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 basis wavefunctions $|\varphi_n\rangle$. Define

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

a_n^k is probability <u>amplitude</u> 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

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

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

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

$$= \mathrm{tr}\left[\hat{\rho} \hat{X}\right] \qquad \mathrm{tr} = \text{"trace"}$$

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 <u>Hermitian</u> 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

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

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

$\Rightarrow$ $\langle\alpha|\hat{\rho}|\beta\rangle = 0$ 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.

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

or

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

$$\delta_{\alpha\beta} = \begin{cases} 1 & \alpha = \beta \\ 0 & \alpha \neq \beta \end{cases}$$ 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 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 the representation in any particular basis

Microcanonical ensemble:

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

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

Canonical ensemble:

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

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

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)

$$\hat{\rho} = \frac{e^{-\beta(\hat{H} - \mu \hat{N})}}{\mathcal{Z}}$$

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

↑ 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

$\langle E \rangle = \hbar\omega\left(\langle n \rangle + 1/2\right)$ where $\langle n \rangle$ is the average level of occupation of the h.o.

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