

lecture 6 - canonical ensemble

- system in thermal contact with environment at temperature T
- $N, V = \text{constant}$, energy fluctuates
- probability to find system at state n of energy ϵ_n

$$p_n = \frac{e^{-\frac{\epsilon_n}{k_B T}}}{Z} \quad (1)$$

- partition function Z

$$Z = \sum_n e^{-\frac{\epsilon_n}{k_B T}} \quad (2)$$

- ratio of probabilities

$$\frac{p_n}{p_m} = \frac{e^{-\frac{\epsilon_n}{k_B T}}}{e^{-\frac{\epsilon_m}{k_B T}}} = e^{-\frac{\epsilon_n - \epsilon_m}{k_B T}} \quad (3)$$

- mean values

$$U = \sum_n p_n \epsilon_n \quad (4)$$

$$S = -k_B \sum_n p_n \ln p_n \quad (5)$$

- free energy $F = U - TS = -k_B T \ln Z$
- free energy (and thus Z) generates all thermodynamic quantities

$$S = -\left. \frac{\partial F}{\partial T} \right|_V \quad (6)$$

$$U = -T^2 \left. \frac{\partial}{\partial T} \left(\frac{F}{T} \right) \right|_V \quad (7)$$

$$C_V = -T^2 \left. \frac{\partial^2 F}{\partial T^2} \right|_V \quad (8)$$