

Quantum Ensembles

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

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

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 $f(q_i, p_i)$ 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 $M \rightarrow \infty$.

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 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

$$\begin{aligned} \langle \hat{X} \rangle &= \frac{1}{M} \sum_{k=1}^M \sum_{n,m} a_n^k a_m^{k*} \langle \varphi_m | \hat{X} | \varphi_n \rangle \\ &= \frac{1}{M} \sum_k \sum_{n,m} a_n^k a_m^{k*} X_{mn} \end{aligned}$$

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

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

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

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

We can write for ensemble averages

$$\begin{aligned} \langle \hat{X} \rangle &= \sum_{n,m} f_{nm} X_{mn} \\ &= \sum_{n,m} \langle \varphi_n | \hat{\rho} | \varphi_m \rangle \langle \varphi_m | \hat{X} | \varphi_n \rangle \\ &= \sum_n \langle \varphi_n | \hat{\rho} \hat{X} | \varphi_n \rangle \\ &= \text{tr} [\hat{\rho} \hat{X}] \quad \text{tr} = \text{"trace"} \end{aligned}$$

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

$$\begin{aligned} \text{tr } \hat{\rho} &= \sum_n \rho_{nn} = \frac{1}{M} \sum_{k=1}^M \sum_n a_n^k a_n^{k*} \\ &= \frac{1}{M} \sum_{k=1}^M \sum_n |a_n^k|^2 \\ &= 1 \end{aligned}$$

Also

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

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

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

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

⇒ 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 $\partial \hat{\rho} / \partial t = 0$.

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

$$\begin{aligned}\langle \alpha | \hat{H} \hat{\rho} | \beta \rangle &= E_{\alpha} \langle \alpha | \hat{\rho} | \beta \rangle \\ &= \langle \alpha | \hat{\rho} \hat{H} | \beta \rangle = E_{\beta} \langle \alpha | \hat{\rho} | \beta \rangle\end{aligned}$$

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

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

So $\hat{\rho}$ only couples eigenstates of equal energy (i.e. 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.

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

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

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

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 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 in perturbation. In general it is useful to have the above representation for $\hat{\rho}$ and

Microcanonical ensemble:

representation in any particular basis

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

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

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

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

Grand Canonical ensemble

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

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

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

↑ state α has energy E_{α} and number of particles N_{α} .
Sum over all states with any number N_{α} .