Statistical Mechanics: Lecture 9

▬ Quantum Statistical Mechanics

Postulates of Quantum Statistical Mechanics

Till now whatever we studied in statistical mechanics, was by using classical laws of motion. However, all systems in nature follow quantum mechanics, which is the more fundamental theory. In many situations it is a good approximation to describe even microscopic classically. For example, large molecules and colloid particles can be described well using classical laws, and hence using classical statistical mechanics suffices. However, 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 as things like Pauli's exclusion principle are important for them. In the following we will formulate statistical mechanics for quantum systems.

The state of a quantum system can be described at any instant of time by its wave function Ψ. In a particular representation, Ψ will be a function of position coordinates of all the particles, and time. In another

representation, it will be a function of momenta of all the particles, and time. In general it can be just be represented as a vector in Hilbert space, $|\Psi\rangle$. $|\Psi\rangle$ 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 $\hat{H}$, the so-called energy eigenstates, given by $\hat{H}|\Phi_n\rangle = E_n|\Phi_n\rangle$. The state of the system can now be written as

$$|\Psi\rangle = \sum_n c_n|\Phi_n\rangle \tag{1}$$

According to quantum mechanics, the expectation value of any observable, represented by $\hat{A}$, is given by

$$\langle A\rangle = \frac{\langle\Psi|\hat{A}|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{\sum_{n,m} c_n^* c_m \langle\Phi_n|\hat{A}|\Phi_m\rangle}{\sum_{n,m} c_n^* c_m \langle\Phi_n|\Phi_m\rangle}$$
$$= \frac{\sum_{n,m} c_n^* c_m \langle\Phi_n|\hat{A}|\Phi_m\rangle}{\sum_n c_n^* c_n} \tag{2}$$

where we have used orthonormality of $|\Phi_n\rangle$. The constants c_n, c_m are in general time-dependent.

Now macroscopic systems can never be considered isolated systems - they continually interact with the environment, although extremely weakly. So, the state

involved should be the state of the system plus environment combined. The state will look something like $|\Psi\rangle = \sum_n d_n|\chi_n\rangle|\Phi_n\rangle$, where $|\chi_n\rangle$ represent certain states of the environment. Formally we can still represent the state $|\Psi\rangle$ by (1), but the c_n should now be identified with $d_n|\chi_n\rangle$. However, c_n are not constants now, but involve states of the environment. The expectation value of an observable can still be given by (2), provided we identify $c_n^* c_m$ with $d_n^* d_m \langle\chi_n|\chi_m\rangle$.

The relation (2) gives the expectation value of the observable at any instant of time. However, when we measure a thermodynamic system, our measurements are never instantaneous, quite simply because atoms and molecules move much faster than what our measuring apparatus can resolve. What we measure is really an time-averaged value of the observable. The time over which the average is done, or rather happens, is much long than typical collision time of atoms and molecules, but much smaller than the resolving time of our apparatus. Thus, the quantity we actually measure, should be given by

$$\langle A \rangle = \frac{\overline{\langle\Psi|\hat{A}|\Psi\rangle}}{\overline{\langle\Psi|\Psi\rangle}} = \frac{\sum_{n,m} \overline{c_n^* c_m} \langle\Phi_n|\hat{A}|\Phi_m\rangle}{\sum_n \overline{c_n^* c_n}}, \quad (3)$$

The term $\overline{c_n^* c_m}$ represents a time average of $d_n^* d_m \langle\chi_n|\chi$

over times much longer than the time-scale of molecular motion, but shorter than the resolution time of the measuring apparatus. This term might look simple in appearance, but is extremely difficult to calculate, as it involves all the states of the environment, and its interaction with the system. In general, this term cannot be calculated, and one can only make guesses about it.

If $\hat{A}$ 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.

Postulate of Equal a Priori Probability

$$\overline{c_n^* c_n} = \begin{cases} 1 \ (E < E_n < E + \Delta E) \\ 0 \ (\text{otherwise}) \end{cases} \tag{4}$$

Simply put, it implies that only those states are allowed which conform to the fixed energy constraint. And all such states are equally probable.

Postulate of Random Phases

$$\overline{c_n^* c_m} = 0 \quad (n \neq m) \tag{5}$$

In quantum mechanics if $|\psi_1\rangle$ and $|\psi_2\rangle$ are two al-

lowed states, any superposition of them, given by $\alpha_1|\psi_1\rangle + \alpha_2|\psi_2\rangle$, is also an allowed state. This postulate implies that quantum superposition of any two *energy eigenstates*, $|\Phi_n\rangle$ and $|\Phi_m\rangle$, is not allowed. This is the effect of the environment on the system, and it grants a special status to energy eigenstates.

It should be emphasized here that the environment with which the system is assumed to be interacting here, is *not* the heat-bath that we have considered in the classical canonical ensemble before. This environment does not exchange energy with the system, interaction being extremely weak. Its most important effect is the killing of quantum superpositions of energy eigenstates of the system.

▃▃▃ Density matrix

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

$$\hat{\rho} = |\psi\rangle\langle\psi|, \tag{6}$$

provided that $|\psi\rangle$ is normalized. For an unnormalized state, one can write $\hat{\rho} = \frac{|\psi\rangle\langle\psi|}{Tr[|\psi\rangle\langle\psi|]}$, where $Tr[\dots]$ represents trace over a complete set of states. The

expectation value of an observable can then be written as

$$\langle A \rangle = Tr[\hat{\rho}\hat{A}] \tag{7}$$

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

$$\langle A \rangle = \sum_{n,m} \langle \Phi_n | \hat{\rho} | \Phi_m \rangle \langle \Phi_m | \hat{A} | \Phi_n \rangle = \sum_{n,m} \rho_{nm} \langle \Phi_m | \hat{A} | \Phi$$
$$\tag{8}$$

where ρ_{nm} is the called the density matrix. For a pure state, described by a single wave function, this density matrix is always non-diagonal - it can be diagonal only when the system is in one of its energy eigenstates. Comparing the above equation with (2), we conclude that the system in (2) can be described by a density matrix given by

$$\rho_{nm} = \frac{\overline{c_n^* c_m}}{\sum_n \overline{c_n^* c_n}}. \tag{9}$$

Furthermore, the postulates of quantum statistical mechanics, stated in the preceding discussion, imply that this density matrix (in the representation of energy eigenstates) is diagonal. To put it mathematically,

$$\rho_{nm} = \frac{\overline{c_n^* c_n}}{\sum_n \overline{c_n^* c_n}} \delta_{nm} \tag{10}$$

The density matrix may be non-diagonal if another set of states, different from the energy eigenstates, are used to take the trace (trace is invariant under change of representation). The average value of an observable can now be written as

$$\langle A \rangle = \sum_n \rho_{nn} \langle \Phi_n | \hat{A} | \Phi_n \rangle. \qquad (11)$$

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, occuring with different probability.

▬ Microcanonical ensemble

With the density matrix formulation discussed above, we are all set to describe various ensembles in quantum statsitical 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:

$$\frac{1}{N!}\frac{1}{\hbar^{3N}}\int dp\,dq \rightarrow \sum_n$$

The density matrix for microcanonical ensemble is given by

$$\rho_{nn} = \frac{\overline{c_n^* c_n}}{\sum_k \overline{c_k^* c_k}} \tag{12}$$

with the condition

$$\overline{c_n^* c_n} = \begin{cases} 1 \ (E < E_n < E + \Delta E) \\ 0 \ \text{(otherwise)} \end{cases} \tag{13}$$

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, $\sum_k \overline{c_k^* c_k}$ is just equal to the number of microstates whose energy eigenvalue lies between E and $E + \Delta E$, let us call it Ω. The microcanonical density matrix can then be written as

$$\rho_{nn} = \begin{cases} \frac{1}{\Omega} \ (E < E_n < E + \Delta E) \\ 0 \ \text{(otherwise)} \end{cases} \tag{14}$$

Canonical ensemble

Canonical ensemble can be formulated exactly as it was done in classical statisitical 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

$$\rho_{nn} = \frac{e^{-\beta E_n}}{Z}, \quad Z = \sum_n e^{-\beta E_n} \quad (15)$$

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

$$\langle A \rangle = \frac{1}{Z} \sum_n e^{-\beta E_n} \langle \Phi_n | \hat{A} | \Phi_n \rangle \quad (16)$$

where $|\Phi_n\rangle$ are the eigenstates of the Hamiltonian of the system.

▬▬ Grand canonical ensemble

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

$$\rho_{ii} = \frac{e^{-\beta(E_i - \mu N_i)}}{\mathcal{Z}}, \quad \mathcal{Z} = \sum_i e^{-\beta(E_i - \mu N_i)} \quad (17)$$

where μ is the chemical potential, and $\mathcal{Z}$ 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 ideal gas of identical particles.