Quantum Ensembles

The classical ensemble was a probability distribution in phase space $\rho(q_i, p_i)$ such that thermodynamic averages of an observable X are given by

$$\langle X \rangle = \left(\prod_i \int dp_i dq_i\right) X(q_i, p_i)\, \rho(q_i, p_i)$$

The ensemble interpretation of thermodynamics imagines that we make many (ideally infinitely many) copies of our system, each prepared identically as far as macroscopic parameters are concerned. The distribution $\rho(q_i p_i)$ is then the probability that a given copy will be found at coordinates (q_i, p_i) in phase space. The average $\langle X \rangle$ above is the average over all copies of the system. The ergodic hypothesis states that this ensemble average over many copies will give the same result as averaging X over the time trajectory of the system in just one copy.

In quantum mechanics, states are described by wavefunctions $|\psi\rangle$ rather than points in phase space (q_i, p_i). To describe a quantum ensemble imagine making many copies of the system. Let $|\psi^k\rangle$ be the state of the system in copy k.

The ensemble average of an observable operator $\hat{X}$ would then be

$$\langle \hat{X} \rangle \equiv \frac{1}{M} \sum_{k=1}^{M} \langle \psi^k | \hat{X} | \psi^k \rangle$$

where in the above we took M copies of the system to make our ensemble. In general $M \to \infty$.

In quantum mechanics it is convenient to express wavefunctions as a linear superposition of some complete set of orthonormal basis wave functions $|\varphi_n\rangle$. Define

$\langle \varphi_m | \varphi_n \rangle = \delta_{mn}$

$$|\psi^k\rangle = \sum_n a_n^k |\varphi_n\rangle$$

a_n^k is probability amplitude for $|\psi^k\rangle$ to be in state $|\varphi_n\rangle$.

$|a_n^k|^2$ is probability for $|\psi^k\rangle$ to be found in state $|\varphi_n\rangle$

normalization $\langle \psi^k | \psi^k \rangle = 1 \Rightarrow \sum_n |a_n^k|^2 = 1$

Now express $\langle \hat{X} \rangle$ in terms of the basis states

$$\langle \hat{X} \rangle = \frac{1}{M} \sum_{k=1}^{M} \sum_{n,m} a_n^k a_m^{k*} \langle \varphi_m | \hat{X} | \varphi_n \rangle$$

$$= \frac{1}{M} \sum_k \sum_{n,m} a_n^k a_m^{k*} X_{mn}$$

where $X_{mn} \equiv \langle \varphi_m | \hat{X} | \varphi_n \rangle$ is the matrix of $\hat{X}$ in the basis $|\varphi_n\rangle$.

We can now define the density matrix that describes the ensemble

$$\rho_{nm} \equiv \frac{1}{M} \sum_{k=1}^{M} a_n^k a_m^{k*}$$

ρ_{nm} is just the matrix of the density operator $\hat{\rho}$ in the basis $|\varphi_n\rangle$

$$\hat{\rho} \equiv \sum_{n,m} |\varphi_n\rangle \rho_{nm} \langle \varphi_m|$$

We can write for ensemble averages

$$\langle \hat{X} \rangle = \sum_{n,m} \rho_{nm} X_{mn}$$

$$= \sum_{n,m} \langle \varphi_n | \hat{\rho} | \varphi_m \rangle \langle \varphi_m | \hat{X} | \varphi_n \rangle$$

$$= \sum_{n} \langle \varphi_n | \hat{\rho} \hat{X} | \varphi_n \rangle$$

$$= \mathrm{tr}\left[\hat{\rho} \hat{X} \right]$$

tr = "trace"

Note: ρ_{nn} is the probability that a state, selected at random from the ensemble, will be found to be in $|\varphi_n\rangle$

$$\mathrm{tr}\,\hat{\rho} = \sum_n \rho_{nn} = \frac{1}{M}\sum_{k=1}^{M}\sum_n a_n^k a_n^{k*}$$

$$= \frac{1}{M}\sum_{k=1}^{M}\sum_n |a_n^k|^2$$

$$= 1$$

Also

$$\rho_{nm} = \frac{1}{M}\sum_k a_n^k a_m^{k*}$$

$$\Rightarrow \rho_{mn}^* = \frac{1}{M}\sum_k a_m^{k*} a_n^k = \rho_{nm}$$

so $\hat{\rho}$ is an Hermitian operator

$\Rightarrow$ ρ_{nn} can be diagonalized and its eigenvalues are real.

So a quantum mechanical ensemble is described by a Hermitian density matrix $\hat{\rho}$ such that $\mathrm{tr}\,\hat{\rho} = 1$, and ensemble averages are given by $\mathrm{tr}[\hat{\rho}\hat{X}]$. What additional conditions must $\hat{\rho}$ satisfy if it is ~~to~~ describe thermal equilibrium?

As for any operator in the Heisenberg picture, its equation of motion is

$$i\hbar\frac{\partial\hat{\rho}}{\partial t} = [\hat{H}, \hat{\rho}]$$

quantum analog of Liouville's eqn

$\hat{H}$ is Hamiltonian

$\Rightarrow$ if $\hat{\rho}$ is to describe a stationary equilibrium, it is necessary that $\hat{\rho}$ commutes with $\hat{H}$, $[\hat{H}, \hat{\rho}] = 0$, so $\partial\hat{\rho}/\partial t = 0$.

$\Rightarrow$ $\hat{\rho}$ is diagonal in the basis formed by the energy eigenstates. If these states are $|\alpha\rangle$ then

$$\langle\alpha|\hat{H}\hat{\rho}|\beta\rangle = E_\alpha \langle\alpha|\hat{\rho}|\beta\rangle$$
$$= \langle\alpha|\hat{\rho}\hat{H}|\beta\rangle = E_\beta \langle\alpha|\hat{\rho}|\beta\rangle$$

$$E_\alpha \langle\alpha|\hat{\rho}|\beta\rangle = E_\beta \langle\alpha|\hat{\rho}|\beta\rangle$$

$$\Rightarrow \langle\alpha|\hat{\rho}|\beta\rangle = 0 \quad \text{unless } E_\alpha = E_\beta$$

So $\hat{\rho}$ only couples eigenstates of equal energy (ie degenerate states) but since $\hat{\rho}$ is Hermitian, it is diagonalizable $\Rightarrow$ we can always take appropriate linear combinations of degenerate eigenstates to make eigenstates of $\hat{\rho}$. In this basis $\hat{\rho}$ is diagonal.

$$\hat{H}|\alpha\rangle = E_\alpha|\alpha\rangle, \quad \hat{\rho}|\alpha\rangle = \rho_\alpha|\alpha\rangle$$

or $$\langle\alpha|\hat{H}|\beta\rangle = E_\alpha \delta_{\alpha\beta}, \quad \langle\alpha|\hat{\rho}|\beta\rangle = \rho_\alpha \delta_{\alpha\beta}$$

$$\delta_{\alpha\beta} = \begin{cases} 1 & \alpha = \beta \\ 0 & \alpha \neq \beta \end{cases} \quad \text{Kronecker delta}$$

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

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

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

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

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

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

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

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

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

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

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

$= \psi(1, 2, \ldots, N)$ $\qquad s_i$ = 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 interchanges

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

2) ψ is antisymmetric under pair enterchanges

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

(1) = Bose-Einsten 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 $\quad \psi_{BE} = \frac{1}{\sqrt{N_p}} \sum_{\mathbb{P}} \mathbb{P}\psi \leftarrow \psi = \phi_1 \phi_2 \cdots \phi_N$ as above

$\uparrow$ normalization $\qquad$ $\leftarrow$ 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 $\phi_{i_1}, \phi_{i_2}, \dots \phi_{i_N}$, the total energy is

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

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

then when we construct

particles 1 and 2 in same state ϕ_1

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

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 $n_j = 0, 1, 2, 3, \dots$ 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.

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:

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

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

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

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

In spherical coords

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

$$= 2\pi\, \sigma^2 \cdot \sqrt{2\pi\sigma^2} = (2\pi\sigma^2)^{3/2}$$ 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 $\int_0^\infty dr\, r^2 e^{-r^2/2\sigma^2}$ by making two integrations by parts.

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

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

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!