Quantum Ensembles

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

$$\langle X \rangle = \left( \prod_{i} dp_i dq_i \right) X(g_i, p_i) f(g_i, p_i)$$

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 $f(g_i, p_i)$ is the probability that a given copy will be found at coordinates $(g_i, p_i)$ 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 $(g_i, p_i)$. To define 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

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

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 basis wave functions \( |\phi_n\rangle \). Define

\[
|\psi^k\rangle = \sum_n a_n^k |\phi_n\rangle
\]

\( a_n^k \) is probability amplitude for \( |\psi^k\rangle \) to be in state \( |\phi_n\rangle \).

\( |a_n^k|^2 \) is probability for \( |\psi^k\rangle \) to be found in state \( |\phi_n\rangle \).

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 state

\[
\langle \hat{X} \rangle = \frac{1}{M} \sum_{k=1}^{M} \langle \psi^k | \hat{X} | \psi^k \rangle = \sum_{n,m} a_n^k a_m^k \langle \phi_m | \hat{X} | \phi_n \rangle
\]

\( = \sum_{n,m} \frac{1}{M} \sum_{k} a_n^k a_m^k X_{mn} \)
where $X_{mn} = \langle \varphi_m | \hat{X} | \varphi_n \rangle$ is the matrix of $\hat{X}$ in the basis $| \varphi_n \rangle$.

We can now define the density matrix that describes the ensemble

$$
P_{nm} = \frac{1}{M} \sum_{k=1}^{\infty} d_n^k a_k^* a_k
$$

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

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

We can write for ensemble averages

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

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

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

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

Note: $p_{nn}$ is the probability that a state, selected at random from the ensemble, will be found to be in $| \varphi_n \rangle$.
\[
\text{tr} \hat{\rho} = \sum_{n} p_{nn} = \frac{1}{M} \sum_{k=1}^{M} a_{n}^{k} a_{n}^{k*} = \frac{1}{M} \sum_{k=1}^{M} |a_{n}^{k}|^2 = 1
\]

Also
\[
p_{nm} = \frac{1}{M} \sum_{k} a_{n}^{k} a_{m}^{k*}
\]

\[
\Rightarrow p_{nm} = \frac{1}{M} \sum_{k} a_{m}^{k*} a_{n}^{k} = p_{mn}
\]

so \( \hat{\rho} \) is an Hermitian operator

\[
\Rightarrow p_{nm} \text{ can be diagonalized and its eigenvalues are real.}
\]

So a quantum mechanical ensemble is described by a Hermitian density matrix \( \hat{\rho} \) such that \( \text{tr} \hat{\rho} = 1 \), and ensemble averages are given by \( \text{tr}[\hat{\rho} \hat{O}] \). 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 eq

\( \hat{H} \) is Hamiltonian
⇒ if $\hat{\beta}$ is to describe a stationary equilibrium, it is necessary that $\hat{\beta}$ commutes with $\hat{A}$, $[\hat{A}, \hat{\beta}] = 0$, so $\partial \hat{\beta} / \partial t = 0$.

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

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

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

⇒ $\langle \alpha | \hat{\beta} | \beta \rangle = 0$ unless $E_\alpha = E_\beta$

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

$$\hat{\beta} | \alpha \rangle = E_\alpha | \alpha \rangle \quad \hat{\beta} | \alpha \rangle = p_\alpha | \alpha \rangle$$

$$\langle \alpha | \hat{H} | \beta \rangle = E_\alpha \delta_{\alpha \beta} \quad \langle \alpha | \hat{\beta} | \beta \rangle = p_\alpha \delta_{\alpha \beta}$$

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

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 useful 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 $\hat{H}^1$ as perturbation. In general it is useful to have the above representation for $\hat{\rho}$ and $\langle \hat{X} \rangle = \text{tr}(\hat{X} \hat{\rho})$ in an operator form that is indep of $\hat{H}$.

**Microcanonical ensemble:**

$$\hat{\rho} = \sum_{\alpha} |\alpha\rangle \rho_{\alpha} \langle \alpha|$$

with $\rho_{\alpha} = \begin{cases} \text{const} & E \leq E_{\alpha} \leq E + \Delta \\ 0 & \text{otherwise} \end{cases}$

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

**Canonical ensemble:**

$$\hat{\rho} = \sum_{\alpha} |\alpha\rangle \rho_{\alpha} \langle \alpha|$$

with $\rho_{\alpha} = \frac{e^{-\beta E_{\alpha}}}{\Omega N}$

where $\Omega N = \sum_{\alpha} e^{-\beta E_{\alpha}}$.
can also write \( Q_N = \sum_{x} e^{-\beta E_x} = \sum_{x} \langle x | e^{-\beta \hat{H}} | x \rangle \)

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

\[ \hat{\varphi} = \frac{e^{-\beta \hat{H}}}{Q_N} \quad \langle \hat{X} \rangle = \frac{\text{tr} (\hat{X} e^{-\beta \hat{H}})}{\text{tr} (e^{-\beta \hat{H}})} \]

**Grand Canonical Ensemble**

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

\( \hat{\varphi} \) should commute with both \( \hat{H} \) (so it is stationary) and with \( \hat{N} \) (so it doesn't mix states with different \( N \)).

\[ \beta = \frac{e^{-\beta (\hat{H} - \mu \hat{N})}}{Z} \]

with \( Z = \text{trace} \left( e^{-\beta (\hat{H} - \mu \hat{N})} \right) = \sum_{\alpha} e^{-\beta (E_{\alpha} - \mu N_{\alpha})} \]

\[ \langle \hat{X} \rangle = \frac{\text{tr} (\hat{X} e^{-\beta \hat{H}} e^{\beta \mu \hat{N}})}{\text{tr} (e^{-\beta \hat{H}} e^{\beta \mu \hat{N}})} \]

\[ = \sum_{N=0}^{\infty} z^N \langle \hat{X} \rangle_N Q_N \]

\[ \sum_{N=0}^{\infty} z^N Q_N \]
Example: The harmonic oscillator

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

The canonical partition function will be

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

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

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

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

We could write

\[
\langle E \rangle = \hbar \omega (\langle n \rangle + \frac{1}{2}) \quad \text{where} \quad \langle n \rangle \text{ is the average level of occupation of the h.o.}
\]

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