Canonical Ensemble

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 $S = -k_B \int d^6X \rho(X) \ln[CN\rho(X)]$
subject to the constraints related to normalization and average energy:

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

Apply calculus of variation with two Lagrange multipliers:

$$\delta \int_{\Gamma} d^6X \{-k_B\rho \ln[CN\rho] + \alpha_0\rho + \alpha_UH\rho\} = 0$$

$$\Rightarrow \int_{\Gamma} d^6X \delta\rho\{-k_B\ln[CN\rho] - k_B + \alpha_0 + \alpha_UH\} = 0.$$

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

Determine the Lagrange multipliers $\alpha_0$ and $\alpha_U$:

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

$$\int_{\Gamma} d^6X \rho(X)\{\cdots\} = 0 \Rightarrow S - k_B + \alpha_0 + \alpha_UU = 0.$$

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

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

Canonical partition function: $Z_N = \frac{1}{CN} \int_{\Gamma} d^6X \exp (-\beta H(X)), \beta = \frac{1}{k_BT}$.

Probability density: $\rho(X) = \frac{1}{Z_NCN} \exp (-\beta H(X))$.

Canonical ensemble in quantum mechanics:

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