Even though a stationary $\hat{\rho}$ is diagonal in the basis of energy eigenstates, we can always express it in terms of any other complete basis states

$$\rho_{nm} = \langle n|\hat{\rho}|m\rangle = \sum_{\alpha\beta} \langle n|\alpha\rangle\langle\alpha|\hat{\rho}|\beta\rangle\langle\beta|m\rangle$$

$$= \sum_{\alpha} \langle n|\alpha\rangle \rho_\alpha \langle\alpha|m\rangle$$

in this basis, $\hat{\rho}$ need not be diagonal

This will be usefull because we may not know the exact eigenstates for $\hat{H}$. If $\hat{H} = \hat{H}^0 + \hat{H}^1$ we might know the eigenstates of the simpler H^0, but not the full $\hat{H}$. In this case it may be convenient to express $\hat{\rho}$ in terms of the eigenstates of $\hat{H}^0$ and treat $\hat{H}^1$ in perturbation. In general it is useful to have the above representation for $\hat{\rho}$ and $\langle\hat{X}\rangle = \mathrm{tr}(\hat{X}\hat{\rho})$ in an operator form that is indep of its representation in any particular basis

Microcanonical ensemble:

$$\hat{\rho} = \sum_{\alpha} |\alpha\rangle\rho_\alpha\langle\alpha| \quad \text{with } \rho_\alpha = \begin{cases} \text{const} & E \le E_\alpha \le E+\Delta \\ 0 & \text{otherwise} \end{cases}$$

$$\text{and } \sum_{\alpha}\rho_\alpha = 1$$

Canonical ensemble:

$$\hat{\rho} = \sum_{\alpha} |\alpha\rangle\rho_\alpha\langle\alpha| \quad \text{with } \rho_\alpha = \frac{e^{-\beta E_\alpha}}{Q_N}$$

$$\text{where } Q_N = \sum_{\alpha} e^{-\beta E_\alpha}$$

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

$$= \mathrm{trace}\,(e^{-\beta\hat{H}})$$

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

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

state α has energy E_α and number of particles N_α
Sum over all states with any number N_α

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

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

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

$\langle E \rangle = \hbar\omega\left(\langle n \rangle + 1/2\right)$ 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

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

Indentical 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 interchange

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

2) ψ is antisymmetric under pair interchange

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

(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 $\Rightarrow$ $\mathbb{P}\psi = \psi$

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

Consider <u>non-interacting</u> particles

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

sum of single particle Hamiltonians

$$\Rightarrow \psi(1,2,\ldots,N) = \phi_{i_1}(1)\,\phi_{i_2}(2)\cdots\phi_{i_N}(N)$$

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

normalization

$\Leftarrow$ 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 operators give

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

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

then when we construct

particles 1 and 2 in same state ϕ_1

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

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

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

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

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

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

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.

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