Quantum Many particle systems

N identical particles described by a wavefunction

$$\psi(\vec{r}_1 s_1, \vec{r}_2 s_2, \dots, \vec{r}_N s_N) \qquad \vec{r}_i = \text{position particle } i$$
$$= \psi(1, 2, \dots, N) \qquad s_i = \text{spin of particle } i$$

Identical particles $\Rightarrow$ prob distribution $|\psi|^2$ should be symmetric under interchange of any pair of coordinates: $|\psi(1, \dots i, \dots, j, \dots N)|^2 = |\psi(1, \dots, j, \dots, i, \dots N)|^2$

$\Rightarrow$ two possible symmetries for ψ

1) ψ is symmetric under pair interchanges
$$\psi(1, \dots, i, \dots, j, \dots, N) = \psi(1, \dots, j, \dots, i, \dots N)$$
2) ψ is antisymmetric under pair interchanges
$$\psi(1, \dots, i, \dots, j, \dots N) = -\psi(1, \dots, j, \dots i, \dots N)$$

(1) = Bose-Einstein statistics - particles called "bosons"
(2) = Fermi-Dirac statistics - particles called "fermions"

For a general permutation $\mathbb{P}$ that interchanges any number of pairs of particles

(1) BE $\Rightarrow$ $\mathbb{P}\psi = \psi$

(2) FD $\Rightarrow$ $\mathbb{P}\psi = (-1)^p \psi$ where p = # pair interchanges
$$= \begin{cases} +\psi & \text{for even permutation} \\ -\psi & \text{for odd permutation} \end{cases}$$

BE statistics are for particles with integer spin, $s = 0, 1, 2, \dots$
FD statistics are for particles with half integer spin, $s = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$
(proved by quantum field theory)

Consider non-interacting particles

$$\mathcal{H}(1,2,3,\dots N) = \mathcal{H}^{(1)}(1) + \mathcal{H}^{(1)}(2) + \cdots \mathcal{H}^{(1)}(N)$$

sum of single particle Hamiltonians

$$\Rightarrow \quad \psi(1,2,\dots,N) = \phi_1(1)\phi_2(2)\cdots\phi_N(N)$$

where ϕ_i is an eigenstate of single particle $\mathcal{H}^{(1)}$ with energy ϵ_i.

But ψ above does not have proper symmetry.

for BE $\quad \psi_{BE} = \frac{1}{\sqrt{N_P}} \sum_{\mathbb{P}} \mathbb{P}\psi \quad \leftarrow \psi = \phi_1 \phi_2 \cdots \phi_N$ as above

$\leftarrow$ sum over all permutations $\mathbb{P}$

N_p = # possible permutations of N particles $= N!$

normalization

for FD $\quad \psi_{FD} = \frac{1}{\sqrt{N_P}} \sum_{\mathbb{P}} (-1)^P \mathbb{P}\psi$

You can verify that the above symmetrizing operators give

$$\left\{ \begin{array}{l} \mathbb{P}_0 \psi_{BE} = \psi_{BE} \\ \mathbb{P}_0 \psi_{FD} = (-1)^{P_0} \psi_{FD} \end{array} \right\} \text{ as desired}$$

For ψ described by the N single particle eigenstates $\phi_{i_1}, \phi_{i_2}, \dots \phi_{i_N}$, the total energy is

$$E = \epsilon_{i_1} + \epsilon_{i_2} + \dots + \epsilon_{i_N} = \sum_j n_j \epsilon_j$$

where n_j is the number of particles in state ϕ_j.

For FD statistics, $n_j = 0$ or 1 only possibilities.

This is because if $\psi(1,2,\dots,N) = \phi_1(1)\phi_1(2)\phi_{i_3}(3)\cdots\phi_{i_N}(N)$

particles 1 and 2 in same state ϕ_1

then when we construct

$$\psi_{FD} = \frac{1}{\sqrt{N_p}} \sum_P (-1)^p P\psi$$

then for every term in the sum $\phi_1(i)\phi_1(j)\phi_{i_3}(k)\cdots\phi_{i_N}(l)$
there must also be a term $(-1)\phi_1(j)\phi_1(i)\phi_{i_3}(k)\cdots\phi_{i_N}(l)$
so these cancel pair by pair
and we find $\psi_{FD} = 0$

$\Rightarrow$ Pauli Exclusion Principle — no two ~~particles~~ fermions can occupy the same state, or no two fermions can have the same "quantum numbers".

For BE statistics there is no such restriction and $n_j = 0, 1, 2, 3, \dots$ any integer.

The specification of any non-interacting N particle quantum state is given by the occupation numbers $\{n_i\}$. Each set of $\{n_i\}$ corresponds to one N particle state.

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 $E = \frac{\hbar^2}{2m}(k_1^2 + k_2^2)$

The eigenstates are symmetrized plane waves

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

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

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

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

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.

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

$$|\langle \vec r_1 \vec r_2 | \vec k_1 \vec k_2\rangle|^2 = \frac{2 \pm e^{i\vec k_1\cdot \vec r_{12}}\, e^{-i\vec k_2\cdot \vec r_{12}} \pm e^{-i\vec k_1\cdot \vec r_{12}}\, e^{i\vec k_2\cdot \vec r_{12}}}{2V^2}$$

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 $\alpha = \dfrac{\beta\hbar^2}{m}$

$$\langle \vec r_1 \vec r_2 | e^{-\beta \hat H} | \vec r_1 \vec r_2\rangle = \frac{1}{2!\,V^2}\sum_{\vec k_1 \vec k_2} e^{-\frac{\alpha}{2}k_1^2}\, e^{-\frac{\alpha}{2}k_2^2}\left(1 \pm \mathrm{Re}\left[e^{i\vec k_1\cdot\vec r_{12}}\, e^{-i\vec k_2\cdot \vec r_{12}}\right]\right)$$

for large V, $\dfrac{1}{V}\sum\limits_{\vec k} = \displaystyle\int \frac{d^3k}{(2\pi)^3}$

$$\langle \vec r_1 \vec r_2 | e^{-\beta \hat H} | \vec r_1 \vec r_2\rangle = \frac{1}{2\,(2\pi)^6}\int d^3k_1 \int d^3k_2\, e^{-\frac{\alpha k_1^2}{2}}\, e^{-\frac{\alpha k_2^2}{2}}\left(1 \pm \mathrm{Re}\left[e^{i\vec k_1\cdot\vec r_{12}}\, e^{-i\vec k_2\cdot \vec r_{12}}\right]\right)$$

We need the following integrals

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

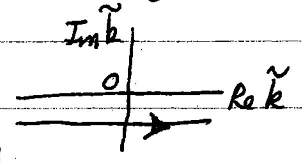
$$\int d^3k\, e^{-\frac{\alpha}{2}k^2 + i\vec k\cdot \vec r} \qquad \text{do by "completing the square"}$$

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

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

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

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



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

So $\langle \vec{r}_1 \vec{r}_2 | e^{-\beta \hat{H}} | \vec{r}_1 \vec{r}_2 \rangle = \dfrac{1}{2(2\pi)^6} \left(\dfrac{2\pi}{\alpha}\right)^3 \left[1 \pm e^{-r_{12}^2/\alpha} \right]$

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

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 $\vec{R} = \dfrac{\vec{r}_1 + \vec{r}_2}{2}$, $\vec{r} = \vec{r}_1 - \vec{r}_2 = \vec{r}_{12}$

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

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

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

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

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

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

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

Consider two classical 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) 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 $v(r_{12}) \to 0$ as $r_{12} \to \infty$ sufficiently fast

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

$$\approx V^2$$

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

compare with our expressions from quantum statistics

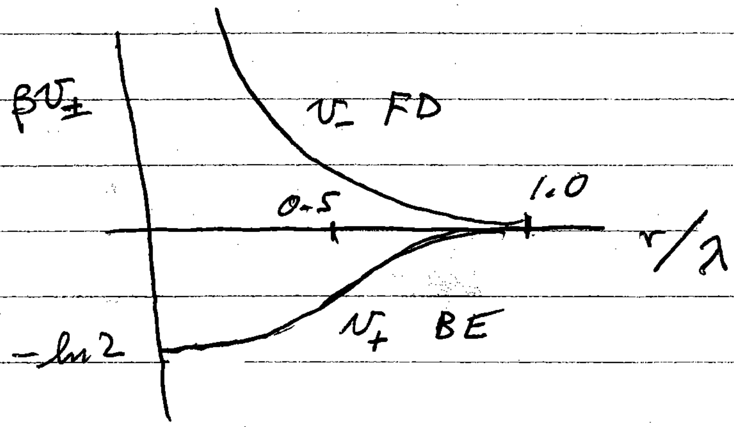
$$\langle \vec{r}_1\vec{r}_2|\hat{\rho}|\vec{r}_1\vec{r}_2\rangle = \frac{1}{V^2}\left[1 \pm e^{-2\pi r_{12}^2/\lambda^2}\right]$$

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

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

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

$r \lesssim \lambda$

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 $\mathbb{P}1 = 2$, $\mathbb{P}2 = 3$ ad $\mathbb{P}3 = 1$

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

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

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 $\sum_{\mathbb{P}} \sum_{\vec{k}}$ 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

$$\langle \vec r_1 \cdots \vec r_N | e^{-\beta \hat H} | \vec r_1 \cdots \vec r_N \rangle =$$

$$\frac{1}{N!\, V^N} \sum_{\vec k_1 \cdots \vec k_N} e^{-\frac{\beta \hbar^2}{2m}(k_1^2 + \cdots + k_N^2)} \sum_{\mathbb{P}} (\pm 1)^p \, e^{i \sum_i \vec k_i \cdot (\vec r_i - \mathbb{P}\vec r_i)}$$

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

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

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

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

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 $\frac{V^N}{N!\,\lambda^{3N}}$ 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.