Thermodynamics

Statistical Thermodynamics – I

Byeong-Joo Lee

POSTECH - MSE

calphad@postech.ac.kr

1. Stirling's approximation

$$\ln (x!) \approx \int_1^x \ln x \ dx = x \ln x - x + 1 \approx x \ln x - x$$

2. Evaluation of the Integral $\displaystyle\int_{-\infty}^{\infty} e^{-x^2} dx$

$$\int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi} \qquad \int_0^{\infty} e^{-x^2} dx = \frac{1}{2}\sqrt{\pi} \qquad \int_0^{\infty} e^{-ax^2} dx = \frac{1}{2}\sqrt{\frac{\pi}{a}}$$

3. Lagrangian Undetermined Multiplier Method

View Point

Macroscopic vs. Microscopic

State

Macrostate vs. Microstate

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$$

$$\nabla^2\psi + \frac{2m}{\hbar^2}E\psi = 0 \qquad\qquad \sqrt{\frac{2mE}{\hbar^2}}L = n\pi$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \qquad\qquad n = 1, 2, 3, \dots$$

$$E(n_x, n_y, n_z) = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2)$$

for 66 : 8,1,1   7,4,1,   5,5,4

System with particles – Microstates of a System

Table 2.1 Possible Distributions of Three Particles Among Three Different Energy Levels

Energy Level	Configurations									
	A	B	C	D	E	F	G	H	I	J
III at 0.2 eV	3	2	2	1	1	0	1	0	0	0
II at 0.1 eV	0	1	0	2	1	3	0	2	1	0
I at 0 eV	0	0	1	0	1	0	2	1	2	3
Total energy of configuration, eV	0.6	0.5	0.4	0.4	0.3	0.3	0.2	0.2	0.1	0
Ω (sum = 27)	1	3	3	3	6	1	3	3	3	1

$$\underbrace{3 \quad 3}_{6} \qquad \underbrace{6 \quad 1}_{7} \qquad \underbrace{3 \quad 3}_{6}$$

| P_i at 1000 K (sum = 1.00)[a] | 3×10^{-4} | 0.003 | 0.021 | | 0.077 | | 0.209 | | 0.334 | 0.356 |

[a] The symbol Ω denotes the thermodynamic probability of the configuration.

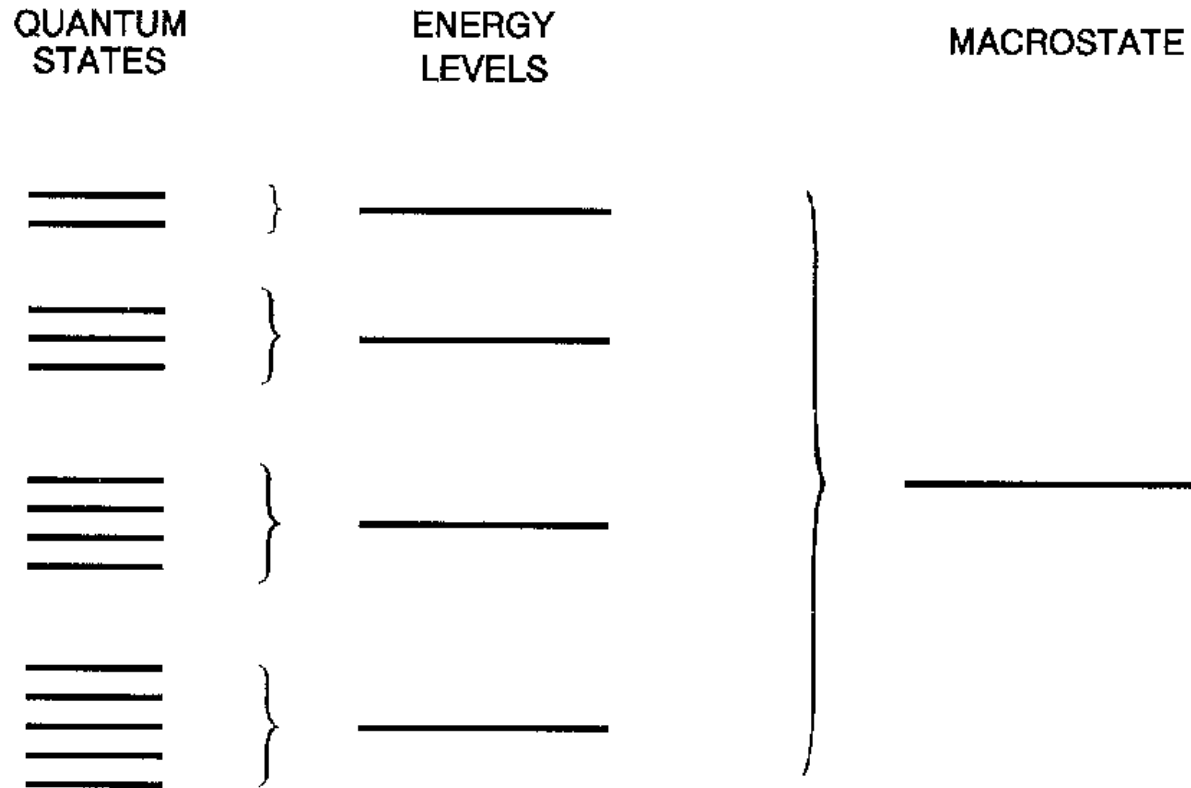# Macrostate / Energy Levels / Microstates –

Figure 6.1   The hierarchy of quantum states, energy levels, and macrostates. In general, many quantum states (microstates) will be consistent with a given macrostate. Quantum states having the same energy, but differing in some other observable way, are grouped in energy levels.

Scope and Fundamental Assumptions of Statistical Mechanics

▷ each probable case defined by (n_1, n_2, …, n_k) to make a macrostate
  → microstate

▷ mental collection of macrostates, quantum mechanically accessible
  to a system → ensemble

➢ all microstates in the same energy level have a same probability

➢ Ensemble average = time average

▷ 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 $\quad \dfrac{(g_i + n_i - 1)!}{(g_i - 1)! n_i!}$

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

▷ Indistinguishable with Pauli exclusion principle

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

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

$$W = \frac{N!}{n_1! n_2! \cdots n_k!} (g_1)^{n_1} (g_2)^{n_2} \cdots (g_k)^{n_k}$$

$$\ln W = N \ln N + \sum (n_i \ln g_i - n_i \ln n_i)$$

$$\delta \ln W_{max} = \sum \delta n_i \ln\left(\frac{g_i}{n_i}\right) = 0$$

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

$$\sum \varepsilon_i \delta n_i = 0 \qquad \sum \beta \varepsilon_i \delta n_i = 0$$

$$\ln\left(\frac{n_i}{g_i}\right) + \alpha + \beta \varepsilon_i = 0 \qquad\qquad n_i = g_i e^{-\alpha} e^{-\beta \varepsilon_i}$$

$$e^{-\alpha} = \frac{N}{\sum g_i e^{-\beta \varepsilon_i}} = \frac{N}{Z} \qquad\qquad n_i = \frac{N}{Z} g_i e^{-\beta \varepsilon_i}$$

Bose-Einstein Distribution

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

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

Fermi-Dirac Distribution

$$W = \prod_i \frac{g_i!}{(g_i - n_i)! n_i!} \qquad n_i = \frac{g_i}{e^\alpha e^{\beta \varepsilon_i} + 1}$$

Definition of Entropy and Significance of β

▷ Consider an Isolated System composed of two part in thermal contact.
  Equilibrium condition ?
    Classical Thermodynamics → maximum entropy (S)
    Statistical mechanics → maximum probability (Ω)

▷ S and Ω have a monotonic relation:

$$S = f(\Omega) \qquad\qquad S_{A-B} = f(\Omega_A \cdot \Omega_B) = f(\Omega_A) + f(\Omega_B)$$

$$S = k' \ln \Omega$$

$$dS = -k'\sum dn_i \ln n_i = k'\sum dn_i(\beta\varepsilon_i - \ln\frac{N}{P}) = k'\beta\sum\varepsilon_i dn_i - k'\ln\frac{N}{P}\sum dn_i = k'\beta \ dU$$

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

$$k' \ \beta = \frac{1}{T} \qquad\qquad \rightarrow \qquad\qquad \beta = \frac{1}{k'T}$$

Calculation of Macroscopic Properties from the Partition Function

$$S = k \ln \Omega = -k \sum n_i \ln\left(\frac{n_i}{N}\right) = -k \sum n_i \ln\left(\frac{1}{Z} e^{-\varepsilon_i / kT}\right) = k \sum n_i \left(\varepsilon_i / kT + \ln Z\right)$$

$$S = \frac{U}{T} + Nk \ln Z$$

$$F \equiv U - ST = -NkT \ln Z$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = Nk \ln Z + NkT \left(\frac{\partial \ln Z}{\partial T}\right)_V$$

$$U = NkT^2 \left(\frac{\partial \ln Z}{\partial T}\right)_V$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = NkT \left(\frac{\partial \ln Z}{\partial V}\right)_T$$

Ideal Mono-Atomic Gas

$$Z = \sum_{\substack{energy \\ level \ i}} g_i e^{-\varepsilon_i / kT}$$

$$Z = \sum_{state} e^{-\varepsilon_i / kT}$$

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

$$Z = \sum e^{-(h^2/8mkT)\,(n_x^2/a^2)} \sum e^{-(h^2/8mkT)\,(n_y^2/b^2)} \sum e^{-(h^2/8mkT)\,(n_z^2/c^2)}$$

$$Z = \int_0^\infty e^{-(h^2/8mkT)\,(n_x^2/a^2)}\, dn_x \int_0^\infty e^{-(h^2/8mkT)\,(n_y^2/b^2)}\, dn_y \int_0^\infty e^{-(h^2/8mkT)\,(n_z^2/c^2)} dn_z$$

$$\int_0^\infty e^{-ax^2}\, dx = \frac{1}{2}\sqrt{\frac{\pi}{a}}$$

$$Z = \left[\frac{a}{2}\sqrt{\frac{8\pi mkT}{h^2}}\right]\left[\frac{b}{2}\sqrt{\frac{8\pi mkT}{h^2}}\right]\left[\frac{c}{2}\sqrt{\frac{8\pi mkT}{h^2}}\right] = V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}$$

$$Z = V \left(\frac{2\pi m k T}{h^2} \right)^{3/2} \qquad \ln Z = \ln V + \frac{3}{2} \ln T + \frac{3}{2} \ln \left(\frac{2\pi m k}{h^2} \right)$$

$$P = N k' T \left(\frac{\partial \ln Z}{\partial V} \right)_T = N k' T \cdot \frac{1}{V} \equiv \frac{nRT}{V}$$

$$U = N k T^2 \left(\frac{\partial \ln Z}{\partial T} \right)_V = N k T^2 \frac{3}{2T} = \frac{3}{2} N k T$$

$$S = N k \ln P + N k T \left(\frac{\partial \ln P}{\partial T} \right)_V = \frac{3}{2} N k \ln T + N k \ln V + \frac{3}{2} N k \ln \left(\frac{2\pi m k}{h^2} \right) + \frac{3}{2} N k$$

for 1 mol of gas

$$s = c_v \ln T + R \ln V + s_o$$

Entropy – S = *k* ln W