Thermodynamics

Statistical Thermodynamics – III

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Properties of the Partition Function

For a system consists of two parts A' and A" which interacts only weakly with each other.

→ Two different distinguishable groups of particles

→ Two different sets of degree of freedom of the same groups of particles

$$E_{rs} = E_r' + E_s''$$

$$Q = \sum_{r,s} e^{-\beta(E_r' + E_s'')} = \sum_{r,s} e^{-\beta E_r'} e^{-\beta E_s''} = (\sum_r e^{-\beta E_r'})(\sum_s e^{-\beta E_s''})$$

$$Q = Q'Q'' \qquad \ln Q = \ln Q' + \ln Q''$$

Gibbs Paradox: Consider combination of two identical part with N' and V'

$$S = S' + S'' = 2S'$$

$$S' = S'' = N'k\left[\frac{3}{2}\ln T + \ln V' + s_o\right] \qquad S = 2N'k\left[\frac{3}{2}\ln T + \ln(2V') + s_o\right] \neq 2S'$$

$$Q \rightarrow \frac{Q}{N!} \qquad S = Nk\left[\frac{3}{2}\ln T + \ln\frac{V}{N} + s_o + 1\right]$$

System Energy vs. Particle Energy

Neglecting inter-particle interaction

$$E = \varepsilon_a + \varepsilon_b + \varepsilon_c + \cdots$$

$$q_a = \sum_j e^{-\varepsilon_{a_j}/kT}, \qquad q_b = \sum_j e^{-\varepsilon_{b_j}/kT}, \qquad \cdots$$

$$\varepsilon_a = \varepsilon_a(V) \qquad \textit{and} \qquad q = q(V,T)$$

$$q_a \cdot q_b = e^{-(\varepsilon_{a_1}+\varepsilon_{b_1})/kT} + e^{-(\varepsilon_{a_2}+\varepsilon_{b_1})/kT} + e^{-(\varepsilon_{a_3}+\varepsilon_{b_1})/kT} + e^{-(\varepsilon_{a_1}+\varepsilon_{b_2})/kT} + \cdots$$

$$Q = \sum_i e^{-E_i/kT} = q_a \cdot q_b \cdot q_c \cdots$$

Independent, identical, distinguishable particle system $\quad Q = q^N$

Independent, identical, indistinguishable particle system $\quad Q = \dfrac{q^N}{N!}$

Independence of Modes of Energy Storage

$$\varepsilon_a = \varepsilon_{a_{trans}} + \varepsilon_{a_{rot}} + \varepsilon_{a_{vib}} + \cdots$$

Translational motion $$\varepsilon_i = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$

Rotational motion $$\varepsilon_i = \frac{h^2}{8\pi^2 mr^2}(j)(j+1)$$

Motion in a Potential Field $$\varepsilon_i = (i+1)\ h\nu$$

Motion of an electron in a Coulomb Potential $$U = -\left(\frac{ze^2}{r}\right)$$

$$\varepsilon_i = -\left(\frac{mz^2e^4}{8\varepsilon_o^2 h^2 n^2}\right)$$

$$q_{trans} = \sum_i e^{-\varepsilon_i / kT}$$

$$q_a = \sum_i e^{-(\varepsilon_{a_{trans}} + \varepsilon_{a_{rot}} + \varepsilon_{a_{vib}} + \cdots)/kT} = q_{trans} \cdot q_{rot} \cdot q_{vib} \cdots$$

Ensemble for Isolated System – Microcanonical ensemble

Number of NVE systems: $\tilde{N} = \sum_i n_i$

$$W\{n_i\} = \frac{\tilde{N}!}{n_1!n_2!\cdots n_k!}$$

$$\ln W = \tilde{N}\ln\tilde{N} - \sum n_i \ln n_i$$

$$d\ln W_{\max} = -\sum dn_i \ln n_i = 0$$

$$\sum dn_i = 0 \qquad \sum \alpha\delta n_i = 0$$

$$\ln n_i + \alpha = 0 \qquad n_i = e^{-\alpha} \qquad e^{-\alpha} = \frac{\tilde{N}}{number\ of\ \ states\ at\ H = E}$$

$$p_i = \frac{n_i}{\tilde{N}} = \frac{1}{\Omega_{NVE}}$$

$$\Omega_{\tilde{N}}\{n_i\} = \frac{\tilde{N}!}{n_1!n_2!\cdots n_k!}$$

Microcanonical Ensemble – Entropy

$$S_{\tilde{N}} = k \ln \Omega_{\tilde{N}} = k \; [\tilde{N} \ln \tilde{N} - \sum n_i \ln n_i]$$

$$S = \frac{S_{\tilde{N}}}{\tilde{N}} = -k \sum_i \left(\frac{n_i}{\tilde{N}} \right) \ln \left(\frac{n_i}{\tilde{N}} \right) = -k \sum_i p_i \ln p_i$$

$$S \equiv < -k \ln p_i >$$

$$S = -k \ln \frac{1}{\Omega_{NVE}} = k \ln \Omega_{NVE}$$

Computation of Ω_{NVE} and state density *g(E)* is critical but generally difficult

System in contact with a heat reservoir – Canonical ensemble

Number of NVT systems with E_i: $\tilde{N} = \sum_i n_i$

Average Energy of a system: $U \equiv \langle E_i \rangle = \sum_i p_i E_i$ $\tilde{N}U = \sum_i n_i E_i$

$$\ln W = \tilde{N} \ln \tilde{N} - \sum n_i \ln n_i$$

$$d \ln W_{\max} = -\sum dn_i \ln n_i = 0$$

$$\sum dn_i = 0 \qquad \sum \alpha \delta n_i = 0$$

$$\sum E_i dn_i = 0 \qquad \sum \beta E_i dn_i = 0$$

$$\ln n_i + \alpha + \beta E_i = 0 \qquad n_i = e^{-\alpha} e^{-\beta E_i} \qquad e^{-\alpha} = \frac{\tilde{N}}{\sum_i e^{-\beta E_i}}$$

$$p_i = \frac{n_i}{\tilde{N}} = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} \qquad U = \langle E_i \rangle = \frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$$

Canonical Ensemble – Free Energy & Thermodynamic Relations

$$S \equiv < -k \ln p_i > = -k \sum_i p_i (-\beta E_i - \ln Q) = k\beta U + k \ln Q$$

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN$$

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T} = k\beta \qquad \beta = \frac{1}{kT}$$

$$F_{NVT} \equiv U - ST = -kT \ln Q$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = k \ln Z + kT \left(\frac{\partial \ln Q}{\partial T}\right)_{V,N} \qquad P = -\left(\frac{\partial F}{\partial V}\right)_{N,T} = kT \left(\frac{\partial \ln Q}{\partial V}\right)_{N,T}$$

$$U = -\frac{\partial \ln Q}{\partial \beta} \qquad C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = \left(\frac{\partial U}{\partial \beta}\right)_{V,N} \left(\frac{\partial \beta}{\partial T}\right) = k\beta^2 \left(\frac{\partial^2 \ln Q}{\partial \beta^2}\right)_{V,N}$$

Canonical Ensemble – Ideal Gas

$$Q_{NVT} = \frac{q^N}{N!} = \frac{V^N}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{3N/2}$$

$$F_{NVT} = -kT\ln Q$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{N,T} = \frac{NkT}{V}$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = Nk\left[\frac{5}{2} + \ln\frac{V}{N} + \frac{3}{2}\ln T + s_o\right]$$

$$U = -\frac{\partial \ln Q}{\partial \beta} = \frac{3}{2}NkT$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = \frac{3}{2}Nk$$

Canonical Ensemble – relation with Microcanonical Ensemble

$$U \equiv \langle E \rangle = -\frac{\partial \ln Q}{\partial \beta}$$

$$\langle E^2 \rangle = \frac{1}{Q}\sum_i E_i^2 e^{-\beta E_i} = \frac{1}{Q}\frac{\partial^2 Q}{\partial \beta^2}$$

$$\langle E^2 \rangle - \langle E \rangle^2 = \frac{1}{Q}\frac{\partial^2 Q}{\partial \beta^2} - \left(-\frac{1}{Q}\frac{\partial Q}{\partial \beta}\right)^2 = \frac{\partial}{\partial \beta}\left(\frac{1}{Q}\frac{\partial Q}{\partial \beta}\right) = -\frac{\partial U}{\partial \beta}$$

$$\langle (\Delta E)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2 = -\frac{\partial U}{\partial \beta} = kT^2\left(\frac{\partial U}{\partial T}\right) = kT^2 C_V$$

$$\frac{\sqrt{\langle (\Delta E)^2 \rangle}}{\langle E \rangle} = \frac{\sqrt{kT^2 C_V}}{U} \propto \frac{1}{\sqrt{N}}$$

Open System with a heat reservoir – Grand Canonical ensemble

Number of μVT systems with E_i & N_r: $\tilde{N} = \sum_{i,r} n_{i,r}$

Average Energy of a system: $U \equiv \langle E_i \rangle = \sum_{i,r} p_{i,r} E_i$ $\tilde{N}U = \sum_{i,r} n_{i,r} E_i$

Average # of ptl. of a system: $\langle N \rangle = \sum_{i,r} p_{i,r} N_r$ $\tilde{N} \langle N \rangle = \sum_{i,r} n_{i,r} N_r$

$$\ln W = \tilde{N} \ln \tilde{N} - \sum n_i \ln n_i$$

$$d \ln W_{\max} = -\sum dn_i \ln n_i = 0$$

$$\sum dn_{i,r} = 0 \qquad \sum \alpha \delta n_{i,r} = 0$$

$$\sum E_i dn_{i,r} = 0 \qquad \sum \beta E_i dn_{i,r} = 0$$

$$\sum N_r dn_{i,r} = 0 \qquad \sum \gamma \; N_r dn_{i,r} = 0$$

$$\ln n_{i,r} + \alpha + \beta E_i - \gamma N_r = 0 \qquad n_{i,r} = e^{-\alpha} e^{-\beta E_i + \gamma N_r} \qquad e^{-\alpha} = \frac{\tilde{N}}{\sum_{i,r} e^{-\beta E_i + \gamma N_r}}$$

$$p_{i,r} = \frac{n_{i,r}}{\tilde{N}} = \frac{e^{-\beta E_i + \gamma N_r}}{\sum_{i,r} e^{-\beta E_i + \gamma N_r}} \qquad U = \frac{\sum_{i,r} E_i e^{-\beta E_i + \gamma N_r}}{\sum_{i,r} e^{-\beta E_i + \gamma N_r}} \qquad \langle N \rangle = \frac{\sum_{i,r} N_r e^{-\beta E_i + \gamma N_r}}{\sum_{i,r} e^{-\beta E_i + \gamma N_r}}$$

Grand Canonical Ensemble – Thermodynamic Relations

$$S \equiv < -k \ln p_{i,r} > = -k \sum_{i,r} p_{i,r}(-\beta E_i + \gamma N_r - \ln Q_G) = k\beta U - k\gamma < N > + k \ln Q_G$$

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN$$

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T} = k\beta \qquad \beta = \frac{1}{kT}$$

$$\left(\frac{\partial S}{\partial N}\right)_{U,V} = -\frac{\mu}{T} = -k\gamma \qquad \gamma = \frac{\mu}{kT}$$

$$Q_G = \sum_{i,r} e^{-\beta E_i} e^{\beta \mu N_r} = \sum_N Q_{NVT} (e^{\beta\mu})^N = \sum_N Q_{NVT}\ z^N \qquad \textit{Fugacity} \qquad z = e^{\frac{\mu}{kT}}$$

$$-kT \ln Q_G = U - TS - \mu N \equiv \Phi_{\mu VT} = -(PV)$$

$$d\Phi = dU - TdS - SdT - \mu dN - Nd\mu = -SdT - PdV - Nd\mu$$

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_{V,\mu} \qquad P = -\left(\frac{\partial \Phi}{\partial V}\right)_{T,\mu} \qquad N = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V}$$

Grand Canonical Ensemble – Ideal Gas

$$Q_G = \sum_{N=0} Q_{NVT} \ z^N = \sum_{N=0} \frac{1}{N!}(q_{1VT} \cdot z)^N = e^{q_{1VT} \cdot z}$$

$$\Phi_{\mu VT} = -kT \ln Q_G = -kTzq_{1VT}$$

$$q_{1VT} = V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}$$

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_{V,\mu}$$

$$P = -\left(\frac{\partial \Phi}{\partial V}\right)_{T,\mu}$$

$$N = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V}$$

Examples

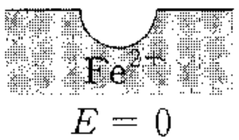
▷ Paramagnetism: ideal two state (up & down)

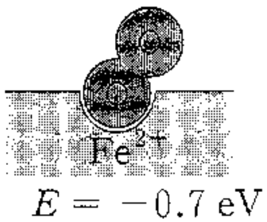
$$Z = e^{+\beta\mu B} + e^{-\beta\mu B} = 2\cosh(\beta\mu B)$$

$$\overline{E} = \sum_s E(s)P(s) = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\mu B \tanh(\beta\mu B)$$

$$\overline{\mu_z} = \sum_s \mu_z(s)P(s) = \mu \tanh(\beta\mu B)$$

▷ 헤모글로빈 분자 위에서의 산소 흡착





$$Z_G = \sum_{i,r} e^{-\beta E_i} e^{\beta\mu N_r}$$

$$Z_G = \sum_N e^{-\beta(\varepsilon-\mu)N} = 1 + e^{-(\varepsilon-\mu)/kT}$$

Quantum Statistics – Number of ways of distribution

▷ Distinguishable without Pauli exclusion principle

$$\sum W = (g_1 + g_2 + \cdots + g_k)^N$$

$$W = \frac{N!}{n_1! n_2! \cdots n_k!}(g_1)^{n_1}(g_2)^{n_2}\cdots(g_k)^{n_k} = N!\prod\left(\frac{g_j^{\,n_j}}{n_j!}\right)$$

▷ Indistinguishable without Pauli exclusion principle

for g_i with n_i $\quad \frac{(g_i + n_i - 1)!}{(g_i - 1)! n_i!}$

$$W = \prod_i \frac{(g_i + n_i - 1)!}{(g_i - 1)! n_i!}$$

▷ Indistinguishable with Pauli exclusion principle

for g_i with n_i $\quad \frac{g_i!}{(g_i - n_i)! n_i!}$

$$W = \prod_i \frac{g_i!}{(g_i - n_i)! n_i!}$$

Bose-Einstein Distribution

$$W = \prod_i \frac{(g_i + n_i - 1)!}{(g_i - 1)!n_i!} \quad \rightarrow \quad W = \prod_i \frac{(g_i + n_i)!}{(g_i - 1)!n_i!}$$

$$n_i = \frac{g_i}{e^{\alpha} e^{\beta \varepsilon_i} - 1}$$

Fermi-Dirac Distribution

$$W = \prod_i \frac{g_i!}{(g_i - n_i)!n_i!}$$

$$n_i = \frac{g_i}{e^{\alpha} e^{\beta \varepsilon_i} + 1}$$

※ **Photon Statistics**

Quantum Statistics – mean # of particles in a single-particle state s

$$E_R = n_1\varepsilon_1 + n_2\varepsilon_2 + n_3\varepsilon_3 + \cdots = \sum_r n_r \varepsilon_r$$

$$\sum_r n_r = N$$

$$Q = \sum_R e^{-\beta E_R} = \sum_R e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + n_3\varepsilon_3 + \cdots)}$$

$$\bar{n}_s = \frac{\sum_R n_s e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + n_3\varepsilon_3 + \cdots)}}{\sum_R e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + n_3\varepsilon_3 + \cdots)}} = \frac{1}{Q}\sum_R \left(-\frac{1}{\beta}\frac{\partial}{\partial \varepsilon_s}\right) e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + n_3\varepsilon_3 + \cdots)} = -\frac{1}{\beta Q}\frac{\partial Q}{\partial \varepsilon_s}$$

$$\bar{n}_s = -\frac{1}{\beta}\frac{\partial \ln Q}{\partial \varepsilon_s}$$

Quantum Statistics – Photon Statistics

$$Q = \sum_{R} e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + n_3\varepsilon_3 + \cdots)}$$

$$Q = \sum_{n_1, n_2, \cdots} e^{-\beta n_1 \varepsilon_1} e^{-\beta n_2 \varepsilon_2} e^{-\beta n_3 \varepsilon_3} \cdots$$

$$Q = (\sum_{n_1=0} e^{-\beta n_1 \varepsilon_1})(\sum_{n_2=0} e^{-\beta n_2 \varepsilon_2})(\sum_{n_3=0} e^{-\beta n_3 \varepsilon_3})\cdots$$

$$Q = \left(\frac{1}{1-e^{-\beta\varepsilon_1}}\right)\left(\frac{1}{1-e^{-\beta\varepsilon_2}}\right)\left(\frac{1}{1-e^{-\beta\varepsilon_3}}\right)\cdots$$

$$\ln Q = -\sum_{r} \ln \ (1 - e^{-\beta\varepsilon_r})$$

$$\bar{n}_s = -\frac{1}{\beta}\frac{\partial \ln Q}{\partial \varepsilon_s} = \frac{e^{-\beta\varepsilon_s}}{1-e^{-\beta\varepsilon_s}} = \frac{1}{e^{\beta\varepsilon_s} - 1}$$

Quantum Statistics – Bose-Einstein/Fermi-Dirac Statistics

$$Q_G(\mu,V,T) = \sum_{i,N} e^{-\beta E_i} e^{\beta\mu N} = \sum_{\{n_i\}} e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\cdots)} e^{\beta\mu(n_1+n_2+\cdots)}$$

$$= \sum_{\{n_i\}} e^{-\beta \sum_k n_k(\varepsilon_k-\mu)}$$

$n_k = 0, 1$ Fermion

$n_k = 0, 1, 2, 3, \ldots, \infty$ Boson

$$Q_G^{F-D} = \prod_{k=1} \sum_{n_k=0}^{1} e^{-\beta(\varepsilon_k-\mu)n_k} = \prod_{k=1} (1+e^{-\beta(\varepsilon_k-\mu)})$$

$$Q_G^{B-E} = \prod_{k=1} \sum_{n_k=0}^{\infty} e^{-\beta(\varepsilon_k-\mu)n_k} = \prod_{k=1} \frac{1}{1-e^{-\beta(\varepsilon_k-\mu)}}$$

Quantum Statistics – Bose-Einstein/Fermi-Dirac Statistics

$$\bar{n}_s = -\frac{1}{\beta}\frac{\partial \ln Q}{\partial \varepsilon_s}$$

$$\ln Q_G^{F-D} = \sum_k \ln(1 + e^{-\beta(\varepsilon_k - \mu)})$$

$$\ln Q_G^{B-E} = \sum_k \ln \frac{1}{1 - e^{-\beta(\varepsilon_k - \mu)}}$$

$$n^{F-D}(\varepsilon) = f^{F-D}(\varepsilon) = \frac{e^{-\beta(\varepsilon-\mu)}}{1 + e^{-\beta(\varepsilon-\mu)}} = \frac{1}{e^{\beta(\varepsilon-\mu)} + 1}$$

$$f^{B-E}(\varepsilon) = \frac{e^{-\beta(\varepsilon-\mu)}}{1 - e^{-\beta(\varepsilon-\mu)}} = \frac{1}{e^{\beta(\varepsilon-\mu)} - 1}$$