Course 4. Quantum statistics

) Maxwell - Boltzmann, Bose - Einstein, Fermi - Dirac

- many-body wave function

- MB statistics

- Grand canonical description of BE statistics

- " FD "

- Classical limit and $\bar{n}_r$

Application I

- Fermions : conduction electrons in solids

- Ideal Bose gas : Bose - Einstein condensation

- photons : black-body radiation

Application II

(1) Maxwell - Boltzmann (MB),

Bose - Einstein (BE),

Fermi - Dirac (FD)

○ Many-body wave functions

N identical particles in volume V

(Q_i : coordinate of the ith particle (spatial & spin)
(S_i : quantum number

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

	classical MB	BE, boson	FD, fermion
total spin angular momentum		integer	half integer
		photon, He^4,	electron, He^3,
	distinguishable	indistinguishable symmetric	indistinguishable antisymmetric
	$\psi_i(Q_A)\psi_j(Q_B)$	$\Psi(\cdots Q_j \cdots Q_i \cdots) = \Psi(\cdots Q_i \cdots Q_j \cdots)$ $\Psi_i(Q_A)\Psi_j(Q_B) + \Psi_i(Q_B)\Psi_j(Q_A)$	$\Psi(\cdots Q_j \cdots Q_i \cdots) = -\Psi(\cdots Q_i, \cdots, Q_j \cdots)$ $\Psi_i(Q_A)\Psi_j(Q_B) - \Psi_i(Q_B)\Psi_j(Q_A)$
Any # of particles in the same single particle state	Yes	Yes	No. Pauli exclusion principle

supp.

symmetric / antisymmetric wave fn.

fermion $\Psi^{A}_{k_1 \cdots k_N}(\vec{r}_1, \cdots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \underset{\substack{\uparrow \\ \text{permutation}}}{\sum_P} (-1)^P \underset{\substack{\uparrow \\ \text{permutation operator}}}{\hat{P}} \phi_{k_1}(\vec{r}_1) \cdots \phi_{k_N}(\vec{r}_N)$

$$= \frac{1}{\sqrt{N!}} \det \begin{pmatrix} \phi_{k_1}(\vec{r}_1) & \cdots & \phi_{k_1}(\vec{r}_N) \\ \vdots & & \vdots \\ \phi_{k_N}(\vec{r}_1) & \cdots & \phi_{k_N}(\vec{r}_N) \end{pmatrix}$$

Slater determinant

boson $\Psi^{S}_{k_1 \cdots k_N}(\vec{r}_1 \cdots \vec{r}_N) = \underbrace{\mathrm{Norm}}_{\downarrow} \sum_P \hat{P} \phi_{k_1}(\vec{r}_1) \cdots \phi_{k_N}(\vec{r}_N)$

depends on how many of the quantum numbers $k_1, \cdots, k_N$ are equal.

$N = \sum_i n_i$. n_i : # of bosons in the state k_i

$\Rightarrow \mathrm{Norm} = [N! \, n_1! n_2! \cdots]^{-1/2}$

fractional statistics

$$\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3 \cdots, \vec{r}_N) = e^{\pm i\pi\nu} \Psi(\vec{r}_2, \vec{r}_1, \vec{r}_3 \cdots \vec{r}_N)$$

ν : $2n$ boson

$2n+1$ fermion

fractional value

※ Origin of phase :

$$|\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \cdots, \vec{r}_N)|^2 = |\Psi(\vec{r}_2, \vec{r}_1, \vec{r}_3, \cdots, \vec{r}_N)|^2 \quad \because \text{indistinguishabl}$$

$$\Rightarrow \Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \cdots) = e^{\pm i\pi\nu} \Psi(\vec{r}_2, \vec{r}_1, \vec{r}_3, \cdots)$$

⊙ MB statistics

a gas of identical particles in a volume V

in equilibrium at the temperature T.

$$\left(\begin{array}{llll} \text{many-body state index} : R & \to \text{energy } E_R & \text{particle \# } N \\ \text{single-particle} \;\; \text{"} \;\; \text{"} : r & \to \text{energy } \epsilon_r, & \text{particle \# } n_r \end{array} \right.$$

$$\left(\begin{array}{l} E_R = \sum_r n_r \epsilon_r \\ N = \sum_r n_r \end{array} \right. \quad , \quad n_r = 0, 1, 2, \cdots$$

$$Z = \sum_{R\{n_1, n_2 \ldots\}} e^{-\beta E_R} \times \frac{N!}{n_1! n_2! \cdots}$$

$\because$ for given values of $\{n_1, n_2 \cdots\}$

we have $\dfrac{N!}{n_1! n_2! \cdots}$ possible ways

of arrangements.

Distinguishability $\to$ each of these arrangements

should be regarded as a distinct

state.

$$\Rightarrow Z = \sum_{n_1, n_2 \cdots} \frac{N!}{n_1! n_2! \cdots} \left(e^{-\beta \epsilon_1}\right)^{n_1} \left(e^{-\beta \epsilon_2}\right)^{n_2} \cdots$$

$\nwarrow$ multinomial distribution

$$= \left(e^{-\beta \epsilon_1} + e^{-\beta \epsilon_2} + \cdots\right)^N$$

$$\ln Z = N \ln \left(\sum_r e^{-\beta \epsilon_r} \right)$$

$$\bar{n}_s = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \epsilon_s} \qquad \left(= \cancel{\sum n_s e} \left(\sum n_s e^{-\beta E_R}\right) / Z \right)$$

$$= N \frac{e^{-\beta \epsilon_s}}{\sum_r e^{-\beta \epsilon_r}} .$$

) Grand canonical description of BE statistics

Grand canonical partition function $\mathcal{Z}$

$$\mathcal{Z} = \sum_R e^{-\beta(n_1\epsilon_1 + \cdots)} \quad e^{-\alpha(n_1+n_2+\cdots)}$$

Grand canonical $\Rightarrow$ We have no restriction such as $N = \sum_r n_r$.

$\Rightarrow$ $\mathcal{Z}$ is easier to be evaluated.

$$\mathcal{Z} = \sum_{n_1, n_2, \cdots} e^{-(\alpha+\beta\epsilon_1)n_1} \quad e^{-(\alpha+\beta\epsilon_2)n_2} \cdots$$

$$= \prod_r \left(\sum_{n_r}^{\infty} e^{-(\alpha+\beta\epsilon_r)n_r} \right)$$

$$= \prod_r \frac{1}{1 - e^{-(\alpha+\beta\epsilon_r)}}$$

To achieve the convergence of the series

※ $e^{-(\alpha+\beta\epsilon_r)} < 1$.

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

Remember: $\bar{E} - TS - \mu\bar{N} = -kT \ln \mathcal{Z}$, $\alpha = -\beta\mu$ (see the next page)

$\bar{E} - TS = -kT \ln Z(N)$

$\Rightarrow$ $\ln Z(\bar{N}) = \alpha\bar{N} + \ln \mathcal{Z}$

$$\bar{N} = \frac{1}{\mathcal{Z}} \sum_{n_1, n_2 \cdots}^{\infty} (n_1 + n_2 + \cdots) e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \cdots)} \quad e^{-\alpha(n_1+n_2+\cdots)}$$

$$= -\frac{\partial \ln \mathcal{Z}}{\partial \alpha} = \sum_r \frac{e^{-\alpha-\beta\epsilon_r}}{1 - e^{-\alpha-\beta\epsilon_r}} = \sum_r \frac{1}{e^{\alpha+\beta\epsilon_r} - 1}$$

$$\bar{N} = \sum_r \frac{1}{e^{\alpha+\beta\epsilon_r} - 1}$$

Similarly,

$$\bar{n}_s = \frac{1}{\mathcal{Z}} \sum n_s \cancel{e^{\ldots}}\, e^{-\beta(\epsilon_1 n_1 + \epsilon_2 n_2 + \cdots)}\, e^{-\alpha(n_1+n_2+\cdots)}$$

$$= +\frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial(-\beta\epsilon_s)}$$

$$= -\frac{1}{\beta}\frac{\partial \ln \mathcal{Z}}{\partial \epsilon_s}.$$

$$= \frac{e^{-\alpha-\beta\epsilon_s}}{1-e^{-\alpha-\beta\epsilon_s}} = \frac{1}{e^{\alpha+\beta\epsilon_s}-1}$$

(※ $\sum_r \bar{n}_r = N$ is automatically satisfied.)

(※ $\alpha = 0 \Rightarrow$ the case of photon.)

$$\mu = \frac{\partial F}{\partial N} = -kT\frac{\partial \ln Z}{\partial N} = -kT\alpha$$

$$\Rightarrow \alpha = -\beta\mu$$

Notice: $\bar{n}_s \in (0, \infty)$

$\Rightarrow$ The convergent condition $e^{-\beta(\epsilon_r-\mu)} < 1$

is consistent with the result $\bar{n}_s \in (0, \infty)$.

→ For a Bose gas, $\beta(\epsilon_r - \mu) > 0$ is always ~~sti~~ satisfied.

But for a fermi gas, there is no restriction on the sign of $\beta(\epsilon_r-\mu)$.

$\beta(\epsilon_r-\mu)$ can be either positive or negative.

(See the next page.)

① Grand canonical description of FD statistics

$n_r = 0$ and 1 for each r.

(Pauli exclusion principle)

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

$$= \left(\sum_{n_1=0}^{1} e^{-(\alpha+\beta\epsilon_1)n_1}\right)\left(\sum_{n_2=0}^{1} e^{-(\alpha+\beta\epsilon_2)n_2}\right)\left(\sum_{n_3=0}^{1} e^{-(\alpha+\beta\epsilon_3)n_3}\right)\cdots$$

$$= \prod_{r=1} \left(1 + e^{-\alpha-\beta\epsilon_r}\right)$$

$$\ln \mathcal{Z} = \sum_r \ln\left(1 + e^{-\alpha-\beta\epsilon_r}\right)$$

$$N = \bar{N} = -\frac{\partial \ln \mathcal{Z}}{\partial \alpha} = \sum_r \frac{e^{-\alpha-\beta\epsilon_r}}{1 + e^{-\alpha-\beta\epsilon_r}} = \sum_r \frac{1}{e^{\alpha+\beta\epsilon_r} + 1}$$

$$\Rightarrow \boxed{N = \sum_r \frac{1}{e^{\alpha+\beta\epsilon_r} + 1}}$$

$$\bar{n}_s = -\frac{1}{\beta}\frac{\partial \ln \mathcal{Z}}{\partial \epsilon_s} = -\frac{1}{\beta}\frac{(-\beta)e^{-\alpha-\beta\epsilon_s}}{1 + e^{-\alpha-\beta\epsilon_s}} = \frac{1}{e^{\alpha+\beta\epsilon_s} + 1}$$

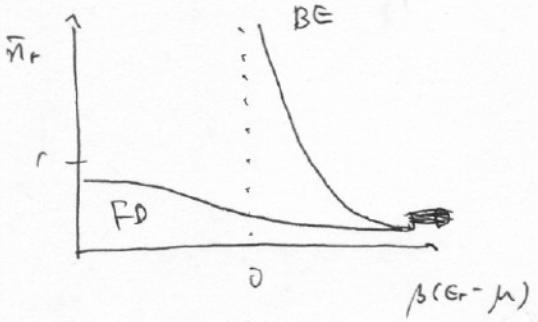
$$\ln \mathcal{Z} = -\alpha N + \ln Z$$

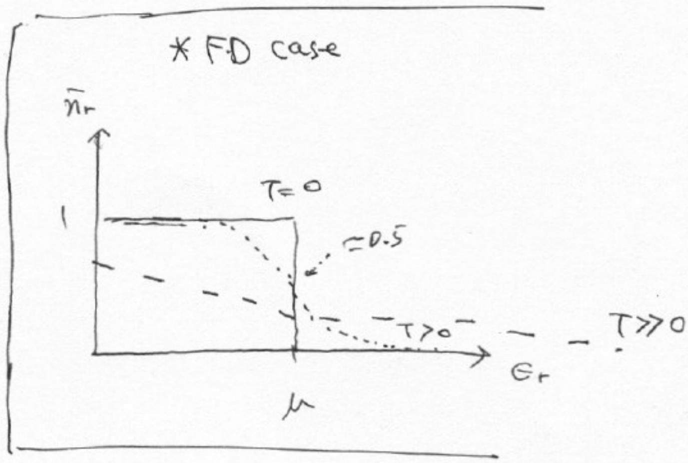
$$\Rightarrow \ln Z = \alpha N + \sum_r \ln\left(1 + e^{-\alpha-\beta\epsilon_r}\right)$$

※ Note : see $0 \le \bar{n}_s \le 1$

⊙ $\bar{n}_r$

$$\bar{n}_r = \begin{cases} \dfrac{1}{e^{\beta(\epsilon-\mu)} \pm 1} & +: \text{FD} \quad -: \text{BE} \\[2ex] \dfrac{N e^{-\beta\epsilon_r}}{\sum_r e^{-\beta\epsilon_r}} & \text{MB} \end{cases}$$





* $\beta(\epsilon_r-\mu) \gg 1$:

FD. BE. and MB are identical.

a classical limit
- high temperature and fixed $N = \sum_r \bar{n}_r$
- very dilute ($\bar{n}_r \ll 1$)

Note : Do not confuse that this limit seems to occur at low temperatures. At high temperatures, one can find this limit, since μ is a function of (T, N, V)

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

$\beta(\epsilon_r - \mu) \gg 1 \Rightarrow \bar{n}_r \simeq e^{-\beta(\epsilon_r-\mu)}$

$$= N \frac{e^{-\beta\epsilon_r}}{\sum_s e^{-\beta\epsilon_s}}$$

$\rightarrow$ MB.

$$e^{+\beta\mu} = \frac{N}{\sum_r e^{-\beta\epsilon_r}}$$

$(\because N = \sum \bar{n}_r)$

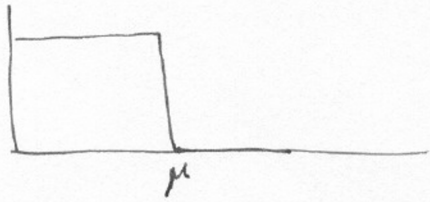
* μ : Boson : $\bar{n}_r$ diverges as $\beta(\epsilon_r - \mu) \to 0^+$

$\Leftrightarrow \bar{n}_r \in [0, N]$

$\Leftrightarrow$ the convergence condition $e^{-(\alpha+\beta\epsilon_r)} < 1$

$\rightarrow \mu \le \epsilon_r$ for all r

Fermion :



To add one more fermion to the system, we need the energy cost of μ. (∵ Pauli exclusion principle)

* fluctuations of n_r

$$\overline{\Delta n_r^2} = \overline{n_r^2} - \overline{n_r}^2$$

$$= \left(-\frac{1}{\beta}\frac{\partial}{\partial \epsilon_r}\right)^2 \ln Z$$

$$= -\frac{1}{\beta}\frac{\partial}{\partial \epsilon_r}\overline{n_r} = \frac{e^{\beta(\epsilon_r-\mu)}}{\left(e^{\beta(\epsilon_r-\mu)} \pm 1\right)^2}$$

$+$: FD
$-$: BE

$$\Rightarrow \frac{\overline{\Delta n_r^2}}{\overline{n_r}^2} = \exp(\beta(\epsilon_r-\mu)) = \frac{1}{\overline{n_r}} - (\pm 1)$$

$+$: FD
$-$: BE

For boson, the fluctuations are larger.

* partition function

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

$$\simeq \alpha N \pm \underbrace{\sum_r \pm e^{-\alpha-\beta\epsilon_r}}_{\simeq N}$$

$$= \alpha N + N.$$

$$e^{-\alpha} = \frac{N}{\sum_r e^{-\beta\epsilon_r}} \Rightarrow \alpha = -\ln N + \ln \sum_r e^{-\beta\epsilon_r}$$

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

$$= \ln Z_{MB} - \ln N!$$

$$\Rightarrow Z = \frac{1}{N!} Z_{MB}$$

Gibbs factor

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

~~① Ideal gas~~

- Fermions : conduction electrons in solids

- Ideal Bose gas : Bose-Einstein condensation

- photons : black-body radiation