Basic Statistical Mechanics

- In the Boltzmann distribution, the probability of a configuration r^N with energy $U_s(r^N)$ is,

$$\pi_s(r^N) \propto \exp\left[-\beta U_s(r^N)\right] \text{ (unnormalized)}$$

$$\rho_s(r^N) = \exp\left[-\beta U_s(r^N)\right]/Z_s \text{ (normalized)}$$

- A partition function is the normalizing constant of the Boltzmann distribution

$$Q_s = \int \pi_s(r^N) dr^N$$

- The free energy difference is related to a ratio of partition functions

$$\beta(A_1 - A_0) = -\ln\left(\frac{Q_0}{Q_1}\right)$$

The Zwanzig Relation: Derivation

- From before, $\beta(A_1 - A_0) = -\ln\left(\frac{Q_0}{Q_1}\right)$.
- Substituting in partition functions, $\beta(A_1 - A_0) = -\ln\left(\frac{\int e^{-\beta U_1(r^N)}dr^N}{\int e^{-\beta U_0(r^N)}dr^N}\right)$.
- Multiplying by one, $\beta(A_1 - A_0) = -\ln\left(\frac{\int e^{-\beta U_1(r^N)+\beta U_0(r^N)-\beta U_0(r^N)}dr^N}{\int e^{-\beta U_0(r^N)}dr^N}\right)$.
- Defining the potential energy difference $\Delta U(r^N) = U_1(r^N) - U_0(r^N)$,

$$\beta(A_1 - A_0) = -\ln\left(\frac{\int e^{-\beta \Delta U(r^N)}e^{-\beta U_0(r^N)}dr^N}{\int e^{-\beta U_0(r^N)}dr^N}\right)$$