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 $\hat{H} = \hat{H}^0 + \hat{H}'$ 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 $\hat{H}'$ 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:

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

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

Canonical ensemble:

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

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

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

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

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

<u>Grand Canonical ensemble</u>

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

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

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

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

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

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

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

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

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

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

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

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

$\Rightarrow$ two possible symmetries for ψ

1) ψ is symmetric under pair interchange
$$\psi(1, \ldots, i, \ldots, j, \ldots, N) = \psi(1, \ldots, j, \ldots, i, \ldots N)$$
2) ψ is antisymmetric under pair interchange
$$\psi(1, \ldots, i, \ldots, j, \ldots N) = -\psi(1, \ldots, j, \ldots i, \ldots N)$$

(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

$\sum_{\mathbb{P}} \leftarrow$ 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

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

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

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 $\psi_{FD} = 0$

$\Rightarrow$ 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 set of $\{n_i\}$ corresponds to one N particle state.