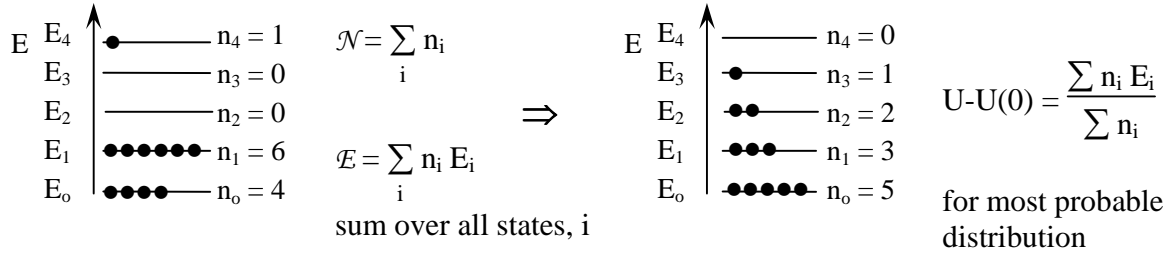


## The Boltzmann Distribution Gives the Equilibrium State



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

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

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

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

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

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

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

**Lagrange multipliers:**

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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