we can treat the 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

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

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

compare with our expressions from quantum statistics

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

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

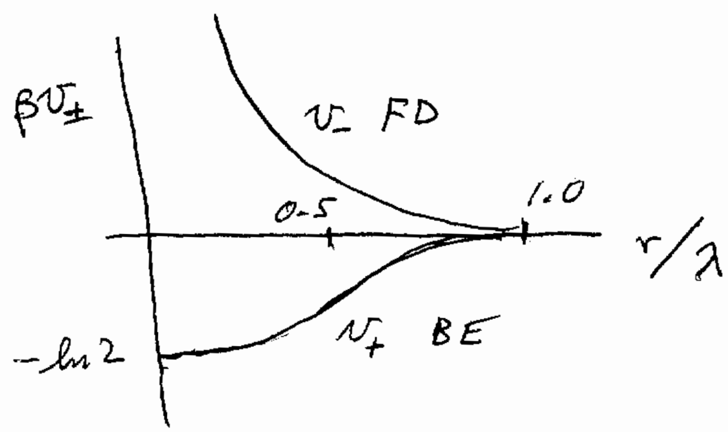
$\hbar = \frac{h}{2\pi}$

$+$ for BE , $-$ for FD

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

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

$r \lesssim \lambda$

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

Partition function

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

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

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

The next ~~term in~~ 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

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

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

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

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.

We are now ready to compute the Partition function. for <u>non-interacting</u> 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. ⇒ go to <u>grand canonical</u> 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

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

$\sum_n$: sum over all possible occupations of state i

$\prod_i$: 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

Compare these to what one has <u>Classically</u>

If single particle states are labeled by energy ϵ_i with

$$E = \sum_i n_i \epsilon_i \qquad n_i = \#\text{ particles in state } i$$
$$N = \sum_i n_i$$

Then if the particles are <u>distinguishable</u>, then for N particles with n_1 in state 1, n_2 in state 2, etc, the number of microstates corresponding to a given set of occupation numbers $\{n_i\}$ would be

$$\frac{N!}{n_1!\,n_2!\cdots} = \#\text{ ways to distribute } N \text{ particles so that } n_i \text{ are in state } i$$

So we would have

$$Q_N = \sum_{\{n_i\}} \delta\Big(\sum_i n_i - N\Big) \frac{N!}{n_1!\,n_2!\cdots} e^{-\beta \sum_i \epsilon_i n_i}$$

But we now recall Gibb's correction factor $1/N!$ for <u>indistinguishable</u> particles, to get in this case

$$Q_N = \sum_{\{n_i\}} \delta\Big(\sum_i n_i - N\Big) \frac{1}{n_1!\,n_2!\cdots} e^{-\beta \sum_i \epsilon_i n_i}$$

$$= \sum_{\{n_i\}} \delta\Big(\sum_i n_i - N\Big) \prod_i \left(\frac{1}{n_i!}\left(e^{-\beta\epsilon_i}\right)^{n_i}\right)$$

Classically, the state $|n_1, n_2, \ldots\rangle$ which counts with weight 1 in QM, counts with weight $\dfrac{1}{n_1!\,n_2!\cdots}$.

This is because classically, when we divide by $N!$ to avoid over counting, that is really only correct for states in which each particle is at a different point in phase space. If two or more particles were at exact same point in phase space, then we should not correct our counting. This is not important classically since the probability for any two particles to be at the exact same point in the continuous phase space is vanishingly small. But in QM where energy eigenstates can be discrete, this can make a difference. (see Bose condensation)

Grand Canonical for non-interacting classical particles using occupation number represntation

$$\mathcal{L} = \sum_{N=0}^{\infty} z^N Q_N = \sum_{\{n_i\}} \prod_i \frac{1}{n!} \left(z e^{-\beta \epsilon_i} \right)^{n_i}$$

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

$$= \prod_i \exp\left[z e^{-\beta \epsilon_i} \right] = \exp\left[z \sum_i e^{-\beta \epsilon_i} \right]$$

$$= \exp\left[z Q_1 \right]$$

where $Q_1 = \sum_i e^{-\beta \epsilon_i}$ is single particle partition function
"i" labels the single particle states

$$\frac{pV}{k_B T} = \ln \mathcal{L} = z Q_1$$

$$N = z \frac{\partial \ln \mathcal{L}}{\partial z} = z Q_1$$

$$\Rightarrow \frac{pV}{k_B T} = N$$

get ideal gas law independent of what the single particle energy values ϵ_i are.

Recall, above is the same result we got from our earlier classical phase space calculation of $\mathcal{L}$

$$\mathcal{L} = \sum_N z^N Q_N = \sum_N z^N \frac{Q_1^N}{N!} = e^{z Q_1}$$