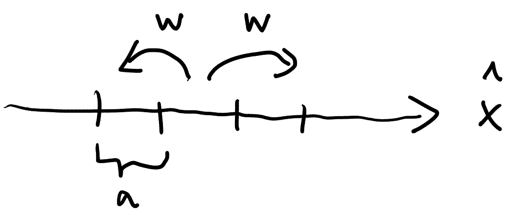
$$\langle i \rangle_t = i_0 \qquad \langle i^2 \rangle_t = i_0^2 + 2wt$$

$$\Rightarrow \quad \text{MSD} \quad \langle \Delta_i^2 \rangle_t = 2 \underbrace{wa^2}_{D} t = 2Dt$$

$$\Delta_i = a(i - i_0)$$



$$D = wa^2 = \frac{\text{length}^2}{\text{time}}$$ diffusion constant

generalize to 3D: $\vec{r} = a(i, j, k)$ integer labels of box

initial pos: $\vec{r}_0 = a(i_0, j_0, k_0)$

displacements:
$$\Delta_i = a(i - i_0)$$
$$\Delta_j = a(j - j_0)$$
$$\Delta_k = a(k - k_0)$$

3D MSD: $\langle (\vec{r} - \vec{r}_0)^2 \rangle_t$

$$= \langle a^2(i-i_0)^2 + a^2(j-j_0)^2 + a^2(k-k_0)^2 \rangle_t$$

$$= \underbrace{\langle \Delta_i^2 \rangle_t}_{2Dt} + \underbrace{\langle \Delta_j^2 \rangle_t}_{2Dt} + \underbrace{\langle \Delta_k^2 \rangle_t}_{2Dt}$$

$$= 6Dt \qquad (3D)$$

2D MSD $= 4Dt \qquad (2D)$

compare to "ballistic" motion: const. vel. v

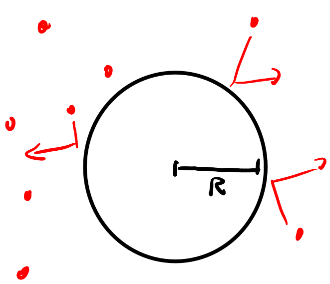
dist. $L = v\,t$

$L^2 = v^2 t^2 \propto t^2$

versus diffusion: $\langle (\vec{r} - \vec{r}_0)^2 \rangle_t \sim t$

RMSD $\quad L \sim \sqrt{\langle (\vec{r} - \vec{r}_0)^2 \rangle_t} \sim t^{1/2}$

How to estimate D?



sphere in a fluid

fluid viscosity η

temp. T

Stokes law $\quad D = \dfrac{k_B T}{6 \pi \eta R}$

$R = 1$ nm

$D = 245\ \mu m^2/s$

$k_B = 1.38 \times 10^{-23}$ J/K

$T = 298$ K

$\eta = .89 \times 10^{-3}$ Pa·s (water)

$$MSD \sim L^2 = 6 D t \Rightarrow t \approx \frac{L^2}{6D}$$

rough time to cover a distance L for diffusion

How to solve for $p_i(t)$?

$$\frac{dp_i}{dt} = \sum_j \Omega_{ij} p_j$$

$\left.\begin{array}{l} \text{grid} \rightarrow \text{small} \\ a \rightarrow 0 \\ N = \frac{L}{a} \rightarrow \infty \end{array}\right\}$ continuum limit

discrete pos: $\underset{\substack{\uparrow \\ \text{integer}}}{x = i\,a}$ $\longrightarrow$ continuous position x

probability $p_i(t)$ $\longrightarrow$ $p(x,t)$ = prob. density to be at x at time t

$$\sum_i p_i(t) = 1 \longrightarrow \int dx\, \underbrace{p(x,t)}_{\text{units: } 1/\text{Length}} = 1$$

$p(x,t)\,dx$ = prob. to be b/t x + $x+dx$ at time t

$$a \longrightarrow dx$$

Next time: show master equation

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

diffusion equ.