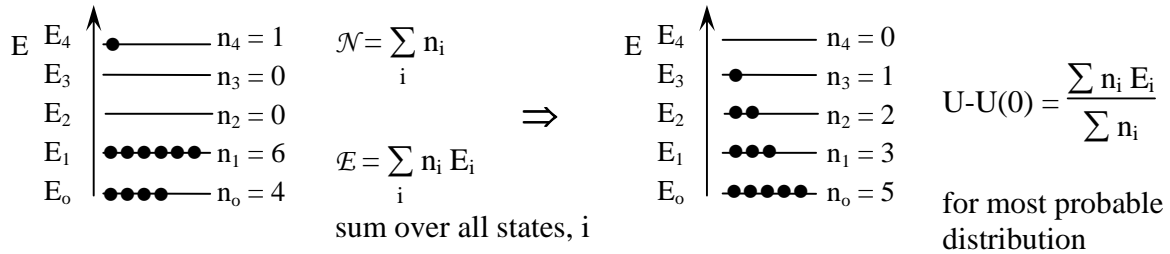


The Boltzmann Distribution Gives the Equilibrium State



$$S = -k \sum_i p_i \ln p_i$$

$$dS = -k \sum_i (p_i \ln p_i + \ln p_i dp_i)$$

$$d \ln p_i = 1/p_i dp_i$$

$$dS = -k \sum_i (1 + \ln p_i) dp_i = -k \sum_i dp_i - k \sum_i \ln p_i dp_i$$

$$dS = -k \sum_i \ln p_i dp_i$$

$$dS = -k \sum_i \ln p_i dp_i = 0 \quad (\text{most probable})$$

$$\sum p_i = 1 \text{ and } \sum E_i p_i = \mathcal{E}. \quad \rightarrow \quad \sum dp_i = 0 \text{ and } \sum E_i dp_i = 0$$

Lagrange multipliers:

$$\alpha \sum_i dp_i = 0 \quad \text{and} \quad \beta \sum_i E_i dp_i = 0 \quad (\text{constraints})$$

$$dS = -k \sum_i \ln p_i dp_i + \alpha \sum_i dp_i + \beta \sum_i E_i dp_i = 0 \quad (\text{most probable})$$

$$dS = -k \sum_i (\ln p_i + \alpha + \beta E_i) dp_i = 0 \quad (\text{most probable})$$

$$\ln p_i + \alpha + \beta E_i = 0 \quad (\text{most probable})$$

$$p_i = e^{-\alpha} e^{-\beta E_i} \quad (\text{most probable})$$

$$\sum_i p_i = \sum_i e^{-\alpha} e^{-\beta E_i} = e^{-\alpha} \sum_i e^{-\beta E_i} = 1$$

$$e^{-\alpha} = \frac{1}{\sum_i e^{-\beta E_i}}$$

$$p_i = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} \quad (\text{most probable})$$

$$Q \equiv \sum_i e^{-\beta E_i} \quad (\text{canonical ensemble})$$

$$p_i = \frac{e^{-\beta E_i}}{Q} \quad (\text{most probable})$$

$$\ln p_i = -\beta E_i - \ln Q \quad (\text{equilibrium})$$

$$dS = -k \sum_i (-\beta E_i - \ln Q) dp_i \quad (\text{equilibrium})$$

$$dS = k\beta \sum_i E_i dp_i + k \ln Q \sum_i dp_i \quad (\text{equilibrium, cst. V})$$

$$dS = k\beta \sum_i E_i dp_i \quad (\text{equilibrium, cst. V})$$

$$U - U(0) = \langle E \rangle \quad dU = d\langle E \rangle$$

$$dU = d\langle E \rangle = \sum_i E_i dp_i \quad (\text{cst. V})$$

$$\left(\frac{\partial S}{\partial U} \right)_V = k\beta \quad (\text{cst. V, equilibrium})$$

$$(\partial S / \partial U)_V > 0 \quad \beta > 0$$