Fundamentals of Statistical Thermodynamics

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Lecture – 19

The Canonical Partition Function

Welcome to the next lecture of Statistical Thermodynamics. So far, we have discussed molecular partition function and then we have connected the molecular partition function with various thermodynamic quantities. For example, with internal energy and with entropy. But specifically, the molecular partition function when we were discussing, then we were restricting to one system in which the number of particles or number of molecules are fixed and also the total energy is fixed. What I mean is that the molecular partition function Q is equal to $\sum_j e^{-\beta E_j}$. This was discussed for the system in which there are total number of particles or molecules is fixed that means $\sum_i n_i$ is equal to N and also the total energy is fixed that means $\sum_i n_i \varepsilon_i$ is equal to E.

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The Canonical Ensemble

$$q = \sum_j e^{-\beta \varepsilon_j}$$

$$\sum_i n_i = N$$

$$\sum_i n_i \varepsilon_i = E$$

And all our discussion was based upon the assumption that the molecules do not interact with each other. That means the total energy that we talk about is the sum of individual molecules present in different energy levels. And since we were not allowing the molecules to interact, therefore the contribution to total energy from any intermolecular interaction was neglected. And if now let us say we allow the molecules to interact.

Once you allow the molecules to interact, there can be attractive interaction, there can be repulsive interactions, we can list several type of interactions. Some of the interactions can be exothermic, some of the interactions can be endothermic. If exothermic interactions take place, heat is released and if endothermic interactions take place, heat is taken in. And therefore, the energy is going to be changed. It is not then simply the energy possessed by each molecule and their summation.

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The Canonical Ensem

- The crucial new concept we need whe of interacting particles is the 'ensemble'

- Like so many scientific terms, the term has basically its normal meaning of 'collection', but it has been sharpened and refined into a precise significance

- To set up an ensemble, we take a closed system of specified volume, composition, and temperature, and think of it as replicated $\bar{N}$ times

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Then in addition to that the interaction energy has also to come in. Now we will switch over to the systems which will permit interaction between the molecules. That means we will discuss a system in which the energy of the overall system can change. That means we are allowing the molecules to interact with each other. To begin that discussion, let me introduce the concept of ensemble.

So what is an ensemble? Let us start discussing. The comment if you read here, what is written over here, is the crucial new concept now we need when treating systems of interacting particles is ensemble. The literal meaning of ensemble is collection. So therefore, like so many scientific term, the term has basically its normal meaning of collection, but it has been sharpened and refined into a precise significance. We will discuss a little bit more details of this.

So how do we set up an ensemble? First let us take a closed system of specified volume, composition and temperature. What I mean is consider this one block, consider this as a system. What we have is n fixed, when you say n fixed and volume fixed, that means composition is fixed, volume is fixed, temperature is fixed, but energy is not fixed, because if the molecules interact the energy may change. So therefore, let us first consider a system in which the number of molecules is fixed, the volume is fixed, the temperature is fixed. In other words, a closed system, remember the definition of open system, closed system, isolated system.

A closed system is the one in which matter cannot go out, the energy can go out and here the matter cannot go out is contained in this definition that the number of molecules will not change. So, a closed system of specified volume, composition and temperature and then you think of it replicated several times. So that means if you consider this system, now you replicate this system in all directions. This is an imaginary replication. So this can be n, this special symbol whatever is given n times.

This n that is the number of the systems in this replication can be infinity, n can tend to infinity. So, focus on this N, V, T which is fixed and then it is replicated in all direction multiple times and how many times? Here we are giving this n, this value can be infinity. That means this one particular box which represents a system of fixed composition, volume and temperature can replicate infinity times. Now carefully try to understand this concept now. Temperature everywhere in each system is constant.

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Microcanonical ensemble:	N, V, E common
Canonical ensemble:	N, V, T common
Grand canonical ensemble:	μ, V, T common

That means you are maintaining a thermal contact of each system with each other. That is all the identical closed systems are regarded as being in thermal contact with one another so they can exchange it actually. Suppose if you have a system in which the molecules can interact with each other and then if you want to maintain isothermal condition, when you maintain temperature that means you are maintaining isothermal conditions. How you can

maintain isothermal condition? Even if you consider construction of some calorimeter or some system in which you carry out a reaction the interactions take place, but you want to maintain isothermal conditions. Then the excess heat which is generated or the heat which is consumed that has to be compensated for.

That means excess heat generated should go out or if the heat is taken in it produces some cooling, then some more heat should transfer. So that is the meaning of being in thermal contact with one another so that they can exchange energy. Now you are allowing the molecules to interact with each other. Now the total energy of the systems is let us say I give another special symbol to it. This is the total energy of all the systems.

That means this system plus this system plus this system plus this system add up the energy of all these systems let this be designated by the special E character. Now because they are in thermal equilibrium with one another they all have the same temperature and how to maintain the same temperature we just discussed that means you let the energy be exchanged energy be compensated fine. This imaginary collection of replications of the actual system with a common temperature is called canonical ensemble. What it means is you have one system you have defined its NVT properties that means energy can change and this is an imaginary replication in all the direction and this as a whole is called canonical ensemble. Let us discuss this concept of canonical ensemble in a little more detail.

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Microcanonical ensemble:	N, V, E common
Canonical ensemble:	N, V, T common
Grand canonical ensemble:	μ, V, T common

- In the microcanonical ensemble the condition of constant temperature is replaced by the requirement that all the systems should have exactly the same energy: each system is individually isolated.

- In the grand canonical ensemble the volume and temperature of each system is the same, but they are open, which means that matter can be imagined as able to pass between the systems; the composition of each one may fluctuate, but now the chemical potential is the same in each system

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The word canon means according to a rule you are setting up a rule over here. An ensemble means collection which is literally in captured into the definition of canonical ensemble. All the identical closed systems are regarded as being in thermal contact with one another so they can exchange energy. This is the thing that we have already discussed that in order to maintain a thermal contact in order to maintain a fixed temperature you have to allow exchange of energy. There are different types of ensembles. You can fix NVT common that is what we have just discussed. You can fix the composition constant. You can fix the volume constant. You can fix the temperature constant and that one is called canonical ensemble. So remember canonical ensemble is a collection of systems their imaginary replication in which NVT are common.

You can also now consider a system in which you do not want to maintain temperature constant. You want to maintain energy constant that will be NVE common. So, if energy is held constant that means now you have to allow the temperature to change. Such an ensemble is called microcanonical ensemble. So, what is microcanonical ensemble? Collection of systems in which each system has fixed number of molecules, fixed volume and fixed energy. There is another type of ensemble which is possible and that is called grand canonical ensemble. And in grand canonical ensemble what is common is chemical potential, volume and temperature. Remember our discussion in chemical thermodynamics. It was stressed upon at that time that chemical potential is central to

chemistry. Chemical potential is change in free energy with addition of one mole of a species when the temperature, pressure and composition of all the other species in the mixture is constant. And there the concept of chemical potential was expanded or it was applied to derive many useful relations and to discuss many useful observations. So that means you can base your discussion on the basis of any of these three ensembles. One is microcanonical ensemble, second is canonical ensemble and the third is grand canonical ensemble. It is up to you that which ensemble you would like to use for further discussion. For further discussion over here in a major way we are going to focus on canonical ensemble that is NVT is constant. That means you allow the energy of the system to change that in other words means that you allow the molecules to interact with each other. So let us now read the comments. In the microcanonical ensemble the condition of constant temperature is replaced by the requirement that all the systems should have exactly the same energy that is what is NBE. What does that mean? That means each system is individually isolated. You are not allowing the energy to change.

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If you don't allow the transfer of mass and energy then the system becomes isolated. In the grand canonical ensemble, the volume and temperature of each system is same volume and temperature but they are open. Open means you are not fixing the number of molecules.

You are not fixing the energy therefore it becomes an open system. So therefore in the grand canonical ensemble the volume and temperature of each system is the same but they are open which means that the matter can be imagined as able to pass between the systems. The composition of each one may fluctuate but now the chemical potential is the same in each system. So, depending upon the system which you are considering one of these ensembles can be used and further theories can be developed. The important point about an ensemble is that it is a collection of imaginary replications of the system. So that means you are free to let the number of members be as large as you like.

It can be even infinity. That means this total number of replications, total number of systems can even become infinite. The number of members of the ensemble in a state with energy E_i is denoted N_i. One system may have some energy, second system may have some another energy, third system may have energy of number one, fourth system may have some different energy. So, in general the number of members of the ensemble in a state with energy E_i is denoted by this special character N_i. This is one member, this is second member, this is third member of the whole ensemble.

So how to write the total number of members of ensemble in a state E_i is we are calling this as special character N_i. And similarly, now you can talk about weight of a configuration as we discussed earlier while talking about molecular partition function. There we talked about only one system. Remember there we talked about only one system in which N and E were fixed. Here we have several systems and that forms an ensemble and there can be certain members with certain energy and therefore, their number and population can be defined. And by the same arguments that we discussed earlier, we can talk about the weight of the configuration of the ensembles and this special character W. Let us define that as the weight of the configuration of the ensemble. Remember this N special character N which is the total number of members is not related to this N is not related to number of molecules in a given system. Don't get confused with that. This special character of N is the sum of each member means 1, 2, 3, 4, 5, 6, 7, 8, 9, 10.

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This is the 20. That means here this special character N is 20, but this N the number of molecules in each system is different. So, this is unrelated. These two are unrelated. So by the same arguments when we were discussing instantaneous configurations and there we talked about the dominating configurations. It is very unlikely that the whole of the total energy which is represented by this character will accumulate in one system.

Some of the configurations of the ensemble will be very much more probable than others. It depends upon the weight of the configuration. So, we can anticipate that there will be dominating configuration and that we can evaluate the thermodynamic properties by taking average over ensemble using that single most probable configuration. Same argument that we discussed earlier while talking about molecular partition function and the thermodynamic limit can be that the total number of systems can tend to infinity and this dominating configuration is overwhelmingly the most probable and it dominates the properties of the system virtually completely. We have to keep that in mind. So how do we now define the weight of a configuration? Now we have several systems and the addition or that means the total number of systems is this special n character and let there be n_0 number of members in 0th energy state. Remember n_0, n_1, n_2 they represent how many members of this ensemble are in ground state, first excited state, second excited state etcetera. So that means when we talk about an ensemble and weight of a configuration will be given by this n factorial over n_0 factorial, n_1 factorial, n_2 factorial etcetera etcetera. Now

let us go back to our discussion of molecular partition function. We will adopt the same procedure that we adopted in molecular partition function.

There we searched for the configuration which has maximum weight. We discussed in terms of log w then d log w we set that equal to 0 and try to find out the expression for Boltzmann distribution. The precision to be adopted here is exactly the same that is the configuration of greatest weight subject to constraints that the total energy of the ensemble is e. Constraints you remember earlier while discussing molecular partition function we had two constraints that is the sum of the number of particles in each state has to remain same and second the total energy of the system must remain same. Here what are the constraints to be used is that the total energy of the ensemble is e and that the total number of members is fixed at n.

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We are not going to do those derivations again because the procedure is same, but simply let us now discuss the result. Remember earlier it was n_i upon n is equal to $e^{-\beta\varepsilon_i}$ divided by molecular partition function, but when you do the calculations or derivations for this ensemble what you get here is the number of members in the ith state divided by the total number of members in the ensemble is equal to $e^{-\beta E_i}$. E_i is the ith state in which the n_i number of members are placed and q is the canonical partition function. Now instead of

small q what we write is capital Q. Let us read the comment. The configuration of greatest weight subject to the constraints that the total energy of the ensemble is constant at E and that the total number of members is fixed at N is given by canonical distribution. Remember this is the same format, is the same definition as you used for molecular partition function, but only here this different notations they apply to ensemble and we have this q which is $\sum_i n_i \, \varepsilon_i$. What we have discussed here is that instead of considering only one system if you now consider various systems which allow different properties to be fixed and then you can develop your theory based upon that. For canonical ensemble we chose n v t fixed that means you allow the molecules to interact with each other the energy can be exchanged and we derived a Boltzmann distribution for such an ensemble and came up with a new form of partition function which we no more call molecular partition function, but we call canonical partition function. We will have a little bit more discussion on this canonical partition function and see how to recover molecular partition function from canonical partition function in the next lecture. Thank you.