Introduction to Molecular Thermodynamics
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Lecture - 08
Microstates of a System (Contd.)

Welcome.

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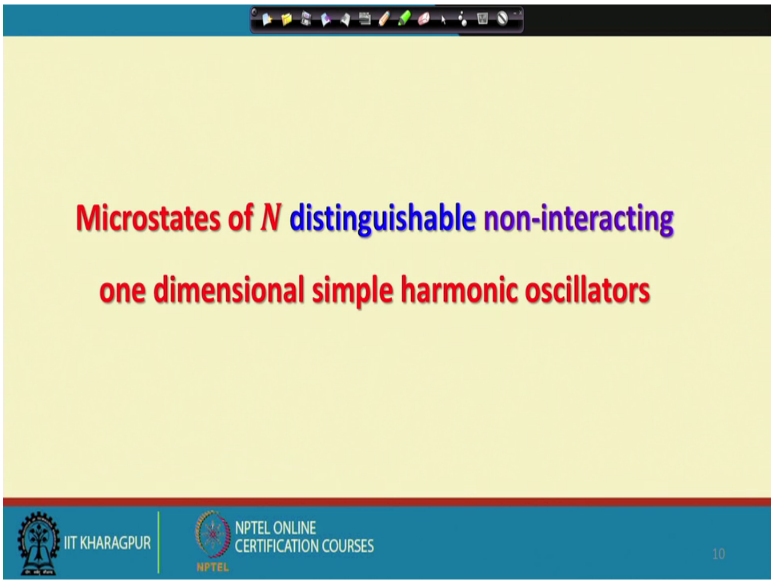

We will continue our discussion on the Microstates of distinguishable non-interacting particles by considering now. A system which is comprised of capital N simple harmonic oscillators and each of these oscillators is present in 1 dimension, and we are trying to find out the number of microscopic states that are allowed for a system like this.

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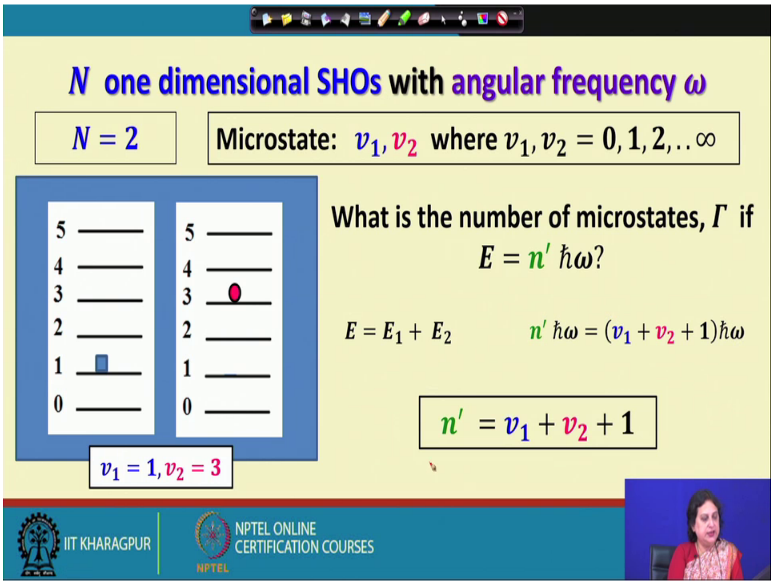

So, once again we will start by looking at the case, where there are only 2 simple harmonic oscillators present. And each of these simple harmonic oscillators we have already seen that they are characterized; they are microscopic state is characterized by a single quantum number.

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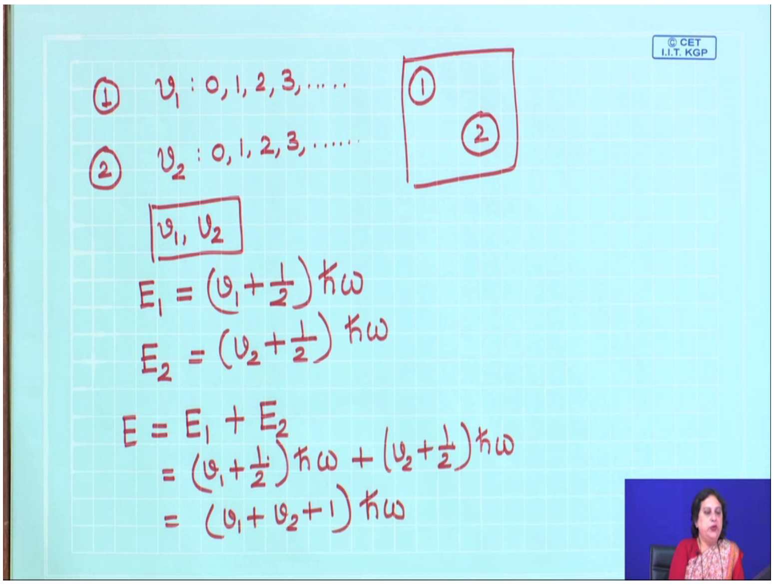

Let me call that the particle 1 is characterized by a quantum number v 1 and the particle 2 is characterized by a quantum number v 2. Since these particles are not interacting with each other in a system where both of them are present 1 and 2 are present, they will still behave as if they are on their own, but for the entire system you can still have v 1 varying from 0 and taking up integer values up to infinity. And similarly we 2 can also take up integer value starting from 0 and going from 1 to 3 and so forth.

Now the question that we ask is, for a composite system that is constituted by 2 such simple harmonic oscillators then, how do I define the microscopic state? The microscopic state obviously now we will be defined in terms of 2 quantum numbers: v 1 and v 2. So, let me have an example of how to define the microscopic state in terms of this quantum numbers. So, this is a typical microscopic state.

So, all you have is a constant volume as shown by this blue box, and here I have highlighted the microstate of oscillator 1 and the microstate of the oscillator 2. Therefore, on the whole the microscopic state of this composite system of 2 oscillators 2 1 dimensional simple harmonic oscillator will be given by v 1 equal to 1 and v 2 equal to 3.

Now the question that I ask here is; what is the number of microstates gamma if the total energy of the system this particular system is equal to something like n prime into h cross omega. Now what is h cross omega? I have already mentioned that each of the simple harmonic oscillators, they are executing this simple harmonic motion with the same angular frequency omega. If that is so, in that case the energy values that are permitted for the particle 1 would be v 1 plus half into h cross omega, and the permitted values of energy for the particle 2 are going to be v 2 plus half h cross omega correct.

And now in the composite system the total energy E is nothing, but E 1 plus E 2 because they are not interacting with each other and therefore, we can say that well if I have a system like this then I must be having E is equal to E 1 plus E 2, and if the total energy is some number some integer n prime multiplied by h cross omega, then n prime h cross omega must be equal to this relationship and that is because I have written down explicitly what E 1 and E 2 are.

So, this is v 1 plus half h cross omega plus v 2 plus half h cross omega, and this will give you v 1 plus v 2 then the 2 halves will make 1 into h cross omega. So, that is how we have arrived at the relationship that I have shown you here. Now once I understand this therefore, I should bother about the limiting condition here on the possible values of v 1 and v 2 and that has been highlighted over here. What I find here is for given values of n prime it must be equal to v 1 plus v 2 plus 1. Now please try to understand although v 1 can itself vary from 0 to an infinite value.

V 2 can have an infinite number of options, but when they are together in the system and there is a restriction on the total energy whatever values v 1 and v 2 can take up is now dictated by the fact that a relationship like this exists. This means that although, I am supposed to vary v 1 and v 2 from their minimum value to their maximum value for all the infinitely possible numbers, here I should be able to vary only v 1 independently and v 2 the value of v 2 will always be decided by satisfying this equation. Now let us actually take one example and see that what would be the number of microstates, if I assign some specific value to n prime.

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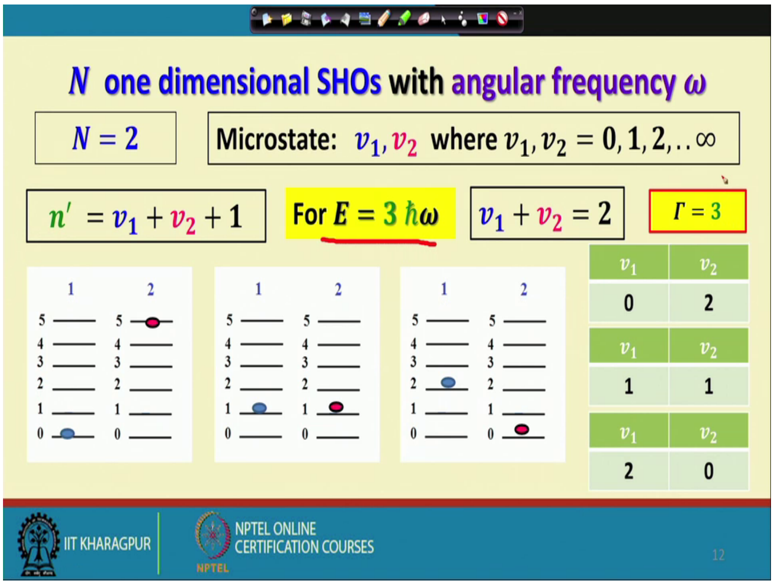

So, let us assume that n prime is equal to 3, and correspondingly I will be having the total energy of the system comprised of the 2 simple one dimensional simple harmonic oscillators would be 3 h cross omega. And in this case what I will be able to show is that then v 1 plus v 2 plus 1 is equal to n prime that is equal to 3 or in other words it is very simple to understand that here for all the microscopic states of the composite system having 2 simple harmonic oscillators, the v 1 and v 2 values would be such that they add up to 2. Now this tells you that well what are the different microstates that are possible now? The different microscopic states that are possible.

I can start with the minimum value of v 1 that is 0. So, what would be the corresponding value of v 2? That would be 2 minus v 1. So, that is 2 and this is a typical representation of what the corresponding microscopic state would look like; as you see the oscillator 1 is occupying the 0 point energy state, and the oscillator 2 is present corresponding to v 2 sorry this 1 should be here v 2 equal to 2. Similarly we can think about visualizing the pictures of other microscopic states. So, this is a microscopic state where oscillator 1 is present with v 1 equal to 1, and oscillator 2 is present with v 2 equal to 1 and the third possibility is that the first oscillator is having v 1 equal to 2, but the second oscillator is having v 2 equal to 0.

Now v 1 in itself could have been 3, but it cannot is it is not possible here because v 1 plus v 2 must be equal to 2 and both v 1 and v 2 are positive integers starting from 0. Therefore, the maximum value of v 1 is associated with the minimum value of v 2 and I have exhausted all my options. Therefore, in this case I can say that well the total number of microscopic states possible for E is equal to 3 h cross omega is equal to 3. Now as you see that this expression or this kind of argument is very very general. So, what we shall see next is, what is the normal of microscopic states that is possible when I have a general value n prime.

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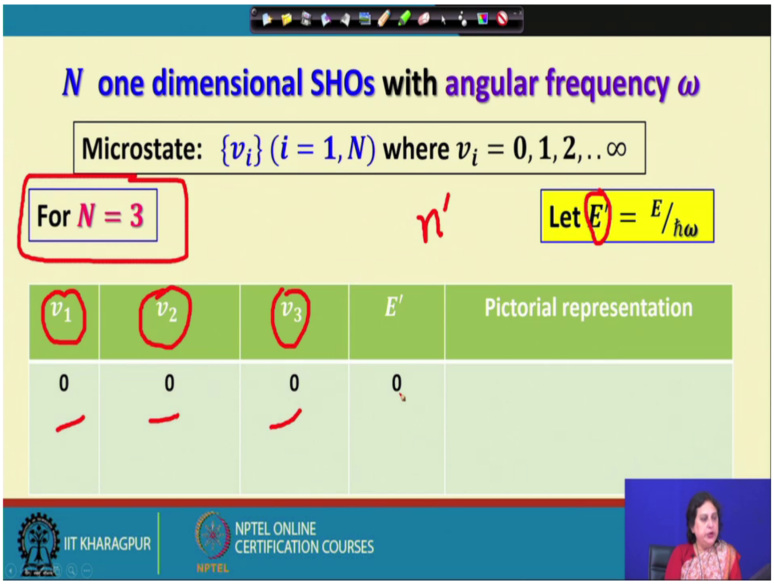

So, this is the typical case for this for capital N one dimensional simple harmonic oscillators, each having the same angular frequency omega. So, as you can see that let me denote here this E prime as capital E by h cross omega. So, I understand that a prime is going to be some number like n prime.

Now if I have a microscopic state, where the first particle if I have a system, where I have 3 one dimensional simple harmonic oscillators. So, this is the lowest energy state, that I can think of all 3 oscillators are present with their respective quantum numbers equal to their respective minimum values. And they add up to E prime which is nothing, but 0. Now I am going to have here a pictorial representation of the situation that is going to be useful for us in the next part of the discussion.

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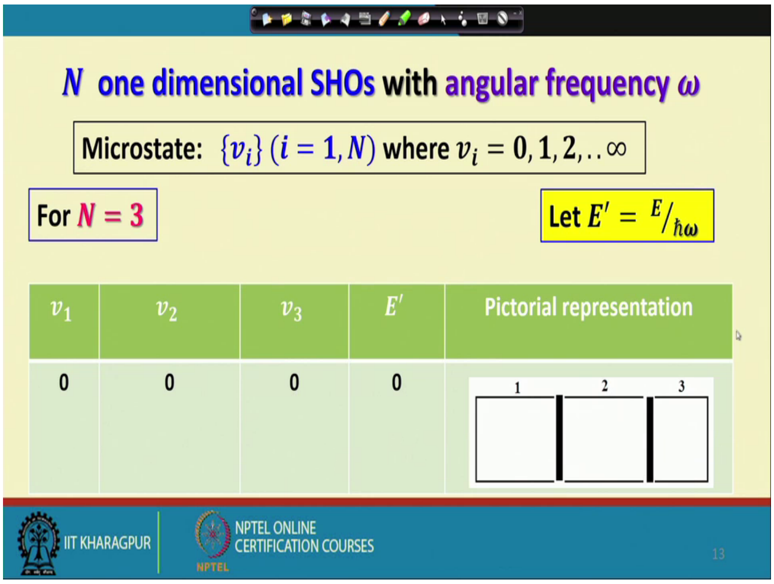

And here I have this as the typical representation of our microscopic state. I have a big box that I have subdivided into 3 compartments using 2 partitions. So, this is my partition number 1 and this is my partition number 2. And my idea is I am going to distribute 0 quantum of energy in each of these boxes, I mean when I distribute 0 quantum of energy I basically leave the boxes empty.

And therefore, this would be a typical representation of the microscopic state, where oscillator 1 has v 1 equal to 0, oscillator 2 has v 2 equal to 0 and oscillator 3 has v 3 equal to 0.

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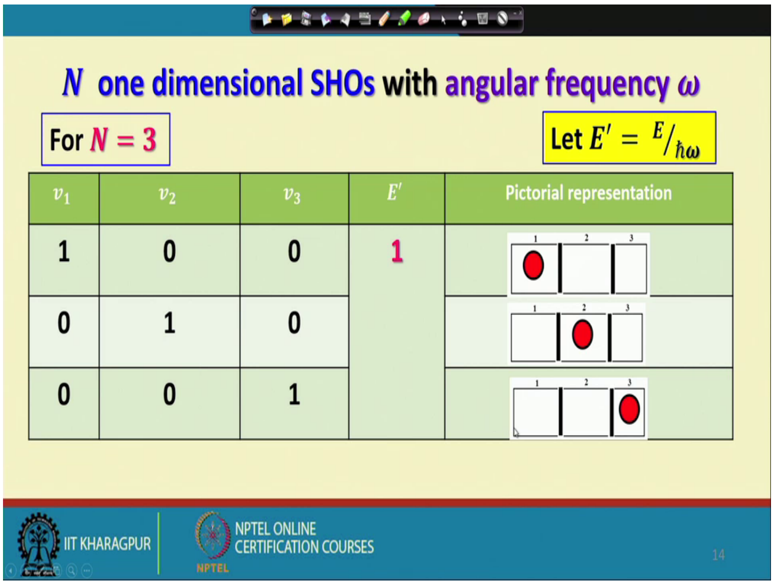

Now, let us consider the same system comprised of 3 one dimensional simple harmonic oscillator, but now with energy that is equal to 1, E prime equal to 1 means that E is equal to h cross omega. Now I can achieve this total energy in 3 possible ways while the second and the third oscillators remain in their corresponding lowest energy states I can have the first oscillator occupying the first excited state.

So, this is v 1 equal to 1. So, similarly in this case, can I have a pictorial representation of the corresponding microstate? And that would look something like this. So, now, you see we have the same box as before, that is separated into 3 compartments 1 2 and 3 corresponding to the 3 oscillators, but now only oscillator 1 has 1 quantum of energy and this has been represented here by putting this red ball in the sub compartment 1. If this is so, then can I say that what would be the typical macroscopic state corresponding the pictorial representation corresponding to this microscopic state.

This is going to look like this and that is simply because the energy quantum now is 1 quantum of energy has been given to this particular oscillator that is oscillator 2. Therefore, this red ball corresponding to 1 quantum of energy has been added to the compartment 2. Similarly this is a pictorial representation of the microscopic state that is characterized by v 1 equal to 0, v 2 equal to 0 and v 3 equal to 1.

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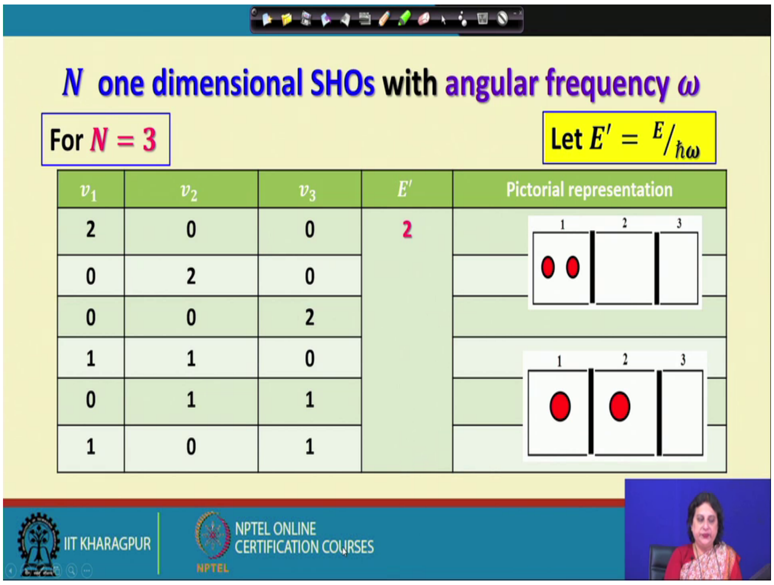

Now, that we have introduced this pictorial representation, let us move over and try to see what is going to be the pictorial representations for the case, where the E prime value is equal to 2. Please try to understand that here I am taking the 0 point energy as the 0 of energy scale and therefore, E prime is going to be just an integer.

Now, coming back what I find here is something very interesting. What I find here is here 1 2 3 4 5 6 there are 6 different ways in which the total energy of the system will be equal to 2. Now what is a typical pictorial representation of any of these 3 states? Here as you see that if I just take this state, here you will find that the first oscillator has 2 quanta of energy the other 2 oscillators do not have any quantum of energy assigned to them and correspondingly the pictorial representation of a typical system like this would be given by this picture. As you see that oscillator 1 has 2 quantum 2 quanta of energy associated with it.

And therefore, you can see that there are 2 red balls presenting the 2 quanta of energy in the compartment 1 allocated to the oscillator 1, these 2 do not have any energy I mean any additional energy other than the 0 point energy. And therefore, each red ball which represents the quantum of energy over and above the 0 point energy I do not have anything here. Similarly you can see that these 3 energy states are also similar. They are similar in this way that here you have 2 particles having 1 quantum of energy h, but the third particle does not have any. So, under such condition what you find is the pictorial representation of a typical microscopic state would look like this. So, here the particle 1 has one quantum of energy the particle 2 has another quantum of energy, and the particle 3 has none above over and above its 0 point energy.

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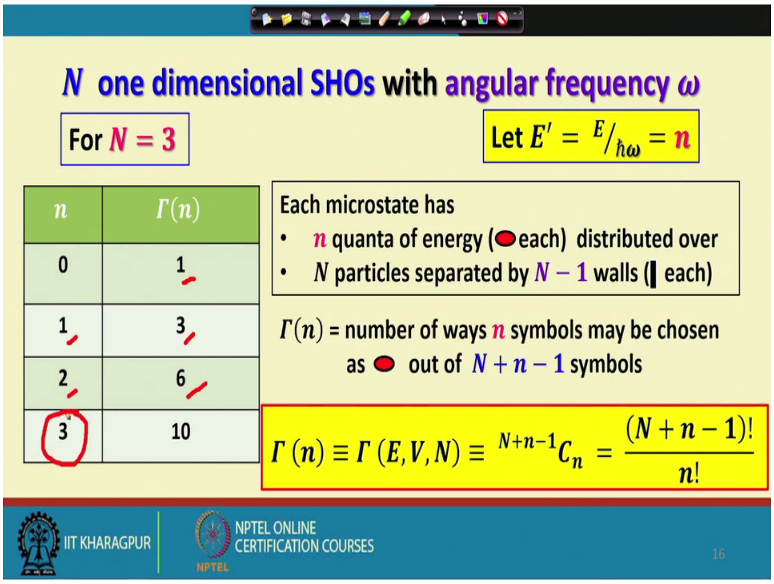

So, then the question is as we can see as before that the number of microscopic states.

They depend on the total amount of energy that is available to the system. So, here I find that well we have already seen when n is equal to 0, gamma is equal to 1; when n is equal to 1 gamma is equal to 3, and when n is equal to 2 gamma is equal to 6, and what is it going to be when a small n is equal to 3, which means if small n quantum or quanta of energy has to be distributed amongst all the microscopic states, how many microscopic states are possible? The answer is 10.

So, the question is well you can go on drawing the different microscopic states like this for example, one of the microscopic states, when I am going to distribute 3 quanta of energy amongst 3 oscillators, these are going to be like this.

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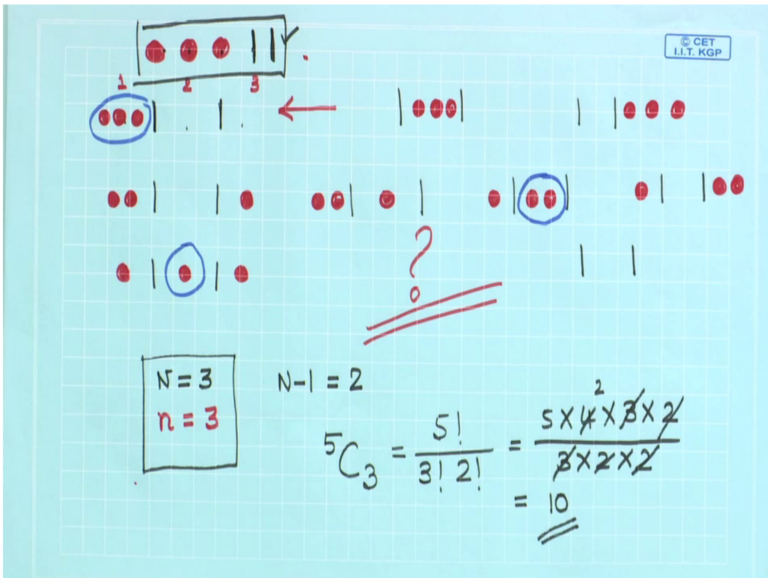

I can have the system I have 2 such separations giving me 1 2 3 sub compartments for the 3 particles. So, 1 possible macroscopic state is this all the 3 quanta are present for particle 1, no energy for energy quantum available for particle 2 or 3. I can also have the situation where particle 1 has 2 quantum of energy and maybe particle 3 as 1 quantum, particle 2 does not have it or it may so happen that each of the particles will have one one quantum of energy each.

As you see in each of these cases first of all you can have you can build microscopic states like this in at least 3 different ways, what are the different ways that you can do it? The other 2 states are going to be like this. So, the particle 2 is going to have both the all the 3 quantum of energy and the particle 1 and 3 would not have anything or else you will have the particle 3 having all the 3 quanta of energy right the next. So, I have 1 2 3 such states, where the all the quanta of energy available is has been taken up by 1 simple harmonic oscillator

Now, about this you can have other microscopic states, like this one or you can have something like this or you can have something like this. Is there any other possibility yes I think I am leaving out onemore possibility and that is I will leave this to you to figure out what are the other possibilities. So, that is a homework, but the point that I would like to highlight over here is this each microstate in my representation has small n quanta of energy when each quantum of energy is represented by a red pellet like this, and these are going to be distributed over capital N particles and these n particles are separated by capital N minus 1 balls, and each of these balls are represented by a black vertical line like this. In this case if the numbers for a general case capital N and small n what is gamma n? Gamma n is the number of ways in which small n symbols may be chosen as the pellets out of a total number of capital N plus small n minus 1 symbols available. So, basically while constructing this kind of a picture, what you were playing around with is 3 such balls and 2 such balls. So, what is the total number of particles? The capital N is equal to 3 how many quanta of energy do you have.

That gives you small n and small n is equal to 3 here, chosen arbitrarily. Now the number of such separators how many are there that they are given by capital N minus 1 which is equal to 2. So, what are the total number of symbols that you have? I have represented them here I have 1 2 3 4 5 I have a total of 5 symbols out of which I will have to choose 3 as pellets, and that can be done in a way that I will say that this would be 5 C 3 and this can be evaluated as factorial 5 by factorial 3 into factorial 2. So, that is 5 into 4 into 3 into 2 divided by 3 into 2 into 2.

So, the result is 10 and I leave it to you to figure out the different microscopic states, that are possible when you have cap capital N is equal to 3, small n is equal to 3 and the total number of microscopic states is equal to 10, I have already drawn quite a few. So, basically what I am doing is I have taken these 3 balls, and then taken these 2 separators and placing them either on one side or like this or like this. So, basically I am playing around with the total 5 symbols, that are present that are available to me and either fixing the position of the 2 walls, and distributing the 3 red balls separately.

And that is exactly how these number of microstates are counted, but you must also realize that in the case of the spins, in that case I if I wanted to find out the kind of pictorial representation I have not done that, but here this kind of count because there the counting was very easy. But here I am doing it simply because as you see that here there is no restriction as to how many balls or how many quantum of energy that you can put in a given box. Here I have put all the 3 here I have put only 1 and in this case I have put 2 two of them in 1 box. So, this kind of counting becomes useful when you have no restriction as to how many quanta of energy can be accommodated by each particle.

That means that each of the particles can have an infinite number of options as far as their own microscopic states are concerned. So, in this case we have learnt several new things and what we have learnt over here is if capital N is a large number, then gamma is going to be a very large number indeed. So, small n that can be a large number or a small number, but the microscopic states number of microscopic states, for a given system with a given quantum of energy is still going to be very large. And in that case once again you can use the stirling approximation to find out the natural logarithm of gamma. So, in conclusion what I would say is as follows.

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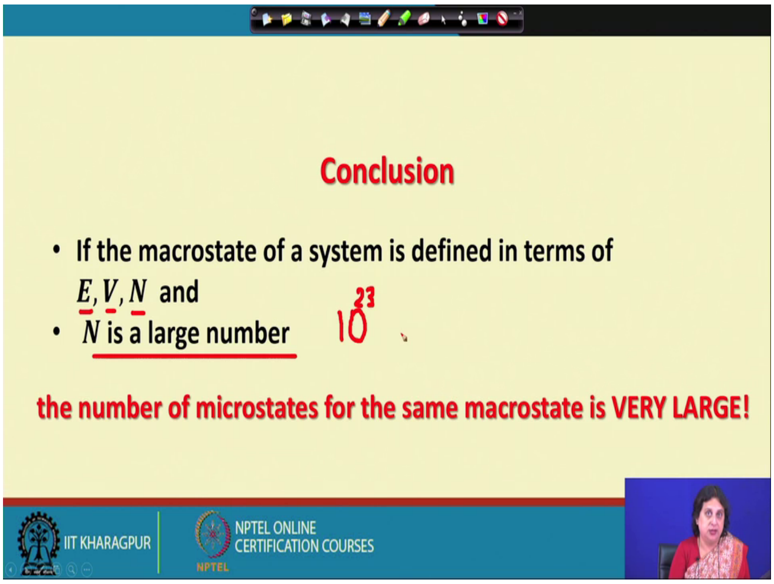

We have learnt now that if the macro state of a system is defined in by giving some specific constant values to its thermodynamic variables like the total energy v and the number of particles and f, and n is a very large number typically of the order of 10 to the power of 23. In that case for every macroscopic state there is a very large number of microscopic states possible for the given thermodynamic state of the system. So, that is a very important observation and provides us with the fundamental concept in developing the language of statistical mechanics.

In the next class we will see how statistical mechanics can be used to connect the microscopic states, to the thermodynamic properties of a given bulk system.

Thank you.