Averages by integration

$$\langle A \rangle = \int dr^N \, A(r^N) \, P(r^N)$$

↑ probability density

$$P(r^N) = \frac{e^{-\beta U(r^N)}}{Z_N}$$

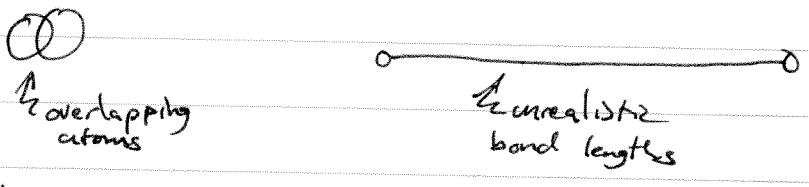
Z_N ← configurational P.F.

Brute force:

$$\langle A \rangle = \frac{\sum_{i=1}^{N_{trial}} A(r_i^N) \, e^{-\beta U(r_i^N)}}{\sum_{i=1}^{N_{trial}} e^{-\beta U(r_i^N)}}$$

each trial corresponds to randomly choosing all $3N$ coordinates of all N atoms each time.

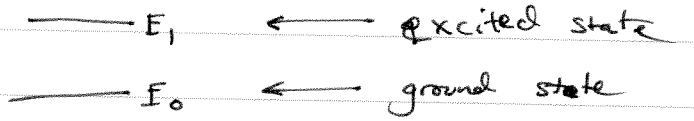
Many of these trials will be "unimportant" parts of space, i.e. where $e^{-\beta U(r_i^N)} \approx 0$



Sampling will be inefficient. How to fix this?

Metropolis MC:

Suppose we have a simple 2 level system:



Further, suppose we know that $e^{-\beta E_0} \approx 2e^{-\beta E_1}$

(Energies are such that ground state is twice as likely as the excited state.)

31-4

So: $$P_0 = \frac{e^{-\beta E_0}}{e^{-\beta E_0} + e^{-\beta E_1}} = \frac{2e^{-\beta E_1}}{2e^{-\beta E_1} + e^{-\beta E_1}} = \frac{2}{3}$$

$$P_1 = \frac{e^{-\beta E_1}}{e^{-\beta E_0} + e^{-\beta E_1}} = \frac{e^{-\beta E_1}}{2e^{-\beta E_1} + e^{-\beta E_1}} = \frac{1}{3}$$

How can we pick states so we visit state 0 twice as often as state 1 ?

We use a ~~transmission~~ matrix Π

$$\begin{pmatrix} P_0(2) \\ P_1(2) \end{pmatrix} = \Pi \begin{pmatrix} P_0(1) \\ P_1(1) \end{pmatrix}$$

← probabilities in 1st step

↑ probabilities after second step

$$\begin{pmatrix} P_0(3) \\ P_1(3) \end{pmatrix} = \Pi \begin{pmatrix} P_0(2) \\ P_1(2) \end{pmatrix}$$

↑ probabilities after 3rd step.

$$\therefore \quad \begin{pmatrix} P_0(n) \\ P_1(n) \end{pmatrix} = \Pi^{n-1} \begin{pmatrix} P_0(1) \\ P_1(1) \end{pmatrix}$$

Π in this very special case is a 2x2 matrix:

$$\Pi = \begin{pmatrix} \frac{1}{2} & 1 \\ \frac{1}{2} & 0 \end{pmatrix}$$

let's try an experiment: Start our system in GS: $\begin{pmatrix} P_0(1) \\ P_1(1) \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$

$$\underset{\sim}{P}(2) = \begin{pmatrix} \frac{1}{2} & 1 \\ \frac{1}{2} & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 1/2 \\ 1/2 \end{pmatrix}$$

$$\underset{\sim}{P}(3) = \begin{pmatrix} \frac{1}{2} & 1 \\ \frac{1}{2} & 0 \end{pmatrix} \begin{pmatrix} 1/2 \\ 1/2 \end{pmatrix} = \begin{pmatrix} 3/4 \\ 1/4 \end{pmatrix}$$

$$\underset{\sim}{P}(4) = \begin{pmatrix} \frac{1}{2} & 1 \\ \frac{1}{2} & 0 \end{pmatrix} \begin{pmatrix} 3/4 \\ 1/4 \end{pmatrix} = \begin{pmatrix} 0.625 \\ 0.375 \end{pmatrix}$$

$$\underset{\sim}{P}(\infty) = \begin{pmatrix} 2/3 \\ 1/3 \end{pmatrix}$$

Suppose we had started the system in state 1:

$$P_0(1) = 0 \qquad P_1(1) = 1$$

$$\underline{P}(2) = \begin{pmatrix} 1/2 & 1 \\ 1/2 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$\vdots$$

$$\underline{P}(\infty) = \begin{pmatrix} 2/3 \\ 1/3 \end{pmatrix}$$

What is special about $\underline{\Pi}$?

$$\underline{P}(\infty) = \Pi \, \underline{P}(\infty)$$

($\underline{P}(\infty)$: large n limit!)

$$\begin{pmatrix} 2/3 \\ 1/3 \end{pmatrix} = \begin{pmatrix} 1/2 & 1 \\ 1/2 & 0 \end{pmatrix} \begin{pmatrix} 2/3 \\ 1/3 \end{pmatrix} = \begin{pmatrix} 2/3 \\ 1/3 \end{pmatrix} \checkmark$$

$\therefore$

$$\sum_i P_i(\infty) \, \Pi_{ij} = P_j(\infty)$$

in an ensemble at equilibrium, the transition matrix must return the equilibrium probability for state j from the equilibrium probability of the other states.

We can try to extract the weights or the equilibrium population information from the purely random part:

$$\Pi_{mn} = \alpha_{mn} P_{mn}$$

- Π_{mn}: transition matrix
- α_{mn}: purely random symmetric "stochastic" matrix (info about how states were chosen)
- P_{mn}: probability of going from state m to n (contains eqm. info P_m & P_n)

31-6

The Metropolis rules:

1) $\pi_{mn} = \alpha_{mn}$ if $\rho_n \geq \rho_m$

2) $\pi_{mn} = \alpha_{mn}\left(\frac{\rho_n}{\rho_m}\right)$ if $\rho_n < \rho_m$

3) $\pi_{mm} = 1 - \sum_{m' \neq m} \pi_{m'm}$

1) if we picked (randomly) a state n which is more probable than original state m, then transition prob is just the prob of picking state in the 1st place, keep the new state!

2) if we picked (randomly) a state n which is less probable than the original, then we might keep the new state. The prob of keeping it depends on the relative probs. of the 2 states.

3) if we happened to pick the same state (at random) we're already in, we have to figure out how likely it is relative to all other states. In practice, this rarely happens:

How we actually do it:

1. Make particles move
2. Did energy go down? If so sample & keep
3. Did energy go up? If so,
   a. pick random on $[0, 1]$
   b. Is this number smaller than $e^{-\beta E_{new}} / e^{-\beta E_{old}}$?
      i. Yes, sample & accept move
      ii. No, sample old again & reject move

Some subtlety in Step 1,

if we make big moves, we will probably reject most of them. This is inefficient sampling. Efficient sampling has

$P_{accept} \approx 0.5$

Make moves:

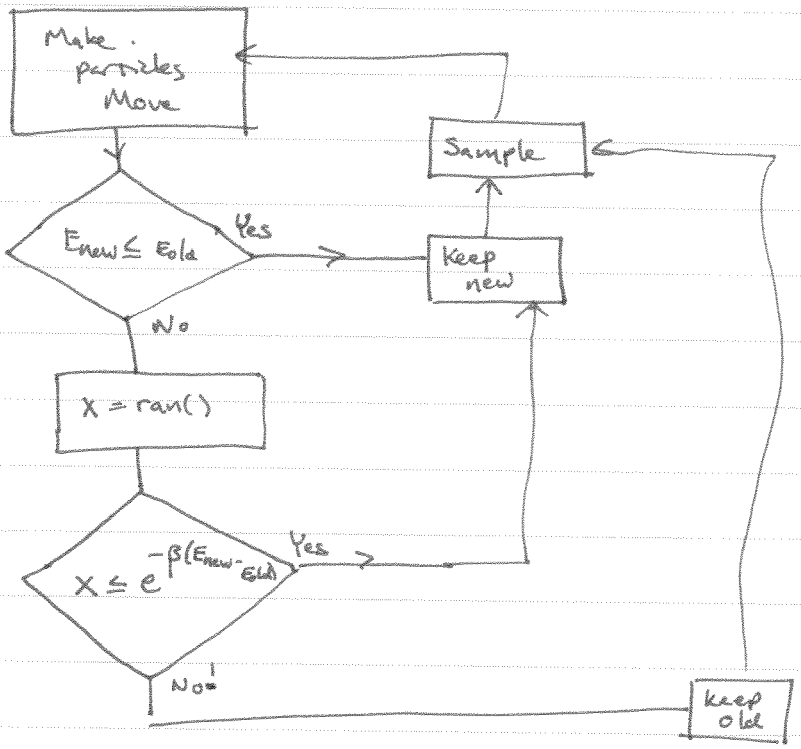
$x_{new} = x_{old} + (2\xi - 1)\,\delta r_{max}$ (ξ: random on $[0,1]$; δr_{max}: max motion allowed in 1 direction)

y

$\vdots$

If Pacc is too small after a few thousand steps, then adjust δr_{max} ↓

If Pacc is too large after a few thousand steps, the adjust δr_{max} ↑



Some subtlety: If we make big moves, we'll probably reject most of them. This is the efficient sampling

Efficient sampling has $P_{accept} \approx 0.5$

Make Moves: $x_{new} = x_{old} + (2\xi - 1)\,\delta r_{max}$ ← max motion along 1 direction

↑ random on [0,1]

If P_{acc} is too small after 1000 steps, then adjust δr_{max} ↓

If P_{acc} is too large after 1000 steps, then adjust δr_{max} ↑

RNGs: $\xi[1]$ = seed

$\xi(i) = (A * \xi[i-1] + B) \bmod M$

modulo arithmetic! ← gives remainder

10 mod 4 = 2 11 mod 4 = 3 12 mod 4 = 0

Linear congruential RNGs:

$$x_n = (a\,x_{n-1} + b) \bmod m \qquad (m \text{ is prime})$$

RANDU

$a = 65539$

$b = 0$

$m = 2^{31} = 2{,}147{,}483{,}648$

$a = 1664525$

$B = 1013904223$

$M = 2^{32} = 4{,}294{,}967{,}296$

x are integers from $0 \to 2^{32}$

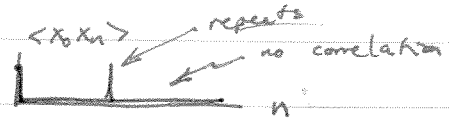
to get reals:

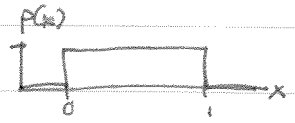
$\frac{x_n}{m} = [0, 1]$

repeats, sometimes poor choices of a & b can give correllated answers

What is a good RNG?

- uniform on [0, 1]
- uncorrelated
- reproducible ← single seed





Other RNGs

Multiple Recursive: $x_n = (a_1 x_{n-1} + a_2 x_{n-2} + \dots a_k x_{n-k}) \bmod p$

period $2^k - 1$

Blum Blum Shub $x_n = (x_{n-1})^2 \bmod m$

$m = pq$ ← 2 large primes $\begin{pmatrix} p = 11 \\ q = 19 \end{pmatrix}$

Mersenne Twister: period $= 2^{19937} - 1$

(Matsumoto & Nishimura 1998)

Generating Gaussian-Distributed Random #s

Box-Muller method (1958)

1. generate 2 random vars, r, a on $[0,1]$

$$X = (-2 \ln r)^{1/2} \cos(2\pi a)$$

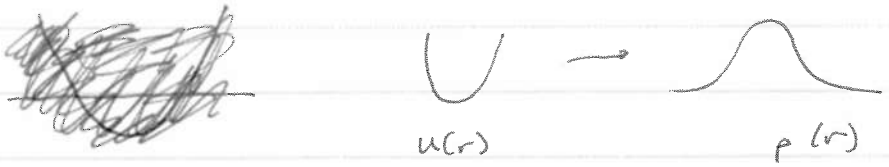
$$y = (-2 \ln r)^{1/2} \sin(2\pi a)$$

↑ these are gaussian distributed (but not independent)

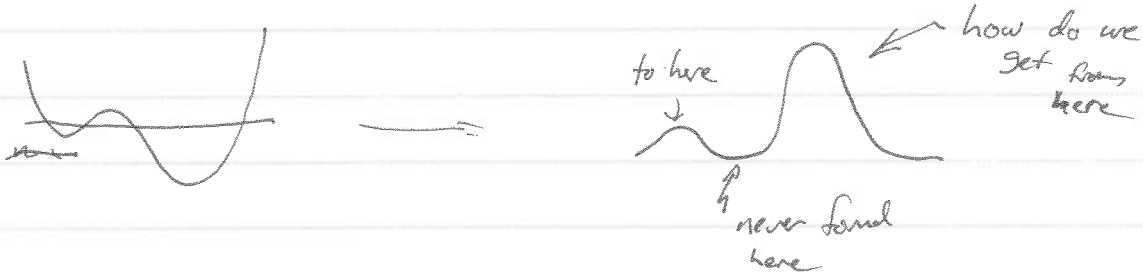
so we use only 1 & start over.

Useful for generating velocities from maxwell boltzmann distribution.

Other subtleties of MC: $p(r) \propto e^{-\beta u(r)}$



MC uses a temperature $\beta = \frac{1}{k_B T}$ to decide on likelihood of uphill moves:



Many methods:

Multiple walkers (good for 1D, hard in higher D)

Simulated annealing

32-4

jump walking
replica exchange MC
} multiple walkers simultaneous

Classical Fluids

$\sigma \rightarrow$ length

$\epsilon \rightarrow$ energy

$m \rightarrow$ mass (also time)

$$U(r^N) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} u_{ij}(r_{ij})$$

$$u_{ij} = 4\epsilon\left(\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right)$$

MC works great for structural properties, but what about time dependent quantities (diffusion, viscosity, thermal conductivity

Start here: $F = ma$

$$m\ddot{\vec{r}}_i = \vec{f}_i = \text{force acting on particle } i$$

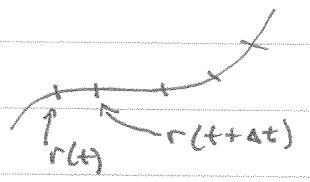
$$= -\frac{\partial}{\partial \vec{r}_i} U(r^N) = -\sum_{j \neq i} \left(\frac{\vec{r}_{ij}}{|r_{ij}|}\right) \frac{du_{ij}(r_{ij})}{dr_{ij}}$$

where $\vec{r}_{ij} = \vec{r}_j - \vec{r}_i$

Newton's equation is a second order coupled differential equation for $3N$ variables: $x_1(t)\ y_1(t), z_1(t) \cdots x_N(t)\ y_N(t), z_N(t)$

$$m\ddot{r}(t) = F[r(t)]$$

To integrate this we imagine a path or trajectory that is locally parabolic in time:

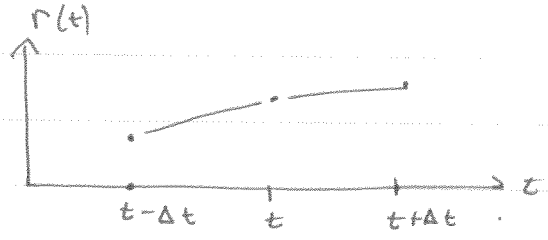


$$r(t+\Delta t) = r(t) + \Delta t\, V(t) + \frac{1}{2}\frac{\Delta t^2}{m} F[r(t)]$$

where

$V(t) = \dot{r}(t)$ is the velocity

We can approximate $v(t)$:



Slope of 1st segment $\quad v_1 \approx \dfrac{r(t) - r(t-\Delta t)}{\Delta t}$

Slope of 2nd segment $\quad v_2 \approx \dfrac{r(t+\Delta t) - r(t)}{\Delta t}$

Average slope: $\quad v(t) = \dfrac{v_1 + v_2}{2} = \dfrac{r(t+\Delta t) - r(t-\Delta t)}{2\Delta t}$

∴ Putting this back in our harmonic expansion:

$$r(t+\Delta t) = r(t) + \Delta t \times \frac{r(t+\Delta t) - r(t-\Delta t)}{2\Delta t} + \frac{\Delta t^2}{2m} F[r(t)]$$

$$\boxed{r(t+\Delta t) = 2r(t) - r(t-\Delta t) + \frac{\Delta t^2}{m} F[r(t)]}$$

Verlet's Leap Frog algorithm, given r at 2 different times and the forces at time t, we can predict the future positions at time $t+\Delta t$

For a LJ fluid:

$$\vec{r}_i^{\,*}(t+\Delta t) = 2\vec{r}_i^{\,*}(t) - \vec{r}_i^{\,*}(t-\Delta t) - (\Delta t^2)^* \left(\frac{48\epsilon}{m\sigma^2}\right) \sum_{j \neq i} \frac{\vec{r}_{ij}^{\,*}}{|r_{ij}^*|} \left[\left(\frac{1}{r_{ij}^*}\right)^{13} - \frac{1}{2}\left(\frac{1}{r_{ij}^*}\right)^{7}\right]$$

Where $\vec{r}_i^{\,*} = \dfrac{\vec{r}_i}{\sigma}$

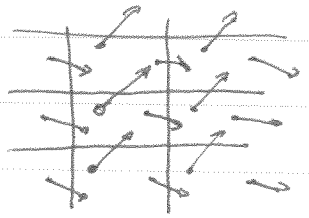
The natural (reduced) unit of time is therefore $\tau = \left(\dfrac{m\sigma^2}{48\epsilon}\right)^{1/2}$

For argon, $\dfrac{\epsilon}{k_B} = 119.8$, $\sigma = 3.405$ Å, $\tau \approx 10^{-13}$ sec $= 0.1$ psec.

The errors in verlet are higher order than $(\Delta t)^2$ and can be made small by setting Δt small. For LJ fluids $\Delta t \approx 0.03\,\tau$ (i.e. 3 fs) is usually sufficient.

Boundary Conditions

We usually imagine a bulk fluid by simulating a portion of an infinitely replicated system:



This is a pretty good model for a bulk system.

No fluctuations larger than the box length can be observed.

Initial conditions:

By equipartition, the total kinetic energy:

$$K = \sum_{i=1}^{N} \tfrac{1}{2} m \vec{v}_i^{\,2} = \sum_{i=1}^{N} \tfrac{1}{2} m_i \left(v_{i,x}^2 + v_{i,y}^2 + v_{i,z}^2 \right)$$

ξ 3N "squared" terms

$$\langle K \rangle = \frac{1}{2} k_B T * 3N$$

$$\langle K \rangle = \frac{3}{2} N k_B T$$

If all velocities are identically distributed:

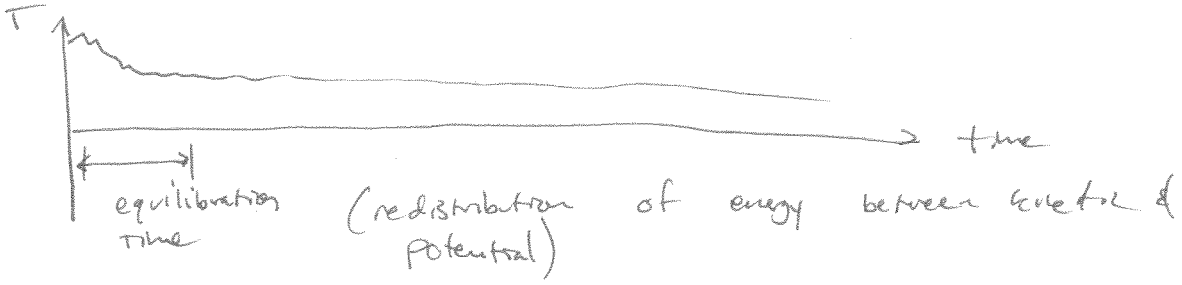
$$3N \left\langle \tfrac{1}{2} m_i v_{ix}^2 \right\rangle = \frac{3N}{2} k_B T$$

$$m_i \langle v_{ix}^2 \rangle = k_B T \qquad \sigma^2 = \frac{k_B T}{m_i}$$

$$\langle v_{ix}^2 \rangle = \frac{k_B T}{m_i} \implies p(v_x) = \frac{\sqrt{m}}{\sqrt{2\pi k_B T}} e^{-m v_{xi}^2 / 2 k_B T}$$

So we can pick initial velocities from a gaussian distribution corresponding to a particular temperature T

If we start the atoms in a regular (FCC) lattice and pick some velocities, do you expect the T to go <u>up</u> or <u>down</u> in time? Why?



<u>Dynamics after equilibration:</u>

By the ergodic hypothesis:

$$\langle G \rangle = \frac{1}{\tau} \int_0^{\tau} dt \; G[r^N(t), v^N(t)]$$

If you focus on a single tagged particle over time, its path would be highly irregular

What do you think this looks like in a <u>solid</u>? In a <u>gas</u>?

Correlations & Time dependence

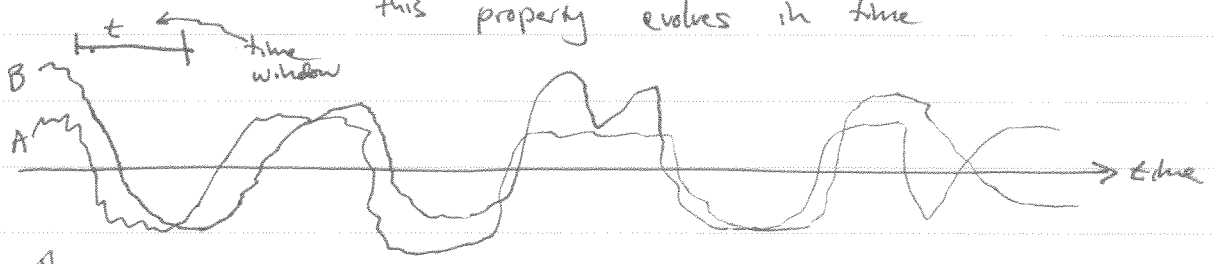
$$C_{AB}(t) = \langle A(0)\,B(t)\rangle = \frac{1}{T-t}\int_0^{T-t} A(t')B(t'+t)\,dt'$$

(T: total run time)

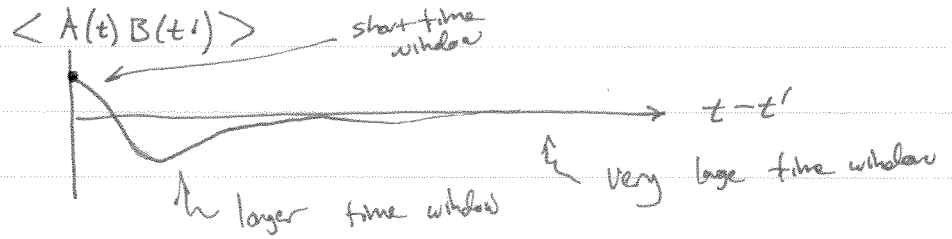
$A(t)$ & $B(t)$ are two (possibly different) variables

$$A(t) = A[r^N(t), p^N(t)]$$

(A: this property evolves in time; $r^N(t), p^N(t)$: these evolve in time)



In this picture, A & B are highly correlated when the time window is small (short time), but are anti-correlated at later times (longer time windows).



At equilibrium:

$$\langle A(t_1)\,B(t_2)\rangle = \langle A(0)\,B(t)\rangle \quad \text{where } t = t_2 - t_1$$

that is, there's nothing special about any particular start time when we're at equilibrium, delay between observations is all that matters.

And:

$$\langle A(0)\,B(t)\rangle = \langle A\rangle\langle B\rangle \quad \text{when } t \to \infty$$

That is, loss of correlation & relaxation are identical concepts.

$C_{AB}(t) = \langle A(0)\, B(t)\rangle$ = A-B cross correlation function

$C_{AA}(t) = \langle A(0)\, A(t)\rangle$ = A auto-correlation function.

$\langle \vec{v}(0)\cdot\vec{v}(t)\rangle$ = velocity auto correlation function

$\langle \vec{\mu}(0)\cdot\vec{\mu}(t)\rangle$ = dipole auto correlation function
↑ related to spectroscopy

$\langle \vec{f}(0)\cdot\vec{f}(t)\rangle$ = force auto correlation function.

$\langle \vec{f}(0)\cdot\vec{v}(t)\rangle$ = force_velocity cross correlation
(related to hydrodynamic friction)

One very special auto-correlation:

$R^2(t)$ = mean squared displacement

$= \langle \left| \vec{r}_1(t) - \vec{r}_1(0) \right|^2 \rangle = \langle (\vec{r}_1(t) - \vec{r}_1(0))\cdot(\vec{r}_1(t) - \vec{r}_1(0)) \rangle$

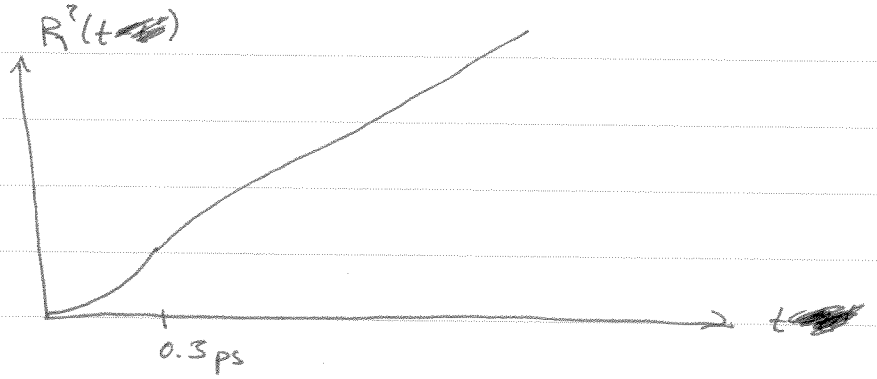
↑ average ↑ separation from initial position in time t

$=$

$\langle r_1^2(t)\rangle - 2\langle \vec{r}_1(t)\cdot\vec{r}_1(0)\rangle + \langle \vec{r}_1^{\,2}(0)\rangle$

↑ explicit auto correlation

Here's what it looks like:



After a short (parabolic) transient, $R^2(t)$ becomes linear in time

↑ ballistic (straight line motion)

Slope of linear regim = 6D where D is the self-diffusion constant:

$$D = \lim_{t\to\infty} \frac{1}{6t} \langle |\vec{r}(t) - \vec{r}(0)|^2 \rangle$$

← Einsteins' relation for macroscopic diffusion in term of microscopic correlations.

For LJ argon, $D \approx 10^{-5} cm^2/s$

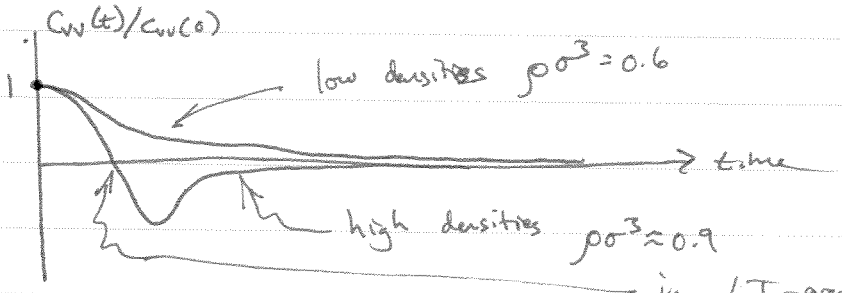
How long will it take an argon atom ($\sigma = 3.4$ Å) to move a distance σ in a liquid?

$$D = \frac{\sigma^2}{6t} \leftarrow \text{what is } t?$$

$$t = \frac{\sigma^2}{6D} = \frac{(3.4 \times 10^{-8} cm)^2}{6\ 10^{-5} cm^2} sec \approx 10\ psec$$

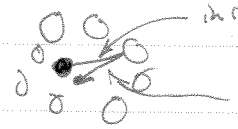
Velocity Auto correlations: ← if all 3 directions are isotropic.

$$C_{VV}(t) = \langle \vec{v}_1(t) \cdot \vec{v}_1(0) \rangle = 3 \langle v_{1z}(0)\, v_{1z}(t) \rangle$$



in LJ-argon ≈ 0.3 ps!

Back scattering at high densities



after 1 collision, the velocity is pointing in the other direction!

Negative-correlation = back-scattering

De-correlation = glancing collisions

Connecting $R^2(t)$ and $C_{vv}(t)$

$$\vec{r}_1(t) = \vec{r}_1(0) + \int_0^t \vec{v}_1(t')\,dt'$$ ← velocity is the derivative of position so if we know $\vec{v}_1(t)$, we can integrate to get the new positions

$$\vec{r}_1(t) - \vec{r}_1(0) = \int_0^t dt'\,\vec{v}_1(t')$$

$$\left|\vec{r}_1(t) - \vec{r}_1(0)\right|^2 = \left(\int_0^t dt'\,\vec{v}_1(t')\right)\left(\int_0^t dt''\,\vec{v}_1(t'')\right)$$ ← two integration times because product involves the entire integral.

$$= \int_0^t \int_0^t dt'\,dt''\;\vec{v}_1(t')\cdot\vec{v}_1(t'')$$

$$\left\langle\left|\vec{r}_1(t) - \vec{r}_1(0)\right|^2\right\rangle = \int_0^t \int_0^t dt'\,dt''\,\left\langle\vec{v}_1(t')\cdot\vec{v}_1(t'')\right\rangle$$

↑ average over particles ; ↑ almost $C_{vv}(t)$

Some important points:

1) Velocity correlation (at equilibrium) is a process that is independent of the origin of time:

$$\langle v(t')\,v(t'')\rangle = \langle v(0)\,v(t''-t')\rangle$$

$$\therefore R^2(t) = \int_0^t \int_0^t dt'\,dt''\,\langle v(0)\,v(t''-t')\rangle$$

2) Eventually, velocity must decorrelate

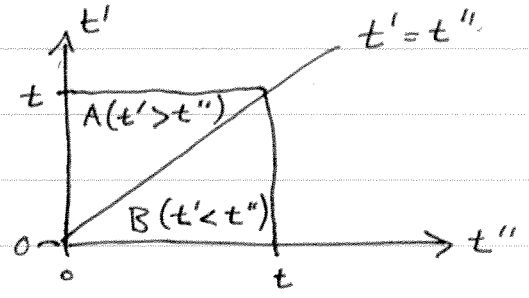
$$\lim_{t\to\infty} \langle v(0)\,v(t)\rangle \longrightarrow 0$$

3) Time is reversible in classical mechanics

$$\therefore \quad \langle v(0)\cdot v(t)\rangle = \langle v(0)\cdot v(-t)\rangle$$

$$\therefore \quad C_{vv}(t) \text{ is an even function of time}$$

Here's how we'll use time reversibility:



Our double integral is over the entire square, but $A + B = 2B$ due to reversibility: $t'' - t' = +(t' - t'')$

So the integral:

$$R^2(t) = 2\int_0^t dt'' \int_0^{t''} dt' \langle v(0)\cdot v(t''-t')\rangle$$

Let's substitute: $y = t'' - t'$ (with limits $(t'', 0)$)

$x = t''$

$$R^2(t) = 2\int_0^t dx \int_0^x dy \langle v(0)\cdot v(y)\rangle$$

Now we can integrate by Parts.

$$u = \int_0^x dy \langle v(0)\cdot v(y)\rangle \qquad dv = dy$$

$$du = \langle v(0)\cdot v(y)\rangle \qquad v = y$$

$$\therefore \quad R^2(t) = 2y\int_0^x dy \langle v(0)\cdot v(y)\rangle \Big|_0^t - 2\int_0^t dy\ y\langle v(0)\cdot v(y)\rangle$$

$$= 2t\int_0^t dy \langle v(0)\cdot v(y)\rangle - 2\int_0^t dy\ y\langle v(0)\cdot v(y)\rangle$$

$$= 2\int_0^t dt'(t-t')\ \langle v(0)\cdot v(t')\rangle$$

Now, since:

$$D = \lim_{t\to\infty} \frac{1}{6t} R^2(t)$$

$$= \lim_{t\to\infty} \frac{1}{3t} \int_0^t dt' \, (t-t') \langle \vec{v}(0) \cdot \vec{v}(t') \rangle$$

as $t \to \infty$ $\quad t - t' \longrightarrow t$

$$D = \frac{1}{3} \int_0^t dt' \langle \vec{v}(0) \cdot \vec{v}(t') \rangle \quad \leftarrow \text{Green Kubo relation for diffusion}$$

$$D = \lim_{t\to\infty} \frac{1}{6t} R^2(t) \quad \leftarrow \text{Einstein relation for diffusion}$$

Other Green-Kubo transport properties:

Shear Viscosity

$$\eta = \frac{1}{V k_B T} \int_0^\infty dt' \langle \sigma^{xy}(t) \, \sigma^{xy}(0) \rangle$$

$$\sigma^{xy} = \sum_{i=1}^{N} \left[m_i v_i^x v_i^y + \frac{1}{2} \sum_{i \neq j} x_{ij} f_y(r_{ij}) \right]$$

Thermal Conductivity

$$\lambda_T = \frac{1}{V k_B T^2} \int_0^\infty dt' \langle q(t) \cdot q(0) \rangle$$

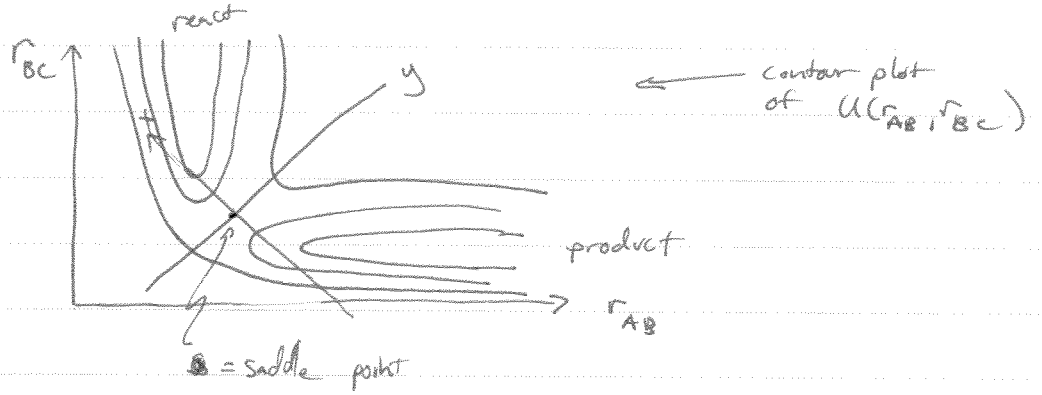
$$q = \frac{d}{dt} \left[\sum_{i=1}^{N} \frac{1}{2} m_i v_i^2 + \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i} u(r_{ij}) \right]$$

Transition state theory:

Consider a reaction:

$$AB + C \longrightarrow A + BC$$

(living in a line: A — B — C, with r_{AB} and r_{BC})

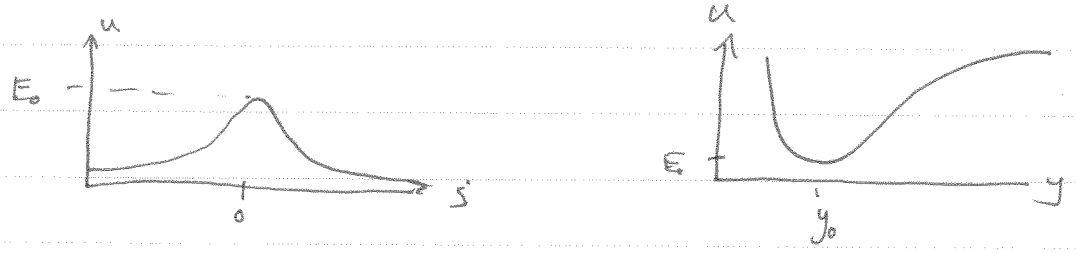


$$s = r_{BC} - r_{AB}$$
$$y = r_{BC} + r_{AB}$$

} new coordinates at saddle point.

s = reaction path

Consider potential along these 2 curves



At the saddle point,

$$\frac{\partial U}{\partial s} = 0, \quad \frac{\partial^2 U}{\partial s^2} < 0$$ ← imaginary frequency at saddle

$$\frac{\partial U}{\partial y} = 0, \quad \frac{\partial^2 U}{\partial y^2} > 0$$ ← real frequency at saddle

Approximate surface near saddle:

$$U(s,y) = \frac{1}{2} C_y (y - y_0)^2 - \frac{1}{2} C_s s^2 + E_0$$

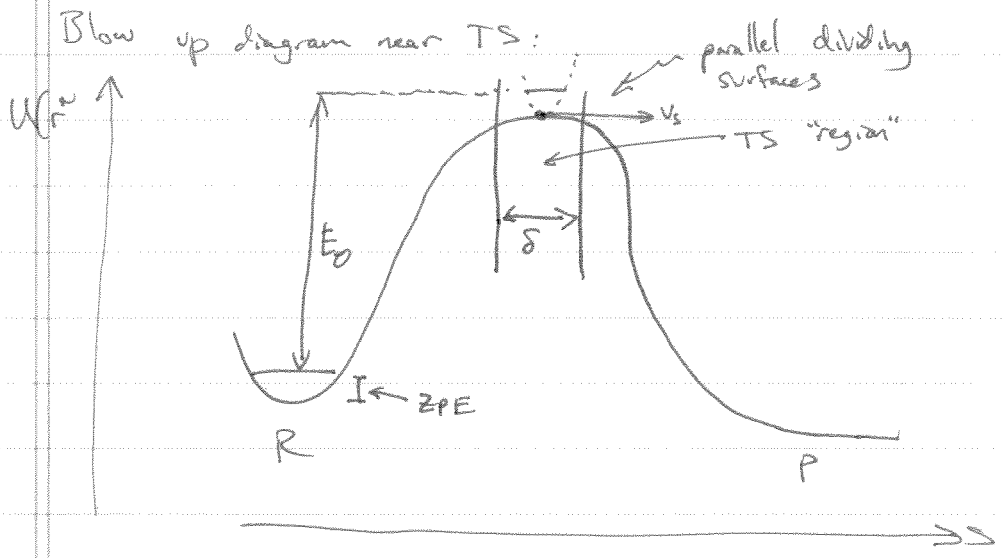
Basic tenets of TST

1) molecules that have crossed the TS in the direction of products can't turn around & form reactants

2) At the TS, motion along reaction coordinate is seperable from other motions and is treated as a translation.

3) TS is in a state of quasi-equilibrium and equilibrium distributions apply. (actually follows from point 1)

Blow up diagram near TS:



Molecules moving forward out of TS region: $N_f^{\ddagger}$

Molecules moving backwards out of TS region: $N_b^{\ddagger}$

$N^{\ddagger} = N_f^{\ddagger} + N_b^{\ddagger}$ ... $K^{\ddagger}$ ... $= \frac{N^{\ddagger}}{[AB][C]}$

or

$$N^{\ddagger} = K^{\ddagger}[AB][C]$$

Now, let's consider only those forward moving states while were still at eqm with reactants:

eqm... $N_f^{\ddagger} = N_b^{\ddagger} = N^{\ddagger}/2$

So: $N_f^{\ddagger} = K^{\ddagger}[AB][C]/2$ ← quasi-equilibrium hypothesis

Net rate of reaction in forward direction

$$\frac{dN}{dt}(r \to p) = \frac{\delta N^{\ddagger}}{\delta t}$$

Now if we know the average velocity $\bar{v}_s$ along RC

δ ← gap between dividing surfaces

$$\bar{v}_s = \frac{\delta}{\delta t}$$

$$\delta t = \delta / \bar{v}_s$$

So:

$$\frac{dN}{dt} = \delta N^{\ddagger} \frac{\bar{v}_s}{\delta}$$

← but this is just half the total population in TS region

$$\delta N^{\ddagger} = \frac{N^{\ddagger}}{2}$$

$$\therefore \quad \frac{dN}{dt} = \frac{N^{\ddagger}}{2} \frac{\bar{v}_s}{\delta}$$ ← all we need is this!

$$\bar{v}_s = \frac{\int_0^{\infty} v_s e^{-(\mu_s v_s^2 / k_B T)} \, dv_s}{\int_0^{\infty} e^{-\mu_s v_s^2 / k_B T} \, dv_s}$$

← equilibrium distribution of velocities at TS

μ_s = reduced mass of reaction coord $= \frac{m_{AB} m_C}{m_{AB} + m_C}$

we only consider forward moving TS

$$\bar{v}_s = \sqrt{\frac{2 k_B T}{\pi \mu_s}}$$

$$\therefore \quad \frac{dN}{dt} = \frac{N^{\ddagger}}{2} \left(\frac{2 k_B T}{\pi \mu_s} \right)^{1/2} \frac{1}{\delta}$$

Now remember that:

$$K_C^{\ddagger} = \frac{N^{\ddagger}}{[AB][C]} = \frac{Q_{tot}^{\ddagger}}{Q_{AB} Q_C} e^{-E_0 / k_B T}$$

← total PF at TS

$$\frac{dN}{dt} = \sqrt{\frac{2kT}{\pi \mu_s}} \frac{1}{2\delta} \frac{Q^{\ddagger}_{tot}}{Q_{AB} Q_C} e^{-E_0/k_B T} [AB][C]$$

$$Q^{\ddagger}_{tot} = Q_s \, Q^{\ddagger} = Q^{\ddagger} \sqrt{\frac{2\pi \mu k_B T}{}} \, \delta / h$$

(Q_s: 1-D translational PF along s; δ: 1-D box size)

$$\frac{dN}{dt} = \frac{k_B T}{h} \frac{Q^{\ddagger}}{Q_{AB} Q_C} e^{-E_0/k_B T} [AB][C]$$

Consider 1st order rate law (rate const)

$$\frac{dN}{dt} = k[AB][C]$$

$$k = \frac{k_B T}{h} \frac{Q^{\ddagger}}{Q_{AB} Q_C} e^{-E_0/k_B T}$$

Everything artificial δ, μ_s, ν_s, factors of $\frac{1}{2}$ have cancelled!

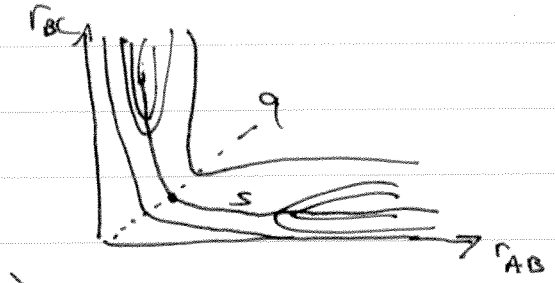
$Q^{\ddagger}$ is the PF for the activated complex with relative motion (s) frozen:

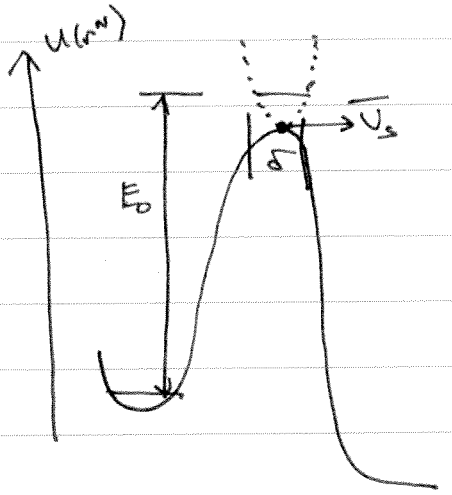
$A \cdots B \cdots C$ → still has 3 translations, still has 3 rotations (but geometry is different)

has $3N-6-1$ vibrations

↑ asymmetric stretch is now s! and has imaginary frequency

$$AB + C \longrightarrow A + BC$$





δ separates II dividing surfaces near TS

E_0 is difference in energies between GS of reactants and TS

$\bar{V}_s$ is the average forward velocity of the product-directed population near TS.

Quasi-equilibrium

$$K^{\ddagger} = \frac{N^{\ddagger}}{[AB][C]}$$

$$\therefore \quad N^{\ddagger} = K^{\ddagger}[AB][C]$$

$$\frac{dN}{dt} = \frac{\delta N_f^{\ddagger}}{\delta t} = \delta N_f^{\ddagger} \cdot \frac{\bar{V}_s}{\delta}$$

$$= \frac{N^{\ddagger}}{2} \sqrt{\frac{2k_B T}{\mu_s \pi}} \frac{1}{\delta}$$

μ_s = reduced mass of rxn coordinate

$$= \frac{m_{AB} \cdot m_C}{m_{AB} + m_C}$$

$$\therefore \quad \frac{dN}{dt} = \frac{K^{\ddagger}}{2\delta} \sqrt{\frac{2k_B T}{\mu_s \pi}} [AB][C]$$

And:

$$K^{\ddagger} = \frac{Q^{\ddagger}_{tot}}{Q_{AB} Q_C} e^{-\beta E_0}$$

$\therefore$

$$\frac{dN}{dt} = \frac{Q^{\ddagger}_{tot}}{Q_{AB} Q_C} e^{-\beta E_0} \frac{1}{2\delta} \sqrt{\frac{2k_B T}{\mu_s \pi}} [AB][C]$$

There are still some artificial things here δ, μ_s

$$Q^{\ddagger}_{tot} = \underbrace{Q_s}_{\text{1d translational partition function along s}} Q^{\ddagger} = Q^{\ddagger} \sqrt{2\pi \mu_s k_B T} \frac{\delta}{h}$$ ← 1-D box size!

$\therefore$

$$\frac{dN}{dt} = \frac{k_B T}{h} \frac{Q^{\ddagger}}{Q_{AB} Q_C} e^{-E_0/k_B T} [AB][C]$$

Consider 1st order rate law — rate constant

$$\frac{dN}{dt} = k [AB][C]$$

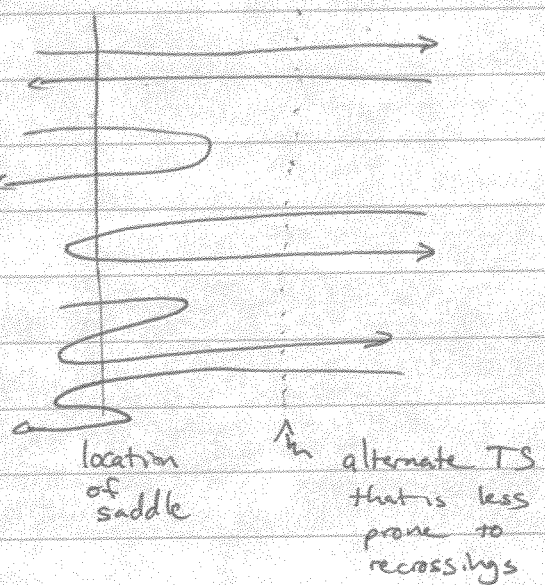
$$\boxed{k = \frac{k_B T}{h} \frac{Q^{\ddagger}}{Q_{AB} Q_C} e^{-E_0/k_B T}}$$

Everything artificial (δ, μ_s, V_s, factors of $\frac{1}{2}$) have cancelled!

$Q^{\ddagger}$ is the P.F. for the activated complex with relative motion (s) frozen

A···B···C → still has 3 translations, still has 3 rotations ← but I is different! has $3N-6-1$ vibrations

Problems with TST



VTST

$$k(T;s^{\ddagger}) = \frac{k_B T}{h} \frac{Q^{\ddagger}(s^{\ddagger})}{Q_{AB}\, Q_C} e^{-E_0(s^{\ddagger})/k_B T}$$

The best TS is the one that minimizes recrossings, and hence maximizes rate.

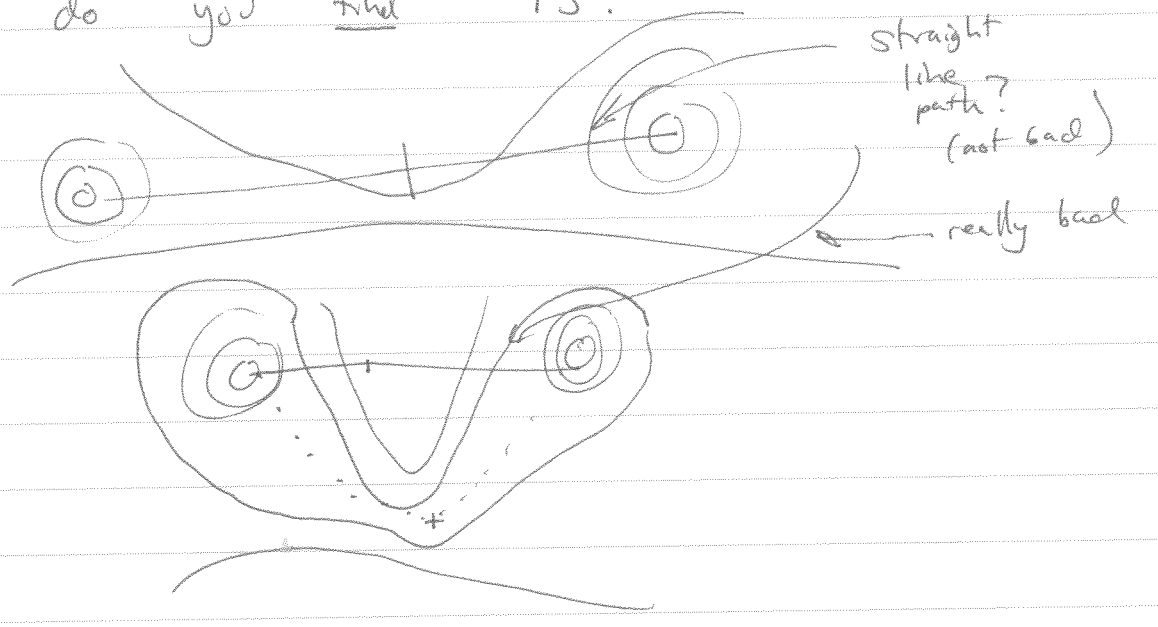
This may not be the same location as the saddle!

$$\frac{d\, k(T;s^{\ddagger})}{ds^{\ddagger}} = 0$$

gives an approximate upper bound on rate constant.

37-2

How do you find TS?

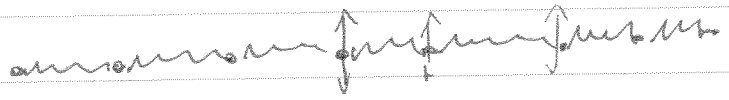


Methods: 1) Shallowest ascent (Cerjian & Miller)

start at R or P and walk uphill along gentlest slope at each point

2) Nudged elastic band (Hannes Jonsson)

place beads connected by springs along straight line path



allow them to walk downhill in a direction perpendicular to the line connecting nearest neighbors!

What do you need at TS?

E_0

$$Q^{\ddagger} = Q^{\ddagger}_{trans}\, Q^{\ddagger}_{vib}\, Q^{\ddagger}_{rot}\, Q^{\ddagger}_{elect}$$

$$\left(\frac{2\pi m^{\ddagger} k_B T}{h^2}\right)^{3/2} V \left(\prod_{i=1}^{N_{vib}} \frac{e^{-h\nu_i/kk_BT}}{1-e^{-h\nu_i/k_BT}}\right) \left[\pi^{1/2} \left(\frac{8\pi^2 I_a kT}{h^2}\right)^{1/2} \left(\frac{8\pi^2 I_b kT}{h^2}\right)^{1/2} \left(\frac{8\pi^2 I_c kT}{h^2}\right)^{1/2}\right]$$

mass — vibrational frequencies — moments of inertia from geometry of TS

$$\times \sum_i g_i e^{-E_i/k_BT}$$

Σ degeneracies & energies of excited states

$S^{\ddagger}$: mass, vibrational freqs, geometry, degeneracies & energies of excited states

Σ These are hardest to get!