An aside on doing Gaussian integrals

$$\int_{-\infty}^{\infty} d^3r\; e^{-\frac{r^2}{2\sigma^2}} = 4\pi \int_0^{\infty} dr\, r^2 e^{-\frac{r^2}{2\sigma^2}}$$

$$\int_{-\infty}^{\infty} d^3r\; r^2 e^{-\frac{r^2}{2\sigma^2}} = 4\pi \int_0^{\infty} dr\, r^4 e^{-\frac{r^2}{2\sigma^2}}$$

in spherical coordinates

In Cartesian coords:

$$\int_{-\infty}^{\infty} d^3r\, e^{-\frac{r^2}{2\sigma^2}} = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz\; e^{-\frac{x^2}{2\sigma^2}} e^{-\frac{y^2}{2\sigma^2}} e^{-\frac{z^2}{2\sigma^2}}$$

$$= \left(\sqrt{2\pi\sigma^2}\right)\left(\sqrt{2\pi\sigma^2}\right)\left(\sqrt{2\pi\sigma^2}\right) = \left(2\pi\sigma^2\right)^{3/2}$$

$$\int_{-\infty}^{\infty} d^3r\, r^2 e^{-\frac{r^2}{2\sigma^2}} = \int dx \int dy \int dz\, (x^2+y^2+z^2)\, e^{-\frac{x^2}{2\sigma^2}} e^{-\frac{y^2}{2\sigma^2}} e^{-\frac{z^2}{2\sigma^2}}$$

all 3 terms contribute equally

$$= 3 \int_{-\infty}^{\infty} dx\, x^2 e^{-\frac{x^2}{2\sigma^2}} \int_{-\infty}^{\infty} dy\, e^{-\frac{y^2}{2\sigma^2}} \int_{-\infty}^{\infty} dz\, e^{-\frac{z^2}{2\sigma^2}}$$

$$= 3\left(\sigma^2\sqrt{2\pi\sigma^2}\right)\left(\sqrt{2\pi\sigma^2}\right)\left(\sqrt{2\pi\sigma^2}\right)$$

$$= 3\sigma^2\left(2\pi\sigma^2\right)^{3/2} = 3(2\pi)^{3/2}\sigma^5$$

All you need to remember is

normalized Gaussian $\displaystyle\int_{-\infty}^{\infty} dx\, \frac{e^{-\frac{x^2}{2\sigma^2}}}{\sqrt{2\pi\sigma^2}} = 1$ $\qquad \displaystyle\int_{-\infty}^{\infty} dx\, \frac{e^{-\frac{x^2}{2\sigma^2}}}{\sqrt{2\pi\sigma^2}}\, x^2 = \sigma^2$

In spherical coords

$$4\pi \int_0^\infty dr\, r^2 e^{-\frac{r^2}{2\sigma^2}} = (4\pi)\left(\tfrac{1}{2}\right)\int_{-\infty}^{\infty} dr\, r^2 e^{-\frac{r^2}{2\sigma^2}}$$

$$= 2\pi\, \sigma^2 \cdot \sqrt{2\pi\sigma^2} = (2\pi\sigma^2)^{3/2} \quad \text{as before}$$

$$4\pi \int_0^\infty dr\, r^4 e^{-\frac{r^2}{2\sigma^2}}$$

would have to either remember this integral or get it into the form $\int^\infty dr\, r^2 e^{-r^2/2\sigma^2}$ by making two integrations by parts.

But even if we dont do integral exactly, we can find the important behavior by a substitution of variables.

$$x = \frac{r}{\sigma} \Rightarrow dr = \sigma\, dx \quad , \quad r = \sigma x$$

integral is then $4\pi\sigma^5 \underbrace{\int_0^\infty dx\, x^4 e^{-x^2/2}}_{\text{a constant}}$

so we know $\int dr\, r^4 e^{-r^2/2\sigma^2} \sim \sigma^5$

--- back to quantum ensembles!

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 $\hat{H}^0$, 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 $Q_N = \sum_\alpha e^{-\beta E_\alpha} = \sum_\alpha \langle \alpha | e^{-\beta \hat{H}} | \alpha \rangle$

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

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

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 doesn't 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

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

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

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

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

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

$\cancel{\psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)}$

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

$= \psi(1, 2, \ldots, N)$ $\quad s_i$ = 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 $\Rightarrow$ $\mathbb{P}\psi = (-1)^p \psi$ $\quad$ 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 $\quad \psi_{BE} = \frac{1}{\sqrt{N_P}} \sum_{\mathbb{P}} \mathbb{P}\psi \quad \leftarrow \psi = \phi_1 \phi_2 \cdots \phi_N$ as above

$\uparrow$ normalization $\quad \leftarrow$ 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 operations give

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

for any permutation $\mathbb{P}_0$

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

then when we construct

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

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 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.