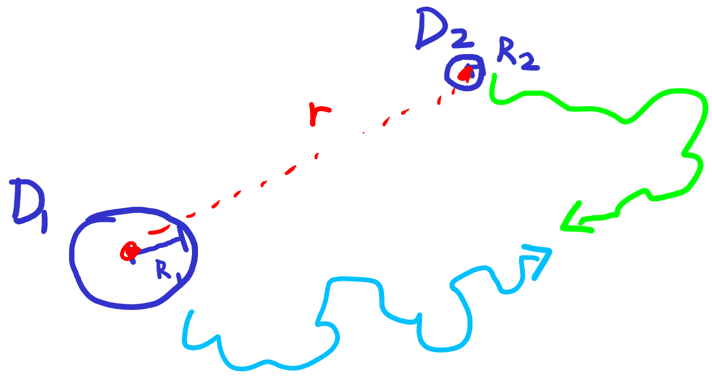
PHYS 320/420 Lecture 10



separation r behaves like a diffusing particle w/ effective diffusivity

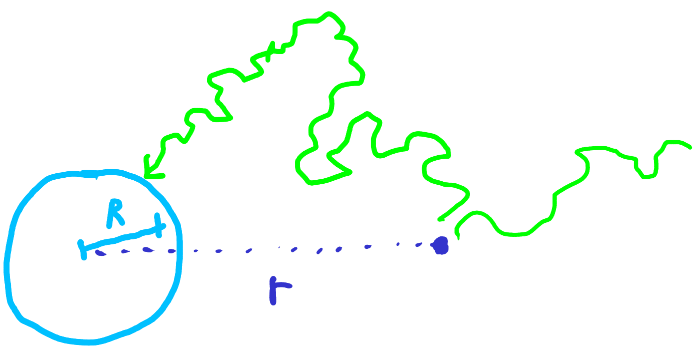
$$D = D_1 + D_2$$

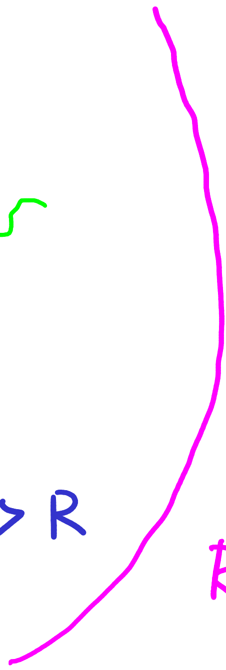
initial sep.

r

final separation ("target")

$$R = R_1 + R_2$$





R_{max} = radius corr. to outer boundary

$R \sim$ nm

$R_{max} >> R$

$R_{max} \sim \mu m$

spherically symm. problem

$\tau(\vec{r})$ = mean first passage time from $\vec{r}$ to a sphere of radius R around origin

$\Downarrow$

$\tau(r)$

just depends on mag. of separation by symmetry

1D

$$D \frac{\partial^2}{\partial x^2} \tau(x) = -1$$

$$\tau(x_c) = 0 \qquad \left.\frac{\partial \tau}{\partial x}\right|_{\text{boundary}} = 0$$

3D

$$D \underbrace{\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right]}_{\nabla^2} \tau(\vec{r}) = -1$$

$$\tau\left(\vec{r} \in \begin{matrix}\text{sphere of} \\ \text{radius } R\end{matrix}\right) = 0$$

$$\nabla \tau(\vec{r})\Big|_{\text{outer boundary}} = 0$$

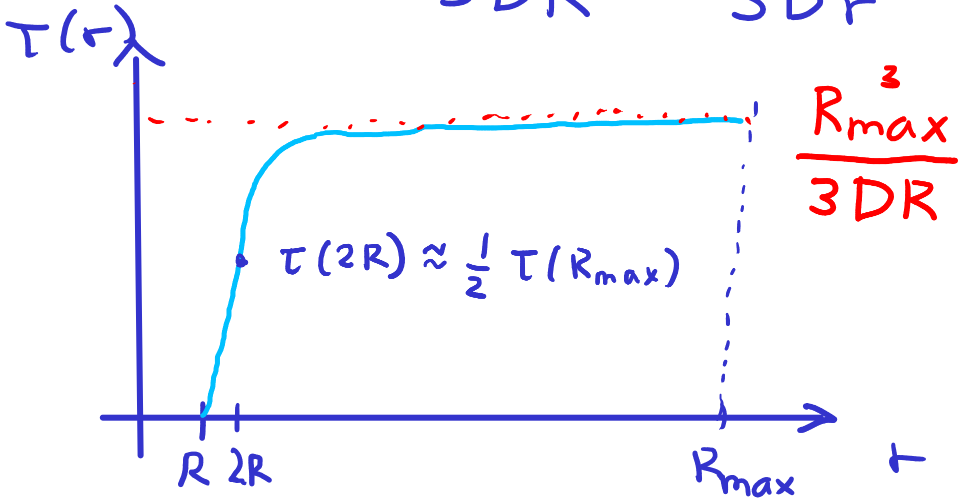
switch to spherical coord. & take advantage of $\tau(\vec{r}) = \tau(r)$

$\vec{r} = (r, \theta, \phi)$

$$\Rightarrow \quad D\left[\frac{\partial^2}{\partial r^2}\tau(r) + \frac{2}{r}\frac{\partial}{\partial r}\tau(r)\right] = -1$$

$$\tau(R) = 0 \qquad \left.\frac{\partial \tau}{\partial r}\right|_{r=R_{max}} = 0$$

$$\Rightarrow \quad \tau(r) = \frac{R_{max}^3}{3DR} - \frac{R_{max}^3}{3Dr} - \frac{r^2}{6D} + \frac{R^2}{6D}$$



once beyond a few nm (a few multiples of R) the time $\tau(r)$ becomes essentially constant

$$\tau \approx \frac{R_{max}^3}{3DR} = \underbrace{\left(\frac{R_{max}^2}{6D}\right)}_{\substack{\text{time to achieve an} \\ \text{MSD of } R_{max}^2 \\ \text{(diffused across entire cell)}}} \underbrace{\left(\frac{2R_{max}}{R}\right)}_{\substack{\text{addit. factor} \\ \text{required for a} \\ \text{collision}}}$$

$$MSD = 6Dt$$

$$t = \frac{MSD}{6D}$$

$R_1 = R_2 = 1$ nm

$D_1 = D_2 = 10\ \mu m^2/s$

$R = 2$ nm

$D = 20\ \mu m^2/s$

$$\tau = (8.3 \times 10^{-3}\ s)(1000)$$

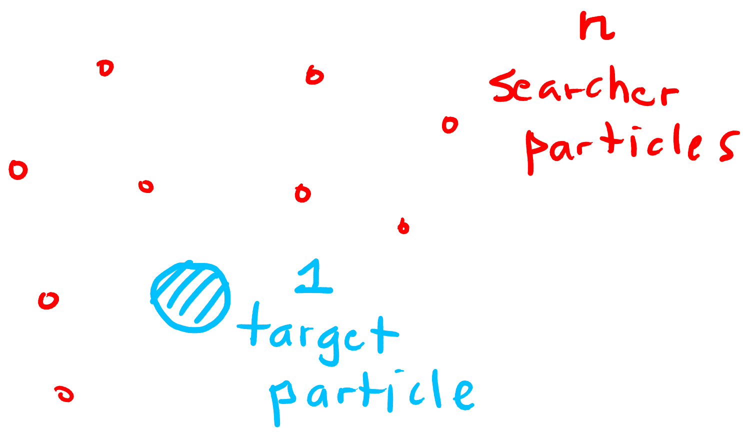
$$= 8.3\ s$$

$R_{max} = 1\ \mu m$

for bacteria

Naive way of speeding this up:

have many particles involved!



how long before one searcher hits the target for first time?

$$\tau = \left(\frac{R_{max}^2}{6D}\right)\left(\frac{2R_{max}}{nR}\right)$$

timescale to explore whole cell

likelihood of collision increases by n

$V = \frac{4}{3}\pi R_{max}^3$ volume confining our particles

$$\Rightarrow \tau = \frac{V}{4\pi D R n} = \frac{1}{4\pi D R c}$$

Concentration of searchers $c = \frac{n}{V}$

rate of searchers hitting target:

$$\boxed{k_{Smol} = \frac{1}{\tau} = 4\pi D R c}$$

Smoluchowski rate: "speed limit" for chemistry

B/c any reaction requires particles to hit first, actual reaction rate will be slower than k_{Smol}

note: this limit is valid when the searchers diffuse purely in 3D. It changes when search is a combo of 3D + lower dim.