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

$$p(\vec{r}_1 \vec{r}_2) = \frac{\sum_{p_1 p_2} e^{-\beta\left[\frac{p_1^2}{2m} + \frac{p_2^2}{2m} + v(r_{12})\right]}}{\sum_{p_1 p_2} \sum_{r_1 r_2} e^{-\beta\left[\frac{p_1^2}{2m} + \frac{p_2^2}{2m} + v(r_{12})\right]}}$$

$$= \frac{e^{-\beta v(r_{12})}}{\sum_{r_1 r_2} e^{-\beta v(r_{12})}}$$

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

$$\sum_{r_1 r_2} e^{-\beta v(r_{12})} = \sum_{\underset{\substack{\uparrow \\ \text{cm coord}}}{R}} \sum_{r_{12}} e^{-\beta v(r_{12})} = V \sum_{r_{12}} e^{-\beta v(r_{12})} \approx V^2$$

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

compare with our expressions from quantum statistics

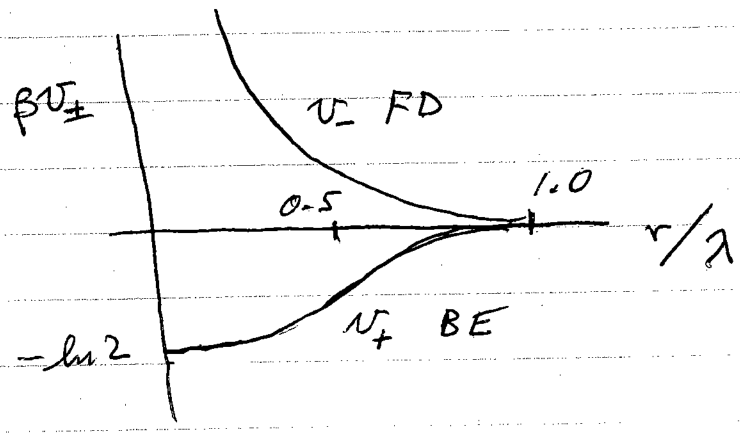
$$\langle \vec{r}_1 \vec{r}_2 | \hat{\rho} | \vec{r}_1 \vec{r}_2 \rangle = \frac{1}{V^2}\left[1 \pm e^{-2\pi r_{12}^2/\lambda^2}\right]$$

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

$+$ for BE , $-$ for FD $\qquad \lambda^2 = \dfrac{2\pi\beta\hbar^2}{m}$

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

$r \lesssim \lambda$

N - particles

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

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

Partition function

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

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

Leading $\overbrace{\text{term is}}^{\text{in the } \sum_{\mathbb{P}}}$ 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

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

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

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

$\uparrow$ 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 <u>grand canonical</u> ensemble

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

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

do $\sum_N$ first to eliminate δ-function

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

$\uparrow$ unconstrained sum over all sets of occupation numbers

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

sum over all possible occupations of state i

product over all single particle eigenstates

For FD, $n = 0, 1$

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

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

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

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

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