

Consider a non-interacting two particle system

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

For free noninteracting 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

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

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

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

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

Note, if we take $\vec{k}_1 \rightarrow \vec{k}_2$ and $\vec{k}_2 \rightarrow \vec{k}_1$, 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. This in taking the sum over all eigenstates, we can replace $\sum_{|\vec{k}_1, \vec{k}_2\rangle}$ 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 $\vec{r}_{12} = \vec{r}_1 - \vec{r}_2$

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

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

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

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

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

We need the following integrals

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

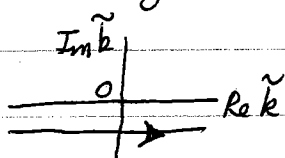
$$\int d^3 k e^{-\frac{\alpha}{2} k^2 + i\vec{k} \cdot \vec{r}} \quad \text{do by "completing the square"}$$

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

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

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

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



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

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

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

It is customary to introduce the thermal wavelength λ by

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

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

$$Q_2 = \int d^3r_1 \int d^3r_2 \langle \vec{r}_1, \vec{r}_2 | e^{-\beta \hat{H}} | \vec{r}_1, \vec{r}_2 \rangle$$

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

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

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

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

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

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

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

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

= 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 the quantum correlation as an effective classical interaction between the two particles. For classical particles with a pairwise 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

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

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

For large V , and assuming $V(r_{12}) \rightarrow 0$ as $r_{12} \rightarrow \infty$ ↓ sufficiently fast

$$\sum_{\vec{r}_1, \vec{r}_2} e^{-\beta V(r_{12})} = \sum_{\vec{R}} \sum_{\vec{r}_{12}} e^{-\beta V(r_{12})} = V \sum_{\vec{r}_{12}} e^{-\beta V(r_{12})}$$

↑
cm coord

$\approx V^2$

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

Compare with our expressions from quantum statistics

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

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

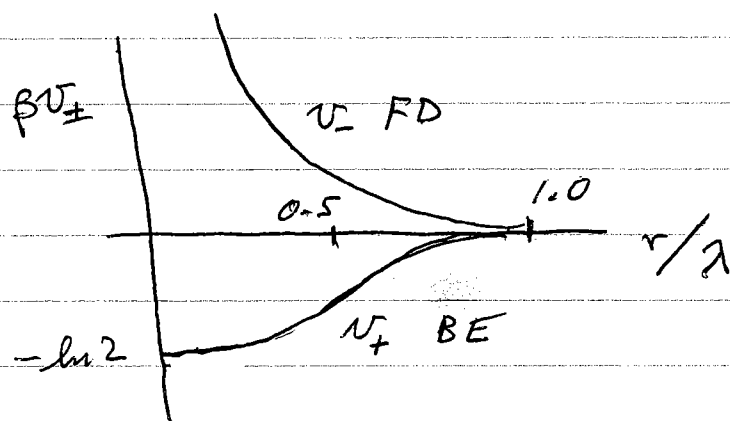
$$\frac{h}{2\pi} = \frac{h}{2\pi}$$

+ for BE, - for FD

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

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

$$r_2 \leq \lambda$$

N-particles

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

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

e.g. if $P(123) = 231$ then $P1 = 2$, $P2 = 3$ and $P3 = 1$

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

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

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

where P'^{-1} is inverse permutation of P'

and $(\pm 1)^P = (\pm 1)^{P'}$

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

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

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

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 $P'^{-1} \vec{k}_i$. So in the above, each term in the $\sum_P$ contributes an equal amount.

We can therefore replace $\sum_P$ by $N!$ times the one term with $P = \mathbb{I}$ the identity. Similarly when we do the sum on eigenstates $\sum_{|\vec{k}_1 \dots \vec{k}_N\rangle}$ we can do independent sums on $\vec{k}_1, \dots, \vec{k}_N$ provided we add a factor $1/N!$ to prevent double counting.

The result is

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

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

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

The integral we did when considering the two body problem.

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

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

$$= \frac{1}{N! \lambda^{3N}} \sum_P (\pm 1)^P \prod_{i=1}^N f(\vec{r}_i - P \vec{r}_i) \quad \text{where } f(r) = e^{-r^2/2\alpha}$$

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

Partition function

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

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

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

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

$$Q_N = \frac{V^N}{N! \lambda^{3N}} \left\{ 1 \pm \sum_{i < j} \int \frac{d^3 r_i}{V} \int \frac{d^3 r_j}{V} f(\vec{r}_i - \vec{r}_j) f(\vec{r}_j - \vec{r}_i) \right. \\
+ \sum_{i < j < k} \int \frac{d^3 r_i}{V} \int \frac{d^3 r_j}{V} \int \frac{d^3 r_k}{V} f(\vec{r}_i - \vec{r}_j) f(\vec{r}_j - \vec{r}_k) f(\vec{r}_k - \vec{r}_i) \\
\left. \pm \dots \right\}$$

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.

We are now ready to compute the Partition function for non-interacting fermions + bosons

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

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

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

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

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

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

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

$$z^N = z^{\sum_i n_i} = \prod_i z^{n_i}$$

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

do $\sum_N$ first to eliminate δ -function

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

↑ unconstrained sum over all sets of occupation numbers

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

$\nwarrow$ sum over all possible occupations of state i
 $\uparrow$ product over all single particle eigenstates

For FD, $n=0,1$

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

$$\text{FD } \mathcal{Z} = \prod_i (1 + z e^{-\beta \epsilon_i}) = \prod_i (1 + e^{-\beta(\epsilon_i - \mu)}) \quad z = e^{\beta \mu}$$

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

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

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

$$\begin{aligned}
 - \frac{\sum}{k_B T} &= \frac{PV}{k_B T} = \ln \mathcal{Z} = \sum_i \ln(1 + e^{-\beta(\epsilon_i - \mu)}) \quad \text{FD} \\
 &= - \sum_i \ln(1 - e^{-\beta(\epsilon_i - \mu)}) \quad \text{BE}
 \end{aligned}$$

can combine above expressions as

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

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