

Basic Statistical Mechanics

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

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

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

- 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 $\Delta U(r^N) = U_1(r^N) - U_0(r^N)$,
$$\beta(A_1 - A_0) = -\ln \left(\frac{\int e^{-\beta \Delta U(r^N)} e^{-\beta U_0(r^N)} dr^N}{\int e^{-\beta U_0(r^N)} dr^N} \right)$$