10.675 LECTURE 21

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1. Today

Rate Constants
→ TPS
→ Commitor Probability Distribution
→ Transition Path Harvesting
→ Chandler-Bennet Formalism for Rate Constants
→ Examples
→ Molden

2. TPS

Many Pathways

Find a saddle point, drop from each side
Approach
→ Postulate q
→ Compute probability distribution
→ If successful, compute $D\ddagger$
→ If not, go back to postulating a new q
Pick any pathway that connects A to B in time τ.
Pick another via a monte carlo pathway in space.
→ Shooting - Take a point along the path and perturb the momentum.
$p_i \rightarrow \delta p_i + p_{io}$

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Run it forward and backward to A and B within time τ
$\rightarrow$ Shifting - Take a path and shift it by Δx and run again.
Stochastic $\rightarrow$ MD to create phase space.
$\frac{Z_{AB}}{Z_A} = K + AB\tau$
How does one choose τ? It's determined by the method you use, and it's usually ¿ 1ps.
It generally needs to be greater than the relaxation time.

3. Chandler-Bennett Formalism

x(t) is a point in phase space (r,p) along a trajectory x at time t
$h_a(x(t)) = 1$ if system is in A, 0 if it's not in A
$h_b(x(t)) = 1$ if system is in B, 0 if it's not in B
$k(t) = \frac{\langle h_a(x(0))h_b(x(t))\rangle}{\langle h_a(x(t))\rangle}$
Related to the rate at which system goes to B
$\approx K_A \rightarrow e^{\frac{-\tau}{t_{rxn}}}$
$\tau_r^{-1} xn = k_{A\rightarrow B} + K_{B\rightarrow A}$
Since system is almost always in A or always in B, $\langle h_a\rangle + \langle h_b\rangle \approx 1$
For barriers $< K_b T$, k(t) reaches a plateau because $e^{\frac{\tau}{t_{rxn}}} \sim 1$
$K_{A\rightarrow B} = \frac{\langle h_a(x(0))h_b(x(t))\rangle}{\langle h_a(x(0))\rangle}$
$K(t) = \nu(t)P(x(\tau)) = \nu(t)P(L)$ Where L is the length, P(L) is the probability
$v(t) = \langle h_b(x(\tau))\rangle_{AB}$
$P(L) = e^{\frac{-\Delta G^{\ddagger}}{K_b T}}$
Recall from TST
$K^{TST} = \frac{K_b T}{h} e^{\frac{\Delta G^*}{K_b T}}$
$K = \kappa \frac{k_b T}{h} e^{\frac{\Delta G^{\ddagger}}{K_b T}}$
If $\Delta G^{\ddagger} \leftrightarrow \Delta G_q^{\ddagger}$
then $\kappa = \frac{h}{k_b T} v(t)$
so, can pick any q, and if you calculate v(t), can back out real reaction rate.
Compute v(t) from harvesting TP trajectories
$\langle h_b\rangle_{AB}$ go from A to B
So, need to (in practice) get to a constant slope very quickly