Statistic Mechanics and Free Energy Calculations

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Stat Mech Basics

- Fundamental postulate of statistical mechanics:

"All accessible microstates are equally probable"

  - Microstates are a particular configuration of particles in a particular quantum state.
  - In contrast, a macrostate is defined by a particular set of properties (e.g., temperature, pressure, density, etc.).

- Entropy (measure of the dispersal of energy):

$\mathbf{S \equiv k \ln w}$, where w is number of states.

- At equilibrium, systems minimize free energy:

Helmholtz (constant V): $\mathbf{F = E - TS = H + PV - TS}$

Gibbs (constant P): $\mathbf{G = H - TS = E - PV - TS}$

Stat Mech Basics

- Internal energy **E** is the total energy in the system (kinetic energy, bond energy, etc.)
- Enthalpy is the "usable" energy under constant pressure. Under constant pressure, the volume can change. This involves work, so **H = E – PV**.
- For solids volume changes are usually small, so PV is generally small at low (e.g., atmospheric) pressure.

Both E and H can only be defined relative to a reference, so it is only ΔE and ΔH (and thus ΔF and ΔG) that are well-defined.

Partition function can be used to calculate free energy differences

$$p(A)/p(B) = \exp[-(G_A-G_B)/kT] \Leftrightarrow G_A-G_B = -kT \ln[p(A)/p(B)]$$

Most Probable Distribution

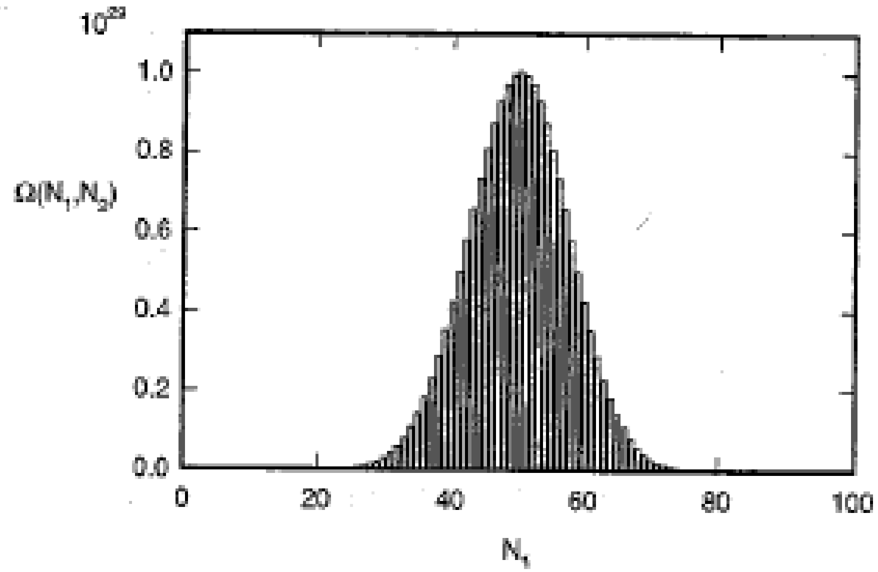
- For large number of particles, entropy dominated by most probable distribution:

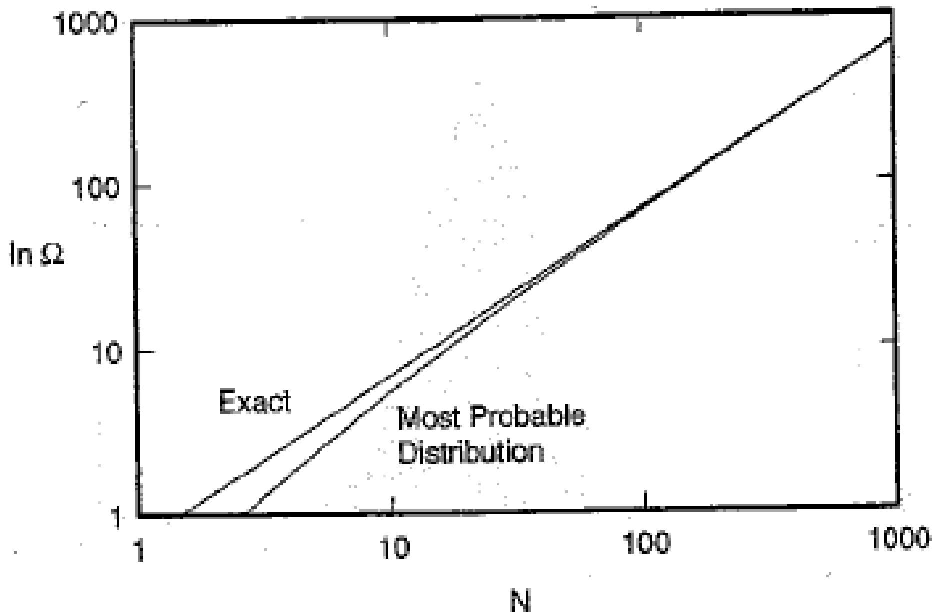
$$S = k \ln w \approx k \ln w_{\text{most probable}}$$

- Example (2 states):

$$W(N_1,N_2) = (N_1+N_2)! \,/\, N_1!\, N_2! = N! \,/\, N_1!\, (N-N_1)!$$

$$W(N) = 2^N$$





Equilibrium

- Continue example of two systems in equilibrium

N = N_1 + N_2, E = E_1 + E_2, V = V_1 + V_2 , w = w_1 w_2

S ≈ k ln $w_{most\ probable}$ is maximized in equilibrium (E fixed)

$$\frac{\partial}{\partial N_1}(w_1 w_2)_{E_1,V_1} = \frac{\partial}{\partial E_1}(w_1 w_2)_{N_1,V_1} = \frac{\partial}{\partial V_1}(w_1 w_2)_{N_1,E_1} = 0$$

$$w_2\left(\frac{\partial w_1}{\partial E_1}\right)_{N_1,V_1} + w_1\left(\frac{\partial w_2}{\partial E_1}\right)_{N_1,V_1} = 0$$

$$\frac{1}{w_1}\left(\frac{\partial w_1}{\partial E_1}\right)_{N_1,V_1} = -\frac{1}{w_2}\left(\frac{\partial w_2}{\partial E_1}\right)_{N_1,V_1} = \frac{1}{w_2}\left(\frac{\partial w_2}{\partial E_2}\right)_{N_2,V_2}$$

$$\left(\frac{\partial[k\ln(w_1)]}{\partial E_1}\right)_{N_1,V_1} = \left(\frac{\partial[k\ln(w_2)]}{\partial E_2}\right)_{N_2,V_2} = \left(\frac{\partial S_1}{\partial E_1}\right)_{N_1,V_1} = \left(\frac{\partial S_2}{\partial E_2}\right)_{N_2,V_2} = \frac{1}{T_1} = \frac{1}{T_2}$$

Equilibrium (cont.)

- Continue by taking derivatives wrt N and V:

$$w_2\left(\frac{\partial w_1}{\partial V_1}\right)_{N_1,E_1}+w_1\left(\frac{\partial w_2}{\partial V_1}\right)_{N_1,E_1}=0$$

$$\left(\frac{\partial S_1}{\partial V_1}\right)_{N_1,E_1}=\left(\frac{\partial S_2}{\partial V_2}\right)_{N_2,E_2}=\frac{p_1}{T_1}=\frac{p_2}{T_2}$$

$$T_1=T_2$$

$$p_1=p_2$$

$$\mu_1=\mu_2$$

$$w_2\left(\frac{\partial w_1}{\partial N_1}\right)_{E_1,V_1}+w_1\left(\frac{\partial w_2}{\partial N_1}\right)_{E_1,V_1}=0$$

$$\left(\frac{\partial S_1}{\partial N_1}\right)_{E_1,V_1}=\left(\frac{\partial S_2}{\partial N_2}\right)_{E_2,V_2}=-\frac{\mu_1}{T_1}=-\frac{\mu_2}{T_2}$$

Thermodynamic Relations

- Using thermodynamic definitions:

$$dS(N,E,V) = \left(\frac{\partial S}{\partial E}\right)_{N,V} dE + \left(\frac{\partial S}{\partial N}\right)_{E,V} dN + \left(\frac{\partial S}{\partial V}\right)_{N,E} dV$$

$$dS(N,E,V) = \frac{1}{T} dE - \frac{\mu}{T} dN + \frac{p}{T} dV = \frac{1}{T} dQ$$

$$dE(S,N,V) = TdS + \mu dN - pdV$$

$$T = \left(\frac{\partial E}{\partial S}\right)_{N,V} ; \mu = \left(\frac{\partial E}{\partial N}\right)_{S,V} ; p = -\left(\frac{\partial E}{\partial V}\right)_{S,N}$$

Ensembles

- Microcanonical: $dE = T\,dS$
- Canonical: $dE = T\,dS - p\,dV$
- Grand canonical $dE = T\,dS - p\,dV + \mu\,dN$

Free Energy Differences

- Partition function can be used to calculate free energy differences:

$$p(A)/p(B) = \exp[-(G_A-G_B)/kT] \Leftrightarrow G_A-G_B = -kT \ln[p(A)/p(B)]$$

- The challenge is simulation time to sample both configurations.
  - Can add bias to allow transitions or favor the configurations of interest
  - Can also break process into steps

Free Energy (Harmonic)

Another approach is to use Harmonic Approximation

- For a harmonic system, free energy can be calculated from vibration (phonon) frequencies.

$$G = H_0 + kT \sum_{\alpha}^{3N} \ln(h\omega_\alpha / kT), \_ where \_ \omega_\alpha = \sqrt{\lambda_\alpha}$$

$$\Gamma = \frac{kT}{2\pi} \frac{\int_S dS \exp(-H/kT)}{\int_\tau d\tau \exp(-H/kT)} = \frac{1}{2\pi} \frac{\prod_{\alpha}^{3N} \omega_\alpha}{\prod_{\alpha}^{3N-1} \omega_{S\alpha}} \exp[-(H_s - H_\tau)/kT]$$

- The λ_α are eigenvalues of the dynamical matrix $(\partial^2 H/\partial r_i \partial r_j)/m_i m_j$.
- The ω_α are vibration frequencies
- In this example, S is transition state (saddle point) and τ is ground state.

Thermodynamic Integration

Make system function of control parameter λ such as:

- Interaction strength
- Configuration constraint

$$\Delta F = \int d\lambda \left(\partial F / \partial \lambda \right)$$

$$\frac{\partial F}{\partial \lambda} =$$

Free Energy (Umbrella Sampling)

Umbrella sampling (histogram method)

- In a fixed volume system, F = -kT ln Z (G for fixed pressure).
- Thus a free energy difference $\Delta F = -kT \ln (Z_1/Z_0)$

$$\Delta F = -kT \ln\left(\int d\boldsymbol{r}^N \exp[-\Phi_1(\boldsymbol{r}^N)/kT] \Big/ \int d\boldsymbol{r}^N \exp[-\Phi_0(\boldsymbol{r}^N)/kT]\right)$$

$$\Delta F = -kT \ln\left(\int d\boldsymbol{r}^N \pi(\boldsymbol{r}^N)[\exp(-\Phi_1/kT)/\pi(\boldsymbol{r}^N)] \Big/ \int d\boldsymbol{r}^N \pi(\boldsymbol{r}^N) \exp(-\Phi_0/kT)/\pi(\boldsymbol{r}^N)]\right)$$

$$\exp(-\Delta F/kT) = \langle \exp(-\Phi_1/kT)/\pi \rangle_\pi \Big/ \langle \exp(-\Phi_0/kT)/\pi \rangle_\pi$$

- $\boldsymbol{r}^n$ is configuration
- $\pi(\boldsymbol{r}^n)$ is probability distribution which spans configurations of systems 1 and 0 (estimation in multiple steps can help)