

CE

$$\begin{aligned}
 Z_N^{CE} &= \sum_i e^{-\beta E_i} \\
 &= \sum_{E_j} \left( \frac{d^{3N} x d^{3N} p}{N! h^{3N}} \right)_{E_j} e^{-\beta E_j} \quad (E_j = N\epsilon) \\
 &= \frac{V^N}{N! h^{3N}} \left[ \int d^3 p e^{-\beta \epsilon} \right]^N \\
 &= \frac{Z_{CE}^N}{N!}
 \end{aligned}$$

GCE

$$\begin{aligned}
 Z^{GCE} &= \sum e^{-\beta(E - \mu N)} \\
 &= \sum_{\alpha} \left( \frac{d^{3N} x d^{3N} p}{N! h^{3N}} \right)_{E_\alpha, N_\alpha} e^{-\beta(E_\alpha - \mu N_\alpha)} \\
 &= \sum_{\alpha} \frac{V^N}{N! h^{3N}} \left[ \int d^3 p e^{-\beta(\epsilon - \mu)} \right]^N \\
 &= \sum_{\alpha} \frac{(e^{\beta \mu} Z_{CE})^{N_\alpha}}{N_\alpha!} \quad (\because \mu_\alpha = N_\alpha \mu)
 \end{aligned}$$

where  $Z = \frac{V}{h^3} \int d^3 p e^{-\beta \epsilon}$  is single/one particle partition function of CE system

$= \frac{V}{\lambda^3}$  for  $\epsilon = \frac{p^2}{2m}$

with  $\lambda = \frac{h}{\sqrt{2\pi m kT}}$  (thermal de Broglie wavelength).

So if we take all possible  $N_\alpha$  from 0 to  $\infty$

$$\begin{aligned}
 Z^{GCE}(\mu, T, V) &= \sum_{N_\alpha=0}^{\infty} \frac{(e^{\beta \mu} Z_{CE})^{N_\alpha}}{N_\alpha!} \\
 &= \exp \{ e^{\beta \mu} Z_{CE} \}
 \end{aligned}$$

$$\begin{aligned}
 \Rightarrow -PV = \Phi &= -kT \ln Z^{GCE} = -kT \{ e^{\beta \mu} Z_{CE} \} \\
 &= -kT \underbrace{\int \frac{V d^3 p}{h^3} e^{-\beta(\epsilon - \mu)}}_N
 \end{aligned}$$

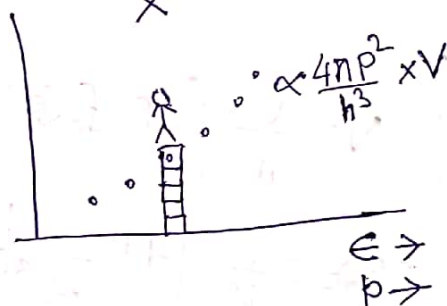
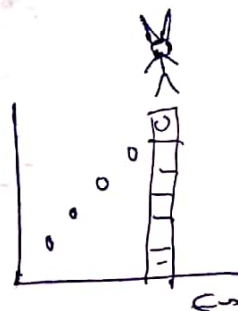
# GCE (classical Ideal gas)

One-particle

Partition function  $Z_1 = \sum e^{-\beta(\epsilon - \mu)}$   
 $= \int \frac{d^3x d^3p}{h^3} e^{-\beta(\epsilon - \mu)}$

Remember

$$\sum \equiv \int \frac{d^3x d^3p}{h^3}$$



Possible Homes or states for one particle

For many or N particle,

Partition function  $Z_N = Z_1 \times Z_2 \times Z_3 \times \dots$

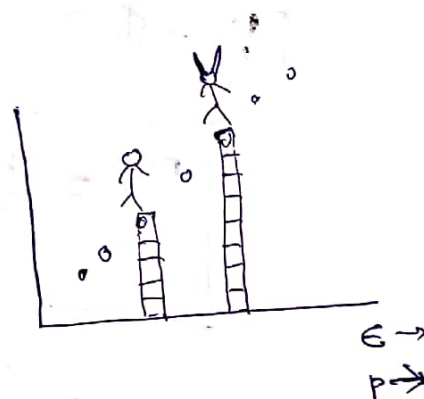
$$= \prod_i Z_i$$

$$= \prod_i e^{-\beta(\epsilon_i - \mu_i)}$$

$$-PV = \Phi = -KT \ln Z_N = -KT \ln \{ \prod_i Z_i \}$$

$$= -KT \sum_i \ln Z_i$$

$$= -KT \int \frac{d^3x d^3p}{h^3} \ln Z$$



$$P = KT \int \frac{d^3p}{h^3} e^{-\beta(\epsilon - \mu)}$$

$$\geq \frac{KT N}{V}$$

$$Z = \exp \{ e^{-\beta(\epsilon - \mu)} \}$$

$$= \sum_{N \geq 0} \frac{\{ e^{-\beta(\epsilon - \mu)} \}^{N \alpha}}{N \alpha !}$$

$$\Phi = -PV = -KT \int \frac{V d^3p}{h^3} e^{-\beta(\epsilon - \mu)} \quad \text{--- (1)}$$

$$\Rightarrow P = \frac{KT}{V} N, \text{ where } N = \frac{V}{h^3} \int d^3p e^{-\beta(\epsilon - \mu)}$$

$$= \frac{V}{h^3} \int d^3p f_0(\epsilon)$$

MB distribution func<sup>n</sup>

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

$$= -(-KT)\beta \int \frac{V d^3p}{h^3} e^{-\beta(\epsilon - \mu)}$$

$$\boxed{N = \frac{V}{h^3} \int d^3p f_0(\epsilon)}$$

$$= V \times \frac{1}{\lambda^3(T)} \text{ for } \epsilon = \frac{p^2}{2m}$$

Thermal distribution function of particle with energy  $\epsilon$ .

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_{\mu,V} = K \underbrace{\int \frac{V d^3p}{h^3} e^{-\beta(\epsilon - \mu)}}_N + KT \underbrace{\left(\frac{\mu - \epsilon}{-KT^2}\right) \int \frac{V d^3p}{h^3} e^{-\beta(\epsilon - \mu)}}_N$$

$$\xrightarrow{\times T} TS = \underbrace{KTN}_{PV} - \mu N + \underbrace{\int \frac{V d^3p}{h^3} \epsilon f_0(\epsilon)}_U$$

$$\Rightarrow TS = U + PV - \mu N$$

Internal Energy

$$\boxed{U = \int \frac{V d^3p}{h^3} [\epsilon] f_0}$$

$$U = \frac{3}{2} NKT$$

$$= \frac{3}{2} KT \left\{ \frac{V}{\lambda^3(T)} \right\} \text{ for } \epsilon = \frac{p^2}{2m}$$

After knowing N, U, we get

$$S = \frac{U + PV - \mu N}{T}$$

$$= \frac{5}{2} NK - \frac{\mu N}{T}$$

Single / One particle

Partition function  $Z = e^{-\beta(\epsilon - \mu)}$  classical

Quantum Degeneracy  $\rightarrow$  if 'n' no of degeneracy is available for energy  $\epsilon$ , then

$$Z = \sum_n e^{-\beta n(\epsilon - \mu)}$$

According Pauli-Exclusion principle  $n=1$  (for fermion)

But for Boson,  $n$  can be any values from  $1, 2, \dots, \infty$

Classical picture also miss  $n=0$  possibility (which is valid for Boson and Fermion).

So  $Z = \sum_{n=0}^1 e^{-\beta n(\epsilon - \mu)}$  for Fermion

$$= [1 + e^{-\beta(\epsilon - \mu)}]$$

$Z = \sum_{n=0}^{\infty} e^{-\beta n(\epsilon - \mu)}$  for Boson

$$= \frac{1}{1 - e^{-\beta(\epsilon - \mu)}}$$

Total partition function  $Z_t = \prod_i Z_i = Z_1 \cdot Z_2 \cdot Z_3 \dots$

$$\Rightarrow \ln Z_t = \ln \{ \prod_i Z_i \}$$

$$= \sum_i \ln Z_i$$



Boson  $\rightarrow$  Spin is integer  $\hbar \Rightarrow s = (0, 1, 2, \dots) \times \hbar$

Fermion  $\rightarrow$  " " half-integer of  $\hbar$   
 $\Rightarrow s = (\frac{1}{2}, \frac{3}{2}, \dots) \times \hbar$

$$-PV = \Phi = -KT \ln Z_t$$

$$= -KT \sum \ln Z = -KT \sum \ln [1 + e^{-\beta(\epsilon - \mu)}] \quad \text{for Fermion}$$

$$= -KT \sum \ln [1 - e^{-\beta(\epsilon - \mu)}]^{-1} \quad \text{for Boson}$$

In general, we can write

$$-PV = \Phi = -\frac{KT}{\eta} \sum \ln [1 + \eta e^{-\beta(\epsilon - \mu)}] \quad \begin{matrix} \nearrow \eta = +1 \text{ (F)} \\ \searrow \eta = -1 \text{ (B)} \end{matrix}$$

$$= -\frac{KT}{\eta} \int \frac{V d^3p}{h^3} \ln [1 + \eta e^{-\beta(\epsilon - \mu)}]$$

$$N = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} = \frac{1}{\eta} \sum \frac{\eta e^{-\beta(\epsilon - \mu)}}{1 + \eta e^{-\beta(\epsilon - \mu)}}$$

$$= \sum \frac{1}{e^{\beta(\epsilon - \mu)} + \eta}$$

$$= \int \frac{V d^3p}{h^3} \frac{1}{e^{\beta(\epsilon - \mu)} + \eta}$$

$$\left. \begin{matrix} N_{FD} \\ N_{BE} \\ N_{MB} \end{matrix} \right\} = \int \frac{V d^3p}{h^3} \int_0^1 \begin{matrix} \nearrow \frac{1}{e^{\beta(\epsilon - \mu)} + 1} \\ \rightarrow \frac{1}{e^{\beta(\epsilon - \mu)} - 1} \\ \searrow e^{-\beta(\epsilon - \mu)} \end{matrix}$$

Classical distribution  $\longrightarrow$  Quantum distribution

$$f_0 = e^{-\beta(\epsilon - \mu)} \text{ (MB)} \begin{cases} \longrightarrow f_0 = \frac{1}{e^{\beta(\epsilon - \mu)} + 1} \text{ (FD)} \\ \longrightarrow f_0 = \frac{1}{e^{\beta(\epsilon - \mu)} - 1} \text{ (BE)} \end{cases}$$

~~$\sum f_0$~~

$\sum f_0 =$

$$N = \frac{V}{h^3} \int d^3p f_0(\epsilon)$$

$$\text{~~1~~ } = \frac{V}{h^3} \int d^3p \frac{1}{e^{\beta(\epsilon - \mu)} + \eta}$$

$\eta = 0 \text{ (MB)}$   
 $\eta = 1 \text{ (FD)}$   
 $\eta = -1 \text{ (BE)}$

$\sum \epsilon f_0 =$

$$U = \frac{V}{h^3} \int d^3p [\epsilon] f_0(\epsilon)$$

$$= \frac{V}{h^3} \int d^3p [\epsilon] \frac{1}{e^{\beta(\epsilon - \mu)} + \eta}$$

$$PV = -\Phi = \frac{KT}{\eta} \sum \ln \{ 1 + \eta e^{\beta(\mu - \epsilon)} \}$$

$$PV = \frac{KT}{\eta} \int \frac{V d^3p}{h^3} \ln \{ 1 + \eta e^{\beta(\mu - \epsilon)} \}$$

$$= \frac{V}{h^3} \int d^3p [?] \frac{1}{e^{\beta(\epsilon - \mu)} + \eta}$$

check!

$$\ln Z = -\frac{1}{\eta} \sum_i \ln [1 + \eta e^{\beta(\mu - \epsilon_i)}]$$

$$= \lim_{\eta \rightarrow 0} \frac{-\sum_i \frac{\partial}{\partial \eta} \ln [1 + \eta e^{\beta(\mu - \epsilon_i)}]}{\frac{\partial \eta}{\partial \eta}}$$

$$= -\sum_i \lim_{\eta \rightarrow 0} \frac{e^{\beta(\mu - \epsilon_i)}}{1 + \eta e^{\beta(\mu - \epsilon_i)}}$$

$$= -\sum_i e^{\beta(\mu - \epsilon_i)}$$

$$pV = \bar{\Phi} = -KT \ln Z = KT \sum_i e^{\beta(\mu - \epsilon_i)} = KT \underbrace{\int \frac{d^3x d^3p}{h^3} e^{-\beta(\epsilon - \mu)}}_N$$

$$N = + \left( \frac{\partial \Phi}{\partial \mu} \right)_{TV} = KT \times \beta \sum_i e^{\beta(\mu - \epsilon_i)} = \int \frac{d^3x d^3p}{h^3} e^{-\beta(\epsilon - \mu)}$$

~~$S = k_B \ln \Omega$~~

$$\left. \begin{array}{l} P_{FD} \\ P_{BE} \\ P_{MB} \end{array} \right\} = \int KT \int \frac{V d^3p}{h^3} \left[ \begin{array}{l} -\ln \{1 + e^{-\beta(\epsilon - \mu)}\} \\ \ln \{1 - e^{-\beta(\epsilon - \mu)}\} \\ e^{-\beta(\epsilon - \mu)} \end{array} \right]$$