Free Energies from Simulations

FS 165-266

- Why do we need the free energy?

Methods

- Hit or miss sampling
- Thermodynamic integration
- Artificial integration
- Grand Canonical MC
- Gibbs ensemble
- Acceptance Ratio method

Why do we need to compute the free energy?

$$e^{-F/kT} = e^{-F_0/kT} \int dR\ e^{-V(R)/kT}$$

•Metastability makes it difficult determine phase transitions, especially first-order ones.

– also different size effects in the different phases.

• Need entropy to determine stability of binding of molecule to site.

• F helps to determine phase transitions

•Free energy (and entropy) is difficult to calculate since ensemble averages are of ratios only.

Hit or miss method

- How about simply sampling R from $p_0(R)$?

$$Z = \int dR\, e^{-\beta V(R)} = \left\langle \frac{e^{-\beta V(R)}}{p_0(R)} \right\rangle_{p_0}$$

- *Trouble*: for a many-body system the estimator is *very highly peaked and the efficiency will be very low*.

- The hit or miss method is not useful for more than 10 particles and especially not for a phase transition!

- Free Energy is difficult to compute but it can be done. Also it is difficult to measure in an experiment!

Thermodynamic Integration

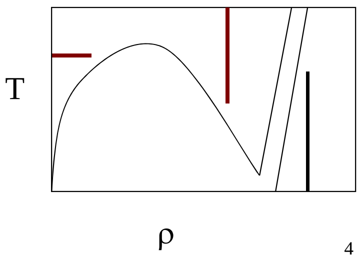
- We can't get free energies but we can compute its derivatives:

$$P = -\left.\frac{\partial F}{\partial V}\right|_{NT} \qquad E = \left.\frac{\partial(\beta F)}{\partial \beta}\right|_{NV}$$

- So pick a path from a known state and integrate to get F.

$$F(T) = F_0(T) + \int_0^{\beta} d\beta' \left(\frac{E(\beta') - E_0(\beta')}{\beta} \right) = F_0(V_0) + \beta N \int_0^{\rho} \frac{d\rho'}{\rho'} \left(\frac{PV'}{Nk_B T} - 1 \right)$$

- **Find path to state where you know F *without crossing phase lines.***
  - Fluid: go to high T or low density.
  - Gas: go to low density.
  - Solid: go to T=0. *(FS Chapter 10)*



Artificial integration

- We are not limited to integrating physical variables like T or V. We can integrate other parameters.
- <u>Use *Coupling constant*.</u>
  - Switch potential from an easy one to a hard one.
  - Make sure the reference state is in the same phase as the perturbed phase.

$$v_\lambda(R) = v_0(R) + \lambda[v(R) - v_0(R)]$$

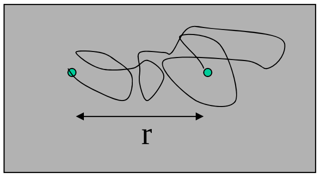
$$\frac{\partial v_\lambda}{\partial \lambda} = v(R) - v_0(R) = \Delta v(R)$$

$$F = F_{\lambda=0} + \int_0^1 d\lambda \left\langle \Delta v(R) \right\rangle_\lambda$$

- *Example: free energy of LDA silicon vs. Tersoff silicon.*

Free energy of a coiled polymer.

- *Constrain ends to be at a distance r apart*.
- Calculate average end-end force: $\mathbf{f}(\mathbf{r}) = \langle -\nabla V \rangle_r$
- Free energy is: $F(a) - F(b) = \int_a^b d\mathbf{r} \bullet \mathbf{f}(\mathbf{r})$



How do we do the integral? What integration formula? How many points?

Particle Insertion Method

Widom Method *(FS pg 173)*

- Chemical potential is given by

$$\mu = \left.\frac{\partial F}{\partial N}\right|_{VT} \approx F(N+1) - F(N)$$

$$\mu \approx -k_B T \ln\left[\frac{Z_{N+1}}{Z_N}\right] = -k_B T \ln\left[\frac{V}{(N+1)\Lambda^3}\right] - k_B T \ln\left\langle e^{-\beta\Delta v}\right\rangle$$

- Insert a particle randomly in the box and find the increase in potential energy.
- What difficulties do you anticipate with this method?

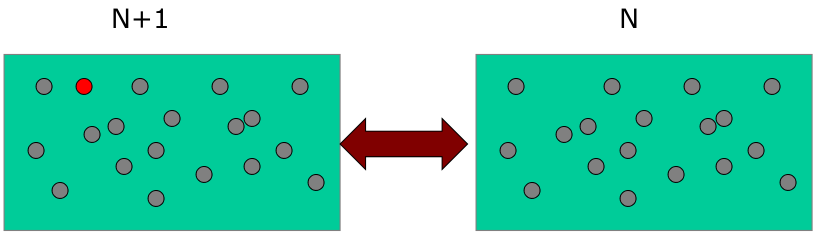
Grand Canonical Ensemble

Norman and Filinov (1969) (FS 126-135)

- Use the (μ, V, T) ensemble. The number of particles is variable, the *chemical potential is fixed*.

$$\Pi(R,N) = \frac{e^{-\beta V(R)+\beta\mu N}\Omega^N}{ZN!\Lambda^{dN}} \qquad \Lambda = \left(\frac{\beta h^2}{2\pi m}\right)^{1/2}$$

- State of system is the number of particles and coordinates.
- Moves change the number of particles by creation and destruction of particles.



GCE moves

$$\Lambda = \left(\frac{\beta h^2}{2\pi m}\right)^{1/2}$$

We pick from several possibilities for moves

1. Ordinary particle displacements
2. Particle destruction

   acceptance probability: $a = \frac{N\Lambda^d}{\Omega} e^{\beta(V_I-\mu)}$

3. Particle creation: $a = \frac{V}{(N+1)\Lambda^d} e^{-\beta(V_x-\mu)}$

- Chemical potential establishes zero of energy.
  - Density will come out.
- Only will work if move 2-3 has a reasonable acceptance ratio. Not at low density or for complicated molecules.
- For a solid, one cannot add and subtract particles. WHY?

Bennett method *(FS 179-183)*

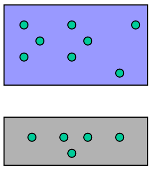
- To compute the free energy difference between two states, with potential energy $V_0(R)$ and $V_1(R)$
  - we enlarge the state space to be (R,s) where s=(0,1).
- Then do a simulation in the enlarged state space including moves which change s (mapping moves).
- The new probability distribution to be sampled if we want to spend 1/2 of the time in each state:

$$\Pi(R,s) = \frac{e^{-\beta V_0(R)}}{2Z_0}\delta_s + \frac{e^{-\beta V_1(R)}}{2Z_1}\delta_{s-1}$$

- Let $Q=Z_1/Z_0$.
  - Make guess to Q and record how many steps we spend on each side. From that we get a better estimate of Q.
- Actually, we don't have to move from 0 to 1, but record would would have happened.
- Example: free energy of vacancy in a solid.

Gibbs ensemble method

Panagiotopoulos (1987) FS Chapter 8



- Method for tracking a phase line say liquid-gas

  Fix temperature, number of particles, and total volume.
- We have two volumes and 3 types of moves:
  - Regular particle displacements
  - Exchange of volumes between the 2 volumes
  - Exchange of particles between the volumes

$$\Pi(V_1,R)=\left(\frac{N!}{(N-N_1)!N_1!}\right)V_1^{N_1}(V-V_1)^{N-N_1}e^{-\beta U(R_1)-\beta U(R_2)}$$

- Put total (V,N) in the 2 phase region.
- The system will phase separate to avoid forming an interface.
- One can track the phase line with single runs. (to study gas-liquid or liquid-liquid equilibrium)