Grandcanonical ensemble [tln60]

Consider an open classical system (volume V, temperature T, chemical potential μ). The goal is to determine the thermodynamic potential $\Omega(T, V, \mu)$ pertaining to that situation, from which all other thermodynamic properties can be derived.

A quantitative description of the grandcanonical ensemble requires a set of phase spaces Γ_N, $N = 0, 1, 2, \ldots$ with probability densities $\rho_N(\mathbf{X})$. The interaction Hamiltonian for a system of N particles is $H_N(\mathbf{X})$.

Maximize Gibbs entropy $S = -k_B \sum_{N=0}^{\infty} \int_{\Gamma} d^{6N}X \, \rho_N(\mathbf{X}) \ln[C_N \rho_N(\mathbf{X})]$
subject to the three constraints

- $\displaystyle\sum_{N=0}^{\infty} \int_{\Gamma_N} d^{6N}X \, \rho_N(\mathbf{X}) = 1$ (normalization),
- $\displaystyle\sum_{N=0}^{\infty} \int_{\Gamma_N} d^{6N}X \, \rho_N(\mathbf{X}) H_N(\mathbf{X}) = \langle H \rangle = U$ (average energy),
- $\displaystyle\sum_{N=0}^{\infty} \int_{\Gamma_N} d^{6N}X \, \rho_N(\mathbf{X}) N = \langle N \rangle = \mathcal{N}$ (average number of particles).

Apply calculus of variation with three Lagrange multipliers:

$$\delta \left[\sum_{N=0}^{\infty} \int_{\Gamma_N} d^{6N}X \left\{ -k_B \rho_N \ln[C_N \rho_N] + \alpha_0 \rho_N + \alpha_U H_N \rho_N + \alpha_N N \rho_N \right\} \right] = 0$$

$$\Rightarrow \sum_{N=0}^{\infty} \int_{\Gamma_N} d^{6N}X \delta\rho_N \left\{ -k_B \ln[C_N \rho_N] - k_B + \alpha_0 + \alpha_U H_N + \alpha_N N \right\} = 0$$

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

Determine the Lagrange multipliers $\alpha_0, \alpha_U, \alpha_N$:

$$\exp\left(1 - \frac{\alpha_0}{k_B}\right) = \sum_{N=0}^{\infty} \frac{1}{C_N} \int_{\Gamma_N} d^{6N}X \exp\left(\frac{\alpha_U}{k_B} H_N(\mathbf{X}) + \frac{\alpha_N}{k_B} N \right) \equiv Z,$$

$$\sum_{N=0}^{\infty} \int_{\Gamma_N} d^{6N}X \, \rho_N(\mathbf{X}) \{\cdots\} = 0 \;\Rightarrow\; S - k_B + \alpha_0 + \alpha_U U + \alpha_N \mathcal{N} = 0$$

$$\Rightarrow U + \frac{1}{\alpha_U} S + \frac{\alpha_N}{\alpha_U} \mathcal{N} = \frac{k_B}{\alpha_U} \ln Z.$$

Compare with $U - TS - \mu\mathcal{N} = -pV = \Omega \;\Rightarrow\; \alpha_U = -\frac{1}{T},\; \alpha_N = \frac{\mu}{T}$.

Grand potential: $\Omega(T, V, \mu) = -k_B T \ln Z = -pV$.

Grand partition function: $Z = \sum_{N=0}^{\infty} \frac{1}{C_N} \int_{\Gamma_N} d^{6N}X\, e^{-\beta H_N(\mathbf{X}) + \beta\mu N},\; \beta = \frac{1}{k_B T}$.

Probability densities: $\rho_N(\mathbf{X}) = \frac{1}{ZC_N}\, e^{-\beta H_N(\mathbf{X}) + \beta\mu N}$.

Grandcanonical ensemble in quantum mechanics:

$$Z = \mathrm{Tr}\, e^{-\beta(H - \mu N)}, \quad \rho = \frac{1}{Z}\, e^{-\beta(H-\mu N)}, \quad \Omega = -k_B T \ln Z.$$

Derivation of thermodynamic properties from grand potential:

$$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu}, \quad p = -\left(\frac{\partial \Omega}{\partial V}\right)_{T,\mu}, \quad \mathcal{N} = \langle N \rangle = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V}.$$

Relation between canonical and grandcanonical partition functions:

$$Z = \sum_{N=0}^{\infty} e^{\mu N / k_B T} Z_N = \sum_{N=0}^{\infty} z^N Z_N, \quad z \equiv e^{\mu/k_B T} \text{ (fugacity)}.$$

Open system of indistinguishable noninteracting particles:

$$Z_N = \frac{1}{N!}\tilde{Z}^N, \quad Z = \sum_{N=0}^{\infty} \frac{1}{N!} z^N \tilde{Z}^N = e^{z\tilde{Z}}$$

$$\Rightarrow\; \Omega = -k_B T \ln Z = -k_B T z \tilde{Z}.$$

Thermodynamic properties of the classical ideal gas in the grandcanonical ensemble are calculated in exercise [tex94].