Quantum Statistical Mechanics

Ref: (a) Statistical Physics of particles – Kardar
(b) Statistical Mechanics – Pathria & Beale
(c) Introduction to Statistical Physics – Salinas

Position, spin, etc

$$\Psi \equiv \Psi(q_1, q_2, \ldots, q_N)$$

$$\Pi_{ij}\Psi = \pm\Psi \quad \begin{cases} + \text{ symmetric (Integer spin)} \Rightarrow \text{e.g., photon, magnon, } ^4He, \text{ etc} \\ - \text{ antisymmetric } (\tfrac{1}{2}\text{-integer spin}) \Rightarrow \text{e.g., } e, p, {}^3He, \text{ etc} \end{cases}$$

Example 1: $\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2$, where, $\mathcal{H}_j = \dfrac{\vec{p}_j^{\,2}}{2m} + V(\vec{r}_j)$

for $j = 1$ & 2.

Eigenfunctions of $\mathcal{H}$ for a given total energy E may be written as $\psi_{n_1}(\vec{r}_1)\,\psi_{n_2}(\vec{r}_2)$

s.t., $\mathcal{H}_1 \psi_{n_1}(\vec{r}_1) = \epsilon_{n_1}\psi_{n_1}(\vec{r}_1)$

& $\mathcal{H}_2 \psi_{n_2}(\vec{r}_2) = \epsilon_{n_2}\psi_{n_2}(\vec{r}_2)$

with $E = \epsilon_{n_1} + \epsilon_{n_2}$.

Symmetry requirement:

$$\psi_S(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}\left(\psi_{n_1}(\vec{r}_1)\psi_{n_2}(\vec{r}_2) + \psi_{n_2}(\vec{r}_1)\psi_{n_1}(\vec{r}_2)\right).$$

$$\psi_A(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}\left(\psi_{n_1}(\vec{r}_1)\psi_{n_2}(\vec{r}_1) - \psi_{n_2}(\vec{r}_1)\psi_{n_1}(\vec{r}_2)\right)$$

Example 2: (a) Two indistinguishable particles A & B occupy orbitals n_1 and n_2 that assume 3 distinct values.

(i) Symmetric choice:

1	2	3	
A	B	–	$\frac{1}{\sqrt{2}}(\psi_1(\vec{r}_1)\psi_2(\vec{r}_2) + \psi_2(\vec{r}_1)\psi_1(\vec{r}_2))$
–	A	B	$\frac{1}{\sqrt{2}}(\psi_2(\vec{r}_1)\psi_3(\vec{r}_2) + \psi_3(\vec{r}_1)\psi_2(\vec{r}_2))$
A	–	B	$\frac{1}{\sqrt{2}}(\psi_1(\vec{r}_1)\psi_3(\vec{r}_2) + \psi_3(\vec{r}_1)\psi_1(\vec{r}_2))$
A, B	–	–	$\psi_1(\vec{r}_1)\psi_1(\vec{r}_2)$
–	A, B	–	$\psi_2(\vec{r}_1)\psi_2(\vec{r}_2)$
–	–	A, B	$\psi_3(\vec{r}_1)\psi_3(\vec{r}_2)$

(ii.) Antisymmetric choice:

1	2	3	
A	B	—	$\frac{1}{\sqrt{2}}(\psi_1(\vec{r}_1)\psi_2(\vec{r}_2) - \psi_2(\vec{r}_1)\psi_1(\vec{r}_2))$
—	A	B	$\frac{1}{\sqrt{2}}(\psi_2(\vec{r}_1)\psi_3(\vec{r}_2) - \psi_3(\vec{r}_1)\psi_2(\vec{r}_2))$
A	—	B	$\frac{1}{\sqrt{2}}(\psi_1(\vec{r}_1)\psi_3(\vec{r}_2) - \psi_3(\vec{r}_1)\psi_1(\vec{r}_2))$

(b.) Distinguishable particles case

1	2	3
A	B	—
B	A	—
—	A	B
—	B	A
A	—	B
B	—	A
A, B	—	—
—	A, B	—
—	—	A, B

——— × ———

Ideal gas of N-indistinguishable particles

Quantum states are characterized by a set of occupation numbers

$$\{n_1, n_2, \ldots, n_j, \ldots\} \equiv \{n_j\}$$

$$n_j = \begin{cases} 0, 1 \ \forall j & \text{Fermions} \\ 0, 1, \ldots, N \ \forall j & \text{Bosons} \end{cases}$$

s.t., $$E\{n_j\} = \sum_j \epsilon_j n_j$$

and $$N \equiv N(\{n_j\}) = \sum_j n_j$$

where, ϵ_j is energy of j^{th} level.

$$\Rightarrow Z(T,V,N) = \sum_{\{n_j\}} \exp\left[-\beta \sum_j \epsilon_j n_j\right]$$

$$\left(\sum_j n_j = N\right)$$

- Restricted sum
- Does not factorize

Define $\mathcal{Z}(T,V,\mu) = \sum_{N=0}^{\infty} \exp(\beta\mu N)\, Z(T,V,N)$

(Grand canonical partition function)

$$= \sum_{N=0}^{\infty} \exp(\beta\mu N) \sum_{\substack{\{n_j\} \\ \sum_j n_j = N}} \exp(-\beta\epsilon_1 n_1 - \beta\epsilon_2 n_2 - \cdots)$$

$$= \sum_{N=0}^{\infty} \sum_{\substack{\{n_j\} \\ \sum_j n_j = N}} \exp\left[-\beta(\epsilon_1-\mu)n_1 - \beta(\epsilon_2-\mu)n_2 - \cdots\right].$$

Restricted sum

All possible restrictions

$$= \sum_{n_1, n_2, \ldots} \exp\left[-\beta(\epsilon_1-\mu)n_1 - \beta(\epsilon_2-\mu)n_2 - \cdots\right]$$

- No restrictions
- Factorizes

$$= \left[\sum_{n_1} \exp\{-\beta(\epsilon_1-\mu)n_1\}\right] \left[\sum_{n_2} \exp\{-\beta(\epsilon_2-\mu)n_2\}\right] \cdots \left[\sum_{n_j} \exp\{-\beta(\epsilon_j-\mu)n_j\}\right] \cdots$$

$$\boxed{\therefore \mathcal{Z}(T,V,\mu) = \prod_j \left[\sum_n \exp\{-\beta(\epsilon_j-\mu)n\}\right]}$$

Also, $\langle n_j \rangle = -\frac{1}{\beta} \frac{\partial \ln \mathcal{Z}(T,V,\mu)}{\partial \epsilon_j}$

Case I: Bose-Einstein statistics

n runs from 0 to ∞.

$$\Rightarrow \mathcal{Z}(T,V,\mu) = \prod_j \Bigg[\underbrace{\sum_{n=0}^{\infty} \exp\{-\beta(\epsilon_j - \mu)n\}}_{\text{infinite geometric progression}} \Bigg].$$

$$= \prod_j \left[1 - \exp\{-\beta(\epsilon_j - \mu)\} \right]^{-1}.$$

$$\therefore \ln \mathcal{Z}(T,V,\mu) = -\sum_j \ln\left[1 - \exp\{-\beta(\epsilon_j - \mu)\}\right]$$

$$\langle n_j \rangle = -\frac{1}{\beta} \frac{\partial \ln \mathcal{Z}(T,V,\mu)}{\partial \epsilon_j} = \frac{1}{\exp\{\beta(\epsilon_j - \mu)\} - 1}.$$

Note: $\langle n_j \rangle \geq 0 \ \forall j$.

Case II: Fermi-Dirac statistics

$n = 0$ or 1.

$$\Rightarrow \mathcal{Z}(T,V,\mu) = \prod_j \left[1 + \exp\{-\beta(\epsilon_j - \mu)\}\right].$$

$$\therefore \ln \mathcal{Z}(T,V,\mu) = \sum_j \ln\left[1 + \exp\{-\beta(\epsilon_j - \mu)\}\right].$$

$$\langle n_j \rangle = -\frac{1}{\beta} \frac{\partial \ln \mathcal{Z}(T,V,\mu)}{\partial \epsilon_j} = \frac{1}{\exp\{\beta(\epsilon_j - \mu)\} + 1}.$$

Note: $0 \leq \langle n_j \rangle \leq 1 \ \forall j$.

In a compact notation

$$\ln \mathcal{Z}(T,V,\mu) = \mp \sum_j \ln\left[1 \mp z \exp(-\beta \epsilon_j)\right].$$

$$\langle n_j \rangle = \frac{1}{z^{-1}\exp(\beta\epsilon_j) \mp 1}.$$

$$z = \exp(\beta\mu)$$

($-$) for Bose-Einstein & ($+$) for Fermi-Dirac cases respectively.

Remarks

- Define Grand thermodynamic potential

$$\Phi(T,V,\mu) = -pV = -\frac{1}{\beta}\ln\mathcal{Z}(T,V,\mu)$$

s.t., $$\frac{pV}{k_BT} = \ln\mathcal{Z}(T,V,\mu)$$

or, $$\boxed{\frac{pV}{k_BT} = \ln\mathcal{Z}(z,T,V)}$$ where, $z = \exp(\beta\mu)$

- In momentum ($\vec{k}$) basis, energy levels are given by $\epsilon_{\vec{k}}$.

Here,

$$\frac{pV}{k_BT} = \ln\mathcal{Z}(z,T,V) = \mp\sum_{\vec{k}}\ln\left(1 \mp z e^{-\beta\epsilon_{\vec{k}}}\right)$$

where, $\begin{cases} (-) \text{ Bose-Einstein statistics} \\ (+) \text{ Fermi-Dirac statistics} \end{cases}$

- $$z\frac{\partial}{\partial z}\ln\mathcal{Z}(z,V,T) = \sum_{\vec{k}}\frac{z e^{-\beta\epsilon_{\vec{k}}}}{1 \mp z e^{-\beta\epsilon_{\vec{k}}}} = \sum_{\vec{k}}\frac{1}{z^{-1}e^{\beta\epsilon_{\vec{k}}} \mp 1}.$$

Now, $$\langle n_{\vec{k}}\rangle = \frac{1}{\mathcal{Z}(z,T,V)}\sum_{N=0}^{\infty} z^N \sum_{\substack{\{n_{\vec{k}}\} \\ \sum_{\vec{k}} n_{\vec{k}} = N}} n_{\vec{k}} \exp\left(-\beta\sum_{\vec{k}}\epsilon_{\vec{k}} n_{\vec{k}}\right).$$

$$= -\frac{1}{\beta}\frac{\partial}{\partial\epsilon_{\vec{k}}}\ln\mathcal{Z}(z,T,V) = \frac{1}{z^{-1}e^{\beta\epsilon_{\vec{k}}} \mp 1}.$$

$$\Rightarrow N = \sum_{\vec{k}}\langle n_{\vec{k}}\rangle = \sum_{\vec{k}}\frac{1}{z^{-1}e^{\beta\epsilon_{\vec{k}}} \mp 1} = z\frac{\partial}{\partial z}\ln\mathcal{Z}(z,T,V).$$

- $\epsilon_{\vec{k}} = \dfrac{\hbar^2 |\vec{k}|^2}{2m}$; $\vec{k} = \left(\dfrac{2\pi}{L}\right)\vec{n}$

$\vec{n}$ has components n_x, n_y, n_z that takes integer values $0, \pm 1, \ldots$

$$\Rightarrow \sum_{\vec{k}} \longrightarrow \frac{V}{(2\pi)^3}\int d^3k = \frac{4\pi V}{(2\pi)^3}\int dk\, k^2$$

I: For Fermi-Dirac Statistics

$$\frac{pV}{k_BT} = \ln \mathcal{Z}(z,T,V) = \sum_{\vec{k}} \ln\left(1 + z e^{-\beta\epsilon_{\vec{k}}}\right)$$

$$= \frac{4\pi V}{(2\pi)^3}\int_0^\infty dk\, k^2 \ln\left(1 + z e^{-\frac{\beta\hbar^2 k^2}{2m}}\right)$$

Let, $\sqrt{\dfrac{\beta\hbar^2}{2m}}\, k = x \quad \Rightarrow k^2 = \dfrac{2m}{\beta\hbar^2}x^2.$

and $\quad dk = \sqrt{\dfrac{2m}{\beta\hbar^2}}\, dx.$

$$\Rightarrow \frac{p}{k_BT} = \frac{1}{2\pi^2}\left(\frac{2m}{\beta\hbar^2}\right)^{3/2}\int_0^\infty dx\, x^2 \ln\left(1 + z e^{-x^2}\right)$$

$$= \frac{1}{8\pi^{3/2}}\left(\frac{2m}{\beta\hbar^2}\right)^{3/2}\frac{4}{\sqrt{\pi}}\int_0^\infty dx\, x^2 \ln\left(1 + z e^{-x^2}\right)$$

$$= \left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2} f_{5/2}(z) = \frac{1}{\lambda^3} f_{5/2}(z).$$

$$f_{5/2}(z) = \frac{4}{\sqrt{\pi}}\int_0^\infty dx\, x^2 \ln\left(1 + z e^{-x^2}\right) = \sum_{l=1}^{\infty}\frac{(-1)^{l+1} z^l}{l^{5/2}}$$

$$\therefore \frac{p}{k_BT} = \frac{1}{\lambda^3} f_{5/2}(z) \quad ; \quad \lambda = \sqrt{\frac{2\pi\hbar^2}{mk_BT}} = \frac{h}{\sqrt{2\pi m k_BT}}$$

(Thermal de Broglie wavelength)

Similarly,

$$N = \sum_{\vec{k}} \langle n_{\vec{k}} \rangle = \sum_{\vec{k}} \frac{1}{z^{-1} e^{\beta \epsilon_{\vec{k}}} + 1}$$

$$= \frac{4\pi V}{(2\pi)^3} \int_0^\infty dk \, \frac{k^2}{z^{-1} e^{\frac{\beta \hbar^2 k^2}{2m}} + 1} .$$

$$\Rightarrow \frac{N}{V} = \frac{1}{v} = \frac{1}{2\pi^2} \left(\frac{2m}{\beta \hbar^2} \right)^{3/2} \int_0^\infty dx \, \frac{x^2}{z^{-1} e^{x^2} + 1} .$$

$$= \left(\frac{m k_B T}{2\pi \hbar^2} \right)^{3/2} \frac{4}{\sqrt{\pi}} \int_0^\infty dx \frac{x^2}{z^{-1} e^{x^2} + 1} .$$

Note: $z \frac{\partial}{\partial z} f_{5/2}(z) = \frac{4}{\sqrt{\pi}} \int_0^\infty dx \, \frac{x^2 \, z \, e^{-x^2}}{1 + z \, e^{-x^2}} = \frac{4}{\sqrt{\pi}} \int_0^\infty dx \frac{x^2}{z^{-1} e^{x^2} + 1} .$

Also $z \frac{\partial}{\partial z} f_{5/2}(z) = \sum_{l=1}^\infty \frac{(-1)^{l+1} z^l}{l^{3/2}} = f_{3/2}(z) .$

$$\therefore \frac{N}{V} = \frac{1}{v} = \frac{1}{\lambda^3} f_{3/2}(z) .$$

$f_{3/2}(z)$.

II) For Bose-Einstein statistics

$$\frac{pV}{k_B T} = - \sum_{\vec{k}} \ln \left(1 - z e^{-\beta \epsilon_{\vec{k}}} \right)$$

and $N = \sum_{\vec{k}} \frac{1}{z^{-1} e^{\beta \epsilon_{\vec{k}}} - 1} .$

Both these quantities diverge as $z \to 1$ for $\epsilon_{\vec{k}} = 0$.

Thus, we split them into $\vec{k} = 0$ term and the leftover integral.

$$\therefore \frac{pV}{k_B T} = - \frac{4\pi V}{(2\pi)^2} \int dk \, k^2 \frac{1}{z^{-1} e^{\frac{\beta \hbar^2 k^2}{2m}} - 1} - \ln(1 - z) .$$

Following a similar substitution as used above for the case of Fermi-Dirac statistics, (i.e., $\sqrt{\frac{\beta\hbar^2}{2m}}\,k = x$

$$\Rightarrow \frac{p}{k_B T} = \left(\frac{1}{\lambda^3}\right)\left(-\frac{4}{\sqrt{\pi}}\int_{0^+}^{\infty} dx\, x^2 \ln\left(1 - z e^{-x^2}\right)\right) - \frac{1}{V}\ln(1-z)$$

$$\therefore \frac{p}{k_B T} = \frac{1}{\lambda^3} g_{5/2}(z) - \frac{1}{V}\ln(1-z).$$

$$\text{where, } g_{5/2}(z) = -\frac{4}{\sqrt{\pi}}\int_{0^+}^{\infty} dx\, x^2 \ln\left(1 - z e^{-x^2}\right) = \sum_{l=1}^{\infty} \frac{z^l}{l^{5/2}}.$$

$$\text{Also, } \frac{N}{V} = \frac{1}{v} = \frac{1}{\lambda^3} g_{3/2}(z) + \frac{1}{V}\left(\frac{z}{1-z}\right).$$

$$\text{where, } g_{3/2}(z) = z\frac{\partial}{\partial z} g_{5/2}(z) = \sum_{l=1}^{\infty} \frac{z^l}{l^{3/2}}.$$

Note: $\frac{N}{V} = \frac{1}{v} = \frac{4\pi V}{(2\pi)^3}\int_0^{\infty} dk\, k^2 \frac{1}{z^{-1} e^{\frac{\beta\hbar^2 k^2}{2m}} - 1} + \frac{1}{V}\left(\frac{z}{1-z}\right).$

- $$U(z,V,T) = \frac{1}{\mathcal{Z}(z,V,T)} \sum_{N=0}^{\infty} z^N \sum_{\substack{\{n_{\vec{k}}\} \\ (\sum_{\vec{k}} n_{\vec{k}} = N)}} \left[e^{-\beta\sum_{\vec{k}} \epsilon_{\vec{k}} n_{\vec{k}}} \sum_{\vec{k}} \epsilon_{\vec{k}} n_{\vec{k}} \right]$$

$$= -\frac{\partial}{\partial\beta}\left[\ln \mathcal{Z}(z,V,T)\right]. \qquad \text{But, } \ln\mathcal{Z} = \frac{pV}{k_B T}.$$

$$= -\frac{\partial}{\partial T}\left(\frac{pV}{k_B T}\right)_{z,V} \Big/ \left(\frac{\partial\beta}{\partial T}\right)$$

$$= k_B T^2 V g_{5/2}(z)\left\{\frac{\partial}{\partial T}\left(\frac{1}{\lambda^3}\right)\right\}$$

For Bose-Einstein statistics

$$= \frac{3}{2} k_B T \frac{V}{\lambda^3} g_{5/2}(z).$$

$$\Rightarrow \frac{U(z,V,T)}{V} = \frac{3}{2}\frac{k_B T}{\lambda^3} g_{5/2}(z)$$

Similarly, for Fermi-Dirac statistics,

$$\frac{U(z,V,T)}{V} = \frac{3}{2}\frac{k_B T}{\lambda^3} f_{5/2}(z).$$

- In a unified notation:

$$\ln \mathcal{Z}_\eta(T,V,\mu) = \eta \sum_{\vec{k}} \ln\left[1+\eta \exp\{\beta(\mu-\epsilon_{\vec{k}})\}\right].$$

$$= \eta \sum_{\vec{k}} \ln\left[1+\eta z e^{-\beta\epsilon_{\vec{k}}}\right]$$

$$\eta = \begin{cases} +1 & \text{Fermions} \\ -1 & \text{Bosons} \end{cases}$$

$$\langle n_{\vec{k}} \rangle = -\frac{\partial \ln \mathcal{Z}_\eta}{\partial(\beta\epsilon_{\vec{k}})} = \frac{1}{z^{-1}e^{\beta\epsilon_{\vec{k}}}+\eta}.$$

$$\therefore \quad N_\eta = \sum_{\vec{k}} \langle n_{\vec{k}} \rangle = \sum \frac{1}{z^{-1}e^{\beta\epsilon_{\vec{k}}}+\eta}.$$

and, $$U_\eta = \sum_{\vec{k}} \epsilon_{\vec{k}} \langle n_{\vec{k}} \rangle_\eta = \sum_{\vec{k}} \frac{\epsilon_{\vec{k}}}{z^{-1}e^{\beta\epsilon_{\vec{k}}}+\eta}.$$

- One-particle states are occupied independently, with a joint probability:

$$P_\eta(\{n_{\vec{k}}\}) = \frac{1}{\mathcal{Z}_\eta}\prod \exp\left[-\beta(\epsilon_{\vec{k}}-\mu)n_{\vec{k}}\right].$$

Non-relativistic Gas.

Considering a spin degeneracy factor, $g = 2s+1$ for a non-relativistic gas in three dimensions,

$$\epsilon_{\vec{k}} = \frac{\hbar^2 k^2}{2m}, \qquad k = |\vec{k}|.$$

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

such that,

$$\beta P_\eta = \frac{1}{V}\ln \mathcal{Z}_\eta = \eta g \int \frac{d^3\vec{k}}{(2\pi)^3} \ln\left[1 + \eta z \exp\left(-\frac{\beta\hbar^2 k^2}{2m}\right)\right].$$

$$n_\eta = \frac{N_\eta}{V} = g\int \frac{d^3\vec{k}}{(2\pi)^3} \frac{1}{z^{-1}\exp\left(\frac{\beta\hbar^2k^2}{2m}\right) + \eta}.$$

$$u_\eta = \frac{U_\eta}{V} = g\int \frac{d^3\vec{k}}{(2\pi)^3} \frac{\hbar^2k^2}{2m} \frac{1}{z^{-1}\exp\left(\frac{\beta\hbar^2k^2}{2m}\right) + \eta}.$$

$$\boxed{\int uv\,dx = u\int v\,dx - \int\left(\frac{du}{dx}\int v\,dx\right)dx}$$

Let, $k = \sqrt{\frac{2mk_BT}{\hbar^2}}\sqrt{x}$

$$\Rightarrow dk = \frac{\sqrt{\pi}}{\lambda} x^{-1/2}\,dx.$$

Thus,

$$\beta P_\eta = \eta \frac{g}{2\pi^2}\frac{4\pi^{3/2}}{\lambda^3}\int_0^\infty dx\, \underbrace{x^{1/2}}_{v}\, \underbrace{\ln(1+\eta z e^{-x})}_{u}$$

$$= \frac{g}{\lambda^3}\frac{4}{3\sqrt{\pi}}\int_0^\infty \frac{dx\, x^{3/2}}{z^{-1}e^x + \eta} = \frac{g}{\lambda^3} h^\eta_{5/2}(z).$$

$$n_\eta = \frac{g}{\lambda^3}\cdot\frac{2}{\sqrt{\pi}}\int_0^\infty \frac{dx\, x^{1/2}}{z^{-1}e^x+\eta} = \frac{g}{\lambda^3} h^\eta_{3/2}(z).$$

$$\boxed{h^\eta_m(z) = \frac{1}{(m-1)!}\int_0^\infty \frac{dx\, x^{m-1}}{z^{-1}e^x + \eta}.}$$

& $$\beta u_\eta = \frac{g}{\lambda^3}\cdot\frac{2}{\sqrt{\pi}}\int_0^\infty \frac{dx\, x^{3/2}}{z^{-1}e^x+\eta} = \frac{3}{2}P_\eta.$$

In the non-degenerate limit, z is small (high temperature) and density is low.

$$h_m^\eta(z) = \frac{1}{(m-1)!}\int_0^\infty \frac{dx\; x^{m-1}}{z^{-1}e^x+\eta} = \frac{1}{(m-1)!}\int_0^\infty dx\; x^{m-1}(ze^{-x})(1+\eta z e^{-x})^{-1}$$

$$= \frac{1}{(m-1)!}\int_0^\infty dx\; x^{m-1}\sum_{j=1}^\infty (ze^{-x})^j(-\eta)^{j+1}.$$

$$= \frac{1}{(m-1)!}\sum_{j=1}^\infty (-\eta)^{j+1} z^j \underbrace{\int_0^\infty dx\; x^{m-1}e^{-jx}}_{\frac{1}{j^m}\Gamma(m)}$$

$$= \sum_{j=1}^\infty (-\eta)^{j+1}\frac{z^j}{j^m}.$$

$$= z - \eta\frac{z^2}{2^m} + \frac{z^3}{3^m} - \eta\frac{z^4}{4^m} + - \cdots$$

$$\Rightarrow \quad \frac{n_\eta\lambda^3}{g} = h_{\frac{3}{2}}^\eta(z) = z - \eta\frac{z^2}{2^{3/2}} + \frac{z^3}{3^{3/2}} - \eta\frac{z^4}{4^{3/2}} + \cdots \qquad \text{— (A.)}$$

and $$\frac{\beta p_\eta\lambda^3}{g} = h_{\frac{5}{2}}^\eta(z) = z - \eta\frac{z^2}{2^{5/2}} + \frac{z^3}{3^{5/2}} - \eta\frac{z^4}{4^{5/2}} + - \cdots \qquad \text{— (B.)}$$

$$\eta = \begin{cases} +1 & \text{Fermions} \\ -1 & \text{Bosons}\end{cases}$$

using (A.)

$$\Rightarrow \quad z = \frac{n_\eta\lambda^3}{g} + \eta\frac{z^2}{2^{3/2}} - \frac{z^3}{3^{3/2}} + - \cdots$$

$$= \left(\frac{n_\eta\lambda^3}{g}\right) + \eta\frac{1}{2^{3/2}}\left(\frac{n_\eta\lambda^3}{g}\right)^2 - \cdots$$

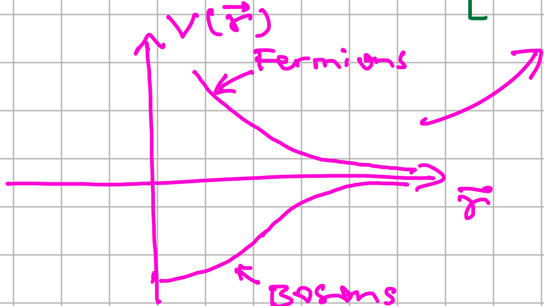
$$= \left(\frac{n_\eta\lambda^3}{g}\right) + \eta\frac{1}{2^{3/2}}\left(\frac{n_\eta\lambda^3}{g}\right)^2 + \left(\frac{1}{4} - \frac{1}{3^{3/2}}\right)\left(\frac{n_\eta\lambda^3}{g}\right)^3 - +$$

(Recursive trick!)

$$\therefore \quad \frac{\beta p_\eta \lambda^3}{g} = \left(\frac{n_\eta \lambda^3}{g}\right) + \frac{\eta}{2^{3/2}}\left(\frac{n_\eta \lambda^3}{g}\right)^2 + \left(\frac{1}{4} - \frac{1}{3^{3/2}}\right)\left(\frac{n_\eta \lambda^3}{g}\right)^3$$

$$- \frac{\eta}{2^{5/2}}\left(\frac{n_\eta \lambda^3}{g}\right)^2 - \frac{1}{8}\left(\frac{n_\eta \lambda^3}{g}\right)^3 + \cdots$$

$$\therefore \quad p_\eta = n_\eta k_B T \left[1 + \frac{\eta}{2^{5/2}}\left(\frac{n_\eta \lambda^3}{g}\right) + \left(\frac{1}{8} - \frac{2}{3^{5/2}}\right)\left(\frac{n_\eta \lambda^3}{g}\right)^2 + \cdots\right]$$



$$\eta = \begin{cases} +1 & \text{Fermions} \\ -1 & \text{Bosons} \end{cases}$$

Note: Quantum effects become more prominent as $n_\eta \lambda^3 \geq g$

(Quantum degenerate limit)

Quantum Statistical Mechanics in other Ensembles

(I.) Canonical Ensemble approach

Product Hilbert space

$$|\vec{k}_1, \vec{k}_2, \ldots, \vec{k}_N\rangle_{\otimes} \equiv |\vec{k}_1\rangle |\vec{k}_2\rangle \cdots |\vec{k}_N\rangle.$$

In coordinate representation,

$$\langle \vec{r}_1, \ldots, \vec{r}_N | \vec{k}_1, \ldots, \vec{k}_N\rangle_{\otimes} = \frac{1}{\sqrt{V^N}} \exp\left(i \sum_{\alpha=1}^{N} \vec{k}_\alpha \cdot \vec{r}_\alpha\right).$$

$$\& \quad \mathcal{H} |\vec{k}_1, \ldots, \vec{k}_N\rangle_{\otimes} = \left(\sum_{\alpha=1}^{N} \frac{\hbar^2}{2m} k_\alpha^2\right) |\vec{k}_1, \ldots, \vec{k}_N\rangle_{\otimes}$$

Note that the above product states do not satisfy the relevant symmetry requirements & we must look at the appropriate subspaces with correct symmetry.

(A.) Fermionic subspace

$$|\vec{k}_1, \vec{k}_2, \ldots, \vec{k}_N\rangle_F = \frac{1}{\sqrt{N!}} \sum_P (-1)^P \, P |\vec{k}_1, \ldots, \vec{k}_N\rangle_{\otimes}$$

(no two $\vec{k}$-labels repeat.)

(B.) Bosonic subspace

$$|\vec{k}_1, \vec{k}_2, \ldots, \vec{k}_N\rangle = \frac{1}{\sqrt{N! \prod_{\vec{k}} n_{\vec{k}}!}} \sum_P P |\vec{k}_1, \ldots, \vec{k}_N\rangle_{\otimes}$$

In general,

$$|\{\vec{k}\}\rangle_\eta = \frac{1}{\sqrt{N_\eta}} \sum_P (-\eta)^P \, P \, |\{\vec{k}\}\rangle$$

with $\eta = \begin{cases} +1 & \text{for Fermions} \\ -1 & \text{for Bosons} \end{cases}$

Set of occupation numbers $\{n_i\}$ are such that $\bullet \sum_{\vec{k}} n_{\vec{k}} = N$.

- For Fermions: $|\{\vec{k}\}\rangle_+ = 0$ unless $n_{\vec{k}} = 0$ or 1.

  & $N_+ = N! \prod_{\vec{k}} n_{\vec{k}}! = N!$.

- For Bosons: $|\{\vec{k}\}\rangle_- \neq 0$ even if $\vec{k}$-labels repeat.

$${}_-\langle\{\vec{k}\}|\{\vec{k}\}\rangle_- = \frac{1}{N_-} \sum_{P,P'} \langle P\{\vec{k}\}| P'\{\vec{k}\}\rangle$$

$$= \frac{N!}{N_-} \sum_{P'} \langle\{\vec{k}\}| P'\{\vec{k}\}\rangle$$

$$= \frac{N! \prod_{\vec{k}} n_{\vec{k}}!}{N_-} = 1.$$

$$\therefore \; N_- = N! \prod_{\vec{k}} n_{\vec{k}}!.$$

In the co-ordinate representation,

$$\langle\{\vec{r}\,'\}|\rho|\{\vec{r}\}\rangle_\eta = {\sum_{\{\vec{k}\}}}' \sum_{P,P'} (-\eta)^P (-\eta)^{P'} \langle\{\vec{r}\,'\}| P'\{\vec{k}\}\rangle \cdot \rho(\{\vec{k}\}) \langle P\{\vec{k}\}|\{\vec{r}\}\rangle \frac{1}{N_\eta}.$$

where, $\rho(\{\vec{k}\}) = \dfrac{\exp\left[-\beta \sum_{\alpha=1}^{N} \frac{\hbar^2 k_\alpha^2}{2m}\right]}{Z_N}$

the sum $\sum'_{\{\vec{k}\}}$ is restricted to ensure that each identical particle state occurs exactly once.

Remove the restriction by dividing by the resulting 'over-counting' factor for Bosons.

$$\sum_{\{\vec{k}\}}{}' = \sum_{\{\vec{k}\}} \frac{\prod n_{\vec{k}}!}{N!}$$

$$\therefore \langle \{\vec{r}\,'\} | \rho | \{\vec{r}\} \rangle = \sum_{\vec{k}} \frac{\prod_{\vec{k}} n_{\vec{k}}!}{N!} \cdot \frac{1}{N! \prod_{\vec{k}} n_{\vec{k}}!} \times Q .$$

where,
$$Q = \sum_{P,P'} \frac{(-\eta)^P (-\eta)^{P'}}{Z_N} \exp\left(-\beta \sum_{\alpha=1}^{N} \frac{\hbar^2 k_\alpha^2}{2m}\right) \langle \{\vec{r}\,'\} | P\{\vec{k}\} \rangle \langle P\{\vec{k}\} | \{\vec{r}\} \rangle$$

In large V limit,

$$\langle \{\vec{r}\,'\} | \rho | \{\vec{r}\} \rangle = \frac{1}{Z_N (N!)^2} \sum_{P,P'} (-\eta)^P (-\eta)^{P'} \int \prod_{\alpha=1}^{N} \frac{V\, d^3\vec{k}_\alpha}{(2\pi)^3} \exp\left(-\frac{\beta \hbar^2 k_\alpha^2}{2m}\right) \times \left\{ \frac{\exp\left[-i \sum_{\alpha=1}^{N} \left(\vec{k}_{P\alpha} \cdot \vec{r}_\alpha - \vec{k}_{P'\alpha} \cdot \vec{r}\,'_\alpha\right)\right]}{V} \right\}$$

$$= \frac{1}{Z_N (N!)^2} \sum_{P,P'} (-\eta)^P (-\eta)^{P'} \prod_{\alpha=1}^{N} \underbrace{\left[\int \frac{d^3\vec{k}_\alpha}{(2\pi)^3} e^{-i\vec{k}_\alpha \cdot \left(\vec{r}_{P^{-1}\alpha} - \vec{r}\,'_{P'^{-1}\alpha}\right)} \times e^{-\beta \frac{\hbar^2 k_\alpha^2}{2m}} \right]}_{\frac{1}{\lambda^3} \exp\left[-\frac{\pi}{\lambda^2}\left(\vec{r}_{P^{-1}\alpha} - \vec{r}\,'_{P'^{-1}\alpha}\right)^2\right]}$$

$$= \frac{1}{Z_N \lambda^{3N} (N!)^2} \sum_{P,P'} (-\eta)^P (-\eta)^{P'} \exp\left[-\frac{\pi}{\lambda^2}\left(\vec{r}_{P^{-1}\alpha} - \vec{r}\,'_{P'^{-1}\alpha}\right)^2\right]$$

Let $\alpha = P\chi$, i.e., $\chi = P^{-1}\alpha$

Thus, $(-\eta)^P = (-\eta)^{P^{-1}}$ & $(-\eta)^{P'^{-1}P} = (-\eta)^{P'P} = \eta^Q$

$Q = P'^{-1}P$

Therefore,

$$\langle\{\vec{r}'\}|\rho|\{\vec{r}\}\rangle = \frac{1}{Z_N \lambda^{3N} N!} \sum_Q (-\eta)^Q \exp\left[-\frac{\pi}{\lambda^2}\sum_{\alpha=1}^{N}(\vec{r}_\alpha - \vec{r}'_{Q\alpha})^2\right].$$

Using normalization condition,

$$\mathrm{Tr}(\rho) = 1 \Rightarrow \int \prod_{\alpha=1}^{N} d^3\vec{r}_\alpha \langle\{\vec{r}\}|\rho|\{\vec{r}\}\rangle = 1.$$

Thus,

$$Z_N = \frac{1}{N!\,\lambda^{3N}} \int \prod_{\alpha=1}^{N} d^3\vec{r}_\alpha \sum_Q (-\eta)^Q \exp\left[-\frac{\pi}{\lambda^2}\sum_{\alpha=1}^{N}(\vec{r}_\alpha - \vec{r}_{Q\alpha})^2\right]$$

<u>Note</u>

- Z_N involves sum over $N!$ permutations.
- For no particle exchange, $Q \equiv 1$ and, $Z_N = \left(\frac{V}{\lambda^3}\right)^N \frac{1}{N!}$ (classical limit).
- Quantum corrections involves a product of factors $\exp\left[-\frac{\pi}{\lambda^2}(\vec{r}_1 - \vec{r}_2)^2\right]$

  these $\xrightarrow[\text{as } T\to\infty \text{ (or, } \lambda\to 0)]{}$ 0 in classical limit.

- First order correction:

  Exchange of two particles 1 & 2 leads to a factor $(-\eta)\exp\left[-\frac{2\pi}{\lambda^2}(\vec{r}_1 - \vec{r}_2)^2\right]$.

  For such pairwise exchanges there are $N(N-1)/2$ terms.

$$\therefore Z_N = \frac{1}{N!\,\lambda^{3N}} \int \prod_{\alpha=1}^{N} d^3\vec{r}_\alpha \left\{1 - \frac{N(N-1)}{2}\eta \exp\left[-\frac{2\pi}{\lambda^2}(\vec{r}_1 - \vec{r}_2)^2\right] + \dots\right\}$$

$$\Rightarrow Z_N = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N \left[1 - \frac{N(N-1)}{2V}\eta \int d^3\vec{r}_{12}\, \exp\left(-\frac{2\pi}{\lambda^2}\vec{r}_{12}^{\,2}\right) + \cdots\right]$$

$$= \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N \left[1 - \frac{N(N-1)}{2V}\left(\frac{\lambda^2}{2}\right)^{3/2}\eta + \cdots\right]$$

with $\eta = \begin{cases} +1 & \text{for Fermions} \\ -1 & \text{for Bosons} \end{cases}$

$$\therefore \quad F = -k_BT \ln Z_N$$

$$= -Nk_BT \ln\left(\frac{V}{\lambda^3}\cdot\frac{e}{N}\right) + \frac{k_BTN^2}{2V}\frac{\lambda^3}{2^{3/2}}\eta + \cdots$$

Using $\ln\left[\frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N\right] = N\ln\left(\frac{V}{\lambda^3}\right) - \ln N!$

$\approx N\ln\left(\frac{V}{\lambda^3}\right) + N - N\ln N$

$\approx N\ln\left(\frac{V}{\lambda^3}\left(\frac{e}{N}\right)\right).$

& $\ln(1+x) \sim x.$

$$\Rightarrow P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{Nk_BT}{V} + \frac{N^2k_BT}{V^2}\frac{\lambda^3}{2^{5/2}}\eta + \cdots$$

$$\therefore \quad P = nk_BT\left[1 + \frac{\eta\lambda^3}{2^{5/2}}n + \cdots\right]$$

with $\eta = \begin{cases} +1 & \text{for Fermions} \\ -1 & \text{for Bosons} \end{cases}$

- The first-order quantum correction is "equivalent" to a second virial coefficient

$$B_2 = \eta\frac{\lambda^3}{2^{5/2}}.$$

(Recall, $P = nk_BT(1 + B_2 n + \ldots)$)

Note that the resulting correction to pressure is negative for Bosons & positive for Fermions as anticipated.

(II.) Micro-canonical ensemble approach

Distribute n_j particles in g_j states

(A) Fermi-Dirac statistics

Number of ways $w_j(n_j) = \dfrac{g_j!}{n_j!\,(g_j-n_j)!}$.

$\therefore$ Number of microstates, $\Omega(\{n_j\}) = \prod_j w_j(n_j)$.

$$= \prod_j \frac{g_j!}{n_j!\,(g_j-n_j)!}.$$

For $g_j, n_j \gg 1$, (use Stirling approximation)

$$\ln\Omega(\{n_j\}) \approx \sum_j g_j\ln g_j - g_j - n_j\ln n_j + n_j - (g_j-n_j)\ln(g_j-n_j) + g_j - n_j.$$

$$= \sum_j \left\{ g_j\ln g_j - n_j\ln n_j - (g_j-n_j)\ln(g_j-n_j) \right\}$$

Also, $N = \sum_j n_j$.

& $U = \sum_j \epsilon_j n_j$.

} constraints

$$\left(\frac{\partial \ln\Omega}{\partial n_j}\right) = -1 - \ln n_j + 1 + \ln(g_j - n_j)$$

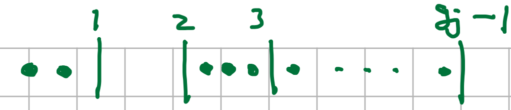
$\therefore$ Using method of Lagrange multipliers, for the most probable distribution $\{\bar{n}_j\}$,

$$\delta\left[\ln\Omega(\{n_j\}) - \alpha\sum_j n_j - \beta\sum_j \epsilon_j n_j\right]_{\{\bar{n}_j\}} = 0.$$

$$\Rightarrow \left[-\ln\bar{n}_j + \ln(g_j-\bar{n}_j) - \alpha - \beta\epsilon_j\right]\delta n_j = 0.$$

As δn_j are arbitrary & also are independent,

$$\Rightarrow \bar{n}_j = \frac{g_j}{e^{\alpha+\beta\epsilon_j}+1}. \quad \text{Fermi-Dirac statistics}$$



(B.) Bose–Einstein statistics

To obtain number of distinct ways to populate g_j cells by n_j particles, we need to find the number of ways to permute $(g_j - 1)$ partitions & n_j particles.

$$\Rightarrow \quad w_j(n_j) = \frac{(n_j + g_j - 1)!}{n_j!\,(g_j - 1)!}.$$

$$\therefore \quad \Omega(\{n_j\}) = \prod_j w_j(n_j)$$

$$= \prod_j \frac{(n_j + g_j - 1)!}{n_j!\,(g_j - 1)!}$$

For $n_j + g_j \gg 1$ and $g_j \gg 1$,

$$\Rightarrow \quad \ln \Omega(\{n_j\}) \approx \sum_j \{(n_j + g_j)\ln(n_j + g_j) - n_j \ln n_j - g_j \ln g_j\}.$$

Using method of Lagrange multipliers (as in the case of Fermi–Dirac statistics),

$$\Rightarrow \left[\ln(\bar{n}_j + g_j) - \ln \bar{n}_j - \alpha - \beta \epsilon_j\right] \delta n_j = 0.$$

$$\therefore \quad \bar{n}_j = \frac{g_j}{e^{\alpha + \beta \epsilon_j} - 1}.$$ Bose–Einstein statistics.

α & β can be obtained using constraint equations.

Note: The Maxwell–Boltzmann way of counting effectively accepts all wavefunctions regardless of symmetry properties under the interchange of coordinates. This set of acceptable wavefunctions is very large compared to the union of the two quantum mechanical scenarios of Bosons & Fermions.