Particle in a box states

For free particles we will often consider the quantum single particle states to be "particle in a box" states

We take our system to have length L in each direction $\hat{x}, \hat{y}, \hat{z}$, volume $V = L^3$. We also use <u>periodic boundary conditions</u>

$$\psi(x+L, y, z) = \psi(x, y, z), \quad \psi(x, y+L, z) = \psi(x, y, z),$$
$$\psi(x, y, z+L) = \psi(x, y, z)$$

energy eigenstates can then be taken as

$$\phi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}} \qquad \text{with energy } \epsilon_k = \frac{\hbar^2 k^2}{2m}$$

$\hbar = \frac{h}{2\pi}$ with h Planck's constant

periodic boundary conditions require

$$\Rightarrow \phi_{\vec{k}}(x+L, y, z) = \frac{1}{\sqrt{V}} e^{ik_x(x+L)} e^{ik_y y} e^{ik_z z}$$
$$\parallel$$
$$\phi_{\vec{k}}(x, y, z) = \frac{1}{\sqrt{V}} e^{ik_x x} e^{ik_y y} e^{ik_z z}$$

$$\Rightarrow e^{ik_x L} = 1 \quad \Rightarrow k_x = \frac{2\pi}{L} n_x \quad \text{with } n_x = 0, \pm 1, \pm 2, \ldots \text{ integer}$$

similarly $k_y = \frac{2\pi}{L} n_y$ and $k_z = \frac{2\pi}{L} n_z$

Spacing between allowed values of k_x (or k_y or k_z) is $\frac{2\pi}{L}$

Consider a non-interacting two particle system

Compute $\langle \vec{r}_1 \vec{r}_2 | \hat{\rho} | \vec{r}_1 \vec{r}_2 \rangle$ diagonal elements of $\hat{\rho}$ in position basis
= probability one particle is at $\vec{r}_1$ and the other is at $\vec{r}_2$

For free non interacting particles, the energy eigenstates are specified by two wave vectors $\vec{k}_1, \vec{k}_2$ with $E = \frac{\hbar^2}{2m}(k_1^2 + k_2^2)$

$\phi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}}$ $\quad \epsilon_k = \frac{\hbar^2 k^2}{2m}$ $\quad$ periodic boundary conditions $\Rightarrow$ $k_x = \frac{2\pi}{L} n_x$, n_x integer

The eigenstates are symmetrized plane waves

$$\langle \vec{r}_1 \vec{r}_2 | \vec{k}_1 \vec{k}_2 \rangle = \frac{e^{i(\vec{k}_1\cdot\vec{r}_1 + \vec{k}_2\cdot\vec{r}_2)} \pm e^{i(\vec{k}_1\cdot\vec{r}_2 + \vec{k}_2\cdot\vec{r}_1)}}{\sqrt{2!}\,(\sqrt{V})^2}$$

+ for BE

− for FD

$$\langle \vec{r}_1 \vec{r}_2 | \hat{\rho} | \vec{r}_1 \vec{r}_2 \rangle = \langle \vec{r}_1 \vec{r}_2 | \frac{e^{-\beta \hat{H}}}{Q_2} | \vec{r}_1 \vec{r}_2 \rangle$$

$$= \sum_{|\vec{k}_1 \vec{k}_2\rangle} \langle \vec{r}_1 \vec{r}_2 | \vec{k}_1 \vec{k}_2 \rangle \frac{e^{-\frac{\beta\hbar^2}{2m}(k_1^2 + k_2^2)}}{Q_2} \langle \vec{k}_1 \vec{k}_2 | \vec{r}_1 \vec{r}_2 \rangle$$

$$= \frac{1}{Q_2} \sum_{|\vec{k}_1 \vec{k}_2\rangle} e^{-\frac{\beta\hbar^2}{2m}(k_1^2 + k_2^2)} |\langle \vec{r}_1 \vec{r}_2 | \vec{k}_1 \vec{k}_2 \rangle|^2$$

Note, if we take $\vec{k}_1 \to \vec{k}_2$ and $\vec{k}_2 \to \vec{k}_1$ then $\langle \vec{r}_1 \vec{r}_2 | \vec{k}_1 \vec{k}_2 \rangle = \pm \langle \vec{r}_1 \vec{r}_2 | \vec{k}_2 \vec{k}_1 \rangle$

Since this matrix element is squared in the above sum, any sign change is canceled out. Thus in taking the sum over all eigenstates, we can replace $\sum_{|k_1 k_2\rangle}$ by independent sums on $\vec{k}_1$ and $\vec{k}_2$ provided we multiply by $\frac{1}{2!}$ so as not to double count $|\vec{k}_1 \vec{k}_2\rangle$ and $|\vec{k}_2 \vec{k}_1\rangle$ which represent the same physical state.

$$\langle \vec{r}_1 \vec{r}_2 | e^{-\beta\hat{H}} | \vec{r}_1 \vec{r}_2 \rangle = \frac{1}{2!} \sum_{\vec{k}_1, \vec{k}_2} e^{-\frac{\beta\hbar^2}{2m}(k_1^2 + k_2^2)} |\langle \vec{r}_1 \vec{r}_2 | \vec{k}_1 \vec{k}_2 \rangle|^2$$

$$|\langle \vec{r}_1 \vec{r}_2 | k_1 k_2 \rangle|^2 = \frac{2 \pm e^{i\vec{k}_1\cdot\vec{r}_{12}} e^{-i\vec{k}_2\cdot\vec{r}_{12}} \pm e^{-i\vec{k}_1\cdot\vec{r}_{12}} e^{i\vec{k}_2\cdot\vec{r}_{12}}}{2V^2}$$

where $\vec{r}_{12} = \vec{r}_1 - \vec{r}_2$

$$= \frac{1 \pm \mathrm{Re}\left[e^{i\vec{k}_1\cdot\vec{r}_{12}} e^{-i\vec{k}_2\cdot\vec{r}_{12}}\right]}{V^2}$$

let $\alpha = \frac{\beta \hbar^2}{m}$

$$\langle \vec{r}_1 \vec{r}_2 | e^{-\beta \hat{H}} | \vec{r}_1 \vec{r}_2 \rangle = \frac{1}{2!\,V^2} \sum_{\vec{k}_1 \vec{k}_2} e^{-\frac{\alpha}{2}k_1^2} e^{-\frac{\alpha}{2}k_2^2} \left(1 \pm \mathrm{Re}\left[e^{i\vec{k}_1\cdot\vec{r}_{12}} e^{-i\vec{k}_2\cdot\vec{r}_{12}}\right]\right)$$

for large V, $\quad \frac{1}{V}\sum_{\vec{k}} = \frac{1}{V(\Delta k)^3} \sum_{\vec{k}} (\Delta k)^3 = \frac{1}{V}\left(\frac{L}{2\pi}\right)^3 \int d^3k = \frac{1}{(2\pi)^3}\int d^3k$

spacing between allowed k_x $\quad \Delta k_x = \frac{2\pi}{L}$

$$\langle \vec{r}_1 \vec{r}_2 | e^{-\beta \hat{H}} | \vec{r}_1 \vec{r}_2 \rangle = \frac{1}{2(2\pi)^6} \int d^3k_1 \int d^3k_2\, e^{-\frac{\alpha k_1^2}{2}} e^{-\frac{\alpha k_2^2}{2}} \left(1 \pm \mathrm{Re}\left[e^{i\vec{k}_1\cdot\vec{r}_{12}} e^{-i\vec{k}_2\cdot\vec{r}_{12}}\right]\right)$$

We need the following integrals

$$\int_{-\infty}^{\infty} d^3k\, e^{-\frac{\alpha}{2}k^2} = \left(\frac{2\pi}{\alpha}\right)^{3/2}$$

$$\int_{-\infty}^{\infty} d^3k\, e^{-\frac{\alpha}{2}k^2 + i\vec{k}\cdot\vec{r}}$$ do by "completing the square"

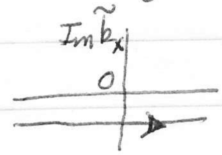
$$-\frac{\alpha}{2}k^2 + i\vec{k}\cdot\vec{r} = -\frac{\alpha}{2}\left(k^2 - \frac{2i}{\alpha}\vec{k}\cdot\vec{r}\right) = -\frac{\alpha}{2}\left[\left(\vec{k} - \frac{i\vec{r}}{\alpha}\right)^2 + \frac{r^2}{\alpha^2}\right]$$

$$= -\frac{\alpha}{2}\vec{\tilde{k}}^2 - \frac{r^2}{2\alpha} \qquad \text{where } \vec{\tilde{k}} = \vec{k} - \frac{i\vec{r}}{\alpha}$$

So $$\int d^3k\, e^{-\frac{\alpha}{2}k^2 + i\vec{k}\cdot\vec{r}} = \int d^3\tilde{k}\, e^{-\frac{\alpha}{2}\tilde{k}^2} e^{-r^2/2\alpha}$$

$$= \left(\frac{2\pi}{\alpha}\right)^{3/2} e^{-r^2/2\alpha}$$

for $\tilde{k}_x$ integration for example



contour of integration over $\tilde{k}$ can be moved back to real axis as it encloses no poles

So $$\langle \vec r_1 \vec r_2 | e^{-\beta \hat H} | \vec r_1 \vec r_2 \rangle = \frac{1}{2(2\pi)^6}\left(\frac{2\pi}{\alpha}\right)^3 \left[1 \pm e^{-r_{12}^2/\alpha}\right]$$

$$= \frac{1}{2\,(2\pi\alpha)^3}\left[1 \pm e^{-r_{12}^2/\alpha}\right]$$

It is customary to introduce the thermal wavelength λ by
$$\lambda^2 = 2\pi\alpha = \frac{2\pi\beta\hbar^2}{m} = \frac{2\pi\hbar^2}{k_B T m} \equiv \frac{h^2}{2\pi m k_B T}$$

Then
$$\langle \vec r_1 \vec r_2 | e^{-\beta \hat H} | \vec r_1 \vec r_2 \rangle = \frac{1}{2\lambda^6}\left[1 \pm e^{-2\pi r_{12}^2/\lambda^2}\right]$$

Now we need

$$Q_2 = \int d^3r_1 \int d^3r_2 \, \langle \vec r_1 \vec r_2 | e^{-\beta \hat H} | \vec r_1 \vec r_2 \rangle$$

$$= \frac{1}{2\lambda^6}\int d^3r_1 \int d^3r_2 \left[1 \pm e^{-2\pi r_{12}^2/\lambda^2}\right]$$

let $\vec R = \frac{\vec r_1 + \vec r_2}{2}$, $\vec r = \vec r_1 - \vec r_2 = \vec r_{12}$

$$= \frac{1}{2\lambda^6}\int d^3R \int d^3r \left[1 \pm e^{-2\pi r^2/\lambda^2}\right]$$

from integral on $\vec R$

$$= \frac{V}{2\lambda^6}\left[V \pm \int_0^\infty dr\, 4\pi r^2 e^{-2\pi r^2/\lambda^2}\right]$$

$$= \frac{1}{2}\left(\frac{V}{\lambda^3}\right)^2 \left[1 \pm \frac{1}{2^{3/2}}\left(\frac{\lambda^3}{V}\right)\right]$$

$$\approx \frac{1}{2}\left(\frac{V}{\lambda^3}\right)^2 \quad \text{as } V \to \infty$$

So $\quad \langle \vec{r}_1 \vec{r}_2 | \hat{\rho} | \vec{r}_1 \vec{r}_2 \rangle = \dfrac{\frac{1}{2\lambda^6}\left[1 \pm e^{-2\pi r_{12}^2/\lambda^2}\right]}{\frac{1}{2}\frac{V^2}{\lambda^6}}$

$$\boxed{\langle \vec{r}_1 \vec{r}_2 | \hat{\rho} | \vec{r}_1 \vec{r}_2 \rangle = \frac{1}{V^2}\left[1 \pm e^{-2\pi r_{12}^2/\lambda^2}\right]} \quad \begin{array}{l} + \text{ bosons} \\ - \text{ fermions} \end{array}$$

= probability one particle is at $\vec{r}_1$ and the other is at $\vec{r}_2$

Consider two <u>classical</u> non-interacting particles. Since the positions of these particles are uncorrelated, we have

$$\langle \vec{r}_1 \vec{r}_2 | \hat{\rho} | \vec{r}_1 \vec{r}_2 \rangle = \frac{1}{V^2}$$

The $\pm e^{-2\pi r_{12}^2/\lambda^2}$ terms are therefore the spatial correlations introduced into the pair probability due to the quantum statistics (+BE, or −FD)

For BE, using the + sign, we see $\langle \vec{r}_1 \vec{r}_2 | \hat{\rho} | \vec{r}_1 \vec{r}_2 \rangle$ is <u>larger</u> than it is classically
$\Rightarrow$ BE statistics give an <u>effective attraction</u>

For FD, using the − sign, we see $\langle \vec{r}_1 \vec{r}_2 | \hat{\rho} | \vec{r}_1 \vec{r}_2 \rangle$ is <u>smaller</u> than it is classically
$\Rightarrow$ FD statistics give an <u>effective repulsion</u>

we can treat this quantum correlation as an effective classical interaction between the two particles. For classical particles with a pair wise interaction $v(|\vec{r}_1-\vec{r}_2|)$, the classical prob to have one particle at $\vec{r}_1$ and the second at $\vec{r}_2$ is

$$p(\vec{r}_1\vec{r}_2) = \frac{\sum_{\vec{p}_1 \vec{p}_2} e^{-\beta\left[\frac{p_1^2}{2m}+\frac{p_2^2}{2m}+v(r_{12})\right]}}{\sum_{\vec{p}_1\vec{p}_2}\sum_{\vec{r}_1\vec{r}_2} e^{-\beta\left[\frac{p_1^2}{2m}+\frac{p_2^2}{2m}+v(r_{12})\right]}}$$

$$= \frac{e^{-\beta v(r_{12})}}{\sum_{\vec{r}_1\vec{r}_2} e^{-\beta v(r_{12})}}$$

For large V, and assuming $v(r_{12}) \xrightarrow{\text{sufficiently fast}} 0$ as $r_{12}\to\infty$

$$\sum_{\vec{r}_1\vec{r}_2} e^{-\beta v(r_{12})} = \underbrace{\sum_{\vec{R}}}_{\text{center of mass coord}} \sum_{\vec{r}_{12}} e^{-\beta v(r_{12})} = V\sum_{\vec{r}_{12}} e^{-\beta v(r_{12})}$$

$$\simeq V^2$$

$$p(\vec{r}_1\vec{r}_2) = \frac{e^{-\beta v(r_{12})}}{V^2}$$

compare with our expressions from quantum statistics

$$\langle \vec{r}_1\vec{r}_2|\hat{\rho}|\vec{r}_1\vec{r}_2\rangle = \frac{1}{V^2}\left[1 \pm e^{-2\pi r_{12}^2/\lambda^2}\right]$$

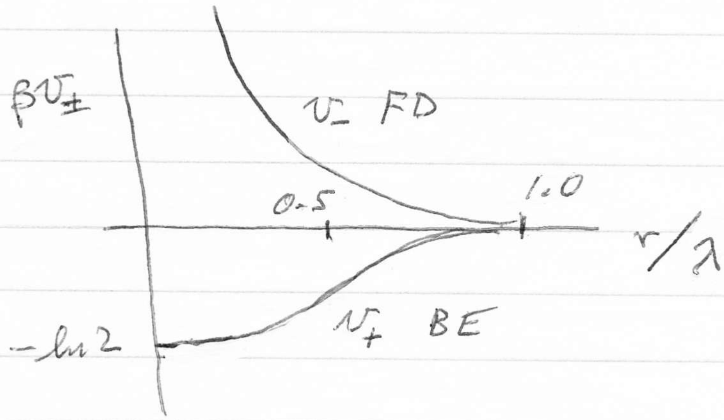
$$\Rightarrow \quad v_\pm(r) = -k_B T \ln\left[1 \pm e^{-2\pi r^2/\lambda^2}\right]$$

$\hbar = \frac{h}{2\pi}$

$+$ for BE , $-$ for FD $\qquad \lambda^2 = \frac{2\pi\beta\hbar^2}{m} = \frac{2\pi\hbar^2}{m k_B T} = \frac{h^2}{2\pi m k_B T}$

we can plot these as

Pathria Fig 5.1



we see that the BE statistics lead to an effective attraction while FD statistics lead to an effective repulsion, for small separations

$r \lesssim \lambda$ $\qquad$ thermal wavelength $\lambda = \sqrt{\frac{h^2}{2\pi m k_B T}}$ sets the length scale below which quantum effects are important for the correlation between the positions of two particles

N - particles

eigenstates $\langle \vec{r}_1 \cdots \vec{r}_N | \vec{k}_1 \cdots \vec{k}_N \rangle = \frac{1}{\sqrt{N!\, V^N}} \sum_{\mathbb{P}} (\pm 1)^P e^{i \sum_i (\mathbb{P} \vec{r}_i) \cdot \vec{k}_i}$

where $\mathbb{P}\vec{r}_i$ is the permutation of position $\vec{r}_i$

ie if $\mathbb{P}(1\,2\,3) = 2\,3\,1$ then $\mathbb{P}1 = 2$, $\mathbb{P}2 = 3$ and $\mathbb{P}3 = 1$

$$\langle \vec{r}_1 \cdots \vec{r}_N | e^{-\beta \hat{H}} | \vec{r}_1 \cdots \vec{r}_N \rangle = \sum_{|k_1 \cdots k_N\rangle} e^{-\frac{\beta \hbar^2}{2m}(k_1^2 + \cdots + k_N^2)} |\langle \vec{r}_1 \cdots \vec{r}_N | \vec{k}_1 \cdots \vec{k}_N \rangle|^2$$

$$|\langle \vec{r}_1 \cdots \vec{r}_N | \vec{k}_1 \cdots \vec{k}_N \rangle|^2 = \frac{1}{N!\, V^N} \sum_{\mathbb{P}} \sum_{\mathbb{P}'} (\pm 1)^{P+P'} e^{i \sum_i [\mathbb{P}\vec{r}_i - \mathbb{P}'\vec{r}_i] \cdot \vec{k}_i}$$

Note: we can write $[\mathbb{P}\vec{r}_i - \mathbb{P}'\vec{r}_i] \cdot \vec{k}_i = [\mathbb{P}(\vec{r}_i - \mathbb{P}^{-1}\mathbb{P}'\vec{r}_i)] \cdot \vec{k}_i$

where $\mathbb{P}^{-1}$ is inverse permutation of $\mathbb{P}$

and $(\pm 1)^P = (\pm 1)^{P^{-1}}$ $\qquad = (\vec{r}_i - \mathbb{P}^{-1}\mathbb{P}'\vec{r}_i) \cdot \mathbb{P}^{-1}\vec{k}_i$

$$|\langle \vec{r}_1 \cdots \vec{r}_N | \vec{k}_1 \cdots \vec{k}_N \rangle|^2 = \frac{1}{N!\, V^N} \sum_{\mathbb{P}} \sum_{\mathbb{P}''} (\pm 1)^{P''} e^{i \sum_i (r_i - \mathbb{P}'' r_i) \cdot \mathbb{P}^{-1} \vec{k}_i}$$

where $\mathbb{P}'' = \mathbb{P}^{-1}\mathbb{P}'$

Now when we sum over the energy eigenstates, we sum over $\vec{k}_i$. Since $\vec{k}_i$ is a dummy index in the sum, it does not matter whether we label it $\vec{k}_i$ or $\mathbb{P}^{-1}\vec{k}_i$. So in the above, each term in the $\sum_{\mathbb{P}}$ contributes an equal amount. We can therefore replace $\sum_{\mathbb{P}}$ by $N!$ times the one term with $\mathbb{P} = \mathbb{I}$ the identity. Similarly when we do the sum on eigenstates $\sum_{|k_1 \cdots k_N\rangle}$ we can do independent sums on $\vec{k}_1 \cdots \vec{k}_N$ provided we add a factor $1/N!$ to prevent double counting.

The result is

$$\langle \vec{r}_1 \cdots \vec{r}_N | e^{-\beta \hat{H}} | \vec{r}_1 \cdots \vec{r}_N \rangle =$$

$$\frac{1}{N!\, V^N} \sum_{\vec{k}_1 \cdots \vec{k}_N} e^{-\frac{\beta \hbar^2}{2m}(k_1^2 + \cdots + k_N^2)} \sum_{\mathbb{P}} (\pm 1)^P e^{i \sum_i \vec{k}_i \cdot (\vec{r}_i - \mathbb{P}\vec{r}_i)}$$

$$= \frac{1}{N!\,(2\pi)^{3N}} \sum_{\mathbb{P}} (\pm 1)^P \prod_{i=1}^{N} \left[\int d^3k_i \, e^{-\frac{\beta \hbar^2}{2m} k_i^2 + i \vec{k}_i \cdot (\vec{r}_i - \mathbb{P}\vec{r}_i)} \right]$$

The integral we did when considering the two body problem.

$$= \frac{1}{N!\,(2\pi)^{3N}} \sum_{\mathbb{P}} (\pm 1)^P \prod_{i=1}^{N} \left[\left(\frac{2\pi}{\alpha}\right)^{3/2} e^{-(\vec{r}_i - \mathbb{P}\vec{r}_i)^2 / 2\alpha} \right] \qquad \alpha = \frac{\beta \hbar^2}{m}$$

$$= \frac{1}{N!\,(2\pi)^{3N}} \left(\frac{2\pi}{\alpha}\right)^{3N/2} \sum_{\mathbb{P}} (\pm 1)^P \prod_{i=1}^{N} f(\vec{r}_i - \mathbb{P}\vec{r}_i)$$

where $f(r) = e^{-r^2/2\alpha}$

$$= \frac{1}{N!\,\lambda^{3N}} \sum_{\mathbb{P}} (\pm 1)^P \prod_{i=1}^{N} f(\vec{r}_i - \mathbb{P}\vec{r}_i)$$

where $\lambda^2 = 2\pi\alpha = \frac{2\pi\beta\hbar^2}{m}$

so $f(r) = e^{-\pi r^2/\lambda^2}$

$f(0) = 1$

Partition function

$$Q_N = \int d^3r_1 \cdots \int d^3r_N \, \langle \vec{r}_1 \cdots \vec{r}_N | e^{-\beta \hat{H}} | \vec{r}_1 \cdots \vec{r}_N \rangle$$

$$= \frac{1}{N!\,\lambda^{3N}} \sum_{\mathbb{P}} (\pm 1)^P \int d^3r_1 \cdots \int d^3r_N \, f(\vec{r}_1 - \mathbb{P}\vec{r}_1) \cdots f(\vec{r}_N - \mathbb{P}\vec{r}_N)$$

in the $\sum_{\mathbb{P}}$

Leading term is when $\mathbb{P} = \mathbb{I}$ the identity. Then $\mathbb{P}\vec{r}_i = \vec{r}_i$ and all the f terms are $f(0) = 1$

The next leading terms are those corresponding to one pair exchange, say $\mathbb{P}\vec{r}_i = \vec{r}_j$ and $\mathbb{P}\vec{r}_j = \vec{r}_i$, for then only two of the f factors are not unity. The next order are terms from permutations $\mathbb{P}\vec{r}_i = \vec{r}_j$, $\mathbb{P}\vec{r}_j = \vec{r}_k$, $\mathbb{P}\vec{r}_k = \vec{r}_i$, three particle exchanges. etc

$$Q_N = \frac{V^N}{N!\,\lambda^{3N}} \Big\{ 1 \pm \sum_{i<j} \int \frac{d^3r_i}{V} \int \frac{d^3r_j}{V} f(\vec{r}_i - \vec{r}_j) f(\vec{r}_j - \vec{r}_i)$$

$$+ \sum_{i<j<k} \int \frac{d^3r_i}{V} \int \frac{d^3r_j}{V} \int \frac{d^3r_k}{V} f(\vec{r}_i - \vec{r}_j) f(\vec{r}_j - \vec{r}_k) f(\vec{r}_k - \vec{r}_i)$$

$$\pm \cdots \Big\}$$

The leading term $\dfrac{V^N}{N!\,\lambda^{3N}}$ is just the classical result,

provided we take the phase space parameter h to be Planck's constant. We get the Gibbs $1/N!$ factor automatically. The higher order terms are the quantum corrections arising from 2-particle, 3-particle, etc, exchanges

For FD, the terms add with alternating signs
For BE, the terms all add with $(+)$ sign.

We are now ready to compute the Partition function for non-interacting fermions + bosons (ie ideal quantum gas)

$$Q_N(T,V) = \sum_{\{n_i\}} e^{-\beta E(\{n_i\})}$$

↑ sum over all $\{n_i\}$ such that $\sum_i n_i = N$

$$= \sum_{\{n_i\}} \delta\left(\sum_i n_i - N\right) e^{-\beta \sum_i \epsilon_i n_i}$$

↑ sum over all $\{n_i\}$, constraint now handled by the δ-function

$$= \sum_{\{n_i\}} \delta\left(\sum_i n_i - N\right) \prod_i e^{-\beta\epsilon_i n_i}$$

Because of the constraint $\sum_i n_i = N$ it is difficult to carry out the summation. $\Rightarrow$ go to grand canonical ensemble

$$\mathcal{L}(T,V,z) = \sum_{N=0}^{\infty} z^N Q_N \qquad z^N = z^{\sum n_i} = \prod_i z^{n_i}$$

$$= \sum_{N=0}^{\infty} \sum_{\{n_i\}} \delta\left(\sum_i n_i - N\right) \prod_i z^{n_i} e^{-\beta\epsilon_i n_i}$$

do $\sum_N$ first to eliminate δ-function

$$\mathcal{L} = \sum_{\{n_i\}} \prod_i \left(z e^{-\beta\epsilon_i}\right)^{n_i}$$

↑ unconstrained sum over all sets of occupation numbers

$$\mathcal{L} = \prod_i \left(\sum_n (z e^{-\beta \epsilon_i})^n \right)$$

sum over all possible occupations of state i

product over all single particle eigenstates

For FD, $n = 0, 1$

$$\Rightarrow \sum_{n=0}^{1} (z e^{-\beta\epsilon_i})^n = 1 + z e^{-\beta \epsilon_i}$$

FD $$\boxed{\mathcal{L} = \prod_i (1 + z e^{-\beta\epsilon_i}) = \prod_i \left(1 + e^{-\beta(\epsilon_i - \mu)}\right)}$$

$z = e^{\beta\mu}$

For BE, $n = 0, 1, 2, \ldots$

$$\Rightarrow \sum_{n=0}^{\infty} (z e^{-\beta\epsilon_i})^n = \frac{1}{1 - z e^{-\beta\epsilon_i}}$$

BE $$\boxed{\mathcal{L} = \prod_i \left(\frac{1}{1 - z e^{-\beta\epsilon_i}} \right) = \prod_i \left(\frac{1}{1 - e^{-\beta(\epsilon_i - \mu)}} \right)}$$

$$-\frac{\Sigma}{k_B T} = \frac{PV}{k_B T} = \ln \mathcal{L} = \sum_i \ln\left(1 + e^{-\beta(\epsilon_i - \mu)}\right) \quad \text{FD}$$

$$= -\sum_i \ln\left(1 - e^{-\beta(\epsilon_i - \mu)}\right) \quad \text{BE}$$

can combine above expressions as

$$\ln \mathcal{L} = \pm \sum_i \ln\left(1 \pm e^{-\beta(\epsilon_i - \mu)}\right)$$

where $(+)$ is for FD, $(-)$ is for BE