Quantum Statistical Mechanics - I

Till now whatever we studied in statistical mechanics, was by using classical laws of motion. Majority of systems which we want to describe using statistical mechanics, are inherently quantum in nature, and classical laws cannot be used to describe them. For example, a gas of free electrons should be described using quantum mechanics.

The state of a quantum system can be described at any instant of time by its wave function Ψ, which is a function of position (or momenta, depending on the representation) coordinates of all the particles, and time. In general, it can be just be represented as a vector in the Hilbert space. $|\Psi\rangle$ can also be written as a linear combination of eigenfunctions of any Hermitian operator of the Hilbert space. We will write it in terms of the eigenstates of the Hamiltonian of the system $\widehat{H}$, the so-called energy eigenstates, given by $\widehat{H} |\Phi_n\rangle = E_n |\Phi_n\rangle$. The state of the system can now be written as

$$|\Psi\rangle = \sum_n c_n |\Phi_n\rangle,$$

where c_n is a complex quantity which can be time dependent and $|\Phi_n\rangle$ are the eigen states. The expectation value of an observable $\widehat{A}$ can be calculated as

$$\langle A \rangle = \frac{\langle \Psi| \widehat{A} |\Psi\rangle}{\langle \Psi|\Psi\rangle} = \frac{\sum_{n,m} c_n^* c_m \langle \Phi_n| \widehat{A} |\Phi_m\rangle}{\sum_{n,m} c_n^* c_m \langle \Phi_n|\Phi_m\rangle}$$

$$\langle A \rangle = \frac{\sum_{n,m} c_n^* c_m \langle \Phi_n| \widehat{A} |\Phi_m\rangle}{\sum_n c_n^* c_n}$$

where we have used the orthonormality of $|\Phi_n\rangle$. Since c_n are time dependent, we can measure the time average expectation value of A as it is should be.

$$\langle A \rangle = \frac{\sum_{n,m} \overline{c_n^* c_m} \langle \Phi_n| \widehat{A} |\Phi_m\rangle}{\sum_n \overline{c_n^* c_n}} \qquad (1)$$

If $\widehat{A}$ represents a measurable macrosocopic observable of a system in thermal equilibrium, the postulates of quantum statistical mechanics are actually postulates about the form of $\overline{c_n^* c_m}$. We write the postulates of quantum statistical mechanics as follows. It clearly says that

1. Postulate of Equal a Priori Probability

$$\overline{c_n^* c_n} = \begin{cases} 1 & E < E_n < E + \Delta E \\ 0 & Otherwise \end{cases}$$

2. Postulate of Random phases

$$\overline{c_n^* c_m} = 0 \ (if \ n \neq m)$$

All of the preceding discussion can also be reformulated in term of density operator, instead of quantum states. A quantum system in a state $|\Psi\rangle$ can be described by a density operator given by

$$\hat{\rho} = |\Psi\rangle\langle\Psi|,$$

Provided $|\Psi\rangle$ is normalized. For an unnormalized state we can write it as

$$\hat{\rho} = \frac{|\Psi\rangle\langle\Psi|}{Tr[\,|\Psi\rangle\langle\Psi|\,]}$$

where $Tr[\ldots]$ represents trace over a complete set of states. The expectation value of an observable can then be written as

$$\langle A\rangle = Tr[\,\hat{\rho}\,\hat{A}\,]$$

If one uses the energy eigenstates of the system to take the trace over states of the system, one gets

$$\langle A\rangle = \sum_{n,m}\langle\Phi_n|\,\hat{\rho}\,|\Phi_m\rangle\langle\Phi_m|\,\hat{A}\,|\Phi_n\rangle$$

$$\langle A\rangle = \sum_{n,m}\rho_{nm}\,\langle\Phi_m|\,\hat{A}\,|\Phi_n\rangle \qquad\qquad (2)$$

Where ρ_{nm} is called the density matrix. If we compare the equations (1) and (2), we can read

$$\rho_{nm} = \frac{\overline{c_n{}^*c_m}}{\sum_n\overline{c_n{}^*c_n}}$$

Or

$$\rho_{nm} = \frac{\overline{c_n{}^*c_n}}{\sum_n\overline{c_n{}^*c_n}}\,\delta_{nm}$$

The average value of an observable can now be written as

$$\langle A\rangle = \sum_{n}\rho_{nn}\,\langle\Phi_n|\,\hat{A}\,|\Phi_n\rangle$$

The above relation represents an average of the observable $\hat{A}$ over an ensemble which consists of copies of the system, in different microstates (quantum states) $|\Phi_1\rangle$, $|\Phi_2\rangle$, $|\Phi_3\rangle$, etc. The microstate (quantum state) $|\Phi_k\rangle$ occurs with a probability ρ_{kk}. Here ρ_{nm} is an example of a mixed-state density matrix. Such a density matrix cannot represent a single system in a particular quantum state. It represents a mixture, or an ensemble of systems in different microstates, occurring with different probability.

Microcanonical ensemble

With the density matrix formulation discussed above, we are all set to describe various ensembles in quantum statistical mechanics. Firstly, the counting of microstates, which was done by calculating the area in phase-space in classical statistical mechanics, is done by counting the quantum states of the system, labelled by suitable quantum numbers:

$$\frac{1}{N!}\frac{1}{h^{3N}}\int dp\, dq\, [..] \rightarrow \sum_n [..]$$

The density matrix for the microcanonical ensemble is given by

$$\rho_{nn} = \frac{\overline{c_n{}^* c_n}}{\sum_n \overline{c_n{}^* c_n}}$$

With the condition

$$\overline{c_n{}^* c_n} = \begin{cases} 1 & E < E_n < E + \Delta E \\ 0 & Otherwise \end{cases}$$

All those $\overline{c_n{}^* c_n}$ are equal to 1 whose E_n lies between E and $E + \Delta E$. The rest are zero. So, $\sum_n \overline{c_n{}^* c_n}$ is the number of microstates whose energy eigenvalue lies between E and $E + \Delta E$. Call it as Ω

$$\rho_{nn} = \begin{cases} \dfrac{1}{\Omega} & E < E_n < E + \Delta E \\ 0 & Otherwise \end{cases}$$

Canonical ensemble

Canonical ensemble can be formulated exactly as it was done in classical statistical mechanics, by having a system and a much bigger heat-bath. Since none of the arguments used in our earlier formulation, was specific to the classical nature of the system, the result can be directly adapted here. The canonical density matrix can be written as

$$\rho_{nn} = \frac{e^{-\beta E_n}}{Z} \qquad where\ Z = \sum_n e^{-\beta E_n}$$

where Z is the canonical partition function. Off-diagonal elements of the density matrix are zero. Ensemble average of an observable can be written as

$$\langle A \rangle = \frac{1}{Z} \sum_n e^{-\beta E_n} \langle \Phi_n| \widehat{A} |\Phi_n \rangle$$

Where $|\Phi_n\rangle$ are the eigen states of the Hamiltonian of the system.

Grand canonical ensemble

The density matrix in the grand canonical ensemble can be written, in general, as

$$\rho_{ii} = \frac{e^{-\beta(E_i - \mu N_i)}}{Z_g} \qquad where \; Z_g = \sum_i e^{-\beta(E_i - \mu N_i)}$$

where μ is the chemical potential, and Z_g the grand partition function. How the microstates of the system are defined, may depend on the specific problem at hand. We will look at it in more detail when studying the quantum statistics of identical particles. Ensemble average of an observable can be written as

$$\langle A \rangle = \frac{1}{Z} \sum_i e^{-\beta(E_i - \mu N_i)} \langle \Phi_n | \widehat{A} | \Phi_n \rangle$$