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

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

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 $\psi(1, 2, \cdots, N) = \phi_1(1)\phi_1(2)\phi_{i_3}(3)\cdots\phi_{i_N}(N)$

particles 1 and 2 in same state ϕ_1

then when we construct

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

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 $\psi_{FD} = 0$

$\Rightarrow$ <u>Pauli Exclusion Principle</u> — 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 $n_j = 0, 1, 2, 3, \ldots$ any integer.

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

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

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

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

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

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.

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

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

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

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

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

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

We need the following integrals

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

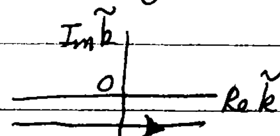
$$\int d^3k\, e^{-\frac{\alpha}{2}k^2 + i\vec k\cdot\vec r}$$ do by completing the square

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

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

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

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

It is customary to introduce the thermal wavelength λ by

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

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

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

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

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

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

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

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

= 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) 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

$$p(\vec{r}_1\vec{r}_2) = \frac{\sum_{p_1p_2} e^{-\beta\left[\frac{p_1^2}{2m}+\frac{p_2^2}{2m}+v(r_{12})\right]}}{\sum_{p_1p_2}\sum_{r_1r_2} e^{-\beta\left[\frac{p_1^2}{2m}+\frac{p_2^2}{2m}+v(r_{12})\right]}}$$

$$= \frac{e^{-\beta v(r_{12})}}{\sum_{r_1r_2} e^{-\beta v(r_{12})}}$$

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

$$\sum_{r_1r_2} e^{-\beta v(r_{12})} = \underbrace{\sum_{R}}_{\text{cm coord}} \sum_{r_{12}} e^{-\beta v(r_{12})} = V\sum_{r_{12}} e^{-\beta v(r_{12})} \approx V^2$$

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

compare with our expressions from quantum statistics

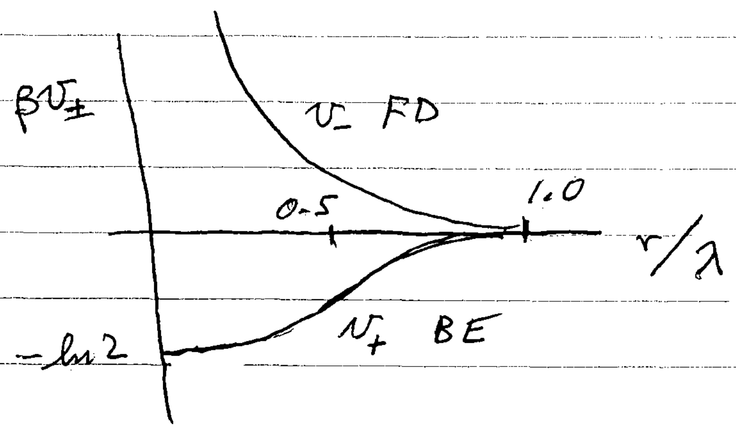
$$\langle \vec{r}_1\vec{r}_2|\hat{\rho}|\vec{r}_1\vec{r}_2\rangle = \frac{1}{V^2}\left[1 \pm e^{-2\pi r_{12}^2/\lambda^2}\right]$$

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

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

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 $\left[\mathbb{P}\vec{r}_i - \mathbb{P}'\vec{r}_i\right] \cdot \vec{k}_i = \left[\mathbb{P}(\vec{r}_i - \mathbb{P}^{-1}\mathbb{P}'\vec{r}_i)\right] \cdot \vec{k}_i$

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

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

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

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.

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

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

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

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

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

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 ~~[illegible]~~ 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.