Canonical Ensemble [tln51]

Consider a closed classical system (volume V, N particles, temperature T). The goal is to determine the thermodynamic potential $A(T,V,N)$ pertaining to that situation, from which all other thermodynamic properties can be derived.

Maximize Gibbs entropy $S = -k_B \int_\Gamma d^{6N}X\, \rho(\mathbf{X}) \ln[C_N \rho(\mathbf{X})]$
subject to the constraints related to normalization and average energy:

$$\int_\Gamma d^{6N}X\, \rho(\mathbf{X}) = 1, \quad \int_\Gamma d^{6N}X\, H(\mathbf{X})\rho(\mathbf{X}) = U.$$

Apply calculus of variation with two Lagrange multipliers:

$$\delta \int_\Gamma d^{6N}X \{-k_B \rho \ln[C_N \rho] + \alpha_0 \rho + \alpha_U H \rho\} = 0$$

$$\Rightarrow \int_\Gamma d^{6N}X\, \delta\rho \{-k_B \ln[C_N \rho] - k_B + \alpha_0 + \alpha_U H\} = 0.$$

$$\Rightarrow \{\cdots\} = 0 \;\Rightarrow\; \rho(\mathbf{X}) = \frac{1}{C_N} \exp\left(\frac{\alpha_0}{k_B} - 1 + \frac{\alpha_U}{k_B} H(\mathbf{X})\right).$$

Determine the Lagrange multipliers α_0 and α_U:

$$\int_\Gamma d^{6N}X\, \rho(\mathbf{X}) = 1 \;\Rightarrow\; \exp\left(1 - \frac{\alpha_0}{k_B}\right) = \frac{1}{C_N} \int_\Gamma d^{6N}X \exp\left(\frac{\alpha_U}{k_B} H(\mathbf{X})\right) \equiv Z_N.$$

$$\int_\Gamma d^{6N}X\, \rho(\mathbf{X}) \{\cdots\} = 0 \;\Rightarrow\; S - k_B + \alpha_0 + \alpha_U U = 0.$$

$$\Rightarrow\; U + \frac{1}{\alpha_U} S = \frac{k_B}{\alpha_U} \ln Z_N. \text{ Compare with } U - TS = A \;\Rightarrow\; \alpha_U = -\frac{1}{T}.$$

Helmholtz free energy: $A(T,V,N) = -k_B T \ln Z_N$.

Canonical partition function: $Z_N = \frac{1}{C_N} \int_\Gamma d^{6N}X \exp(-\beta H(\mathbf{X}))\,,\; \beta = \frac{1}{k_B T}$.

Probability density: $\rho(\mathbf{X}) = \frac{1}{Z_N C_N} \exp(-\beta H(\mathbf{X}))\,.$

Canonical ensemble in quantum mechanics:

$$Z_N = \mathrm{Tr} e^{-\beta H} = \sum_\lambda e^{-\beta E_\lambda}, \quad \rho = \frac{1}{Z_N} e^{-\beta H}, \quad A = -k_B T \ln Z_N.$$