 + z_N^2 \rangle$$

$$= NL^2 + NL^2 + NL^2$$

$$= 3NL^2.$$

So in 3-D

$$\langle \vec{r}_N^{\,2} \rangle = 6 \left(\frac{L^2}{2\Delta t} \right) t$$

$$= 6 D t$$

where

$$D = \frac{L^2}{2\Delta t}$$

and Δt is the step time

$$\Delta t = \frac{t}{N} .$$

Keep in mind that

$$[D] = \frac{L^2}{T} .$$

A more general model of a random walk in one dimension.

Still

$$x_j = x_{j-1} + k_j L$$

but now the mean of k need not be zero

$$\langle k_j \rangle = u,$$

There can be drift (independent of j).

So now

$$\langle x_N \rangle = \langle x_{N-1} + k_N L \rangle$$

$$= \langle x_{N-1} \rangle + L \langle k_N \rangle$$

$$= \langle x_{N-1} \rangle + Lu$$

$$\langle x_1 \rangle = \langle x_0 + k_1 L \rangle = 0 + uL = uL$$

$$\langle x_N \rangle = NLu.$$

Now

$$\mathrm{var}(x_N) = \langle (x_N - \langle x_N \rangle)^2 \rangle$$

$$= \langle (x_N - NuL)^2 \rangle$$

$$= \langle (x_{N-1} + k_N L - NuL)^2 \rangle$$

$$= \langle \left((x_{N-1} - u(N-1)L + (k_N L - uL) \right)^2 \rangle$$

$$= \langle (x_{N-1} - u(N-1)L)^2 \rangle$$

$$+ 2 \langle (x_{N-1} - u(N-1)L)(k_N L - uL) \rangle$$

$$+ \quad L^2 \langle (k_N - u)^2 \rangle$$

Now $x_{N-1} - u(N-1)L$ and $k_N L - uL$

are independent and uncorrelated, so

(by the multiplication rule)

$$\langle (x_{N-1} - u(N-1)L)(k_N L - uL) \rangle$$

$$= \langle x_{N-1} - u(N-1)L \rangle \, L \, \langle k_N - u \rangle = 0$$

since $\langle k_N \rangle = u$. Also

$$\langle x_{N-1} \rangle = (N-1)uL \, .$$

So

$$\text{var}(x_N) = \langle (x_N - \langle x_N \rangle)^2 \rangle$$

$$= \langle (x_{N-1} - \langle x_{N-1} \rangle)^2 \rangle$$

$$+ \; L^2 \langle (k_N - u)^2 \rangle \qquad \text{or}$$

$$\text{var}(x_N) = \text{var}(x_{N-1}) + L^2 \,\text{var}(k)$$

because $\langle k_N \rangle = u$ and

$$\text{var}(k) = \langle (k_N - \langle k_N \rangle)^2 \rangle = \langle (k_N - u)^2 \rangle.$$

So now

$$\text{variance}(x_N) = \langle (x_N - \langle x_N \rangle)^2 \rangle$$

$$= N L^2 \,\text{variance}(k).$$

So

$$\text{var}(x_N) = 2 \left(\frac{L^2 \text{var}(k)}{2\Delta t} \right) t = 2Dt$$

with

$$D = \frac{L^2}{2\Delta t} \text{var}(k).$$

Friction & Diffusion

$$f = ma = m \frac{dv_x}{dt}$$

in one dimension. So

$$v_x = v_{x0} + \frac{f}{m} dt = \frac{dx}{dt}.$$

So

$$\Delta x = \int_0^{\Delta t} v_x \, dt$$

$$= \int_0^{\Delta t} \left(v_{x0} + \frac{f}{m} t \right) dt$$

$$= v_{x0} \Delta t + \frac{1}{2} \frac{f}{m} \Delta t^2 .$$

We <u>assume</u> that v_{x0} is random noise, so

$$\langle v_{x0} \rangle = 0 \quad \text{and so}$$

$$\langle \Delta x \rangle = \frac{1}{2} \frac{f}{m} (\Delta t)^2 .$$

So the brownian drift is

$$v = \frac{\langle \Delta x \rangle}{\Delta t} = \frac{1}{2} \frac{f}{m} \Delta t .$$

In terms of the viscous-frictcoin coefficient

$$\zeta = \frac{2m}{\Delta t},$$

the drift speed v is

$$v = \frac{1}{2} \frac{f}{m} \Delta t$$

$$= f \Big/ \left(\frac{2m}{\Delta t} \right) = f/\zeta .$$

Stokes's formula for the viscous-friction coefficient of a sphere of radius R in a fluid of viscosity η is $\zeta = 6\pi \eta R$.

The viscosity of water at room temperature is

$$\eta \approx 10^{-3} \text{ kg m}^{-1} \text{s}^{-1}.$$

Einstein noticed that the ideal-gas law says

$$pV = m\langle v_x^2\rangle N = NkT$$

So

$$m\langle v_x^2\rangle = kT$$

and

$$m\langle \vec{v}^{\,2}\rangle = 3kT.$$

So he realized that

$$\langle v_x^2\rangle = \frac{kT}{m} = \left\langle\left(\frac{L}{\Delta t}\right)^2\right\rangle.$$

So

$$kT = m\langle v_x^2\rangle = m\left\langle\left(\frac{L}{\Delta t}\right)^2\right\rangle$$

$$= \frac{m}{\Delta t}\frac{L^2}{\Delta t} = \frac{2m}{\Delta t}\frac{L^2}{2\Delta t} = \eta D.$$

Thus k is given by

$$k = \frac{\eta D}{T}$$

in which η, D, and T all are measurable quantities.

We measure η by seeing how fast particles in a fluid settle under the force of gravity

$$v = \frac{f}{\eta} = \frac{mg}{\eta}$$

and $D = \left\langle \frac{\vec{r}^{\,2}}{6t} \right\rangle$ in 3 dimensions.

So for colloidal particles η and D are measurable. Einstein got k as

$$k = \frac{\eta D}{T}.$$

He then got N by

$$pV = NkT$$

or

$$N = \frac{pV}{kT}.$$

Then he knew the mass of a molecule by

$$m = \frac{\text{molar mass}}{N}.$$

And this was in his Ph.D. thesis! And in 1905, Einstein also proposed that the light consists of particles, later called "photons," and that a photon of frequency ν had energy $E = h\nu$ where h is Planck's constant, $h = 6.6 \times 10^{-34}$ Js.