Introduction to Molecular Thermodynamics
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Lecture - 11
Microstates of a System (contd.)

Welcome, today we are going to continue our discussion on the microscopic states of a system in equilibrium and this is a continuation of our discussion on how many microscopic states are associated with, for example, a system comprised of capital N perhaps particles that we have already discussed.

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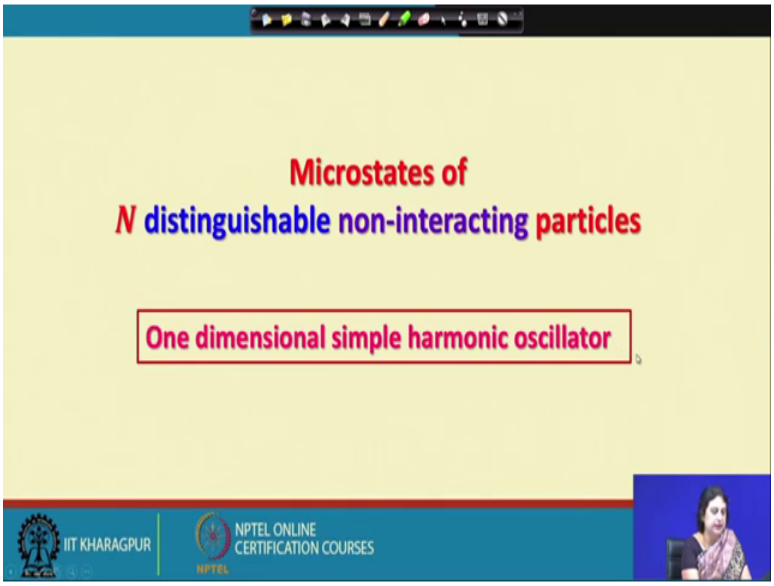

Now in today's lecture, what we are going to do is, we are going to talk about once again the microstates of capital N distinguishable non interacting particles, but in today's discussion we are going to talk in terms of, one dimensional simple harmonic oscillators.

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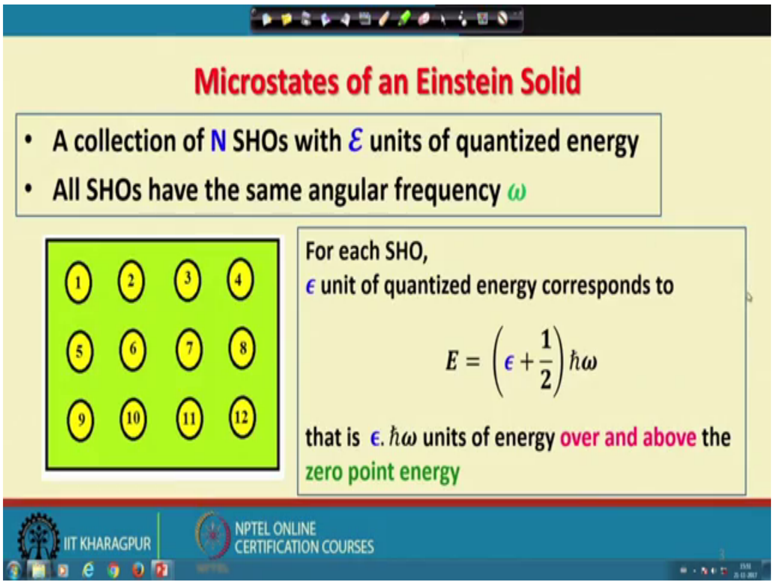

Now, let us see, what the microstate of an Einstein solid is. So, what is an Einstein solid, an Einstein solid is a collection of capital N simple harmonic oscillators, which has a specific total amount of energy which is given as epsilon. So, I have a block of solid with a given volume that is comprised of capital N particles, each of these particles is a simple one dimensional simple harmonic oscillator. Each of them is characterized by an angular frequency omega. So, as you see, that these oscillators are being assumed to be distinguishable and they do not interact with each other. Any such solid that is being modeled, in this way is labeled as an Einstein solid, in the name of the celebrated scientist.

Now, let us see, if such a simple model of solid can give us some information regarding the possible microscopic states under the given condition that the solid is present at the given total energy. When we go back and have a look at what happens with any such system this is the typical pictorial representation of a block of solid, which is comprised of here as in this picture 12 simple harmonic oscillator which by our assumption of the model will have, all of them will have the same angular frequency omega and they do not know how much if the other exists in the sense that all of them behave as an independent simple harmonic oscillator and it is also important to note to that the total energy of the system is given by epsilon units of quantum quantized energies.

In order to understand what it means, let us go and try to see what I mean by these epsilon units of quantized energy. Now for every simple harmonic oscillator, let us say the energy is given by this epsilon plus half this whole thing into h cross omega. So, how much is the 0 point energy of this oscillator half h cross omega? Therefore, this system has epsilon times h cross omega units of energy over and above the 0 point energy.

Since all of the oscillators will be having a same 0 point energy having the same angular frequency, we can assume it to be the 0th level of energy and therefore, whatever energy the system possesses over and above the 0 point energy is what we are going to be interested in for the rest of our lecture.

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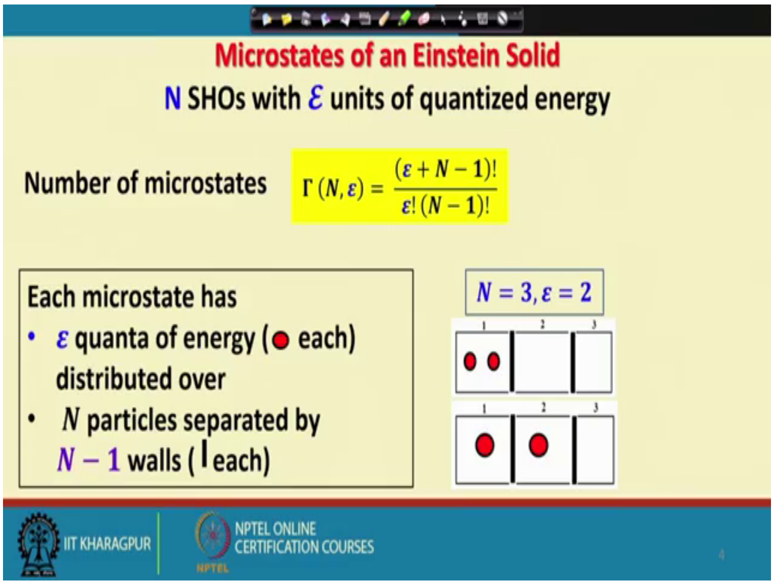

So, let us go and try and have a look at for this system, how do I find out the number of microstates, given that there are capital N simple harmonic oscillators with epsilon unites of quantized energies. We have already covered this and we now know that the number of microstates, they depend on the quant of energy available that is epsilon and the number of particles present in the following way.

Now, we have also discussed that what is the typical way of representing each of the microstate possible for any such system, so let us say that every quantum of energy the over and above the 0 point energy is represented in terms of a red pellet and I am going to use black walls to separate out all the particles, all the N particles that present in the given volume. So, how many walls would you require, to set N particles, obliviously N minus 1 walls.

So, if you look at the corresponding example of N equal to 3 and epsilon equal to 2 what I find is these are the some of the typical microscopic states, where and we will playing around with a total of 3 plus 2 minus 1, 4 symbols. In this case 2 pellets, 2 red pellets and 2 black walls and its possible too, then find out what is the number of microscopic states for different systems.

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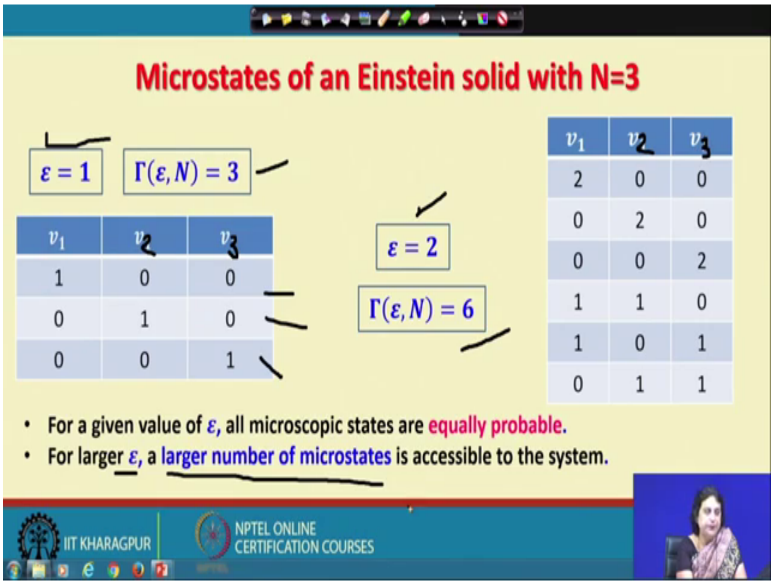

So, if I fix capital N equal to 3, then I find that for epsilon equal to 1, these are the possible microscopic states and correspondingly I would be able to say, that gamma the number of microscopic states that is associated with capital N equal to 3 and epsilon equal to 1 is 3, because I am taking into account 1, 2, 3 these 3 microscopic states.

Now, if I go further and I have 2 quanta of energy to be distributed to the system of 3 simple harmonic oscillators, these are the microscopic states possible. So, as you see that, how many states are possible corresponding to capital N equal to 3 and epsilon equal to 2. 1, 2, 3, 4, 5 and 6 therefore, I would write that the number of microscopic states associated with an Einstein solid where capital N is equal to 3 and epsilon is equal to 2, is 6.

Now, what do I conclude from these data, the conclusions we have already done and we have already learned to the basic principle. So, the first conclusion is, if a given value of epsilon is specified, then all the microscopic states are equally probable.

So, what it means is, if I look at this particular case, I see that for epsilon equal to 1, I have 3 possible microscopic states. Now, is there any reason why one of the, this is v 2 and this is v 3. So, why any of the microscopic states are going to be any different from each of the other, the answer is, we do not have any information on that. So, a priori we are going to assume that all the 3 microscopic states are equally probable.

Now, if I consider this case with this case what is the difference between the 2 total energies, this is the higher value of energy and then you say that look at the number of microscopic states possible, here I have 3 microstates possible, at the higher value of energy, I have 6 microstates possible. So, I conclude, that if I increase the amount of energy available that is for larger values of epsilon, I will lend up with a larger number of microstates for a given value of epsilon.

Once we have revised what we have done before, then we can go ahead and ask this question that what is going to happen to the number of microstates, when I have a very large number of particles and sufficiently large amount of energy.

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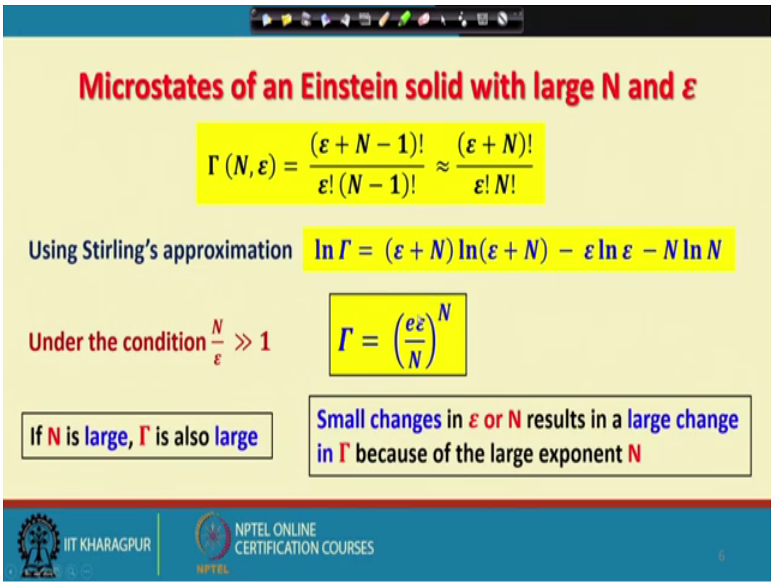

So, let us next address the question of microstates of an Einstein solid with large N and epsilon, so once again I see that, this is an equation that we have seen before and now since capital N is so large I can say that capital N is approximately equal to N minus 1. Obviously, you understand that if you take 1 away from a number like 10 to the power of 20, it does not make any difference; rather you would say that it is I am still in the range of 10 to the power of 20. So, that is the reason why we can write an equation like this.

Now, once we have done this, I understand that whatever number I am dealing with these are very large numbers. So, I can use the Stirling's approximation, do a little bit algebra and this is what I am going to get. I have got the natural logarithm of gamma that is the number of microscopic states possible for this Einstein solid in terms of the large number of simple harmonic oscillators that constitute this solid and the epsilon the quanta of energy available to the system over and above the net 0 point energy of the system.

Now, if I consider this condition, that N by epsilon is much much greater than 1, then it is possible to rewrite this expression as gamma equal to this number to the power of n. Now as you see that in this case, this is a limiting behavior where I have both N and epsilon large, but here I have assumed that well, the amount of energy available is such that this ratio will always be greater than 1. In that case this algebraic simplification is possible and I leave it you to work it out as to how you arrive at this algebraic simplification.

Now, what is it tell us, it tells us that if capital N is large, in that case gamma is also large and if I introduce small changes in the values of epsilon or N there will be a very large change in gamma and that is because I have this very large exponent over here, which is controlling the how the number of microstate is going to respond to the small changes in either epsilon or capital N.

So, what we have learn from here already is that, for a given value of total energy of the system and Einstein solid which is comprised of capital N non interacting distinguishable simple harmonic oscillators, they are going to have a very large number of microscopic states associated with that given value of total energy epsilon.

Now, I am going to take up, some very specific example which is an extension of this and this extension is to describe, still once again we are going to talk about a block of solid, but now this solid is a composite Einstein solid.

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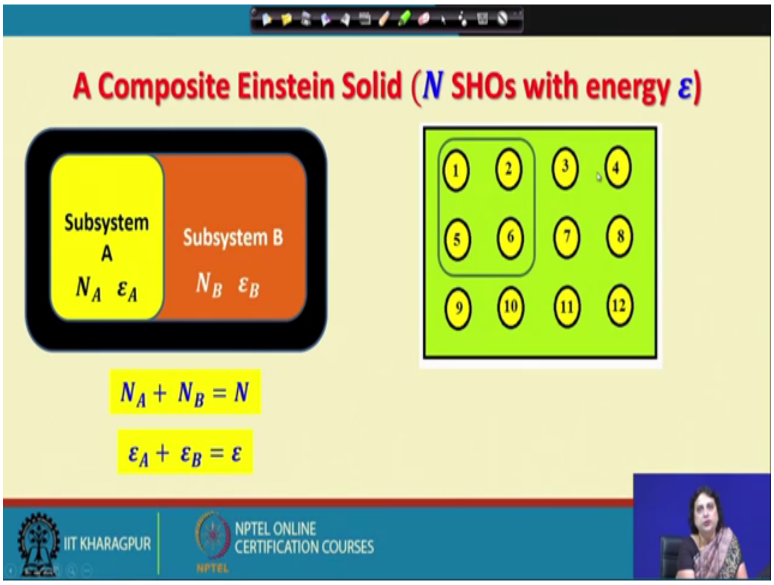

So, let us have a look at how it, what exactly the system that I am considering here. So, here I have this big black box, which tells me that I have a constant volume, in which the solid is placed and the solid now is separated into two compartments, one is what I call the subsystem A and the other one is what I call the subsystem B.

Now, in this case I still assume that, there are a total of capital N simple harmonic oscillators and the total energy of the solid, the block of solid which is the sum of the subsystems A and B that is epsilon, but now just because I separated the entire system into two subsystems, I need to describe the number simple harmonic oscillators that I have in the subsystem A and the associated quanta of energy that they possess.

And similarly I also have N B as a number of simple harmonic oscillators present in the subsystem B with energy epsilon B. So, as you understand that since the entire block of solid I am going to maintain at a constant energy volume and number of particles, I must be having these two mathematical condition satisfied that the number of simple harmonic oscillators in the subsystem A and the number of simple harmonic oscillators in the subsystem B must add up to the total number of simple harmonic oscillators. Similarly the energy of subsystem A, plus energy of subsystem B must add up to the total amount of energy available to the system.

So, pictorially if I consider the example, that I have already taken what I have done is I have just picked up these 4 oscillators and put them in the subsystem A and the rest of the 8 oscillators that I can see here, they now belong to subsystem B. So, in this case N A is equal to 4 and N B is equal to 8.

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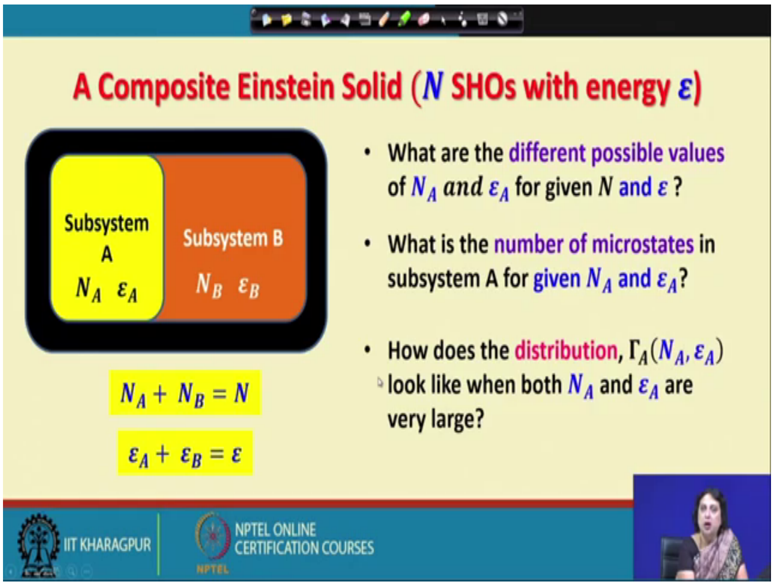

Now, the next thing that we ask here is under these 2 restrictions what are the possible values of N A and epsilon A, if we have specified the total number of simple harmonic oscillators and the total amount of energy available to them, we would also like to ask the question, what is the number of microstates in subsystem A, if you assign epsilon A sum value and N A sum value, but please remember that these two values are always controlled by these two equations and finally, we would like to know how does the distribution of the number of microscopic states in the subsystem A look like when both N A and epsilon A are very very large.

So, you see that we are trying to understand the same issues that we raised, when we talked about the spin systems. So, let us take these questions one by one and try to see if the conclusions, that we derived in the case of the spin system is general enough and applies to the simple harmonic oscillator system as well.

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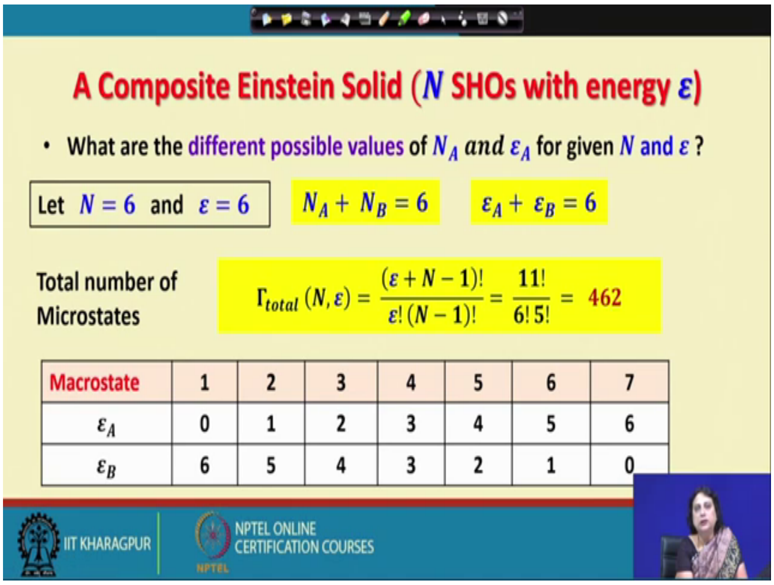

So, let us, next have a look at, what happens to a composite Einstein solid that has, that is comprised of capital N simple harmonic oscillators, with a total energy of epsilon and the question that we ask is, what are the possible values of N A and epsilon A.

Now, as you see that in this case I am going to assume that capital N, for the sake of simplicity is equal to 6 and I am also going to assume and I am going to leave this fixed. Now let me assume that epsilon is equal to 6, when the sum of the 2 energy is the epsilon A and epsilon B are fixed, then what I find is that I must now the 2 constraint equations that I have must look like epsilon A plus epsilon B equal to 6 and N A plus N B equal to 6.

So, it is just an example, where I am now going to calculate the total number of microstates possible. As you see that, here I can very easily find out for the entire solid the total number of microstates and that you can very easily show it to be 462, this is something that you already know. But what is knew here is as follows, these 462 microscopic states these are now describing not all the capital N simple harmonic oscillators together, because of the introduction of the subsystems A and B now I have different macro states possible corresponding to each of the subsystem.

Now, since let me say that here epsilon A, plus epsilon B is all a constant. Therefore, I can vary only one variable like epsilon A from a minimum permissible value to a maximum permissible value and the values of epsilon B will automatically be defined in accordance to this equation. So, how many such macro states are possible for the subsystem A, as you see that the subsystem A has 7 different macro states.

So, under the condition of a constant number of particles and the given value of a total energy of 6 units, you can see that these 7 macro states are possible and there will be many microstates possible for say, epsilon A equal to 0 or may be some other microscopic states associated with epsilon A equal to 5. If I sum up all the possible microscopic states for each of these macro states, I am going to retrieve this number 462.

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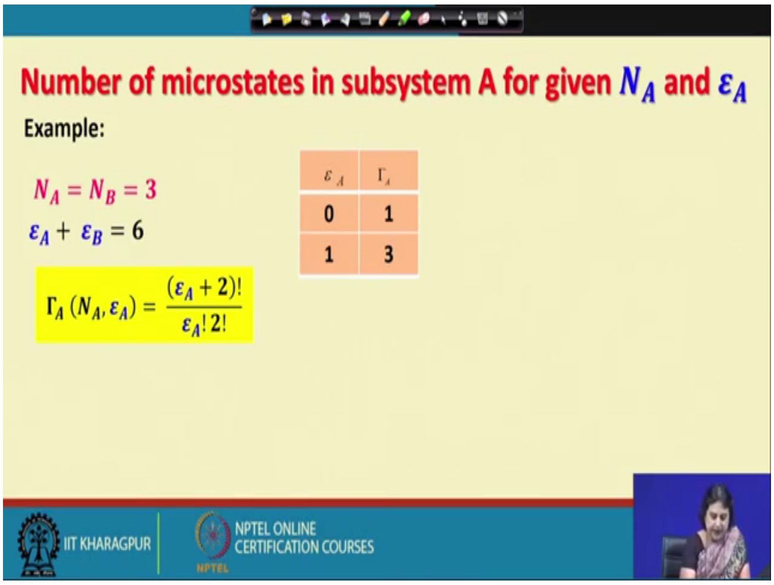

But here, there is something more that I need to consider about this composite solid and that is as follows.

So, in this example we very easily can say, that well the number of microstates for the subsystem a can be obtained by saying that well this is epsilon A plus 2 factorial divided by epsilon A factorial plus 2 into 2 factorial. Now I can generate the different microscopic states, there are 7 of them by changing the value of epsilon A keeping in a fixed at 3, if I do that, then this is what I would get. So, for epsilon A equal to 0, what is the number of microstates associated with gamma A here, given N A is equal to 3, that is 1. So, epsilon A equal to 1, gamma A .

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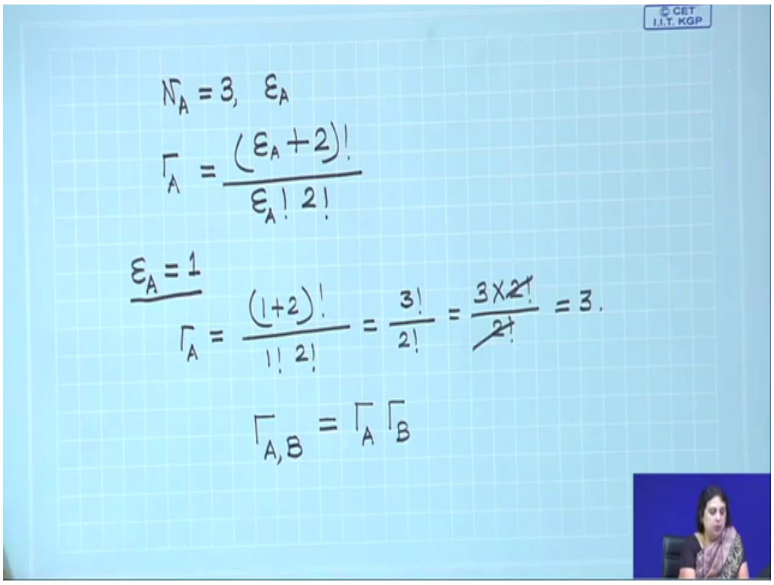

Well we can work it out very easily, that if N A equal to 3 and epsilon A is some given value, we have already seen that gamma A that is going to be given by epsilon A plus 2 factorial divided by epsilon A factorial, then 2 factorial.

Now, I have taken epsilon A is equal to 1, if that is so, then gamma A is going to be 1 plus 2 factorial divided by 1 factorial into 2 factorial. So, this is 3 factorial divided by 2 factorial and the answer is obviously, 3. So, this way I can find out what the different number of microscopic state is associated with a given value of epsilon.

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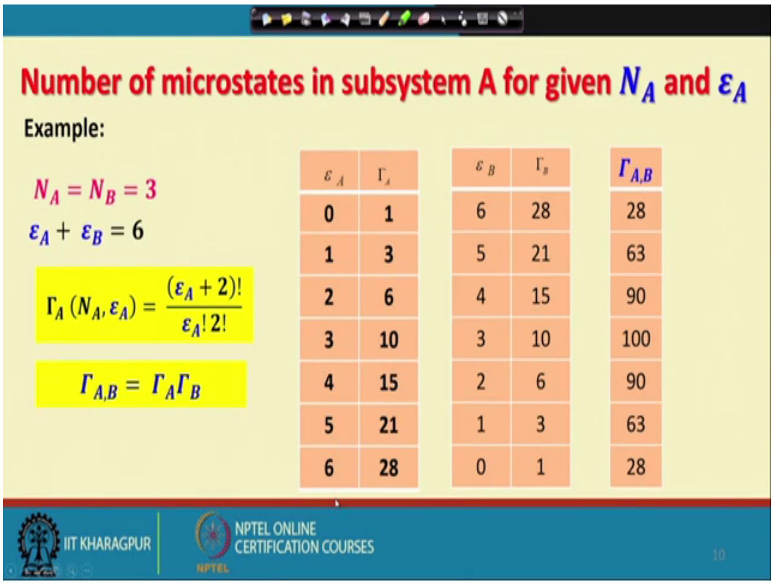

ε_A	Γ_A	ε_B	Γ_B	$\Gamma_{A,B}$
0	1	6	28	28
1	3	5	21	63
2	6	4	15	90
3	10	3	10	100
4	15	2	6	90
5	21	1	3	63
6	28	0	1	28

So, now we can generate all possible values of epsilon A and estimate the corresponding values of gamma A. So, the final value would be epsilon A is equal to 6 and correspondingly the number of microstates possible with N A equal to 3 is 28. Now once I know this, then obviously, I can generate the corresponding values of epsilon B and the associated number of a microscopic states, now this is a symmetric system, as a result of it I have assumed that N A is equal to N B is equal to 3.

And therefore, I see that with complimentary energy value skipping the total energy equal to 6, I get when gamma A is equal to 1, then gamma B is equal to 28 because epsilon A and epsilon B they add up to 6 and the same happens the equivalence situation happens if I look at the other extreme.

Now, at this point the other quantity that is of interest is the total number of microscopic states possible, which tells me what is the number of microscopic states associated when subsystem has energy epsilon A and the subsystem B has the energy epsilon B. Now since A and B, these are 2 subsystems which are not interacting with each other, then following the principles of probability, I would say that this is the conditional probability that the subsystem A has some specific value of the energy epsilon A and at the same time the subsystem B has an energy equal to epsilon B and since they are independent of each other, therefore, I must be having gamma A comma B that is equal to gamma A into gamma B.

So, using this principle we can now find out what these values are. So, now, what I have here is the complete description of all the 7 macro states associated with the subsystem A and the corresponding number of microstates associated with each of them. So, you see that for the lowest value of epsilon A, I have gamma A B equal to 28 and the highest value of epsilon A, once again the gamma value is 28. So, what happens in between is the gamma A B value goes on increasing from 28 to 63, 90,100 and then falls of exactly in the same way to 28.

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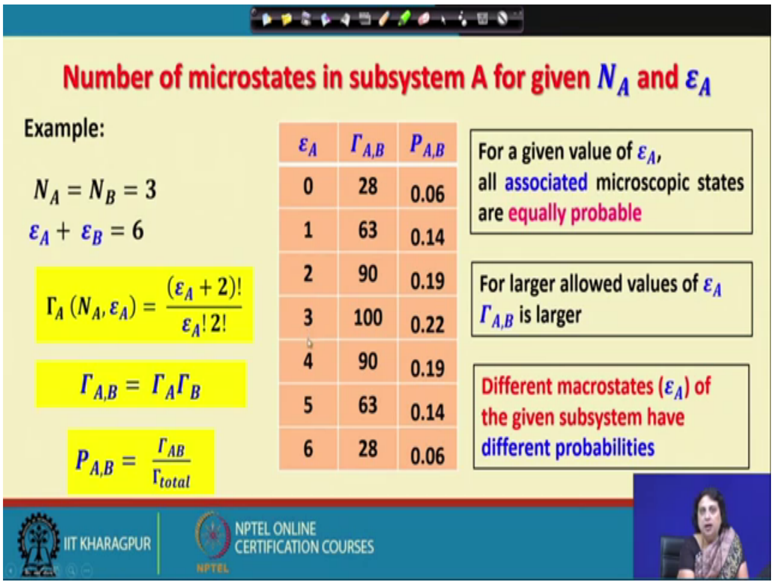

Now, if I go little further I understand that in this system, I know what the total number of microstates are and therefore, if I divide this gamma A B by gamma total what I am going to get is, what is the probability that I find the Einstein solid the composite Einstein solid in such a state that, subsystem A has energy epsilon A and subsystem B has energy epsilon B and there independent of each other and this is given like this.

So, once again following the behavior of gamma A B, what you find is that the probability A B that increases as you go towards the middle of the range of epsilon A and then it falls off. So, basically what we learn here is as follows. For a given value of epsilon A, I understand all associated microscopic states are equally probable.

For example, if I fix my epsilon A at epsilon A equal to 2, how many microstates are available to the system? 90 microstates are available to the system and these 90 microscopic states are equally probable under the given condition.

Now for larger allowed values are epsilon A gamma A B is larger. So, if I go from 2 to 3 as I see, that the number of accessible microscopic states under such condition this is increasing and finally, I understand that there are 7 macro states possible to characterize the subsystem A and what are the probabilities associated with each of them? As you seen in this case the probability is 0.06, it increases as I go to epsilon A equal to 2 and finally, it reaches a maximum and then it tapers off.

So, this means that different macro states, which are characterized by the energy values epsilon A of the given subsystem A, they have different probabilities. Please remember, that these are the probabilities of observing the subsystem A with the total value of epsilon A for energy, given the condition that epsilon A plus epsilon B must always maintain a constancy condition.

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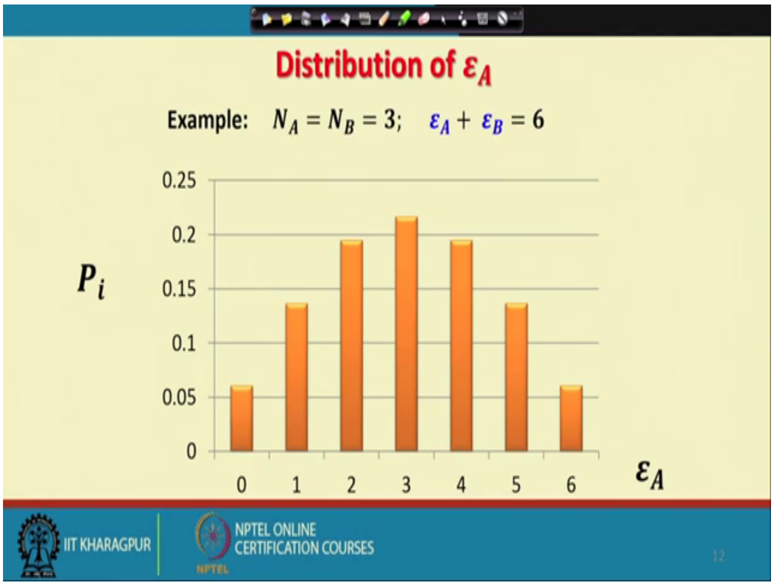

So, this is the distribution of epsilon A as you see here and I can very easily indicate that epsilon A equal to 3 is associated with the highest number of microscopic states and hence this is the most probable state. In the next lecture we are going to see the effect of the large values of N and epsilon on this distribution and conclude what happens in realistic systems, where the number of particle is very large and even the amount of energy available may also be relatively large.

Thank you.