Introduction to Molecular Thermodynamics
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Lecture - 06
Microstates of a System (Contd.)

Welcome back. So, we are talking about the microscopic state of a given system in terms of the possible quantum numbers as allowed by solving the Schrodinger equation within the framework of quantum mechanics. So, the first example that I am going to take today in this class is a particle in a 3 dimensional box.

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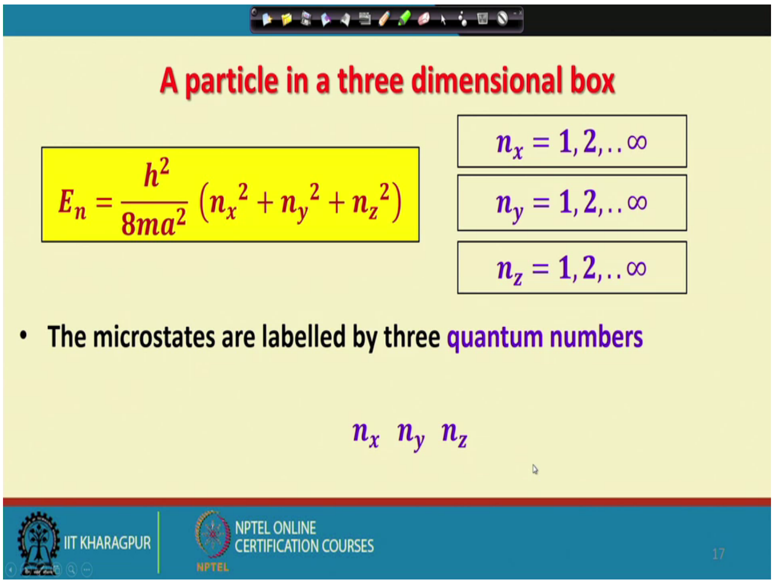

And it is now known that the discrete energy levels here, this will be characterized by 3 different quantum numbers and what are these quantum numbers? N x corresponding to the x direction of the box n y corresponding to the y direction, and n z corresponding to the z direction; each of these quantum numbers can take up an infinite number of possible values, starting from one and these are integers like 1 2 3 and so on and so forth. And given a value of n x n y and n z, the corresponding value of E is defined in terms of this quantity that you have already seen in the case of the one dimensional box, and a summation of square of these 3 quantum numbers.

Now what we learn from here is as follows. So, the microstates here are labelled by 3 quantum numbers, and these 3 quantum numbers are n x n y and n z.

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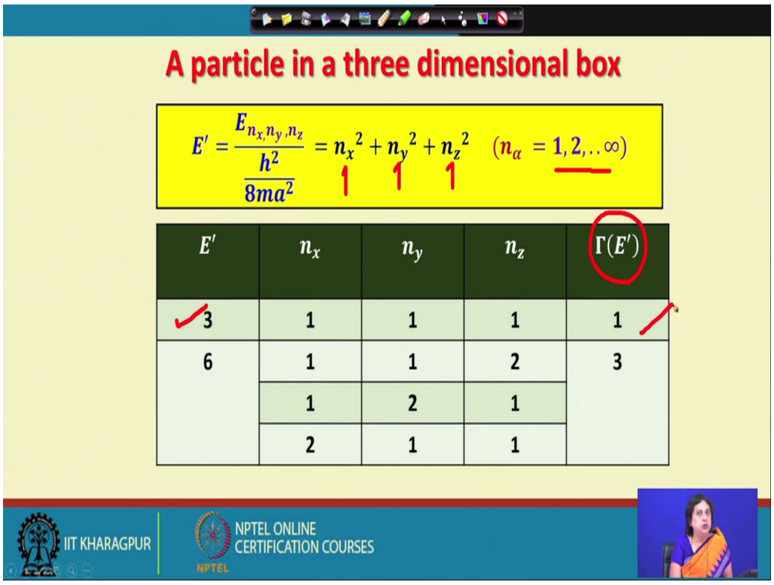

So, if we have a particle in a 3 dimensional box, what we see is something very very interesting. The allowed values of E prime that is the value of the energy divided by this quantity, that is n x square plus n y square plus n z square; where n alpha with alpha equal to x y or z can have values starting from 1 then 2 and up to infinity.

Now, the simplest possible value of epsilon a E prime is going to be 3 because the smallest value of n x is one the smallest value of n y is one and the smallest value of n z is 1. So, if I square each of them and add them what I get is a prime is equal to 3. So, that is the case that I have shown here and here are there any other ways in which the system can have a total energy E prime equal to 3 the answer is no.

So, in this case I find that the number of microscopic states associated with E prime equal to 3 is 1. Now let me look at another situation.

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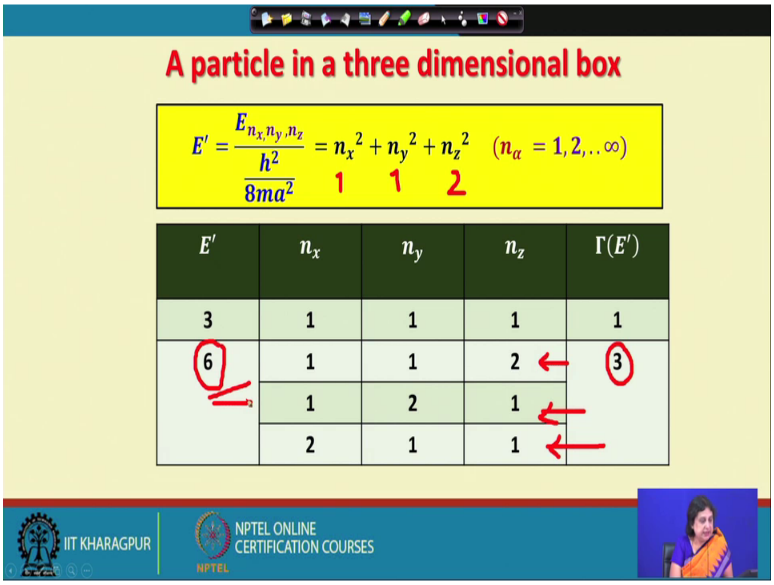

Where I am looking at E prime is equal to 6. Now what are the different microscopic states that can give you E prime equal to 6? Interestingly there are more than one microscopic states here which can give you E prime equal to 6. So, let us have a look at them. Let us say that for n x n y and n z if I give a value 1 here 1 here, but 2 here; 1 plus 1 plus 4 that gives you 6. So, this is the typical microstate that I am talking about.

Now, since x y and z directions are different from each other therefore, it is equally possible that this kind of a microscopic state where along n y along the y direction n y is 2, but the other 2 quantum numbers are 1 or this where I have n x equal to 2, but other 2 quantum numbers 1 that is also possible and in this case I find that 3 different microscopic states are possible for a given value of E prime. So, at this stage we understand that the introduction of an added dimension complicates the situation in such a way that the number of microscopic states associated with a single energy value may be something other than one.

So, at this stage then let us try and talk about a little different system where more than one particle is present.

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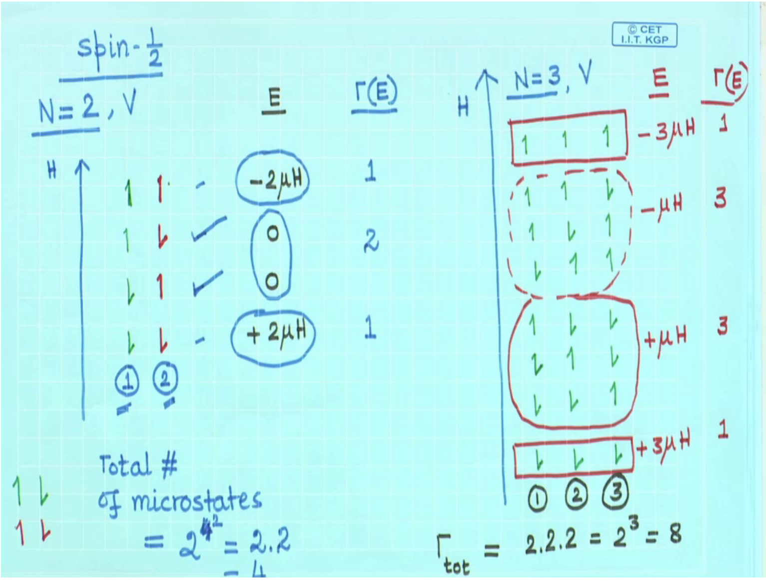

So, once again we go back to the spin half system, and here I am taking N is equal to 2 and let this be the direction of the applied magnetic field and there are 2 spins which are labelled as spin 1 and spin 2 they are present here.

In the system at a constant volume and I am going to look for the different microscopic states that can be obtained for these 2 spins. So, if this is my spin 1 my spin 2 can also have an up spin or if this is my spin 1 corresponding to it my second spin can have a down spin. Spin 1 if it has a down spin spin 2 can have an up spin. And if spin 1 has a down spin, spin 2 can also have a down spin.

Please remember that here the kind of approximations that I am making is in a constant volume there are two particles. N equal to two these are present, and the system is integrated with this field which has been applied in a certain direction I have particle 1 and particle two and these two particles are distinguishable from each other as has been shown by using different colors. Now the particle one can have an up spin or a down spin and similarly the particle 2 also can have an up spin or a down spin.

Now, I have taken the two of them together and I am looking at a system where there are 2 non interacting spin half particles present in the system. So, this is a simplest possible description of two spins together, and the question that I ask is what are the possible microscopic states since I have already mentioned that the 2 spins.

Do not interact with each other how spin 1 is oriented is independent of how spin 2 is oriented. Therefore, if I have spin 1 in the upstate, spin 2 can be either in upstate or in downstate. So, this way I have generated 2 such microscopic states and depending on whether spin 1 is in the downstate I can generate 2 more microscopic states. So, here I have a total number of microscopic states is equal to for this system, the total number of microstates is equal to 2 to the power of 4 and how do I get this 2? Particle one has 2 possible microstates corresponding to each of which, particle 2 has 2 microstates and that gives me 2 sorry 2 to the power of 2 and this is 4.

Now the basic idea here is are all these microscopic states giving me the same value of total energy of the system, let us have a look. So, when I have a look at the different possible values of energy of this system, what I have is as follows. So, energy of this system is minus 2 mu H, energy of this system is 0, energy of this system is 0 and the energy of this system is plus 2 mu H and therefore, if I now count the number of microscopic states associated with each value of energy.

I find that there are 3 values of energy possible; minus 2 mu H 0 and plus 2 mu H how many microscopic states are possible associated with the energy minus 2 mu H, I find that this is one. I find that there are 2 microscopic states that are associated with the energy 0 and there is only one microscopic state associated with the situation, where the energy value is plus 2 mu H and I can see that here all the descriptions are dependent on the fact that spin 1 is not interacting with spin 2. Now under a similar situation if I have 3 spins. So, I will have capital N is equal to 3 present in a volume V and immersed in this filled in this direction H.

So, in this case I can have 3 non interacting distinguishable spins labelled as 1 2 and 3. So, what are the different microstates that are associated with it? These are definitely the microscopic states associated with all 3 pointing parallel, then 2 pointing parallel one pointing anti parallel, then maybe 2 pointing anti parallel and one pointing parallel and all 3 pointing anti parallel. So, do you agree that if I label these 3 particles as particle 1 particle 2 and particle 3; I can distinguish between these particles particle 1 it is possible for particle one to have 2 microscopic states corresponding to each of which, particle 2 can have 2 microscopic states corresponding to each of which particle 3 can have 2 microscopic states.

And therefore, the total number of microscopic states is going to be given by 2 cubed that is equal to 8. Now let us once again have a closer look at the different types of microscopic states we have drawn here. Look at this microscopic state; what is the energy of this microscopic state? Minus 3 mu H; so this is the energy and we also note down the number of microscopic states, possible for any such system. So, the number of microscopic states possible for any such system is 1.Now let us have a look at this set of microscopic states.

Now in this set of microscopic states the energy is given by mu H minus mu H and the number of such microscopic states is 3. If I think of these microscopic states then what I find is the energy is given by plus mu H and once again there are 3 such microscopic states possible. And finally, when all the 3 spins are orienting anti parallel to the applied field, the energy is plus 3 mu H and gamma corresponding to is 2 this energy is 1.

So, we have learnt from here the fact that, whenever you are increasing the number of particles you are increasing the total number of microscopic states. And for every system for every given possible value of the total energy, there may be one or more microscopic states associated with the same value of the total energy. Now this is what we talked about in the case of a spin half system. Let us go about and look at what happens if I have a one dimensional simple harmonic oscillator and I have 2 of them.

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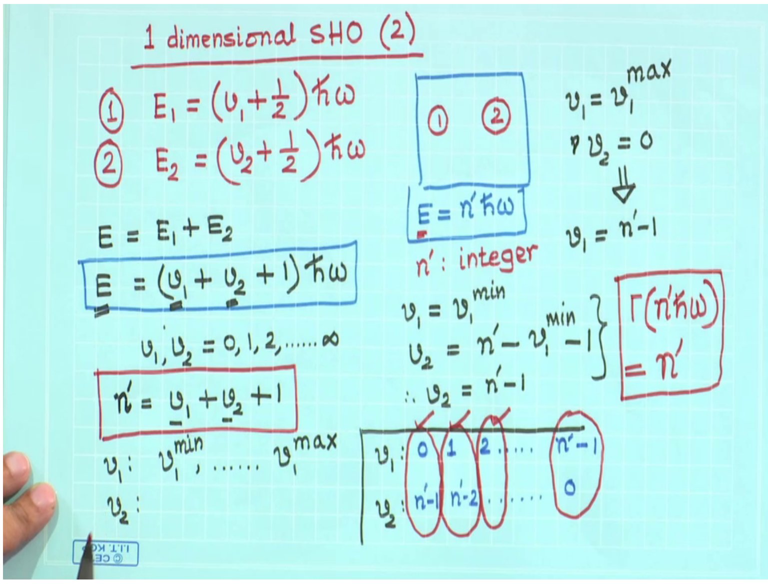

So, my oscillator 1 its energy is given by E 1 that is equal to v 1 plus half.

H cross omega and for my oscillator 2 the energy value is given by E 2 and that is characterized by this quantum number v 2, and I assume that both the oscillators are distinguishable they have the labels one and 2, and they are present in a system where both of them are interacting with each other . So, I have both oscillator 1 and oscillator 2 present in this system, in that case my question is; how should I describe the microscopic states of this composite system the microscopic state. Obviously, is going to be characterized by energy values E, that is equal to E 1 plus E 2 and therefore, I can write that E is going to be v 1 plus 2 plus one into h cross omega. So, what are the allowed values of E?

The allowed values of E are decided by what the values of v 1 and v 2 are. Now the allowed values of v 1 and v 2 are as follows 0, 1, 2. So, integer value starting from 0 and there are an infinite number of possibilities. Now, let me focus on one given energy state of the system, where E is equal to some n prime into h cross omega. So, if I compare these 2 equations that E is given by this and E is also given by this I understand that the relationship like this must hold v 1 plus v 2 plus 1.

Therefore, I would say that can I find out the different possible microscopic states of this composite system, when the total value of energy is given by n prime h cross omega where n prime is some integer. Now in this case if I want to count and find out what the different microscopic states are, I understand that the first oscillator labelled as oscillator 1 its different microstates will have v 1 equal to 0, v 2 equal v 1 equal to one and so on and so forth and for the second particle this is going to be v 2 equal to 0 and so on and so forth. But here since I have given a specific energy of the total system you must realize that now not all possible values of v 1 and v 2 are simultaneously allowed.

So, let us have a look at the constraining equation again. So, I have this is a fixed value and I have 2 variables v 1 and v 2. Because of the presence of this constraint I understand that v 1 will vary from some v 1 minimum so on and so forth up to some v 1 maximum; and when it varies like this v 2 will be given by what? When v 1 is equal to v 1 minimum v 2 is given by n prime minus v 1 minimum minus one now we already know what we one minimum is v 1 minimum is 0. And therefore, I understand that v 2 in that case we will be n prime minus 1.

Similarly I know that when v 2 is; when v 1 is equal to v 1 max, I must be having v 2 equal to 0 to satisfy this condition, as a result under that situation I must be having v 1 equal to n prime minus 1 or in other words I can say let us write down the allowed values of v 1 and v 2. So, the allowed values of v 1 are as follows, the minimum value is 0 the next value is 1 2 and so on and so forth. And it will go up to n prime minus 1. For v 2 what are the allowed values when v 1 is equal to 0. Then I find that v 2 must be equal to n prime minus 1 when v 1 is equal to one then its value is going to be n prime minus 2 and so on and so forth up to 0.

So, now if I want to describe the microstate microscopic states of the given composite system that is comprised of 2 non interacting simple harmonic oscillators, they are going to be characterized like these different values of v 1 and v 2. So, this is one microscopic state where v 1 is 0 and v 2 is equal to n prime minus 1, this is another microscopic state and so on and so forth. So, how many microscopic states do I have as a whole? If you count these you see this is 1 2 3 so on and so forth up to n prime. So, the number of microscopic states associated with the energy value of n prime h cross omega is given by n prime and these n prime energy values are or can be generated by giving different values to the 2 quantum numbers v 1 and v 2 provided this relationship is maintained.

So, as you see once again for a given energy state, if I have more than one particle then more than one energy states is possible. Now once I have understood that how the number of particles introduction of higher number of particles is giving me the problem of a very large number of microscopic states associated with the given energy, let us consider one general case of the spin half system.

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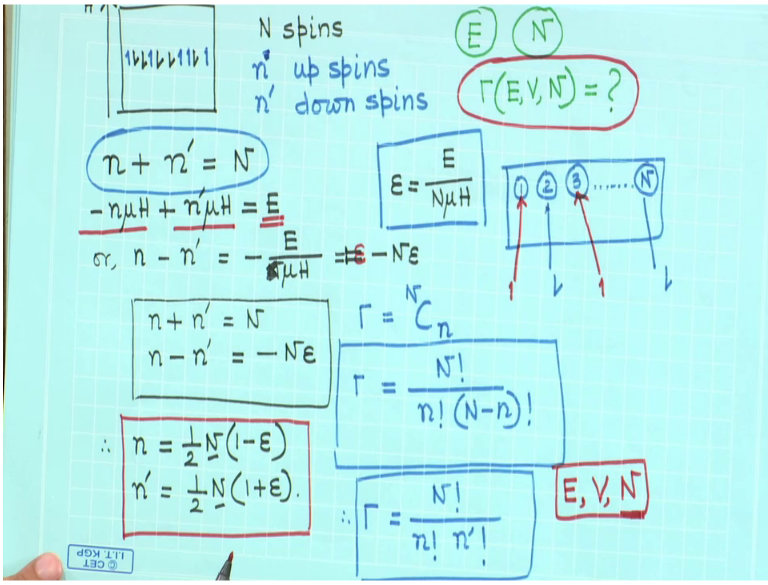

So, once again I have this spin half system, where I have a typical situation where in a box v embedded in the box under the influence of this field h are capital N spins. And this out of this capital N spin values, some of them are pointing up and some of them are pointing down. So, this is a typical microstate that is comprised of n prime up spins or n up spins and n prime down spins. And the question that we ask is as follows if the total energy E of this system is given, and if the total number of particles n is fixed then.

What is the number of microstates associated with this system that is present at a constant energy E a constant volume V and a constant number of particles N. So, this is what we are going to calculate next; is it one is it more than one is it a small number or is it a very big number. So, what we do next is we try and look at exactly what we are dealing with. We have 2 constraints I have small n plus small n prime that must be capital N because the spin half particles having up spin is n and this is a spin half particles having down spins and together they give me the total N spins that I have in my system.

I must also have this relationship that minus n mu H plus n prime mu H that must also be equal to E or I can say that n minus n prime that must be equal to E by mu H or let me define this as some quantity epsilon. So, epsilon is nothing but capital E divided by mu H; now let us have a look at what I have in my hand I have n plus n prime that is equal to capital N and n minus n prime that is equal to let me put and capital N here. So, that is equal to minus N epsilon. So, that is epsilon is equal to capital E by N mu H.

So, I have n minus n prime is equal to E by mu H and that is equal to minus N epsilon. Now I am going to solve for the 2 unknowns quantities capital N a small n and n prime. So, what do I get from these 2 equations? Small n is half of capital N 1 minus epsilon and small n prime is half of n 1 plus epsilon. So, once I know these what I know is a given microscopic state is characterized by certain value of small n that is the number of up spins and small n prime that is the number of down spins, and they are related to the total number of particles present that is capital N and also the energy value epsilon which is defined as capital E divided by capital N mu h.

And once I know small n and n prime as a function of these 2 numbers, I can very easily say that well what is gamma. Gamma must be equal to the number of ways in which you can pick up n up spins and n prime down spins. So, think about this situation, you have particle one particle 2 particle 3 and so on and so forth up to particle n out of these you are going to pick up small n with up spin. So, let us say that a typical microstate will have up spin here up spin here and so on and so forth and some other particles are going to have down spin maybe this one is going to have a down spin.

So, what are the ways in which you can find out the different possible microscopic states? You can find out different possible microscopic states by finding the different combinations of small n and n prime. So, what are the number of ways in which you can pick small n number of up spins out of a capital N number of particles that; obviously, is given by capital N C small n and this is given by N factorial divided by small n factorial into capital N minus small n factorial. So, this is gamma it says that if I have an assembly of non-interacting distinguishable spin half particles whose number is capital n out of them.

I can generate a small n number of up spins in these many possible ways, but I already know that n prime is nothing, but capital N minus small n therefore, I would say that gamma that is equal to n factorial capital n factorial small n divided by small n factorial to small n prime factorial. So, what is the conclusion from this calculation? The conclusion from this calculation is as follows, I have seen that I started by deciding saying that the total energy of the system is given the total volume of the system is given and the total number of particles of the system is fixed for this fixed set of 3 parameters.

My question was what are the number of different microscopic states. What I find is that a typical microscopic state is characterized by small n up spins, and n prime down spins such that their number adds up to the total number capital N f the spin half particles. And also I understand that individual energies of these up spins and the down spins must add up to the total given energy. And then I find that gamma corresponding to this energy E is given by this expression and one can evaluate this gamma for capital n and small n and n prime values that are small. And it is not possible to evaluate gamma for very large number of particles.

And in the next lecture we are going to look at how we can find out the number of possible microscopic states associated with a given value of energy, but a very large number of particles.

Thank you.