can also write $Q_N = \sum_\alpha e^{-\beta E_\alpha} = \sum_\alpha \langle\alpha| e^{-\beta \hat{H}} |\alpha\rangle$

$$= \text{trace}\left(e^{-\beta\hat{H}}\right)$$

$$\hat{\rho} = \frac{e^{-\beta\hat{H}}}{Q_N} \qquad \langle\hat{X}\rangle = \frac{\text{tr}\left(\hat{X}e^{-\beta\hat{H}}\right)}{\text{tr}\left(e^{-\beta\hat{H}}\right)}$$

Grand Canonical ensemble

Here $\hat{\rho}$ is an operator in a space that includes wavefunctions with any number of particles N.

$\hat{\rho}$ should commute with both $\hat{H}$ (so it is stationary) and with $\hat{N}$ (so it doesnt mix states with different N)

$$\hat{\rho} = \frac{e^{-\beta(\hat{H}-\mu\hat{N})}}{\mathcal{L}}$$

with $\mathcal{L} = \text{trace}\left(e^{-\beta(\hat{H}-\mu\hat{N})}\right) = \sum_{\alpha, N} e^{-\beta(E_\alpha - \mu N)}$

$$\langle\hat{X}\rangle = \frac{\text{tr}\left(\hat{X}e^{-\beta\hat{H}}e^{+\beta\mu\hat{N}}\right)}{\text{tr}\left(e^{-\beta\hat{H}}e^{\beta\mu\hat{N}}\right)}$$

$$= \frac{\sum_{N=0}^{\infty} z^N \langle\hat{X}\rangle_N Q_N}{\sum_{N=0}^{\infty} z^N Q_N}$$

Example: The harmonic oscillator

Suppose we have a single harmonic oscillator.
The energy eigenstates are $E_n = \hbar\omega(n + 1/2)$

The canonical partition function will be

$$Q = \sum_n e^{-\beta E_n} = \sum_n e^{-\beta\hbar\omega(n+1/2)} = e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} \left(e^{-\beta\hbar\omega}\right)^n$$

$$Q = \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}}$$

$$\langle E\rangle = -\frac{\partial}{\partial\beta}\ln Q = -\frac{\partial}{\partial\beta}\left[-\beta\frac{\hbar\omega}{2} - \ln\left(1-e^{-\beta\hbar\omega}\right)\right]$$

$$= \frac{\hbar\omega}{2} + \frac{\hbar\omega e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}$$

We could write

$\langle E\rangle = \hbar\omega(\langle n\rangle + 1/2)$ where $\langle n\rangle$ is the average level of occupation of the h.o.

$$\Rightarrow \langle n\rangle = \frac{1}{e^{\beta\hbar\omega}-1}$$

Quantum Many particle systems

N identical particles described by a wavefunction

$\psi(\vec{r}_1 s_1, \vec{r}_2 s_2, \dots, \vec{r}_N s_N)$ $\vec{r}_i$ = position particle i

$= \psi(1, 2, \dots, N)$ s_i = spin of particle i

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

⇒ 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 enterchanges
$$\psi(1, \dots, i, \dots, j, \dots N) = -\psi(1, \dots, j, \dots i, \dots N)$$

(1) = Bose-Einstein statistics - particle called "bosons"

(2) = Fermi-Dirac statistic - particles called "fermions"

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

(1) BE ⇒ $\mathbb{P}\psi = \psi$

(2) FD ⇒ $\mathbb{P}\psi = (-1)^p \psi$ where p = # pair intercha

$$\begin{cases} +\psi & \text{for even permutation} \\ -\psi & \text{for odd permutation} \end{cases}$$

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

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

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

$\uparrow$ normalization

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

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

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 operations 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 $\phi_{i_1}, \phi_{i_2}, \ldots \phi_{i_N}$, the total energy is

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

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 $\psi(1,2,\ldots,N) = \underset{\substack{\uparrow \\ \text{particles 1 and 2 in same state } \phi_1}}{\phi_1(1)\phi_1(2)}\phi_{i_3}(3)\cdots\phi_{i_N}(N)$

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 $\psi_{FD} = 0$

⇒ 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 $n_j = 0, 1, 2, 3, \ldots$ any integer,

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

[illegible] N particle state

onsider 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

$$\langle \vec r_1 \vec r_2 | \vec k_1 \vec k_2 \rangle = \frac{e^{i(\vec k_1 \cdot \vec r_1 + \vec k_2 \cdot \vec r_2)} \pm e^{i(\vec k_1 \cdot \vec r_2 + \vec k_2 \cdot \vec r_1)}}{\sqrt{2!}\,(\sqrt{V})^2}$$

$$\langle \vec r_1 \vec r_2 | \hat\rho | \vec r_1 \vec r_2 \rangle = \langle \vec r_1 \vec r_2 | \frac{e^{-\beta \hat H}}{Q_2} | \vec r_1 \vec r_2 \rangle$$

$$= \sum_{|k_1 k_2\rangle} \langle \vec r_1 \vec r_2 | k_1 k_2 \rangle \frac{e^{-\frac{\beta\hbar^2}{2m}(k_1^2 + k_2^2)}}{Q_2} \langle k_1 k_2 | \vec r_1 \vec r_2 \rangle$$

$$= \frac{1}{Q_2} \sum_{|k_1 k_2\rangle} e^{-\frac{\beta\hbar^2}{2m}(k_1^2 + k_2^2)} |\langle \vec r_1 \vec r_2 | \vec k_1 \vec k_2 \rangle|^2$$

Note, if we take $\vec k_1 \to \vec k_2$ and $\vec k_2 \to \vec k_1$ then $\langle \vec r_1 \vec r_2 | \vec k_1 \vec k_2 \rangle = \pm \langle \vec r_1 \vec r_2 | \vec k_2 \vec k_1$ 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 $\vec k$ 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

$$\langle \vec r_1 \vec r_2 | e^{-\beta \hat H} | \vec r_1 \vec r_2 \rangle = \frac{1}{2!} \sum_{\vec k_1, \vec k_2} e^{-\frac{\beta\hbar^2}{2m}(k_1^2 + k_2^2)} |\langle \vec r_1 \vec r_2 | \vec k_1 \vec k_2 \rangle|^2$$

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

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

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

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

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

We need the following integrals

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

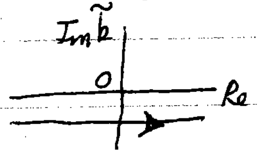
$$\int d^3 k\, e^{-\frac{\alpha}{2} k^2 + i \vec k \cdot \vec r}$$ do by completing the square

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

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

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.

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

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

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

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

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

= 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)