10.675 LECTURE 20

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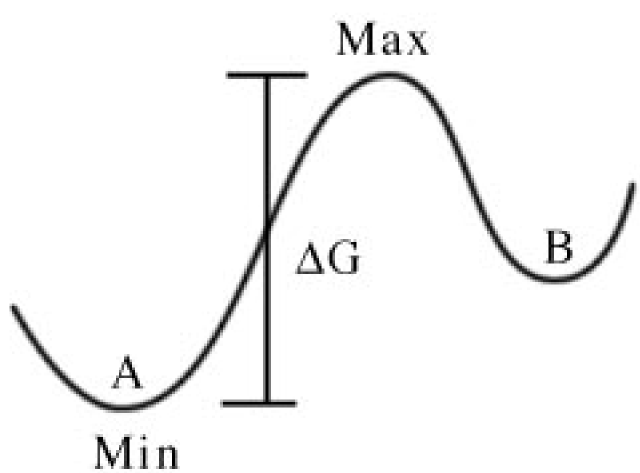
1. Today

⇒ Exploring Complex Free Energy Landscapes
⇒ Course Notes
⇒ Simple vs Complex Free Energy Landscapeds
⇒ PS Time Scales, and what they can do.
⇒ Thermodynamic Integration
⇒ Blue Moon Ensemble (Constrained Dynamics)
⇒ Transition Path Sampling
⇒ Examples

2. Simple System



$K_{AB}, A \rightarrow B$

Date: Fall 2004.

$K_{AB} = \frac{K_bT}{h} e^{\frac{-G\tau}{K_bT}}$
ps (picosecond) time scales in CPMD
What size ΔG can be overcome in 1 ps at room T?
$K_bT = 0.6$ Kcal/mole
$10^{12} s^{-1} = 6x10^{12} s^{-1} e^{\frac{-\Delta G\ddagger}{K_bT}}$
$\Delta G^{\ddagger}$ 1.1 kcal/mole
Can we used information on ps time scales to somehow compute $\Delta G\ddagger$

3. Sampling

For E_{KS}, σ large. Large eV's for ps energies
but, for quantities related to free energy, sigma's are an order of magnitude lower.
Discretize the curve
and small 1.1 kcal/mole variation in each space/region

4. Thermodynamic Integration

$H_1 \rightarrow H_2$ Free energy state function can integrate on non-physical pathway.
$H = (1-\lambda)H_1 + \lambda H_2$ Where H_1 Hamiltonian of state 1, H_2 is the Hamiltonian of state 2.
$\lambda \rightarrow 0$ to 1.
$\Delta F = F_2 - F_1 = \int_0^1 \left\langle \frac{\delta H}{\delta \lambda} \right\rangle_\lambda d\lambda$
And F is obviously the free energy in this case.
Even this approach can only compute small variations accurately.

5. Blue Moon Ensemble

Constrained Dynamics
Compute rare events
→ Carter et al. Chem Phys Lett. 156 (1989, 472)
→ Sprik and Ciccotti JCP, 109 (1998) 7737
$\frac{dF}{dq} = \left\langle \frac{Z^{-1/2}(-f+kTG)}{Z^{-1/2}} \right\rangle_q$
Z, G → Mass weighted matrices
f → Lagrange multiplier on force constraint
If q is a simple distance constraint, $\frac{dF}{dq} = \langle f \rangle_q$

Perform at various q
Most useful with ps timescale
⇒ BUT... how do you know you've chosen the right q?
q can be any constraint.

6. Transition Path Sampling (TPS)

"Throwing enough ropes over mountains in the dark"
Idea is to try many paths over the potential energy surface.
$A \to B$ in many different ways.
Transition path ensemble. Ensemble of all paths of temp, pressure, etc of interest that go from A to B in time τ
$Z_{AB}(\tau)$ is the partition function
$\frac{Z_{AB}(\tau)}{Z_A} = K_b T$

7. Comitter Probability Distribution

One of the tools of TPS
Allows us to test q
1) Choose a point within the trans state ensemble
2) Sample from Maxwell-Boltzmann distribution n, $\vec{v}$ where n is # of trajectories
3) Propagate system forward in time
4) Compute $P_b \to$ the probability that the system goes to B