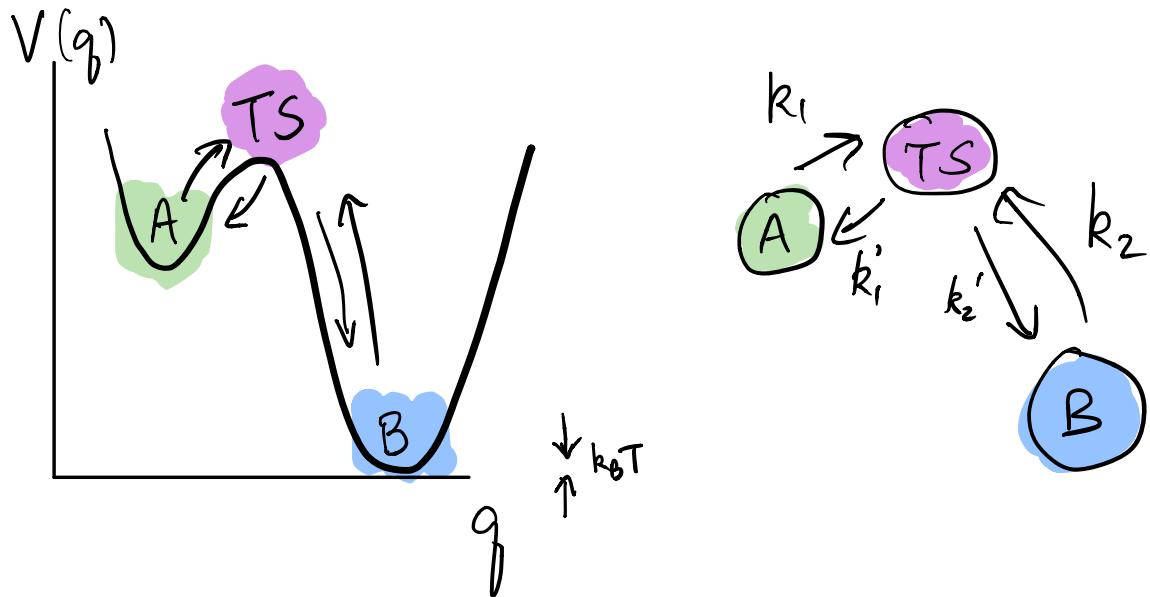


## Lecture 17

Recall from last lecture ...

### Three-state kinetics



Actually solve for  $c(t)$  using math...

$$\frac{dc}{dt} = \underbrace{\begin{pmatrix} -k_1 & k_1' & 0 \\ k_1 & -k_1 - k_2' & k_2 \\ 0 & k_2' & -k_2 \end{pmatrix}}_{\text{W}} c \quad \text{Master equation}$$

$$\Rightarrow c(t) = c^{eq} + x e^{-t/k_1} + y e^{-t/k_2}$$

Approximate solution becomes very good when visiting TS is rare. ( $k_1 \ll k_1' + k_2 \ll k_2'$ )

Steady-state approximation ( $\frac{dc_{TS}}{dt} = 0$ ) leads to an effective two-state kinetics between A & B.

$$\frac{d}{dt} \begin{pmatrix} c_A \\ c_B \end{pmatrix} = \begin{pmatrix} -k_1 k_2' & k_2 k_1' \\ k_1' + k_2' & -k_1 k_2' \\ k_1 k_2' & k_1' + k_2' \end{pmatrix} \begin{pmatrix} c_A \\ c_B \end{pmatrix}$$

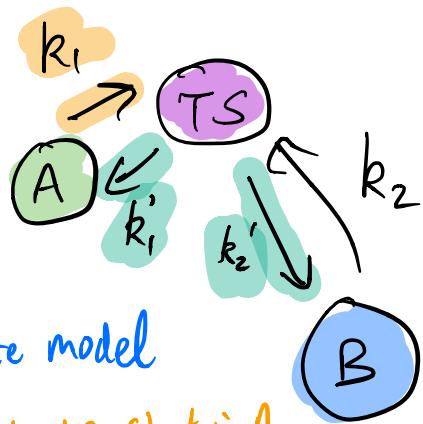
$$= \begin{pmatrix} -k_{BA}^{\text{eff}} & k_{AB}^{\text{eff}} \\ k_{BA}^{\text{eff}} & -k_{AB}^{\text{eff}} \end{pmatrix} \begin{pmatrix} c_A \\ c_B \end{pmatrix}$$

So  $c_{TS} = 0$ ? Then why include it at all?

Just because  $c_{TS} \approx 0$ , doesn't mean it is not important because the only way to go from A  $\rightleftharpoons$  B is to pass through TS.

$$k_{BA}^{\text{eff}} = k_1$$

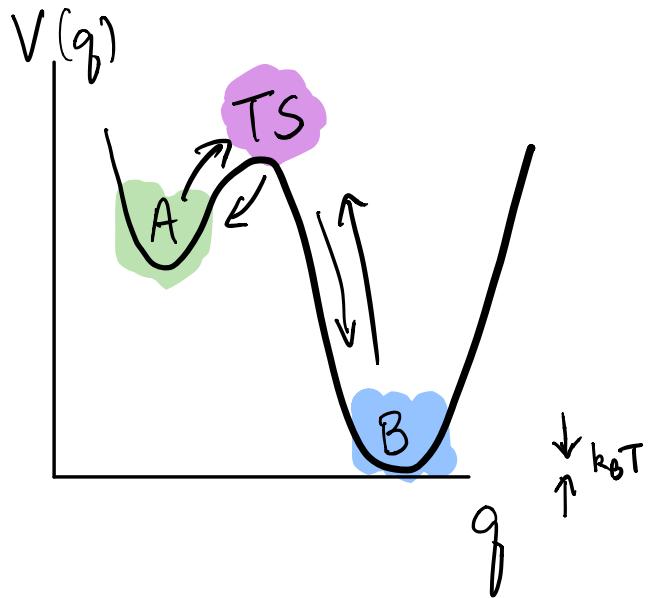
$$\frac{k_2'}{k_1' + k_2'}$$



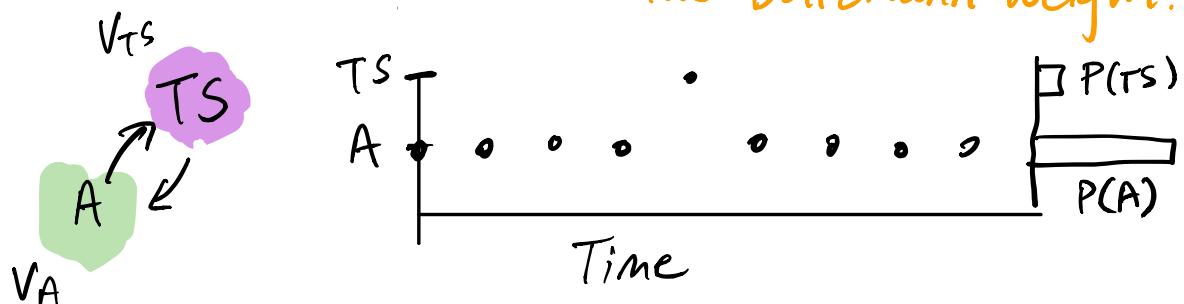
Rate constant if we only had a 2-state model

Probability per unit time to go from A  $\rightarrow$  TS given you start in A

Preference for falling right versus left at the top of the barrier



If dynamics in the "A basin" is effectively equilibrated, a reasonable guess for the probability of reaching TS compared to the probability of being at the bottom of the basin is given by the Boltzmann weight.

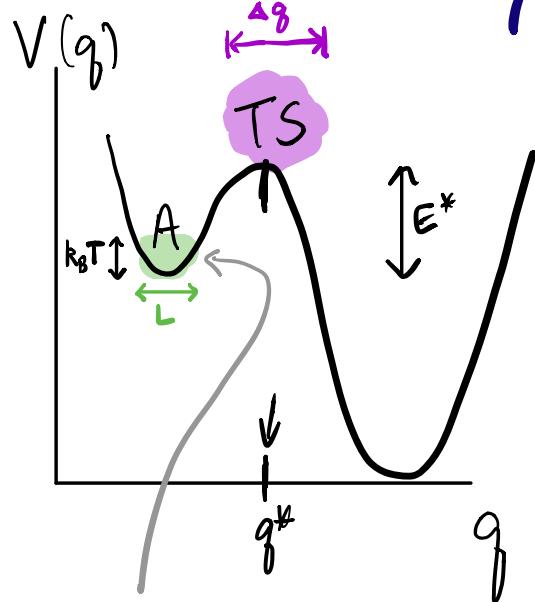


$$P_A = \frac{e^{-\beta V_A}}{Q}$$

$$P_{TS} = \frac{e^{-\beta V_{TS}}}{Q}$$

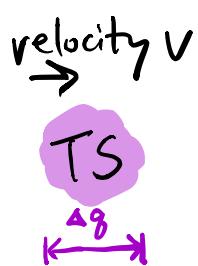
Fraction of time you will randomly reach TS:  $e^{-\beta(V_{TS} - V_A)}$

Transition State Theory: A way to try to estimate a rate using a free energy.



Highly likely states are confined to this region.

$$\frac{\text{Probability of TS}}{\text{Probability of A}} = \frac{\Delta q e^{-\beta E^*}}{L}$$



Average time to get across a distance  $\Delta q$ :

$$\frac{\langle |v| \rangle}{\Delta q}$$

$$k_{BA}^{(TST)} = \frac{\Delta q e^{-\beta E^*}}{L} \frac{\langle |v| \rangle}{\Delta q} \frac{1}{2}$$

$$= \underbrace{\frac{e^{-\beta E^*}}{L}}_2 \frac{\langle |v| \rangle}{2}$$

$$= \frac{Q_{TS}}{Q_A} \frac{\langle |v| \rangle}{2}$$

Probability density at TS surface given confinement to region A.

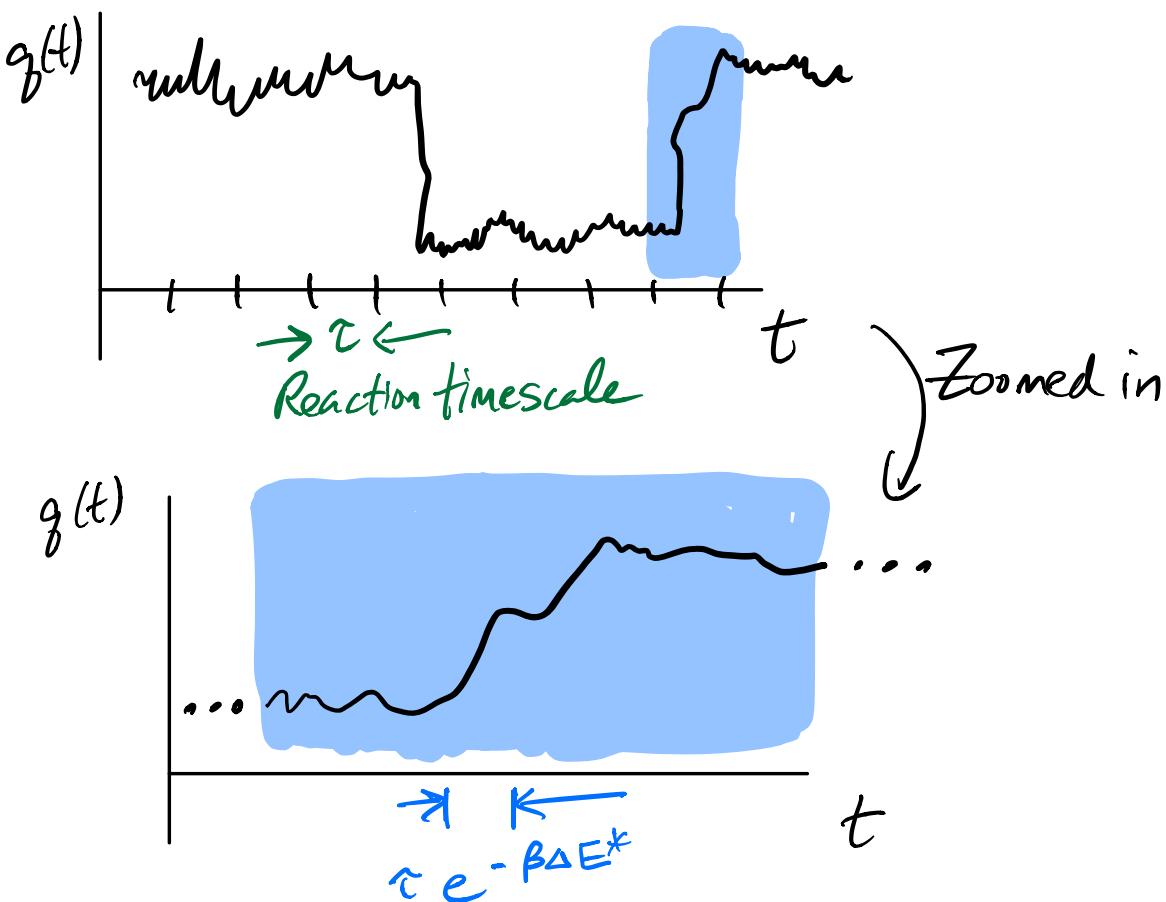
$\therefore$  Rates often go like

$$k = A e^{-E^*/k_B T}$$

↑  
"Prefactor"  
No T-dependence

An "activation energy"  
Arrhenius Rates

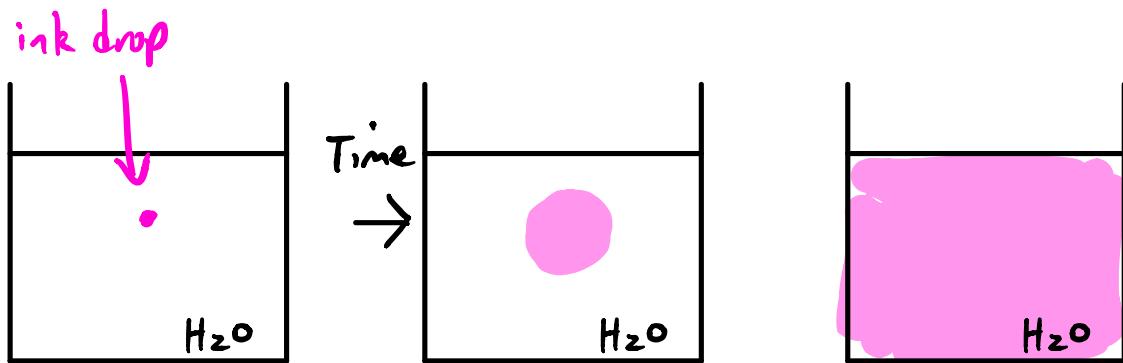
Activated processes have a separation of timescales.



The average rate of a trans-gauche isomerization in alkane chains is  $\sim 10^9 \text{ sec}^{-1}$  per molecule per dihedral angle. ( $\tau \sim 10^{-9} \text{ sec}$ )

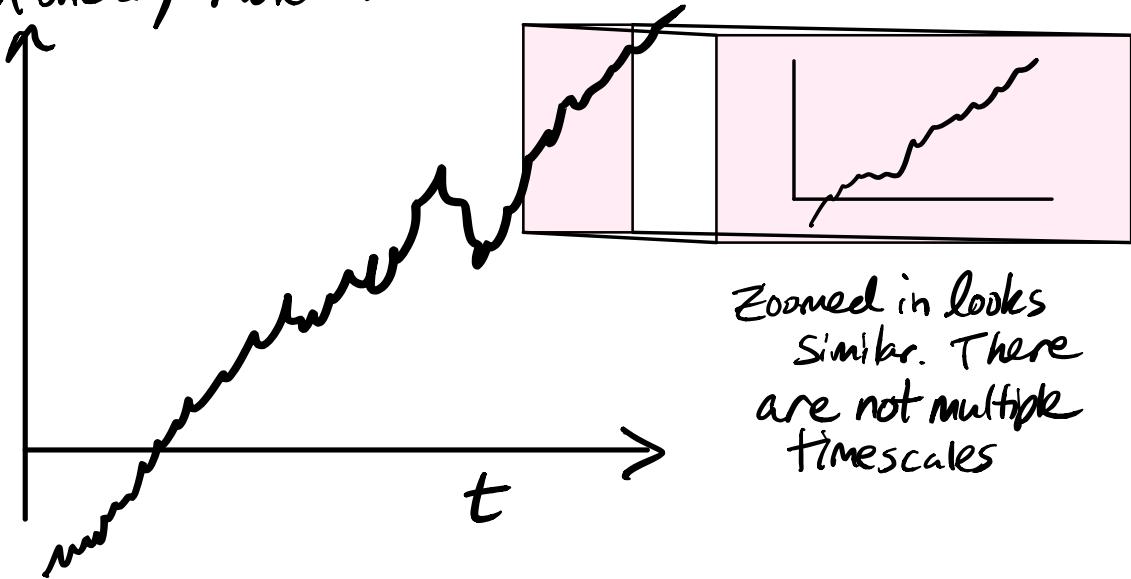
Typical small amplitude fluctuations of the dihedral angles occur on the timescale of  $10^{-12}$  or  $10^{-13} \text{ sec}$ . ( $E^* \approx 6 \text{ or } 7 k_B T$ )

Not all dynamics is activated



Diffusion proceeds via slow and steady progress

$x(t)$  of one dye molecule



How far does a molecule typically move in a fixed amount of time?

First, let's imagine the particle is traveling in vacuum with a fixed velocity  $v$ .  
(No forces)

$$\langle x(t) - x(0) \rangle = vt$$

Every molecule does the exact same thing. No randomness... yet.

$$\Rightarrow \langle (x(t) - x(0))^2 \rangle = v^2 t^2$$

What about if the direction of the velocity were chosen from some (symmetric) distribution?

$$\langle x(t) - x(0) \rangle = 0 \quad (\text{By symmetry})$$

$$\langle S(x(t) - x(0))^2 \rangle = v^2 t^2$$

Mean squared displacement (MSD)

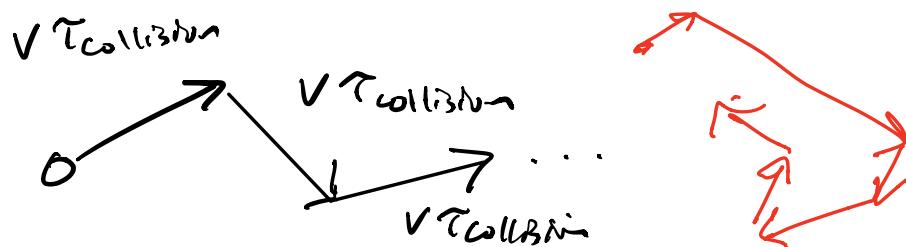
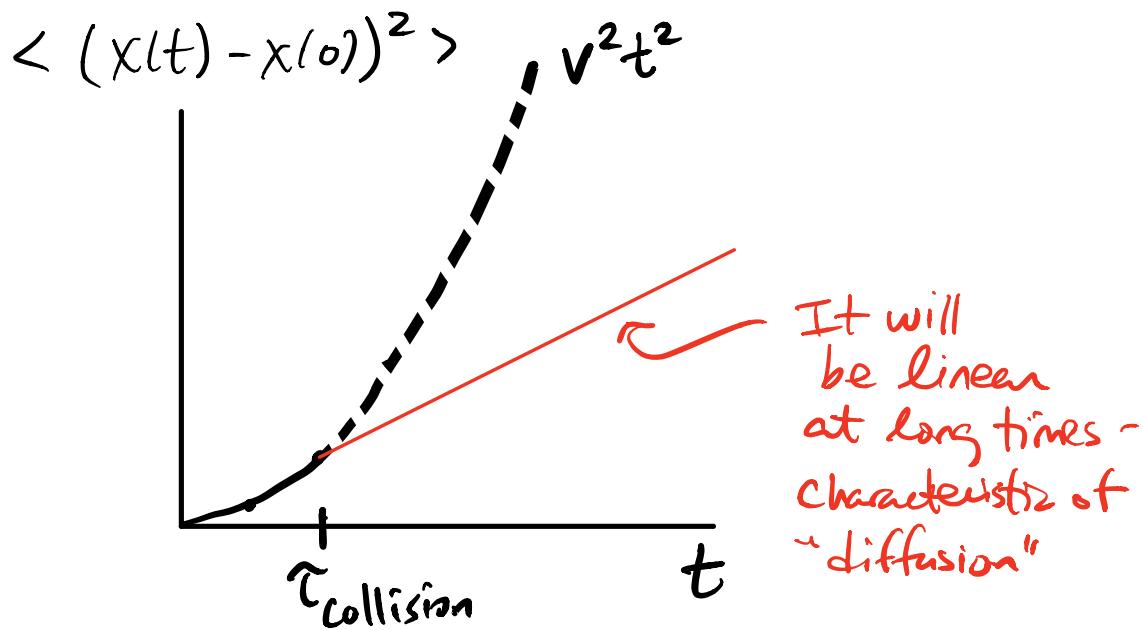
What is a typical distance traveled after time  $t$  by a particle whose initial magnitude is  $v$ ?

$$\sqrt{\langle (x(t) - x(0))^2 \rangle} = vt$$

Root mean squared distance (RMS)

Ballistic Motion.

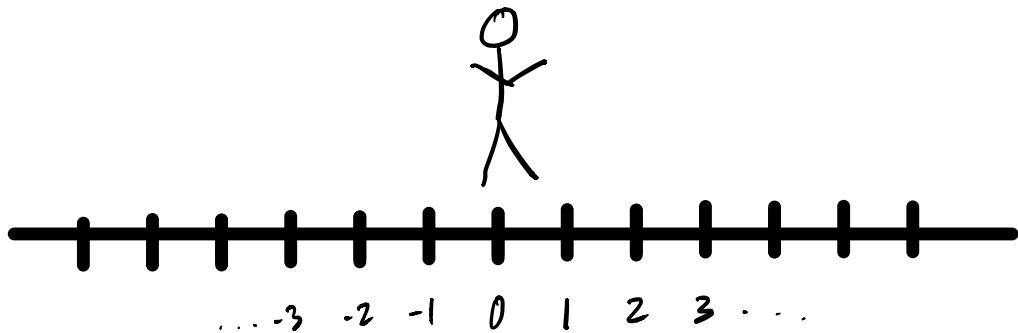
Molecules in solution have collisions.



This looks a lot like our models of polymers. It's a random walker.

"A random walker in 1D"  
 (A model that explains diffusion)

$$\frac{1}{2} \leftarrow \rightarrow \frac{1}{2}$$



$$P_T(x) = \frac{e^{-\frac{x^2}{2T}}}{\sqrt{2\pi T}}$$

$$\langle x \rangle_T = 0$$

(by symmetry)

$$\langle \delta x^2 \rangle = T$$

$$P_T(x) \rightarrow \frac{1}{\sqrt{2\pi T}} e^{-\frac{x^2}{2T}}$$

Notice that  $\langle \delta x^2 \rangle$  is  $\langle (x(t) - x(0))^2 \rangle$  after time  $t$ , so the 1D random walk model predicts

$$\langle (x(t) - x(0))^2 \rangle \propto t \quad (\text{once collisions have kicked in.})$$

Is this limited to 1D? **NO**

Is this limited to a walker that takes equal steps?

(Our velocities would not be the same after each collision, nor would  $\langle v_{\text{collision}} \rangle$  always be a constant.)

**Not limited.** (Central limit theorem)

What determines the slope?

$$\langle (x(t) - x(0))^2 \rangle = \text{Const.} \times t$$

What should we call this constant that controls diffusion?

$$\frac{2d}{\pi} D$$

↑  
Dimensionality

Diffusion Constant

Why is the slope  $2dD$ ?

Why is the slope proportional to  $d$ ?

Let  $\vec{R} = (x, y, z)$  (3D)

What is  $\langle (\vec{R}(t) - \vec{R}(0))^2 \rangle$ ?

$$\begin{aligned}\langle (\vec{R}(t) - \vec{R}(0))^2 \rangle &= \\ \cancel{3D} \quad \langle (x(t) - x(0))^2 + (y(t) - y(0))^2 + (z(t) - z(0))^2 \rangle \\ &= 3 \underbrace{\langle (x(t) - x(0))^2 \rangle}_{1D}\end{aligned}$$

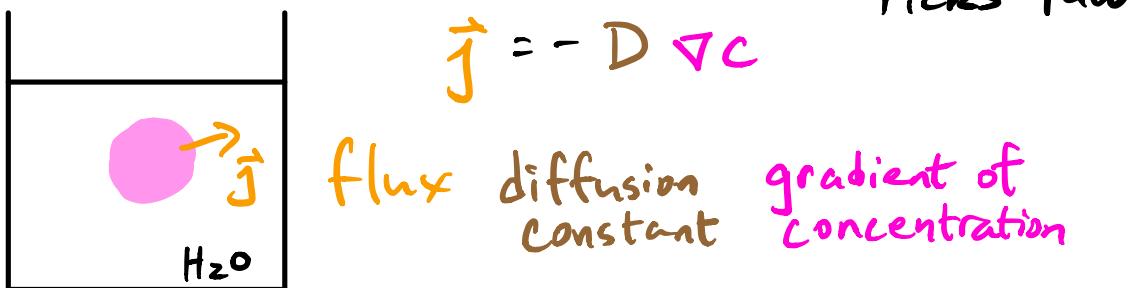
In general, the MSD will be  $d$  times the one-dimensional result (assuming all directions are statistically equivalent)

Why is there a factor of 2?

Ask an engineer about diffusion and they are less likely to start with a random walker.

They will probably start with a continuous space description...

Let  $c(r,t)$  be the concentration of ink at position  $r$  + time  $t$ .



Your engineer friend will tell you about a "continuity equation"

$$\frac{\partial c(r,t)}{\partial t} + \nabla \cdot \vec{j}(r,t) = 0$$

Change in concentration at  $r$  and  $t$  is balanced by fluxes into and out of position  $r$ .

Plugging in Fick's law...

$$\frac{\partial c(r,t)}{\partial t} - D \nabla^2 c(r,t) = 0$$

Start with  $c(r, 0) = \delta(r) \leftarrow$  Dirac  $\delta$  at origin

$$\Rightarrow c(r, t) = \frac{1}{(4\pi D t)^{d/2}} \exp\left(\frac{-r^2}{4Dt}\right)$$

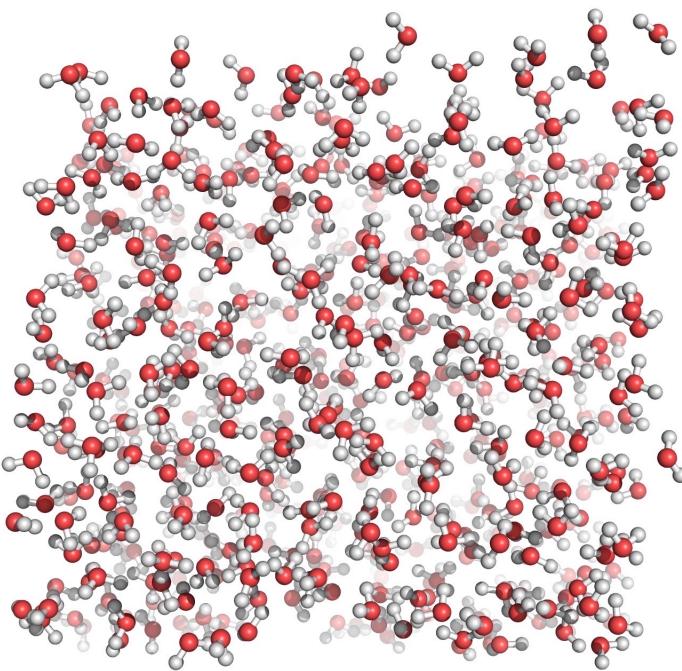
And if we did Gaussian integrals for each dimension we would find

$$\langle (r(t) - \underline{r(0)})^2 \rangle = 2dDt$$

$\uparrow$   
D (origin)

We had to pick whether the MSD's proportionality constant would be called D or whether j's proportionality with  $\nabla c$  would be called D. We couldn't have both.

## Recap of the course ...



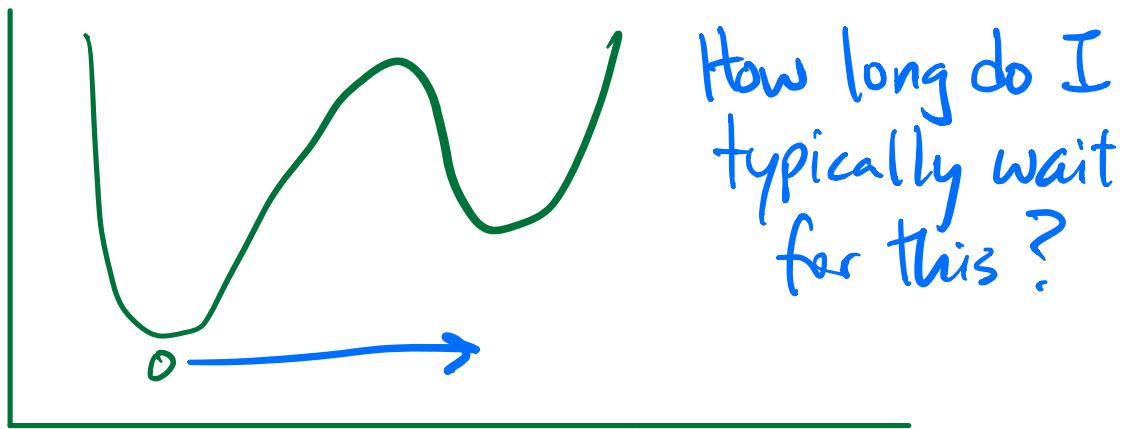
Chemical dynamics is high dimensional and complicated. We cannot hope to track the quantum or classical dynamics of  $O(10^{23})$  degrees of freedom.

In practice we were only ever going to measure some of the degrees of freedom, so we sought theories to describe only those preferred coordinates.

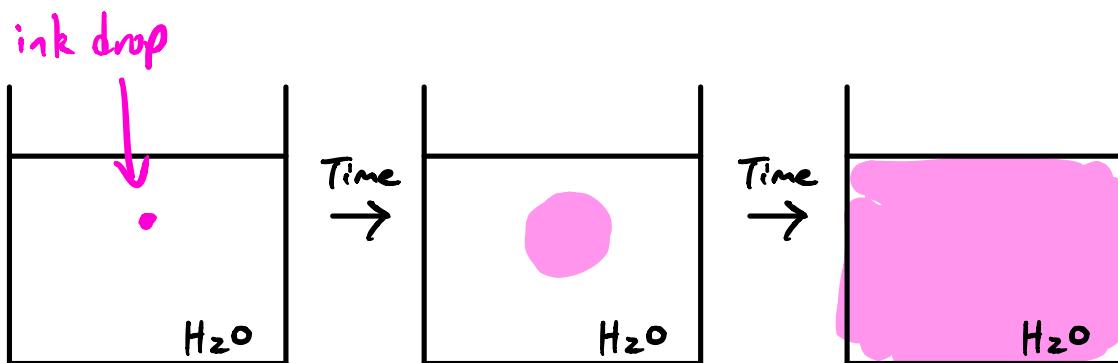
## Kinetics

How do the preferred coordinate(s) change in time

- Rate



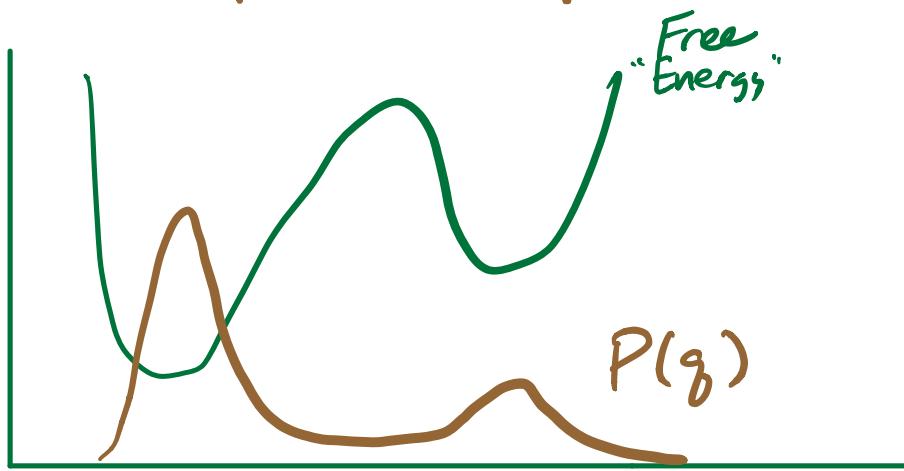
## Preferred "Reaction" Coordinate



How long do I typically wait for this?

# Statistical Mechanics

If I make measurements after waiting a long time, what probability distribution do I expect to sample



Preferred "Reaction" Coordinate  $q$

$(q, \overset{x}{\underset{\sim}{x}})$  ← Microstate  $\nu$   
Everything else

$\rho(q, x)$ : Probability density for microstate  $\nu$

$$\Rightarrow \rho(g) = \int dx \rho(g, x) = Q(g) \leftarrow$$

Marginal distribution for the coordinate I measure

Average over all  $x$  with fixed  $g$ .  
Partition Function

Remember

$$\text{Free energy} \quad -\beta A = \ln Q \quad \text{Partition Function}$$

↓

$$\underline{A = -k_B T \ln \rho(g)}$$

Free energy  $\Leftrightarrow$  Reversible Work

The work it takes to change  $g$  is determined by the distribution that  $g$  would sample in "natural" undriven dynamics.

## Thermodynamics

In the limit of very large systems the statistical mechanical description becomes deterministic (distributions are dominated by a single value) and the impact of microscopic fluctuations all gets clumped into material properties.

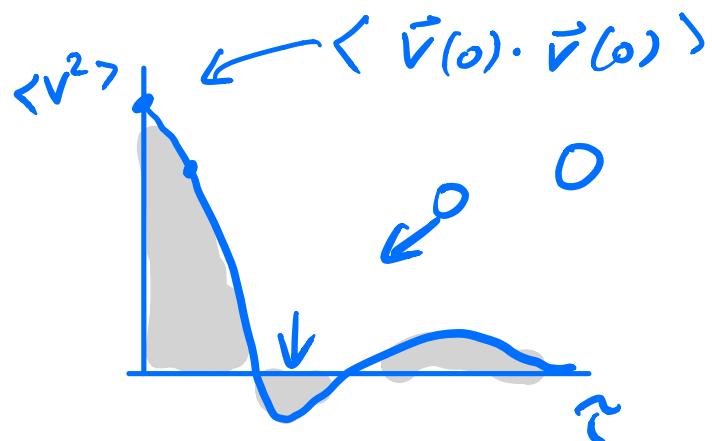
Ex.

Heat capacity at constant volume

$$C_V = \frac{\langle \delta E^2 \rangle}{k_B T^2}$$

$$D = \frac{1}{\pi} \int_0^\infty d\tau \langle \vec{v}(0) \cdot \vec{v}(\tau) \rangle$$

Velocity autocorrelation function



Green-Kubo Relation.