Chapter 5

Fundamentals of Quantum Statistical Mechanics

5.1 Noninteracting Identical Particles

Q_i: a set of position and spin of the ith particle

S_i: a quantum state

Ψ: wavefunction of the system

$$\Psi = \Psi_{(S_1,\cdots,S_N)}(Q_1, \cdots, Q_N) \tag{5.1}$$

$$\text{Particle} \left\langle \begin{array}{l} \text{Boson: integral spin, e.g. photon} \\ \text{Fermion: odd multiples of } 1/2\text{, e.g. electron} \end{array} \right.$$

1) Bose-Einstein Statistics (Boson)

Ψ: symmetric under exchange of any two particles

$\downarrow$

$$\Psi_{(S_1,\cdots,S_i,\cdots,S_j,\cdots,S_N)}(Q_1, \cdots, Q_i, \cdots, Q_j, \cdots, Q_N) = \Psi_{(S_1,\cdots,S_i,\cdots,S_j,\cdots,S_N)}(Q_1, \cdots, Q_j, \cdots, Q_i, \cdots, Q_N)$$

2) Fermi-Dirac Statistics (Fermion)

Ψ: antisymmetric under exchange of any two particles

$$\Psi_{(S_1,\cdots,S_i,\cdots,S_j,\cdots,S_N)}(Q_1, \cdots, Q_i, \cdots, Q_j, \cdots, Q_N) = -\Psi_{(S_1,\cdots,S_i,\cdots,S_j,\cdots,S_N)}(Q_1, \cdots, Q_j, \cdots, Q_i, \cdots, Q_N)$$

$S_i = S_j \Longrightarrow\ \Psi = 0$: Any two particles cannot be in the same state (Pauil exclusion principle)

e.g. $^{\exists}$two particles: particle A & particle B

$^{\exists}$3 single particle states: S_i, $i = 1, 2, 3$

$\varphi_S(Q)$: 1 particle wavefunction with coordinate Q and in state S

$$\text{Boson}: \ \varphi_i(Q_A) \cdot \varphi_i(Q_B),\ \ i = 1,2,3: \ \ 3\text{개} \tag{5.2}$$

$$\varphi_i(Q_A) \cdot \varphi_j(Q_B) + \varphi_i(Q_B) \cdot \varphi_j(Q_A), \ \ i > j, \ \ i \,\&\, j = 1,2,3: \ \ 3\text{개} \tag{5.3}$$

$$\text{Fermion}: \ \varphi_i(Q_A) \cdot \varphi_j(Q_B) - \varphi_i(Q_B) \cdot \varphi_i(Q_A), \ \ i > j, \ \ i \,\&\, j = 1,2,3: \ \ 3\text{개} \tag{5.4}$$

3) Maxwell-Boltzman statistics ('classical' particle)

'classical' particle: No symmetric requirement on the wavefunction when two particles are interchanged:

$$\varphi_i(Q_A) \cdot \varphi_j(Q_B), \ \ i \,\&\, j = 1,2,3: \ \ 9\text{개} \tag{5.5}$$

In C. P., identical particles can be distinguishable

M.B. Statistics

1	2	3
AB		
	AB	
		AB
A	B	
B	A	
A		B
B		A
	A	B
	B	A

3^2

(A=B)
B.E. Statistics

1	2	3
AA		
	AA	
		AA
A	A	
A		A
	A	A

${}_3H_2$

(A=B)
F.D. Statistics

1	2	3
A	A	
A		A
	A	A

${}_3C_2$

$$\mathcal{H} = \sum_i h_i, \quad h_i \mid r >= \varepsilon_r \mid r > \tag{5.6}$$

G: No. of single particle states

N: No. of particles

n_r : Occupation No. in the r-state

$R = \{n_r\}$: microstate of the system

$E(R) = \sum_r n_r \cdot \varepsilon_r, \quad N = \sum_r n_r$

Ω : No. of microstates R

$\Omega^{(d)}_{M.B.} = G^N \longrightarrow \Omega^{(i)}_{M.B.} = G^N/N!$ ($N!$: correct Boltzman counting)

$\Omega_{B.E.} = {}_GH_N = {}_{G+N-1}C_N$

$\Omega_{F.D.} = {}_GC_N \ (G \geq N)$

$$\text{For } N > 1,\ \Omega^{(d)}_{M.B.} > \Omega_{B.E.} > \Omega^{(i)}_{M.B.} > \Omega_{F.D.}$$

$$\text{For } N = 1,\ \Omega^{(d)}_{M.B.} = \Omega_{B.E.} = \Omega^{(i)}_{M.B.} = \Omega_{F.D.}$$

$$g(\{n_r\}) : \text{ No. of degeneracies}$$

$$g^{(d)}_{M.B.}(\{n_r\}) : \ \frac{N!}{\prod_r n_r!} = {}_NC_{n_1} \cdot {}_{N-n_1}C_{n_2} \cdots$$

$$g_{B.E.}(\{n_r\}) = 1 = g_{F.D.}(\{n_r\}) : \text{ indistinguishable}$$

- **Canonical Ensemble**

$$Q^{(d)}_{M.B.} = \sum_{\{n_r\}, \sum n_r = N} \frac{N!}{\prod_r n_r!} e^{-\beta \sum_r n_r \cdot \varepsilon_r} \tag{5.7}$$

$$= (e^{-\beta\varepsilon_1} + \cdots + e^{-\beta\varepsilon_G})^N \tag{5.8}$$

$$= q^N \ \text{(q: single particle partition function)} \tag{5.9}$$

$$Q^{(i)}_{M.B.} = Q^{(d)}_{M.B.}/N! \tag{5.10}$$

$$Q_{B.E.} = \sum_{\{n_r\},\, \sum n_r = N} e^{-\beta \sum_r n_r \cdot \varepsilon_r}, \quad n_r = 0, 1, 2, \cdots \tag{5.11}$$

$$Q_{F.D.} = \sum_{\{n_r\},\, \sum n_r = N} e^{-\beta \sum_r n_r \cdot \varepsilon_r}, \quad n_r = 0, 1 \tag{5.12}$$

As $\beta \longrightarrow 0$ $(T \longrightarrow \infty)$, all accessible states에 있을 확률이 같게된다.

$$Q^{(d)}_{M.B.} \longrightarrow G^N = \Omega^{(d)}_{M.B.} \tag{5.13}$$

$$Q^{(i)}_{M.B.} \longrightarrow \Omega^{(i)}_{M.B.} = G^N/N! \tag{5.14}$$

$$\left.\begin{array}{l} Q_{B.E.} \longrightarrow \Omega_{B.E.} = {}_G H_N \\ Q_{F.D.} \longrightarrow \Omega_{F.D.} = {}_G C_N \end{array}\right) \xrightarrow[G \to \infty]{} G^N/N! \tag{5.15}$$

$(G \longrightarrow \infty :$ states이 거의 continuum$)$

- **Grand Canonical Ensemble**

$$Q_G = \sum_{N=0}^{\infty} z^N Q_N, \quad z = e^{\beta\mu} \tag{5.16}$$

$$= \sum_{N=0}^{\infty} z^N \cdot \sum_{\{n_r\},\, \sum n_r = N} g(\{n_r\}) e^{-\beta \sum_r \varepsilon_r \cdot n_r} \tag{5.17}$$

$$< n_r > = \sum_{N=0}^{\infty} \cdot \sum_{\{n_r\},\, \sum n_r = N} n_r \cdot z^N g(\{n_r\}) e^{-\beta \sum_r \varepsilon_r \cdot n_r} / Q_G \tag{5.18}$$

$$\begin{aligned} < n_r > &= -\frac{1}{\beta} \left(\frac{\partial \ln Q_G}{\partial \varepsilon_r} \right)_{z, T, \{\varepsilon_r\}'}, \; < E > = \sum_r \varepsilon_r \cdot < n_r >, \; < N > = \sum_r < n_r > \\ &= -\frac{1}{\beta} \left(\frac{\partial \ln Q_G}{\partial \varepsilon_r} \right)_{\mu, T, \{\varepsilon_r\}'} \end{aligned} \tag{5.19}$$

$$Q_G^{M.B.^{(d)}} = \sum_{N=0}^{\infty} z^N \cdot q^N = \frac{1}{1 - zq} \quad \text{for } zq < 1 \tag{5.20}$$

$$Q_G^{M.B.^{(i)}} = \sum_{N=0}^{\infty} z^N \cdot \frac{q^N}{N!} = e^{zq} \tag{5.21}$$

$$\therefore \ln Q_G^{M.B.^{(i)}} = zq = \sum_r e^{-\beta(\varepsilon_r - \mu)} \tag{5.22}$$

$$Q_G^{B.E.} = \sum_{N=0}^{\infty} z^N \cdot \sum_{\{n_r\},\, \sum n_r = N} e^{-\beta \sum_r \varepsilon_r \cdot n_r} \tag{5.23}$$

$$= \sum_{n_r=0}^{\infty} e^{-\beta \sum_r n_r(\varepsilon_r - \mu)}, \ \ \mu < \varepsilon_0 \ \ (\varepsilon_0 : \text{ minimum energy state}) \tag{5.24}$$

$$= \prod_r \frac{1}{1 - e^{-\beta(\varepsilon_r - \mu)}} \tag{5.25}$$

$$\therefore \ln Q_G^{B.E.} = -\sum_r \ln(1 - e^{-\beta(\varepsilon_r - \mu)}) \tag{5.26}$$

$$Q_G^{F.D.} = \sum_{N=0}^{\infty} z^N \cdot \sum_{\{n_r\},\, \sum n_r = N} e^{-\beta \sum_r n_r \cdot \varepsilon_r}, \quad n_r = 0, 1 \tag{5.27}$$

$$= \sum_{n_r=0}^{1} e^{-\beta \sum_r n_r(\varepsilon_r - \mu)} \tag{5.28}$$

$$= \prod_r (1 + e^{-\beta(\varepsilon_r - \mu)}) \tag{5.29}$$

$$\therefore \ln Q_G^{F.D.} = \sum_r \ln(1 + e^{-\beta(\varepsilon_r - \mu)}) \tag{5.30}$$

$$< n_r > = -\frac{1}{\beta} \left(\frac{\partial \ln Q_G}{\partial \varepsilon_r} \right)_{T, \mu, \{\varepsilon_r\}'} ? \tag{5.31}$$

$$\left. \begin{array}{l} < n_r >^{M.B.^{(i)}} = e^{-\beta(\varepsilon_r - \mu)} \\ < n_r >^{B.E.} = \frac{1}{e^{\beta(\varepsilon_r - \mu)} - 1} \\ < n_r >^{F.D.} = \frac{1}{e^{\beta(\varepsilon_r - \mu)} + 1} \end{array} \right) \tag{5.32}$$

$$< n_r > = \frac{1}{e^{\beta(\varepsilon_r - \mu)} + a} \quad a = \left(\begin{array}{l} \ \ 0, \ M.B.^{(i)} \\ -1, \ B.E. \\ \ \ 1, \ F.D. \end{array} \right. \tag{5.33}$$

Fluctuation ?

$$< \Delta n_r >^2 = < n_r^2 > - < n_r >^2 \tag{5.34}$$

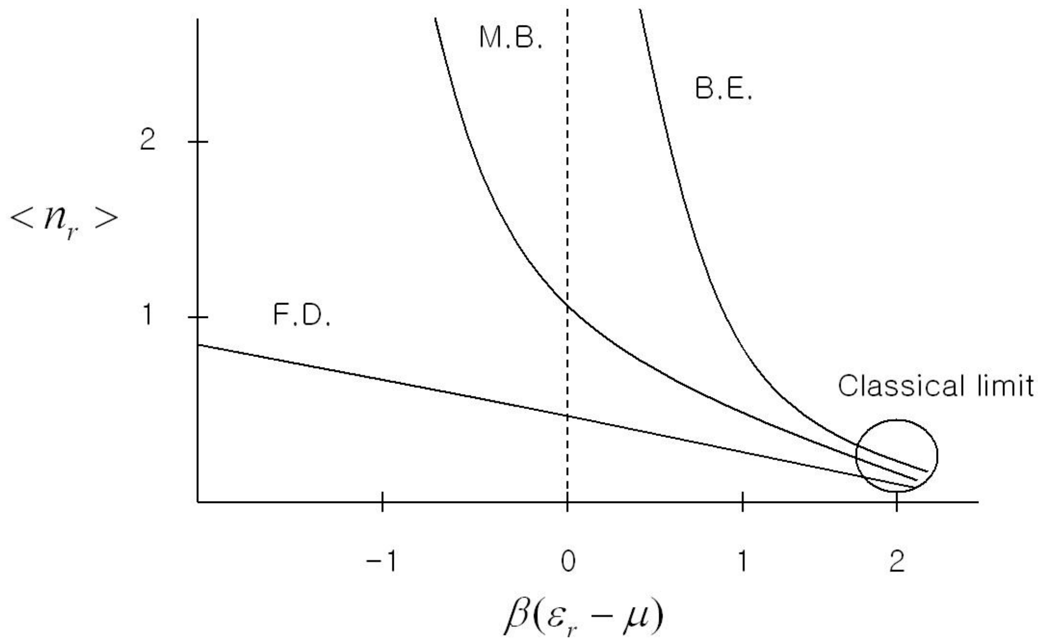
$$< n_r^2 > \;=\; \frac{1}{\beta^2}\cdot\left(\frac{\partial^2 Q_G}{\partial \varepsilon_r^2}\right)/Q_G = \frac{1}{\beta}\frac{\partial}{\partial \varepsilon_r}\left[\frac{1}{\beta}\frac{1}{Q_G}\frac{\partial Q_G}{\partial \varepsilon_r}\right] + \frac{1}{\beta^2}\left(\frac{1}{Q_G}\frac{\partial Q_G}{\partial \varepsilon_r}\right)^2 \tag{5.35}$$

$$= -\frac{1}{\beta}\frac{\partial < n_r >}{\partial \varepsilon_r} + < n_r >^2 \tag{5.36}$$

$$\therefore (\Delta n_r)^2 = -\frac{1}{\beta}\left(\frac{\partial < n_r >}{\partial \varepsilon_r}\right)_{T,\mu} \tag{5.37}$$

$$\frac{(\Delta n_r)^2}{< n_r >^2} = \frac{1}{\beta}\frac{\partial}{\partial \varepsilon_r}\left(\frac{1}{< n_r >}\right) = e^{\beta(\varepsilon_r - \mu)} = z^{-1}\cdot e^{\beta\varepsilon_r} \tag{5.38}$$

$$= \frac{1}{< n_r >} - a, \tag{5.39}$$



1) F.D.

$$0 \leq < n_r >^{F.D.} \leq 1$$

2) B.E.

$\varepsilon_r > \mu$ for all r $\longrightarrow \mu < \varepsilon_0$ (lowest energy level)

($\therefore\ \mu > \varepsilon_r$ for some r $\longrightarrow < n_r > < 0$ (unphysical))

B.E.: ε_0: lowest energy level

$$\mu \longrightarrow \varepsilon_0, < n_0 > \longrightarrow \infty\text{: Bose-Einstein Condensation}$$

$$< n_r > = \frac{1}{e^{\beta(\varepsilon_r - \mu)} + a}, \quad a = 0, \mp 1 \tag{5.40}$$

$$e^{\beta(\varepsilon_r - \mu)} \gg 1 \text{ for all r} \Longrightarrow < n_r >^{B.E.} \ \& < n_r >^{F.D.} \longrightarrow < n_r >^{M.B.^{(i)}} \tag{5.41}$$

$$\Updownarrow$$

$$< n_r >^{B.E.\sim F.D.} \approx e^{-\beta(\varepsilon_r - \mu)} \ll 1 \quad \text{for all r} \tag{5.42}$$

그림에서 오른편으로 갈수록 3개의 curve가 merge.

$$\Updownarrow$$

$$z = e^{\beta\mu} \ll 1 \tag{5.43}$$

$$< N > = V \cdot z/\lambda_T^3 : \quad M.B.^{(i)}, \quad \lambda_T = \frac{h}{(2\pi m k_B T)^{1/2}} \tag{5.44}$$

$$\therefore z = \lambda_T^3/(V/ < N >) \ll 1 \tag{5.45}$$

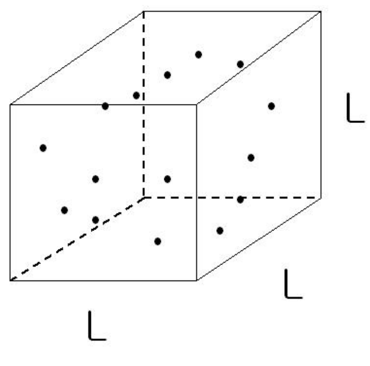
$$\therefore \lambda_T^3 \ll \frac{V}{< N >} : \quad \text{nonoverlap condition} \tag{5.46}$$

$\therefore$ high temperature & low particle density $\longrightarrow$ classical behavior

low temperature & high particle density $\longrightarrow$ quantum behavior

"Quantum Ideal gas with spin S"

$$\mathcal{H} = \sum_i h_i, \quad h_i = \frac{\overrightarrow{p_i^2}}{2m}, \;\; p_i\psi = e\psi, \;\; \psi = C \cdot e^{i\,\overrightarrow{k}\cdot\overrightarrow{r}} \tag{5.47}$$



λ: De Brogie wavelength of the particle

$L \gg \lambda \longrightarrow$ the fraction of particles near the wall $\sim \frac{L^2\lambda}{L^3} \sim \frac{\lambda}{L} \ll 1$

$\therefore$ the detailed properties of the walls become of negligible significance in describing the behavior of a particle located well inside the container.

periodic bdry condi.: $\psi(x+L,y,z) = \psi(x,y+L,z) = \psi(x,y,z+L)$

$\overrightarrow{k} = \frac{2\pi}{L}\overrightarrow{n}, \ \overrightarrow{n} = (n_x, n_y, n_z) \in z^3$

wall effect elimination (no reflection)

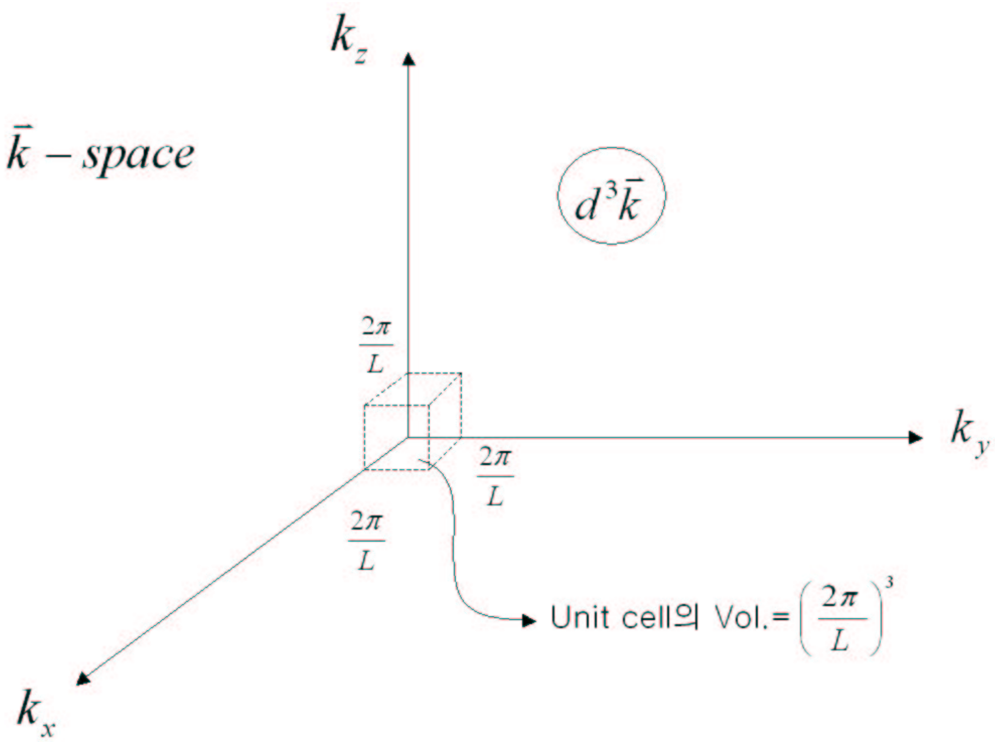
state $r = (\overrightarrow{k}, S)$ ($\overrightarrow{k}$: translational state, S: internal state (e.g. spin)),

$\mathcal{H}_i = \frac{\hbar^2 k^2}{2m}$: indep. of s

$\therefore$ For a given $\overrightarrow{k}$, $^{\exists}g$ (No. of degeneracies) 개 degenerate states

e.g. spin$= s\hbar$

$g = 2s+1$



$$\text{No. of state in } d^3\overrightarrow{k} = \frac{d^3\overrightarrow{k}}{(\frac{2\pi}{L})^3} \tag{5.48}$$

$\frac{N}{L^3} =$ finite & $(N \,\&\, L^3) \longrightarrow \infty \Longrightarrow$ state들이 매우 촘촘히 존재 (거의 연속적으로)

$$\sum_r \longrightarrow g \int \frac{d^3k}{(\frac{2\pi}{L})^3} = g \cdot \frac{V}{(2\pi)^3} \int d^3k \quad (V = L^3 \longrightarrow \infty) \tag{5.49}$$

g: No. of degeneracies for a given $\overrightarrow{k}$

$D(\varepsilon)$: density of states (DOS)

$D(\varepsilon)d\varepsilon =$ No. of state whose energy lies bet. ε and $\varepsilon + d\varepsilon$

$$\therefore D(\varepsilon) = \frac{gV}{(2\pi)^3} \int d^3\overrightarrow{k} \cdot \delta(\varepsilon(\overrightarrow{k}) - \varepsilon) \tag{5.50}$$

$$\text{ideal gas} \longrightarrow \varepsilon = \frac{\hbar^2 k^2}{2m} \longrightarrow k^2 = \frac{2m}{\hbar^2}\varepsilon \longrightarrow dk = \sqrt{\frac{2m}{\hbar^2}} \cdot \frac{1}{2\sqrt{\varepsilon}} d\varepsilon \tag{5.51}$$

$$\begin{aligned} D(\varepsilon) &= \frac{gV}{(2\pi)^3} \cdot \int dk \cdot 4\pi k^2 \cdot \delta(\varepsilon(k) - \varepsilon) && (5.52) \\ &= \frac{gV}{(2\pi)^3} \cdot \int \sqrt{\frac{2m}{\hbar^2}} \cdot \frac{d\varepsilon'}{2\sqrt{\varepsilon'}} 4\pi \frac{2m}{\hbar^2} \varepsilon' \delta(\varepsilon' - \varepsilon) && (5.53) \\ &= \frac{gV}{(2\pi)^3} \cdot \left(\frac{2m}{\hbar^2}\right)^{3/2} 2\pi \int \varepsilon'^{1/2} \delta(\varepsilon' - \varepsilon) \cdot d\varepsilon' && (5.54) \\ &= \frac{gV}{(2\pi)^3} \cdot \left(\frac{2m}{\hbar^2}\right)^{3/2} \cdot \varepsilon^{1/2} && (5.55) \end{aligned}$$

$$\therefore \sum_r \longrightarrow \frac{gV}{(2\pi)^3} \cdot \int d^3k \Longleftrightarrow \frac{gV}{(2\pi\hbar)^3} \cdot \int d^3p, \; (\overrightarrow{p} = \hbar \overrightarrow{h}) \tag{5.56}$$

$$\Updownarrow$$

$$\int d\varepsilon \cdot D(\varepsilon) \tag{5.57}$$