Introduction to Molecular Thermodynamics

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Lecture - 12
Microstates of a System (contd.)

We will continue our discussion on the microstates of simple harmonic oscillator, and we are talking about the solid which is known as the Einstein solid; that is comprised of capital N distinguishable non interacting one dimensional simple harmonic oscillator for which the number of oscillator present is large, and there is a large amount of energy available to it.

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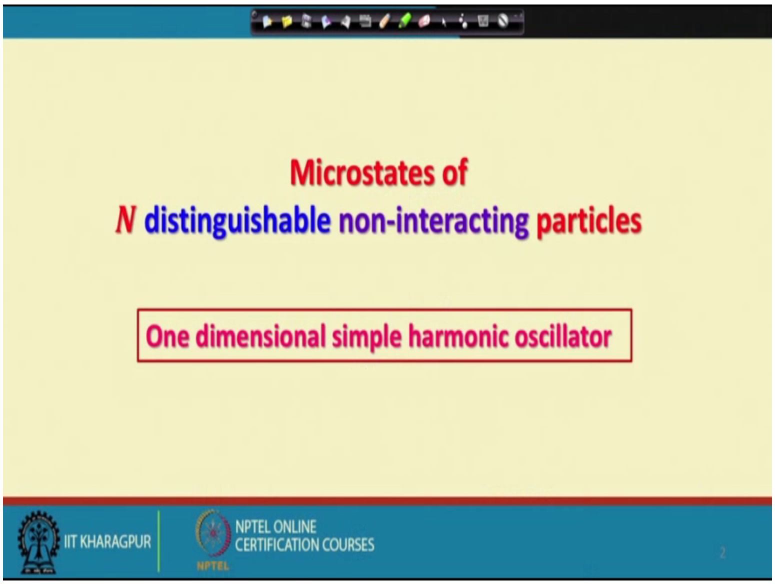

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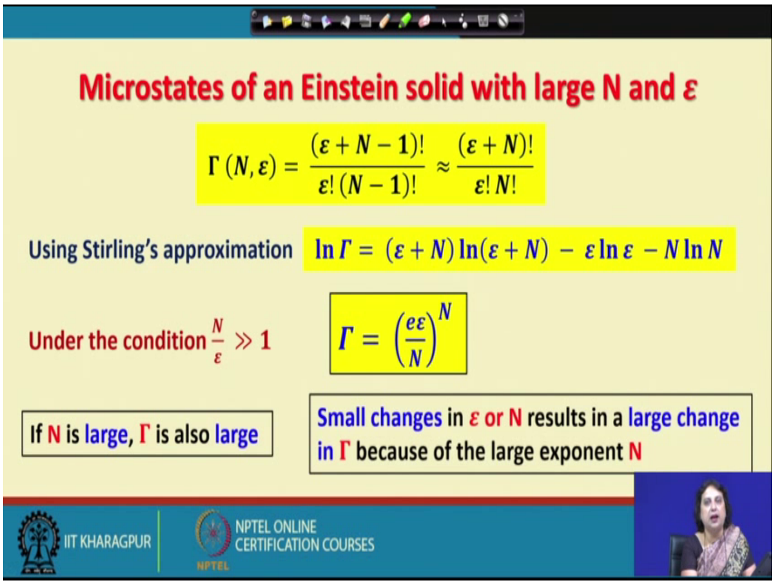

So, we have already seen how to calculate the number of microstates of an Einstein solid, when this particular condition N by epsilon is taken to be N by epsilon much greater than 1, and we find that there will be for each value of epsilon gamma is also very large for a given large number of simple harmonic oscillators.

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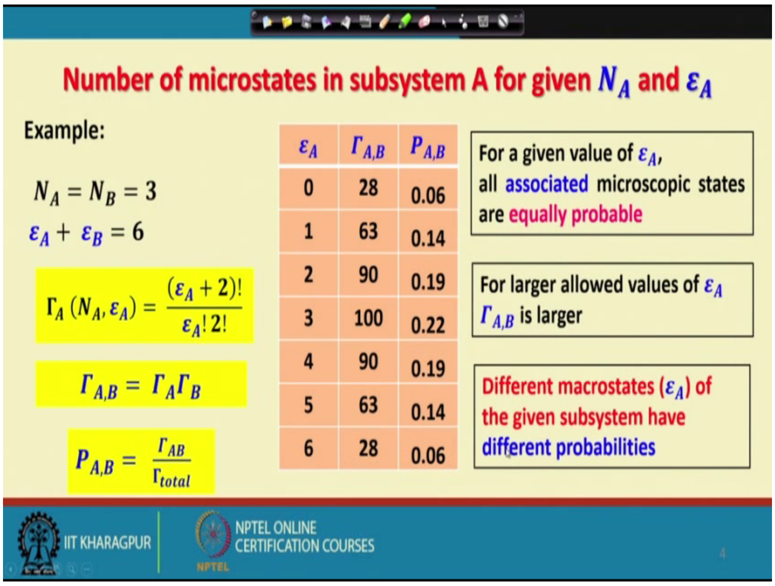

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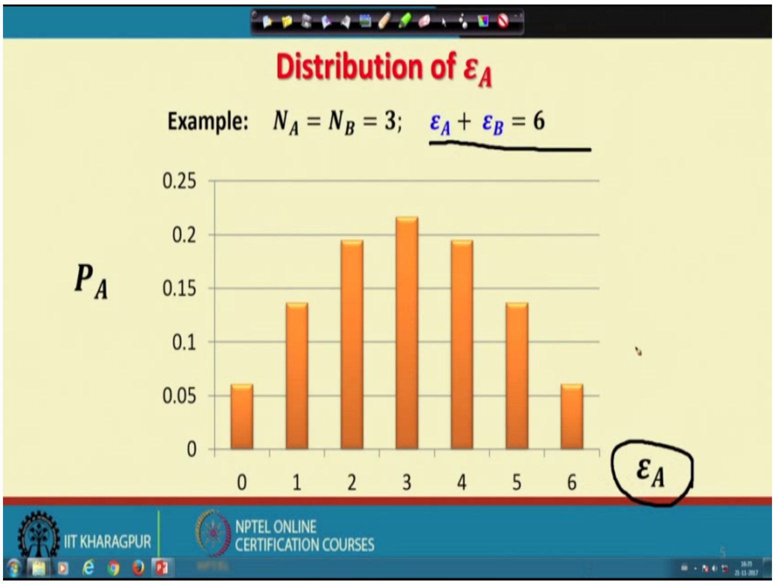

Now, when we talk about the composite solid; we have already seen that there is a set of conclusions that we can derive, and these are summarized here in the slot. So, what we are doing here is along the x axis, I am plotting the energy value that is accessible to the subsystem a and this I denote as epsilon A.

So, under the given condition what are the different values of epsilon A possible; that is decided by this particular relation. Therefore, I understand that epsilon A can take up minimum value of 0 to a maximum value of 6, and corresponding to each of which they has been able to find out the number of microscopic states, that are associated with a given value of epsilon, and then we have also seen how to get the probability of observing that particular value of epsilon A as by dividing the total number of microscopic states gamma total.

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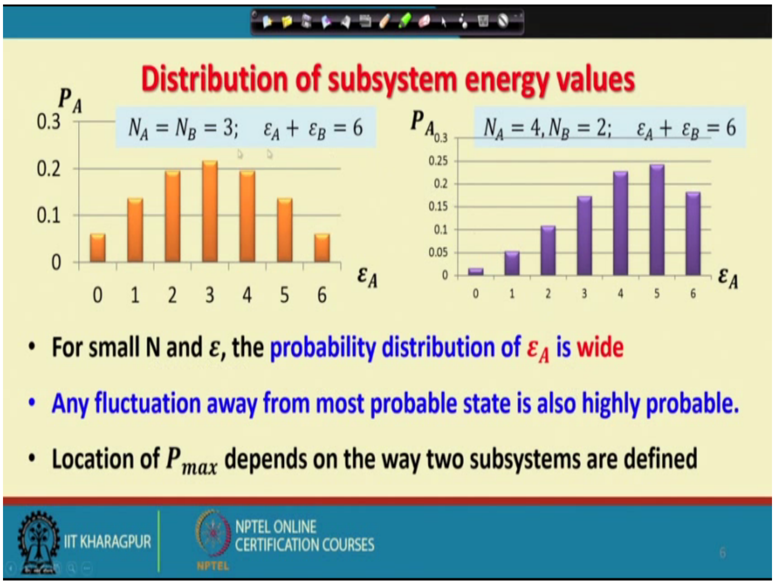

So, from this kind of a picture, then let us now move forward and try and have a look at. What happens during the distribution of subsystem energy values. Please remember that in the first example that I have taken. I have already taken N a equal to N b equal to 3, and I have kept this energy summation of energy constant at some value 6, and this has given me a symmetric distribution about the maximum that appears at epsilon A equal to 3.

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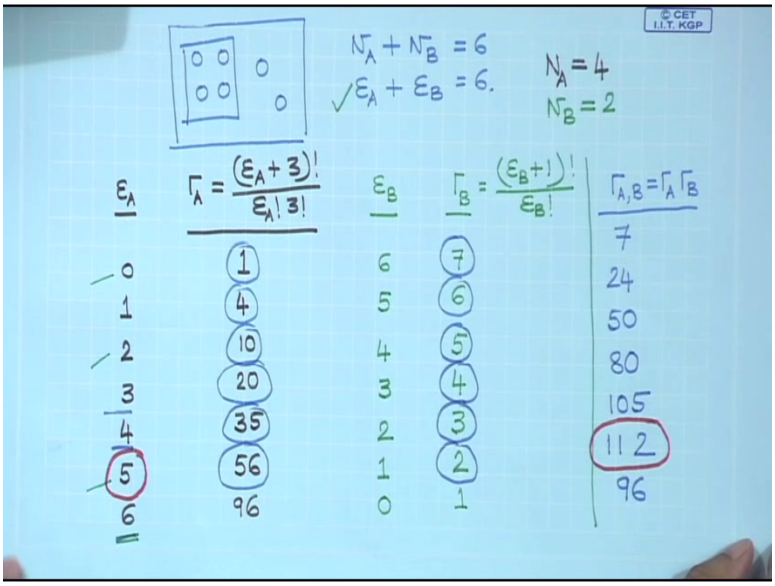

Now, let me have some other case study, where I am taking N a equal to 4 N b equal to 3. So, basically in the previous example in the entire block of the solid, I have now in the subsystem a, how many oscillators 1, 2, 3, 4, oscillators. And in the subsystem b, I have only two oscillators. This; obviously, satisfies the relation that N a plus N b is equal to 6 as required.

Now, I must also satisfy this condition that epsilon A plus epsilon B is equal to 6. Then my question is, if I want to repeat this calculation of the distribution function for possible epsilon A values, what should I be doing. I understand that in this case, I must be having a table as we have prepared before.

So, the first thing that I will write down is epsilon A, the values of epsilon A. For every value of epsilon A given that N a equal to 4. I must be having gamma a given by epsilon A plus 3 factorial divided by epsilon A factorial into 3 factorial clear. Now when epsilon A is equal to 0, what is gamma a. I put epsilon A equal to 0s, that gives me 3 factorial divided by 3 3 3 factorial divided 0 factorial into 3 factorial; obviously, the answer is 1

Now, if I have epsilon A equal to 1, it is very easy to show that the corresponding number of microstates is going to be 4, when epsilon A is equal to 2, the corresponding number is 10. For 3 you will be able to show that the number is 20 for 4 epsilon A equal to 4, the number turns out to be 35.

Now, for epsilon A equal to 5, the number turns out to be 56. And finally, for the highest admissible value of epsilon A which is 6, it is possible to show. Well that is a pretty trivial, that I will be having 6 plus 3 9 factorial divided by 6 factorial into 3 factorial, and the answer is 96. So, corresponding to each of these 7 macro states father composite solid, I am going to have corresponding energy values of epsilon B and the associated number of microscopic states gamma b.

Now, what is gamma b here, it is given that N b is equal to 2, and therefore, gamma b is going to be equal to epsilon B plus 1 factorial divided by epsilon B factorial. So, a quick calculation tells me that corresponding to epsilon 0, epsilon A equal to 0. What is the value of epsilon B. That must be 6, satisfying this equation for epsilon A equal to 1, the corresponding value is going to be 5.

Now, corresponding to epsilon B equal to 6 gamma b is going to be 7, because 6 plus 1 7 factorial divided by 6 factorial that gives you 7. Now for 5 gamma b is equal to 6 then epsilon A is equal to 2 epsilon B has to be equal to 4, and there are now 5 microscopic states associated with gamma epsilon B equal to 4. For this case I will be having the energy of the subsystem b equal to 3 and correspondingly, the number of microscopic states is going to be 4. And finally, we have the number 2 denoting the total energy and the corresponding number of micro state is 3.

Then here when epsilon A is equal to 5 the allowed value of epsilon B is equal to 1 and I have gamma b equal to 2, and then epsilon A is equal to 6. The only possible value of epsilon B is 0 and correspondingly the number of microscopic states is 1. Now the final question that we wanted to know was, what is the number of the total number of microscopic states associated with each of the macro states.

So, that we can very easily find out as gamma a into gamma b for every value of epsilon. So, what I find here. Here if I take the multiplication of these two numbers, I find that this is 7. If I now multiply these two numbers what I get is, 24 .Similarly epsilon A equal to 2 would correspond to a number of 50 obtained by multiplying 5 with 10 for epsilon A equal to 3. I will be multiplying 20 with 4 giving me a total of 80 microscopic states.

Now, for epsilon A equal to 4. Once again I will repeat this exercise and find that this number is 105 epsilon A equal to 5; that is the sixth microscopic state. I am going to multiply these two numbers, and get 112. And finally, for epsilon A equal to 6 I get 96 microscopic states. Now of these as you see that the maximum number of microscopic states is 112, and this is associated with the case where epsilon A is equal to 5.

Now, when I look at a system like this and go back and plot the resultant probability, what I will find is, as follows see here on this side of the slide, I am highlighting the case, where N a is equal to 4 N b is equal to 2, and the total energy epsilon A plus epsilon B as before is equal to 6.

So, what is the difference between the first system and the second system. Here there was an equal distribution of oscillators in the two subsystems, and here I see an unequal distribution of oscillator between the subsystems a and b. So, what is the result that you see in the distribution function of P as a function of epsilon A. Please note that along the x axis I have the same numbers from 0 to 6, but what I find is that the instead of a symmetric curve now I have an asymmetric curve. The common feature is still I have a maximum here. The maximum appears here corresponding to epsilon A equal to 5. The maximum appears here for the system one, where the it appears at epsilon A equal to 3.

Now, the question is, is it possible for me to predict given the definition of the subsystem to find out where these maximum, this maximum in the distribution will appear; that is actually quite possible, but before that, before going into that, let us now make the essential observations from this kind of picture first.

If I have a small value of N and a small finite value of epsilon as in these two cases. The probability distribution of epsilon is fairly wide. As you see that there is non0 probability associated with all the possible values of epsilon A, and therefore, we conclude that any fluctuation away from the most probable state, is also highly probable. As you see that the maximum probable state is associated with a probability of slightly more than 0.2 here.

Once again look at the two states on the two sides. This is epsilon A equal to 4 and epsilon A equal to 2. They are slightly less than 0.2. So, any fluctuation away from the location of the maximum, like epsilon A changing over to epsilon from 3 to 2 or 3 to 4 is nearly as much possible as the observation of epsilon A equal to 3.

even when I have an asymmetric system, I see that here the maximum is closer 2.25, but the nearby states like epsilon A equal to 4 or 6, or even epsilon A equal to 2. They have a substantial probability. Therefore, the system has a non0 probability of residing not only in this state, which is epsilon A equal to 5, but also nearly equal probabilities of residing in the state epsilon A equal to 6 or 4, and would relatively lower, but finite non0 finite probability of being located in any of these states.

Now; obviously, we understand that the location of the maximum in the distribution function depends on how you define the subsystems. So, let us take an example and see how this thing can be worked out. So, the first thing that I show here, is that where does the maximum appear.

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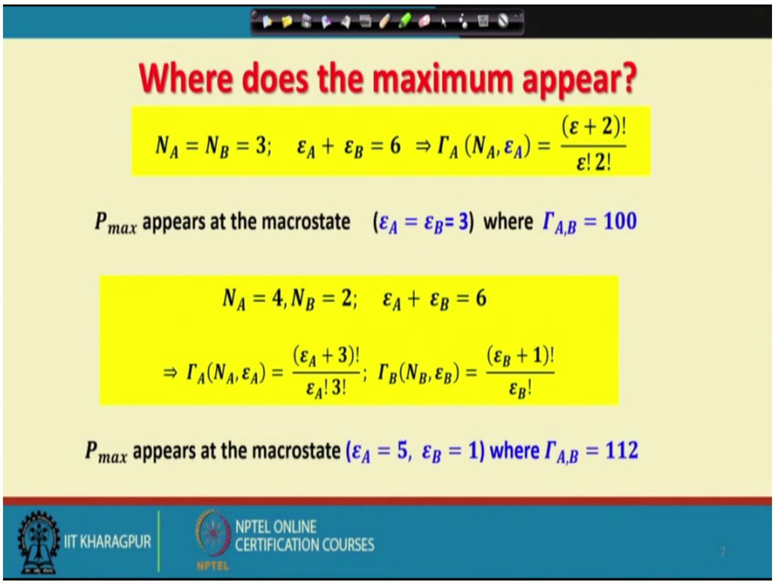

So, when you are given this the particular situation. We have already seen that the P max appears that the macro state, where epsilon A is equal to epsilon B equal to 3, and the associated number of microscopic states is 100.

But; obviously, this is not the case, when I am considering a very general case. So, in that very general case, can I predict what is going to be the position of the maximum in the distribution? This is what we are going to work on next.

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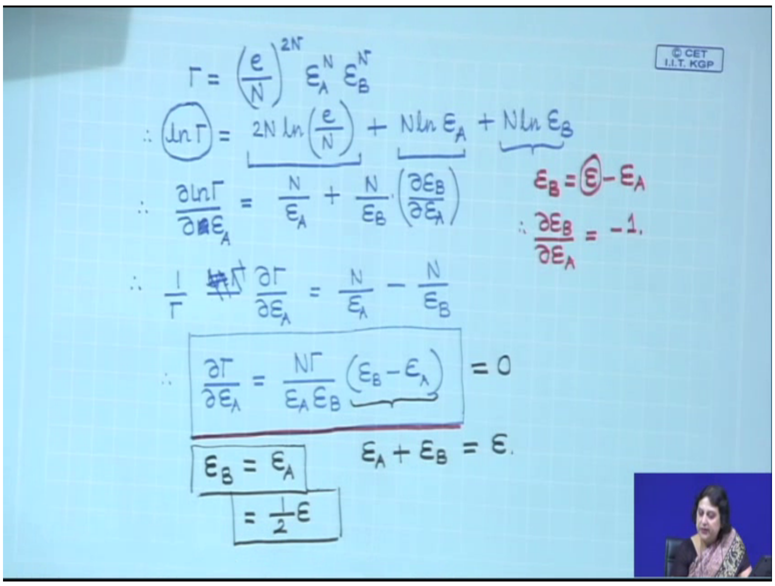

So, we have already discussed that gamma is equal to e by N to the power of 2 N epsilon A to the power of N and epsilon B to the power of n, and this is valid for capital N as a very large number, and N by epsilon in every subsystem is much greater than 1.

Now, let me take a natural logarithm on both sides and this leaves me with 2 N l n e by N plus N l n epsilon plus N l n epsilon B. Now I am expecting a maximum in this function with respect to epsilon A. In order to locate that maximum, the first thing that I do is, I take a derivative of del N l n gamma with respect to. Sorry del epsilon A if I do that; obviously, this particular term, it does not have any dependence on epsilon A. So, there will not be any contribution from this term.

Now, look at this term, this term, when derivative is taken with respect to epsilon A will give me capital N by epsilon n. Now what about this term, when I take a derivative with respect to epsilon A; so; obviously, I am left with capital N by epsilon B into del epsilon B del epsilon A. Now what is this quantity? By definition we know that epsilon B is equal to a constant energy epsilon minus epsilon A. Therefore, I can say that del epsilon B del epsilon A is going to be equal to; obviously, minus 1, under the condition that the total energy epsilon is the constant. Therefore, using this I can now simplify my expression as 1 by gamma l n gamma 1 by gamma. Sorry del gamma del epsilon A; that is given by N by epsilon A minus N by epsilon B.

See if I do a little bit of algebra, what I am going to get is as follows. I am going to get this as N gamma divided by epsilon A into epsilon B and epsilon B minus epsilon A. So, now, I know that if gamma is the number of microscopic states, associated with the condition that subsystem a, a has a total energy of epsilon A, then the first derivative of gamma with respect to epsilon A is given by this relationship if that is. So, in that case we can very easily say. Well if there is a maximum somewhere in gamma with respect to epsilon A, the first derivative finish at that value.

So, let us look for the condition, when this quantity is equal to 0. Now this quantity can become equal to 0, only when this is equal to 0, which means that only under the condition, where epsilon B is equal to epsilon A; now I know that epsilon A plus epsilon B, this is equal to some constant energy value. Therefore, when each of the subsystem energies become equal, I must be having this value to be equal to half of epsilon.

Now, using this we can go back and we can find out, even in the case of the asymmetric situation what would be the position of the maximum. We have already shown that the maximum appears at epsilon A equal to 5 and epsilon B equal to 1, where gamma a b equal to 112 ok.

So, whatever I have been showing you here, the question is, where does the maximum appears. I find that when I have the symmetric case, the maximum appears at epsilon A equal to epsilon B equal to 3, but when I have an asymmetric case, we have already seen that the P max appears at the macro state, where epsilon A is equal to 5 epsilon B equal to 1, and the associated number of microscopic states is equal to 112.

Now, next thing that we are going to discuss is, what happens if unlike the cases that I have discussed, still now with N and epsilon become very large.

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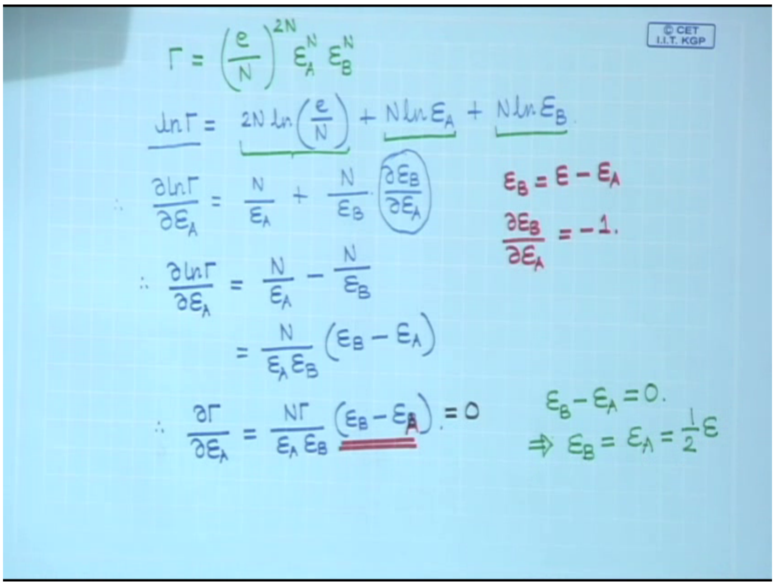

We have already seen that in the such case the number of microscopic states is going to be given by e by N to the power of 2 N into epsilon A to the power of N into epsilon B to the power of n. So, if that is. So, in that case I can try and find out that for very large values of capital N and epsilon, where this peak in the probability corresponding to the different macro, states the different values of epsilon A will appear.

In order to estimate this, what we are going to do is as follows. I am going to take a natural logarithm on both sides, that gives me this simple expression, that all of you must be able to get, if you try it out on paper. Now I am looking for a maximum in this function with respect to epsilon A, and therefore, I will be taking a derivative of this function with respect to epsilon A. And when I do that, I realise that this part is independent of epsilon A. And hence it will not have any contribution to the derivative. So, I will have to concentrate on these two terms.

Now, the first term will give me capital N by epsilon A and the second term will give me capital N by epsilon B into del epsilon B del epsilon A. So, in order to understand what this derivative is, I must know the value of this, but we already know that epsilon B is the total energy epsilon minus epsilon A. Therefore, I must be having del epsilon B del epsilon A; that is equal to minus 1. If that is so, then I can very easily write that del l n gamma del epsilon A that is equal to the simple expression, which I can further modify and say that this is equal to another simple algebraic expression.

So, finally, I can say that del gamma del epsilon A; that is equal to capital N gamma, and a function of the two energies epsilon A and epsilon B. Now if this function gamma has to exhibit a maximum. I must be having this quantity become equal to 0, and under what condition will this first derivative become equal to 0. It can happen this is epsilon B minus epsilon A, that can happen only when this becomes equal to 0. So, at the maximum I must be having this condition satisfied that epsilon B minus epsilon A, that must be equal to 0, but; that means, that I must be having epsilon B equal to epsilon A, or in other words each of these energies must be half of epsilon; that is because these two must sum up to be the total energy epsilon.

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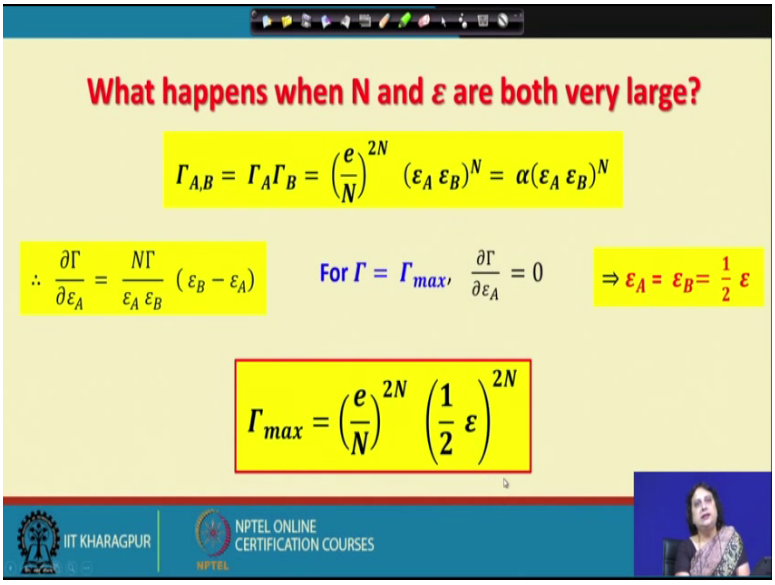

So, this is exactly what we have represented over here, and that tells us that the condition of having a maximum would be, when the two subsystem have equal energies, and if that is so, then the question is, can I then find out what this a number of microscopic states associated with. This maximum that is fairly simple, because I know that the gamma a b that is given in terms of epsilon A and epsilon B; so, I just put back the values of epsilon A and epsilon B at the maximum and this is what I get.

So, as you see that the maximum number of microscopic states associated with the number of microscopic states associated with the maximum probable state is a very large number.

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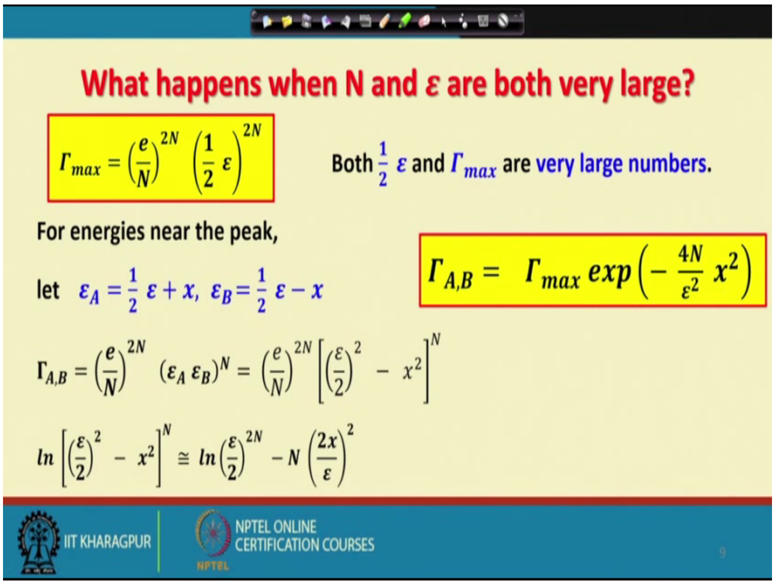

So, how do I understand as you see that gamma max is going to be a very large number, why that is, because when epsilon is the large number epsilon by 2 is also a large number, and when epsilon by 2 is a large number N is a large number. Therefore, gamma max consequently is going to be a very large number ok.

Now, the next question that we ask is, what happens to the energy values near the peak. So, we are going to work this out very simply. So, let us assume that.

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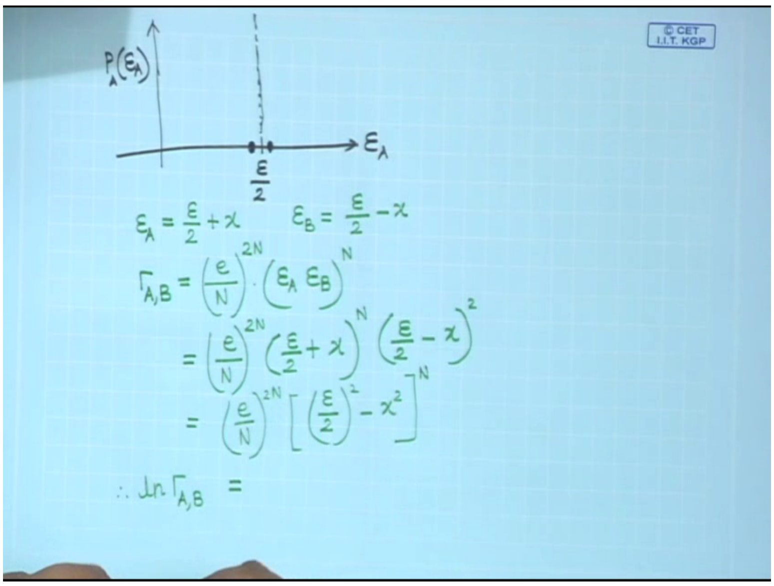

I am looking for. This is the position of the maximum which is epsilon by 2, and I am plotting epsilon A, and probability of this subsystem a having this energy of epsilon A. I know that there is a maximum located over here ok.

Now, I am trying to look at energies which are fairly close to this maximum energy value epsilon by 2. Now let me say that I have a situation where epsilon A is equal to epsilon by 2 plus x. So, what is going to be the corresponding value of epsilon B. Epsilon B is going to be equal to epsilon by 2 minus x. So, that the two of them add up together and give you the total energy epsilon. Under such circumstances what happens. So, basically if x is positive, you are somewhere here. If x is negative you are somewhere here. You are very close to the location of the maximum in the probability distribution.

So, now the consequence of this is that if I want to find out the number of microscopic states associated with the small deviation away from the maximum, I find that this is going to be e by N to the power of 2 N into epsilon A into epsilon B to the power of n. And if I put these two expressions back here, what I find is. This is going to be like epsilon by 2 plus x to the power of N into epsilon by 2 minus x to the power of n. Therefore, this number now looks like, as if it is epsilon by 2 whole square minus x square raised to the power of n.

Now, if I take a log on both sides natural logarithm, then l n of gamma a b; that is going to be something like what you can very easily find out. Now if I do that, then what is the resultant expression. The resultant expression has been shown here. I understand that the log of this number, this is going to be approximated as log of epsilon by 2 it to 2 N raise to the power of 2 N minus capital N into 2 x by epsilon whole square. And if that so happens, then it is very easy to conclude that gamma a b is nothing, but gamma max into exponential of this term.

Now, what kind of. So, this is basically the distribution of the number of microscopic states gamma, when you are looking at the distribution in terms of ah, some quantity x that denotes departure from the equilibrium. Not equilibrium departure from the location of the maximum, and this is the Gaussian distribution which are rapidly falls of two 0 as we go away from the location of the maximum.

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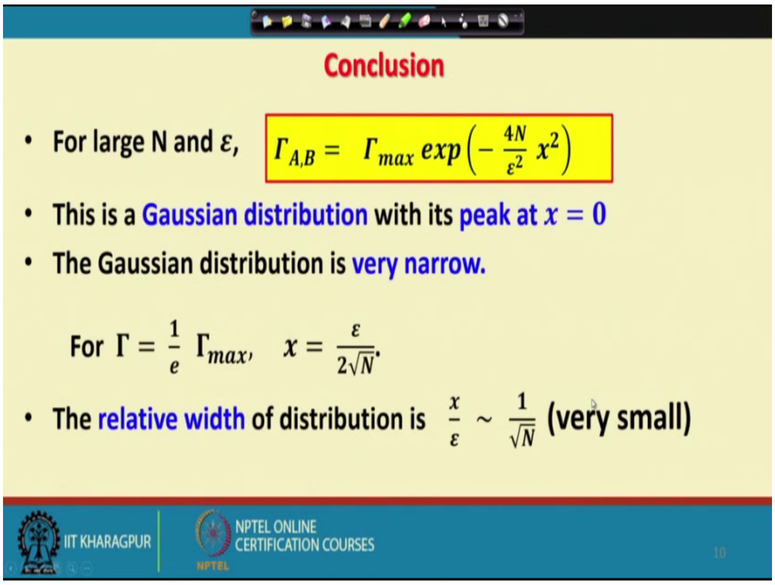

So, the conclusion from all these statements are as follows. We first see that for very large N and gamma the distribution function gamma a b or equivalently gamma a b by gamma total is a Gaussian distribution, with its peak present at x equal to 0. Now this Gaussian distribution is very narrow, because as you see the, that when the number of microstates reduces to 1 by e of the maximum value x is this quantity. So, the relative width of the distribution is proportional to 1 by root n, and for N very large, this must be a very small number, and therefore, this is what we have been able to understand from these lectures.

We have taken up two very different system. The first one the spin half particles, and the second one a collection of simple harmonic oscillators, which I labelled as the Einstein solid. In both the cases the basic learning goal was the same irrespective of the system that you have the microscopic model of the system that you have. What happens if you fix the total energy of the system, and have a very large number of particles present. In both the cases what we found is, that for a given value of energy, there will be a very large number of microstate associated with that particular value of energy, and each of these microstates are going to be equally probable; that is an assumption that I have mentioned

Now, if the system can exist in different total energy values, then what I found is that different total energy values are associated with different number of microscopic states, and if I look for all possible values of this total energy, I can obtain a distribution function either discrete or continuous to represent the probability of observing one particular value of the energy. When I make measurements of, on the system. If I can measure energy of course, or some other quantity related to it

What we found is that, if I look at all possible values of the energies. Usually if I am having a non-interacting system. There is a pronounced maximum present, and the distribution is very sharply picked for very large number of particles about this maximum. So, that concludes our discussion on the different properties of the microscopic states. So, from the next lecture onwards we are going to use this ideas, and see how from the collection of the ensemble of these microstates. Under different conditions we can derive useful thermodynamic information regarding the system.

Thank you.