

(2) Applications I (Rev. chap. 9. Huang chap. 12.3)

~~① Ideal gas~~

- Fermions : conduction electrons in solids
- Ideal Bose gas : Bose-Einstein condensation
- photons : black-body radiation

Fermion : conduction electrons in metals

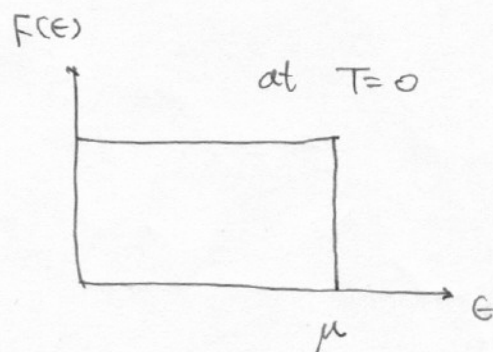
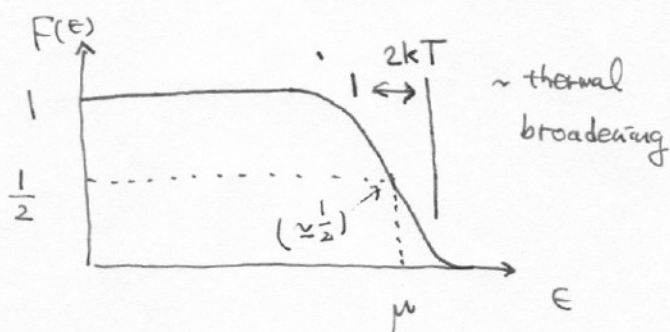
metal $\Rightarrow$ one can neglect electron-electron interactions as a first approximation. So, electrons in metals can be treated as an ideal gas. (cf. Fermi liquid)

But, their density is so high that they can not be described by classical statistics.

$$\bar{n}_s = \frac{1}{e^{\beta(\epsilon_s - \mu)} + 1}$$

$$N = \sum_s \bar{n}_s$$

"Fermi function"
$$F(\epsilon) = \frac{1}{e^{\beta(\epsilon - \mu)} + 1}$$



$\Rightarrow \mu$ is called as the Fermi energy in this case.

note :

$$\begin{cases} \epsilon \ll \mu \Rightarrow F(\epsilon) = 1 \\ \epsilon \gg \mu \Rightarrow F(\epsilon) = e^{\beta(\mu - \epsilon)} \end{cases}$$

At $T=0$, each state with $\epsilon < \mu$ is occupied by one electron

(~~for~~ Pauli exclusion)

② Fermi energy $\mu = \mu_0$ at $T=0$

$$\epsilon = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \quad (\vec{p} = \hbar \vec{k})$$

$$\mu_0 = \frac{P_F^2}{2m} = \frac{\hbar^2 k_F^2}{2m} \rightarrow \text{at } T=0, \text{ all states with } k < k_F \text{ are filled.}$$

$k > k_F$ empty.

the total number of states below μ_0 :

To count the number of states, let's suppose that our system is translationally invariant.

$$\begin{aligned} \psi(x+L_x, y, z) &= \psi(x, y, z) \\ \psi(x, y+L_y, z) &= \psi(x, y, z) \\ \psi(x, y, z+L_z) &= \psi(x, y, z) \end{aligned} \quad \downarrow$$

$$\Rightarrow \psi = e^{i\vec{k} \cdot \vec{r}}, \quad k_x(x+L_x) = k_x x + 2\pi n_x$$

$$\Rightarrow k_x = \frac{2\pi}{L_x} n_x, \quad k_y = \frac{2\pi}{L_y} n_y, \quad k_z = \frac{2\pi}{L_z} n_z.$$

$$\Rightarrow \Delta n_x = \frac{L_x}{2\pi} dk_x$$

$$\Rightarrow \sum_{|\vec{k}| < k_F} 1 = \frac{L_x L_y L_z}{(2\pi)^3} \int_{|\vec{k}| < k_F} d\vec{k} = \frac{V}{(2\pi)^3} \cdot \frac{4}{3} \pi k_F^3$$

By taking into account of spin degeneracy,

$$N = 2 \cdot \frac{V}{(2\pi)^3} \cdot \frac{4}{3} \pi k_F^3$$

$$\Rightarrow k_F = \left(3\pi^2 \frac{N}{V} \right)^{1/3} \quad \lambda_F = 2\pi/k_F$$

$$\mu_0 = \frac{\hbar^2}{2m} k_F^2 = \frac{\hbar^2}{2m} \left(3\pi^2 \frac{N}{V} \right)^{2/3}$$

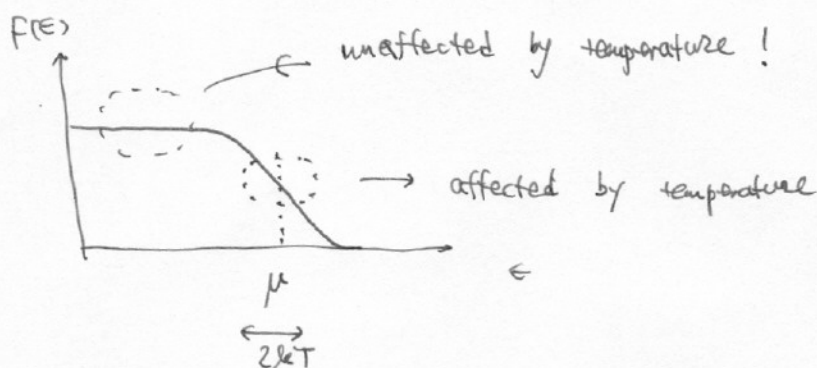
electronic specific heat

estimation :

$$C_v = \left(\frac{\partial \bar{E}}{\partial T} \right)_v$$

classically, $\bar{E} = \frac{3}{2} N k T$, $C_v = \frac{3}{2} N k$.

But, this is not the case in electronic systems.



$$\Rightarrow N_{\text{eff}} \cong N \times \frac{kT}{\mu}$$

$$\rightarrow C_v^{(e)} \cong \frac{3}{2} N_{\text{eff}} k \propto T.$$

$$C_v = \underbrace{C_v^{(e)}}_{\text{electron contribution}} + \underbrace{C_v^{(L)}}_{\text{phonon contribution}}$$

$$C_v^{(e)} = \gamma T.$$

$$C_v^{(L)} = AT^3$$

~~(= 1/12)~~
We will see this later.

detailed calculations ($\beta\mu \gg 1$ limit)

$$\bar{E} = \sum_r \frac{\epsilon_r}{e^{\beta(\epsilon_r - \mu)} + 1} = 2 \int \underbrace{F(\epsilon)}_{\text{spin degeneracy}} \underbrace{\epsilon p(\epsilon) d\epsilon}_{\text{densities of states}}$$

$$= 2 \int_0^\infty \frac{\epsilon}{e^{\beta(\epsilon - \mu)} + 1} p(\epsilon) d\epsilon$$

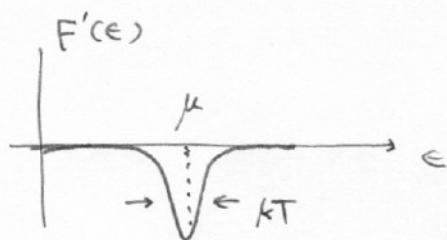
$$N = 2 \int f(\epsilon) p(\epsilon) d\epsilon$$

We will evaluate the integral of the form $\int_0^\infty F(\epsilon) \varphi(\epsilon) d\epsilon$

$$\int_0^\infty F(\epsilon) \varphi(\epsilon) d\epsilon = \underbrace{F(\epsilon) \psi(\epsilon)}_{\text{crossed out}} \Big|_0^\infty - \int_0^\infty F'(\epsilon) \psi(\epsilon) d\epsilon$$

$$\psi(\epsilon) = \int_0^\epsilon \varphi(\epsilon') d\epsilon' \quad (\because F(\epsilon \rightarrow \infty) = 0, \quad \psi(\epsilon \rightarrow 0) = 0)$$

Observe :



$\Rightarrow$ expand $\psi(\epsilon)$ near $\epsilon = \mu$

$$\begin{aligned} \psi(\epsilon) &= \psi(\mu) + \left. \frac{d\psi}{d\epsilon} \right|_\mu (\epsilon - \mu) + \frac{1}{2} \left. \frac{d^2\psi}{d\epsilon^2} \right|_\mu (\epsilon - \mu)^2 + \dots \\ &= \sum_{n=0}^{\infty} \frac{1}{n!} \left[\frac{d^n \psi}{d\epsilon^n} \right]_\mu (\epsilon - \mu)^n \end{aligned}$$

$$\int_0^\infty F'(\epsilon) (\epsilon - \mu)^n d\epsilon = - \int_0^\infty \frac{\beta e^{\beta(\epsilon - \mu)}}{(e^{\beta(\epsilon - \mu)} + 1)^2} (\epsilon - \mu)^n d\epsilon$$

$$= -\beta^{-n} \int_{-\beta\mu}^{\infty} \frac{x^n e^x}{(e^x + 1)^2} dx$$

$$\downarrow \\ x = \beta(\epsilon - \mu)$$

$\boxed{\beta\mu \gg 1}$
(limit)

$$= -\beta^{-n} I_n$$

$$I_n \equiv \int_{-\infty}^{\infty} \frac{e^x x^n}{(e^x + 1)^2} dx = \int_{-\infty}^{\infty} \frac{x^n}{(e^x + 1)(e^{-x} + 1)} dx$$

$$I_0 = 1$$

$$I_n = 0 \quad \text{if } n \text{ is odd}$$

$$\Rightarrow \int_0^\infty F(\epsilon) \varphi(\epsilon) d\epsilon = \psi(\mu) + I_2 \left(\frac{kT}{2} \right)^2 \left[\frac{d^2 \psi}{d\epsilon^2} \right]_\mu + \dots$$

$$I_2 = \frac{\pi^2}{3} \quad (\text{see problems 9.26, 9.27})$$

$$\Rightarrow \bar{E} = 2 \int_0^{\mu} \epsilon p(\epsilon) d\epsilon + \frac{\pi^2}{3} (kT)^2 \left[\frac{d}{d\epsilon} (\epsilon p) \right]_{\mu}$$

$$\left(\begin{aligned} 2 \int_0^{\mu} \epsilon p(\epsilon) d\epsilon &= \underbrace{2 \int_0^{\mu_0} \epsilon p(\epsilon) d\epsilon}_{\equiv \bar{E}_0} + 2 \int_{\mu_0}^{\mu} \epsilon p(\epsilon) d\epsilon \\ &\approx \bar{E}_0 + 2\mu_0 p(\mu_0) (\mu - \mu_0) \\ \frac{d}{d\epsilon} (\epsilon p) &= p + \epsilon p' \end{aligned} \right.$$

$$\Rightarrow \bar{E} = \bar{E}_0 + 2\mu_0 p(\mu_0) (\mu - \mu_0) + \frac{\pi^2}{3} (kT)^2 [p(\mu_0) + \mu_0 p'(\mu_0)]$$

$$N = 2 \int_0^{\mu} p(\epsilon) d\epsilon + \frac{\pi^2}{3} (kT)^2 p'(\mu)$$

$$(\text{from } N = 2 \int f(\epsilon) p(\epsilon) d\epsilon)$$

$$= \underbrace{2 \int_0^{\mu_0} p(\epsilon) d\epsilon}_{=N} + 2 \int_{\mu_0}^{\mu} p(\epsilon) d\epsilon + \frac{\pi^2}{3} (kT)^2 p'(\mu)$$

$$= N + 2p(\mu_0) (\mu - \mu_0) + \frac{\pi^2}{3} (kT)^2 p'(\mu)$$

$$\Rightarrow (\mu - \mu_0) = - \frac{\pi^2}{6} (kT)^2 \frac{p'(\mu_0)}{p(\mu_0)}$$

$$\Rightarrow \bar{E} = \bar{E}_0 - \frac{\pi^2}{3} (kT)^2 \mu_0 p'(\mu_0) + \frac{\pi^2}{3} (kT)^2 (p(\mu_0) + \mu_0 p'(\mu_0))$$

$$= \bar{E}_0 + \frac{\pi^2}{3} (kT)^2 p(\mu_0)$$

$$\Rightarrow C_V^{(0)} = \frac{\partial \bar{E}}{\partial T} = \frac{2\pi^2}{3} k^2 p(\mu_0) T$$

$$p(\epsilon) d\epsilon = \frac{V}{(2\pi)^3} \cdot 4\pi k^2 \frac{dk}{d\epsilon} d\epsilon = \frac{V}{4\pi^2} \frac{(2m)^{3/2}}{\hbar^3} \sqrt{\epsilon} d\epsilon$$

$$\mu_0 = \frac{\hbar^2}{2m} \left(3\pi^2 \frac{N}{V} \right)^{\frac{2}{3}}$$

$$\Rightarrow p(\mu_0) = V \frac{m}{2\pi^2 \hbar^2} \left(3\pi^2 \frac{N}{V} \right)^{\frac{1}{3}} = \frac{3}{4} \frac{N}{\mu_0}$$

$$\Rightarrow C_V = \frac{\pi^2}{2} k N \frac{kT}{\mu_0}$$

① Ideal Bose gas : Bose - Einstein Condensation

(i) Classical ~~Boltzmann~~ Boltzmann gas $\leftarrow$ Bose gas at $\left(\begin{array}{l} \text{high temperature} \\ \text{low density} \end{array} \right)$

$$\frac{N}{V} \left(\frac{h^2}{2\pi m k T} \right)^{3/2} \ll 1$$

$$\ln \mathcal{Z}(T, V, \mu) = - \sum_k \ln (1 - \exp(-\beta(\epsilon_k - \mu)))$$

$$\frac{N}{V} \lambda^3 \ll 1$$

$$N = \sum_k \frac{1}{e^{-\beta(\epsilon_k - \mu)} - 1}$$

To evaluate the above summations,

$$\begin{aligned} \sum_k &\rightarrow \frac{V}{(2\pi)^3} \int d^3k = \frac{2\pi V}{h^3} (2m)^{3/2} \int \sqrt{\epsilon} d\epsilon \\ &\quad \left(\epsilon_k = \frac{(\hbar k)^2}{2m} \right) \\ &= \int \rho(\epsilon) d\epsilon \end{aligned}$$

Note: $\beta(\epsilon_k - \mu) \geq 0$ for all $k \Rightarrow \mu \leq 0$, $e^{\beta\mu} \in [0, 1]$

BUT, this approximation is very bad for small energies $\epsilon \rightarrow 0$.

Notice: In a box with volume V (periodic boundary condition),

there exists a state with $\epsilon=0$, $\psi_0(\mathbf{r}) = \frac{1}{\sqrt{V}}$.

This state is not counted in the approximation.

One can not neglect this special state with the lowest energy.

$$\begin{aligned} \Rightarrow \ln \mathcal{Z}(T, V, \mu) &= - \int_0^\infty \rho(\epsilon) d\epsilon \ln(1 - e^{-\beta(\epsilon - \mu)}) - \underbrace{\ln(1 - e^{\beta\mu})}_{\text{contributed from } \psi_0} \\ &= \frac{2\pi V}{h^3} (2m)^{3/2} \frac{2}{3} \beta \int_0^\infty d\epsilon \frac{\epsilon^{3/2}}{e^{\beta(\epsilon - \mu)} - 1} - \ln(1 - e^{\beta\mu}) \\ N(T, V, \mu) &= \frac{2\pi V}{h^3} (2m)^{3/2} \int_0^\infty d\epsilon \frac{\sqrt{\epsilon}}{e^{\beta(\epsilon - \mu)} - 1} + \frac{1}{e^{-\beta\mu} - 1} \\ N_0 &= \frac{1}{e^{-\beta\mu} - 1} \end{aligned}$$

Let's denote $z_f \equiv e^{+\beta\mu}$, which is called as "fugacity"

use
$$g_n(z) = \frac{1}{\Gamma(n)} \int_0^\infty \frac{x^{n-1} dx}{z_f^{-1} e^x - 1}, \quad 0 \leq z_f \leq 1$$

$n \in \mathbb{R}$

$$x \leftarrow \beta \epsilon$$

$\Gamma(n) \sim$ gamma function.

$$\Rightarrow \ln \mathcal{Z}(T, V, \mu) = \frac{V}{\lambda^3} g_{5/2}(z_f) - \ln(1 - z_f)$$

$$N(T, V, \mu) = \frac{V}{\lambda^3} g_{3/2}(z_f) + N_0(z_f)$$

$$\lambda \equiv \sqrt{\frac{h^2}{2\pi m k T}}$$

$$\left(\frac{h^2}{2m} \frac{1}{\lambda^2} \right)^2 = \frac{h^2}{2m} \cdot \frac{2\pi m k T}{h^2} = \pi k T$$

$$\frac{1}{z_f^{-1} \exp(x) - 1} = z_f \exp(-x) \frac{1}{1 - z_f e^{-x}}$$

$$= \sum_{k=1}^{\infty} z_f^k \exp(-kx)$$

note: $z_f^{-1} \exp x = e^{\beta \epsilon - \mu} \geq 1$

$$\Rightarrow g_n(z_f) = \frac{1}{\Gamma(n)} \sum_{k=1}^{\infty} z_f^k \int_0^\infty x^{n-1} e^{-kx} dx$$

$$z_f \in [0, 1]$$

$$= \frac{1}{\Gamma(n)} \sum_{k=1}^{\infty} \frac{z_f^k}{k^n} \int_0^\infty y^{n-1} e^{-y} dy$$

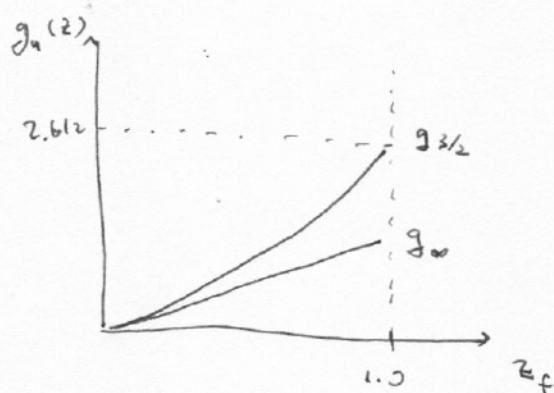
$$= \sum_{k=1}^{\infty} \frac{z_f^k}{k^n}, \quad z_f \in [0, 1]$$

$g_n(z_f)$ is finite for $n > 1$ for $z_f \in [0, 1]$.

for $z_f = 1$ ($\mu = 0$), $g_n(1) = \sum_{k=1}^{\infty} \frac{1}{k^n} = \zeta(n)$, $n > 1$

$\rightarrow$ Riemann's Zeta function $\zeta(n)$

$$\zeta(1) \rightarrow \infty, \quad \zeta(3/2) \approx 2.612$$



Study first
$$N(T, V, \mu) = \underbrace{\frac{V}{\lambda^3} g_{3/2}(z_f)}_{N_e} + N_0(z_f).$$

$$N_e^{\max} = \frac{V}{\lambda^3} g_{3/2}(z_f=1)$$

$$= \frac{V}{\lambda^3} \zeta\left(\frac{3}{2}\right)$$

Let's consider the thermodynamic limit ($N \rightarrow \infty$, $V \rightarrow \infty$, $N/V = \text{constant}$).

$$N = N_e + N_0$$

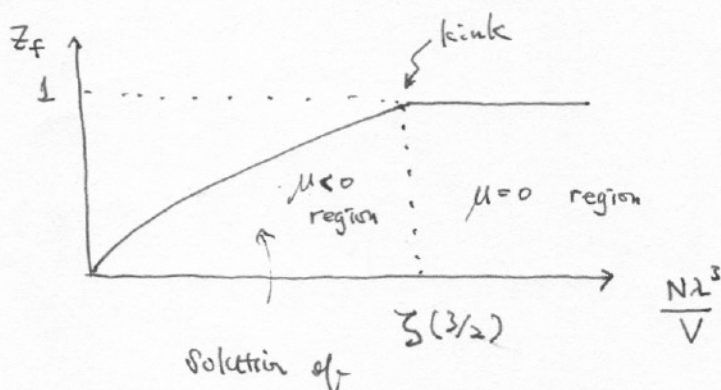
$z_f \neq 1 \rightarrow N_0/N \rightarrow 0$, all particles occupy excited states.

$z_f = 1 \rightarrow N_e = N_e^{\max}$, $N_0 = N - N_e^{\max}$

Cross-over occurs at

$$N = N_e^{\max} = \frac{V}{\lambda^3} \zeta(3/2)$$

$$(\because z_f \neq 1 \Rightarrow N = \frac{V}{\lambda^3} g_{3/2}(z_f))$$



$$N = \frac{V}{\lambda^3} g_{3/2}(z_f)$$

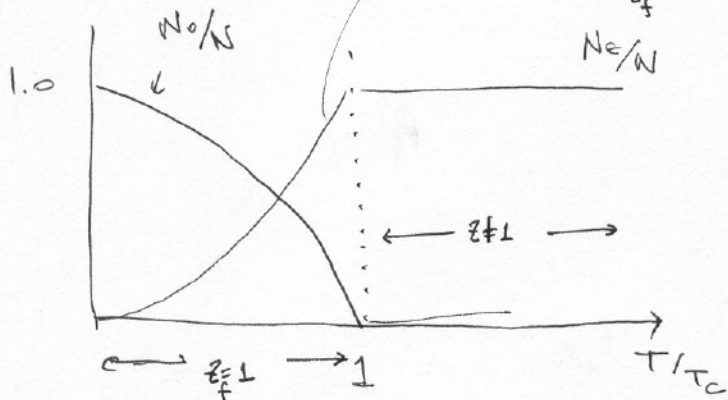
($\therefore$ For finite N , z_f is determined by

$$N = N_e(z_f) + N_0(z_f) \Rightarrow \text{No kink.} \quad (\text{But smooth curve.})$$

$$\frac{N \lambda^3}{V} \geq \zeta(3/2) \Rightarrow T < T_c, \quad kT_c = \left(\frac{N}{V}\right)^{2/3} \frac{h^2}{2\pi m (\zeta(3/2))^{2/3}}$$

$$(N > N_e^{\max})$$

$$\frac{N_E^{\max}}{N} = \left(\frac{T}{T_c} \right)^{3/2}$$



$$\frac{N_0}{N} = 1 - \frac{N_E}{N}$$

Base - Einstein condensation. (Example: ^4He)

* pressure:

$$E = TS - pV + \mu N$$

$$\Rightarrow -\frac{1}{\beta} \ln \mathcal{Z} = E - TS + \mu N = -pV$$

$$\ln \mathcal{Z} = \frac{V}{\lambda^3} g_{5/2}(z_f) - \ln(1 - z_f)$$

$$\Rightarrow p = \frac{kT}{\lambda^3} g_{5/2}(z_f) - \frac{kT}{V} \ln(1 - z_f)$$

$$\text{as } V \rightarrow \infty, N \rightarrow \infty$$

$$N/V = \text{constant}$$

$$\text{if } z_f < 1.$$

$$N_0 = \frac{z_f}{1 - z_f} \rightarrow 1 - z_f = \frac{1}{N_0 + 1}$$

$$\frac{\ln(1 - z_f)}{V} \sim \frac{\ln(N_0 + 1)}{V} \sim \frac{\ln N}{V} \rightarrow 0$$

$$\text{as } V \rightarrow \infty, N \rightarrow \infty, N/V = \text{constant.}$$

$\Rightarrow \psi_0$ does not contribute

to pressure.

$\Rightarrow \psi_0$ has no kinetic energy.

at $T < T_c$,

$$p = \frac{kT}{\lambda^3} \zeta(5/2) \quad (z_f = 1)$$

$\sim$ independent of V, N .

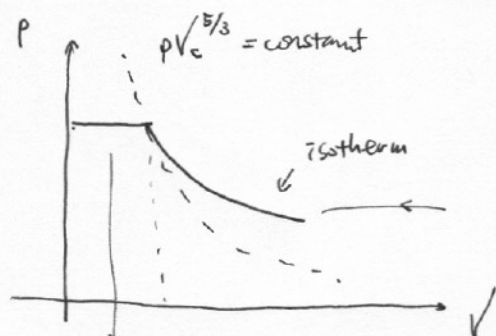
$\therefore$ If one adds one more ~~to~~ particles into the system with $T < T_c$, it would sit in ψ_0 .

Fix temperature and change volume V :

$$\left(\frac{N\lambda^3}{V_c} = \zeta\left(\frac{3}{2}\right) \right) \Rightarrow V_c = \frac{N\lambda^3}{\zeta(3/2)}$$

$$P = \frac{kT}{\lambda^3} \zeta\left(\frac{5}{2}\right)$$

By eliminating T , $P V_c^{5/3} = \text{constant}$



$$P = \frac{kT}{\lambda^3} g_{5/2}(z_f)$$

We already know

$$z_f(T, V, \mu)$$

from the equation

$$N = \sum_r \frac{1}{e^{\beta(\epsilon_r - \mu)} - 1}$$

* classical limit: $\frac{N\lambda^3}{V} \ll 1$

$$\frac{N\lambda^3}{V} = g_{3/2}(z) \quad \text{and} \quad g_{3/2}(z) \simeq z_f \quad \text{for} \quad z_f \ll 1$$

$$\Rightarrow \frac{N\lambda^3}{V} = z_f$$

$$(g_{3/2}(z_f) = z_f + \frac{z_f^2}{2^{3/2}} + \dots)$$

$$g_{5/2}(z_f) = z_f + \frac{z_f^2}{2^{5/2}} + \dots$$

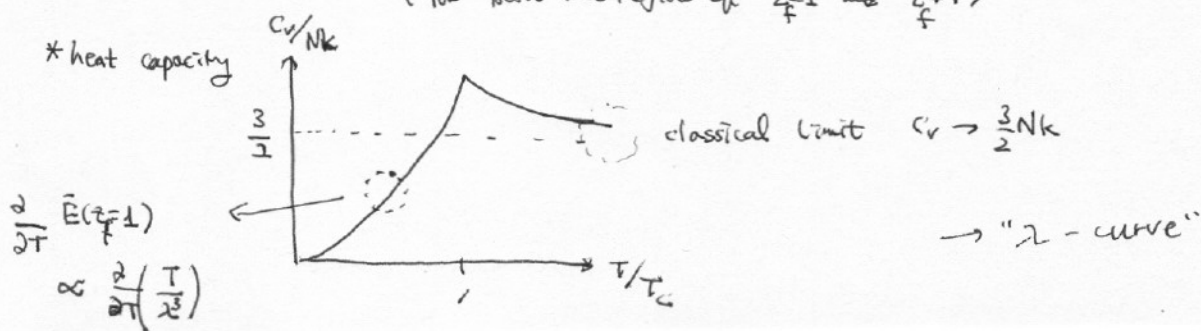
$$P = \frac{kT}{\lambda^3} g_{5/2}(z_f) \approx \frac{kT}{\lambda^3} z_f = \frac{kT}{\lambda^3} \cdot \frac{N\lambda^3}{V} = \frac{1}{V} NkT$$

* energy:

$$E = -\frac{\partial}{\partial \beta} \ln \mathcal{Z} = \frac{3}{2} kT \frac{V}{\lambda^3} g_{5/2}(z_f)$$

$$\Rightarrow \bar{E} = \frac{3}{2} PV \quad \rightarrow \text{classical limit} \quad \bar{E} = \frac{3}{2} NkT$$

(for both the regions of $z_f \ll 1$ and $z_f \gg 1$)



$\rightarrow$ "lambda-curve"

BE condensation does not occur in 1D and 2D systems without any bound states.

V-20

② photon : black-body radiation



The atoms in the walls of the cavity will constantly emit and absorb electromagnetic radiation.

Cavity : volume V

The wall of cavity is heated to a given temperature T .

Quantize EM field $\Rightarrow$ photon.

the total # of photons inside cavity (even in closed cavity) is NOT conserved.

$\Rightarrow$ Using canonical partition function -

$$Z = \sum_{n_1, n_2, \dots} e^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \dots)}$$

$\Rightarrow$ unrestricted summation

$$= \left(\sum_{n_1=0}^{\infty} e^{-\beta n_1 \epsilon_1} \right) \left(\sum_{n_2=0}^{\infty} e^{-\beta n_2 \epsilon_2} \right) \dots$$

$$= \prod_{r=1}^{\infty} \frac{1}{1 - e^{-\beta \epsilon_r}}$$

$$\downarrow e^{-\beta \epsilon_r} < 1$$

($\epsilon_r > 0$)

$$\ln Z = - \sum_r \ln(1 - e^{-\beta \epsilon_r})$$

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

electric field $\vec{E}$

4-22

$$\left(\begin{array}{l} \nabla^2 \vec{E} = \frac{1}{c^2} \frac{\partial^2 \vec{E}}{\partial t^2} \\ \nabla \cdot \vec{E} = 0 \end{array} \right.$$

$$\vec{E} = \vec{A} e^{i(\vec{k} \cdot \vec{r} - \omega t)}$$

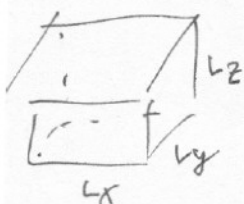
$$\Rightarrow |\vec{k}| = \omega/c, \quad \underbrace{\vec{k} \cdot \vec{E} = 0}_{\text{for given } \vec{k}},$$

there are two possible directions of $\vec{E}$,
(polarization)

quantization

$$\left(\begin{array}{l} E = \hbar \omega \\ \vec{p} = \hbar \vec{k} \end{array} \right.$$

$$\Rightarrow \# \text{ of degeneracy} = 2$$



$$L \gg \lambda = 2\pi/|\vec{k}|$$

$$\sum_n \rightarrow \frac{V}{(2\pi)^3} \int d\vec{k}$$

$$\Rightarrow \underline{f(\vec{k}) d^3\vec{k}} = \left(\frac{d^3\vec{k}}{(2\pi)^3} \right) \cdot \frac{1}{e^{\beta \hbar \omega} - 1}$$

mean # of photons (per unit volume) with $\vec{k} \in [\vec{k}, \vec{k} + d\vec{k}]$

$\Rightarrow$ mean # of photons (") of both directions of polarization
with $\omega \in [\omega, \omega + d\omega]$

$$= 2 \times f(k) 4\pi k^2 dk = \frac{8\pi}{(2\pi c)^3} \frac{\omega^2 d\omega}{e^{\beta \hbar \omega} - 1}$$

$$\bar{E} = \int \hbar \omega \cdot 2 f(k) 4\pi k^2 dk$$

$$= \frac{\hbar}{\pi^2 c^3} \left(\frac{kT}{\hbar} \right)^4 \int_0^\infty \frac{q^3 dq}{e^q - 1} \quad q = \beta \hbar \omega$$

$$\propto T^4$$

$\sim$ Stefan - Boltzmann law.

* radiation pressure

4-23

$$\bar{p} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V}$$

$$= \sum_s \bar{n}_s \left(- \frac{\partial \epsilon_s}{\partial V} \right)$$

$$\begin{aligned} \epsilon_s &= \hbar \omega = \hbar c k = \hbar c \sqrt{k_x^2 + k_y^2 + k_z^2} = \hbar c \left(\frac{2\pi}{L} \right) (n_x^2 + n_y^2 + n_z^2)^{1/2} \\ &= \boxed{a} V^{-1/3} \end{aligned}$$

$$\frac{\partial \epsilon_s}{\partial V} = -\frac{1}{3} \boxed{a} V^{-4/3} = -\frac{1}{3} \frac{\epsilon_s}{V}$$

$$\Rightarrow \bar{p} = \sum_s \bar{n}_s \epsilon_s \left(+\frac{1}{3} \right) = \frac{\bar{E}}{3V}$$

$$= \frac{1}{3} \bar{u}_0$$

$$\bar{u}_0 \equiv \frac{\bar{E}}{V} \sim \text{mean energy density.}$$