Introduction to Molecular Thermodynamics
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Lecture - 07
Microstates of a System (Contd.)

Welcome. We will continue our discussion on the description of microstates of a system in the today's class. So, we are talking about how to define microstates of a system in equilibrium, when the macro state has been defined in terms of the thermodynamic properties as we have seen before. And now we are going to talk about the microstates of distinguishable, non-interacting particles. As you would understand that the solution of the Schrodinger equation is going to be very difficult if we have a large number of interacting particles.

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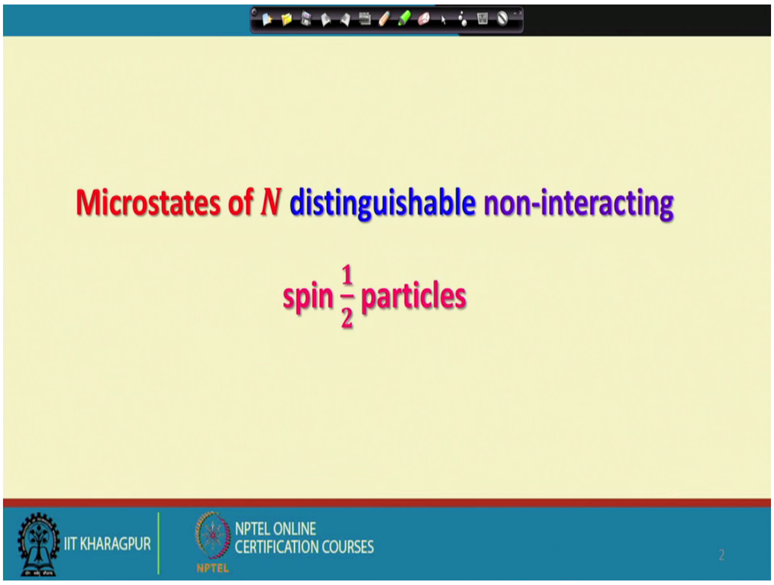

So, that is the reason why at the starting point, we have chosen to talk about distinguishable non-interacting particles, for which for each of which the solution to the Schrodinger equation is exactly known.

So, let us now go back and look at how to define the microstates for a system comprised of capital N particles, and these particles are distinguishable and non-interacting. We will talk first about the spin half particles, for which we have seen how to define the microscopic states when a single particle is present.

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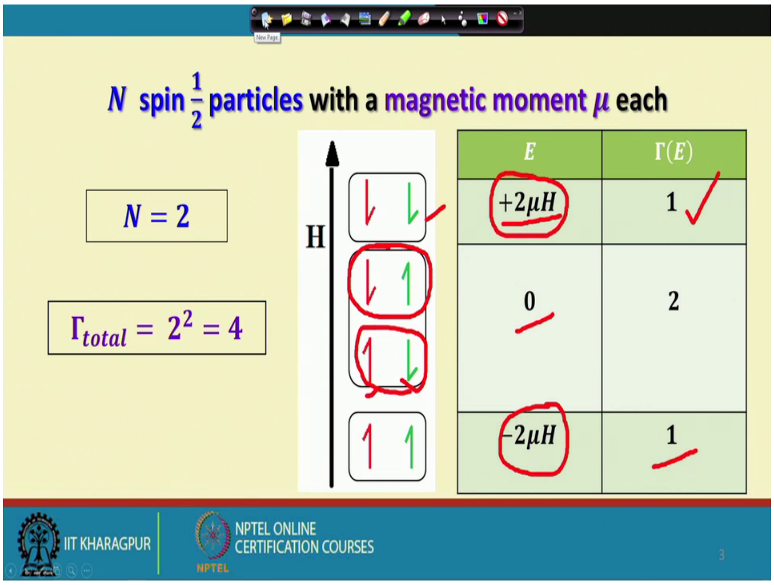

So, in today's lecture we will start by taking simple examples where we assign specific values of N. So, this is the case where N is equal to 2, and as you can see that I have a box in which I put 2 spins, their colours are different so that we know that they are distinguishable. And each spin can take up an up orientation or a down orientation with respect to the direction of an applied field that is embedded in this system. And these 4 states are the possible microscopic states allowed by the solution of the Schrodinger equation for any such system.

So, this is my microstate number 1 this is my microstate number 2, this is my microstate number 3 and this is my microstate number 4. So, the question that I would like to ask here is if I have 2 particles like this and they are not interacting with each other, and each particle can have 2 possible microstates, then what is the total number of microscopic states here? Just because we will assume that particle 1 that is the spin half particle 1 shown in red is independent of the spin half particle shown in the colour green, for each orientation of particle 1 I will have 2 orientations of particle 2; now how many orientations or microstates can the red particle have? 2.

So, the total number of microscopic states possible is 2 square which is 4, and these are the 4 microscopic states as defined for this system. So, here I am highlighting these microscopic states by grouping them in 3 different boxes, and what do I mean by this? This is what I mean when I say that if I look at only this microscopic state, each spin contributes minus mu H through the energy of the system. Therefore, since both the spins are aligned parallel to the direction of the field, the total energy of the system permitted by the solution of the Schrodinger equation is minus 2 mu H.

Now, the question is, when this energy of the total system comprised of these 2 spins how is minus 2 mu H then how many microscopic states are possible? As you see that there is only one such microscopic state possible. Now consider the other extreme case where I have the particle 1 having a down spin and particle 2 also having a down spin. So, each spin contributes plus mu H to the overall energy of the system, correspondingly the energy of the system is total energy of the system is plus 2 mu H, and there is only one way in which this energy can be attained and therefore, gamma E the number of microscopic states associated with this particular value of energy is equal to 1.

Now, consider the case where one spin is up and one spin is down therefore, while one the up spin gives you a contribution of minus mu H to the overall energy, the down spin gives you a plus mu H contribution to the overall energy, as a result the net energy corresponding to this microscopic state is going to be equal to 0. Now if that happens we can also argue that there is another microscopic state that can give the same energy where particle 1 is having a down spin, and particle 2 is having an up spin. Therefore, if we have a look at the microscopic states here even for this very simple system, where each particle has a finite number. Only 2 energy states possible in that 2 states possible in the microscopic level, in that case we find that different values of the total energy of the system comprised of these 2 particles these are different.

With this energy I have only one microstate, with this energy I have this microstate, but when the energy is equal to 0, I have a total of 2 microscopic states possible. Now if I look at the next level of complication by introducing an additional particle in this system.

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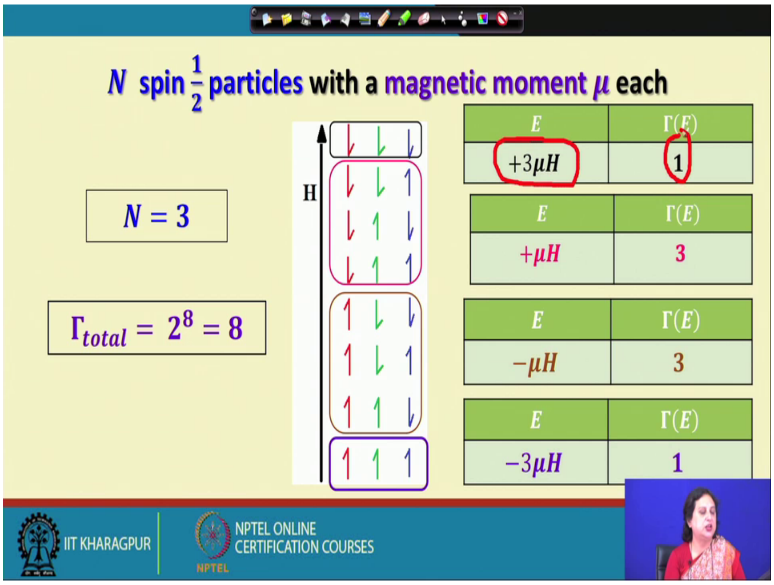

So, we will be dealing with capital N equal to 3 and these are the possible microscopic states that has been generated by assigning the up spin on the down spin state to particle 1, corresponding to each of which you can assign up spin and down spin to the particle 2 and corresponding to each of these combinations, you have 2 possible the orientations of particle 3 that is up spin and down spin.

Correspondingly the total number of microscopic states here is now given by sorry this is 2 to the power of 3, you have 2 states for each particle and you have 3 particles. So, this is 2 to the power of 3. So, there will be a total number of 8 microscopic states. And these microscopic states are tabulated here, this is the microscopic state having the lowest energy and this is the microscopic state having the highest energy. Now when we look at and these microscopic states, and try to group them exactly the way we have done in the last slide where I had N equal to 2 this is what I shall get.

I have a unique microscopic state, where you can see that you have 3 spins, all 3 of them oriented parallel to the direction of the applied field, and correspondingly the energy of the system is minus 3 mu H. And if you have 3 particles each of which can have either up spin or down spin in that case that is only one way, in which this kind of situation can be arrived at and therefore, the number of microscopic states associated with this energy value is equal to 1.

Now let us consider the next set where I have 2 spins up and one spin down. This obviously, would give me an energy value that is minus mu H that is because there will be cancelation of contribution from these 2 pair and only the positive only contribution will be made by the unbalanced spin oriented parallel to the direction of the field. It is possible to have 3 such micro states. And therefore, gamma corresponding to this mu value is equal to 3. The next set corresponds to mu H equal the E is equal to plus mu H. Now E equal to plus mu H tells you that now the microscopic states must be corresponding to 2 spins down and one spin up. So, that is exactly what is has been shown in this set of microstates and once again you see that there are 3 such microstates possible giving you the gamma value equal to 3.

And finally, when we talk about the highest possible microscopic states, what we find is when all the 3 spins are oriented anti parallel to the direction of the applied field, then the energy value turns out to be plus 3 mu H and there is only one such microstate, that will correspond to this energy value. So, as we see that the variety of the problem is going on increasing as we increase the number of particles.

So, the next question; obviously, that we can ask is if I have this general case of capital N spin half particles, each of which are distinguishable and non-interacting with the other spins present in the system. And the system is present under the condition that the total number of spins is constant, and they are present in a constant volume then the question that we pose is, is it possible to find out the total number of microscopic states associated with the system specification.

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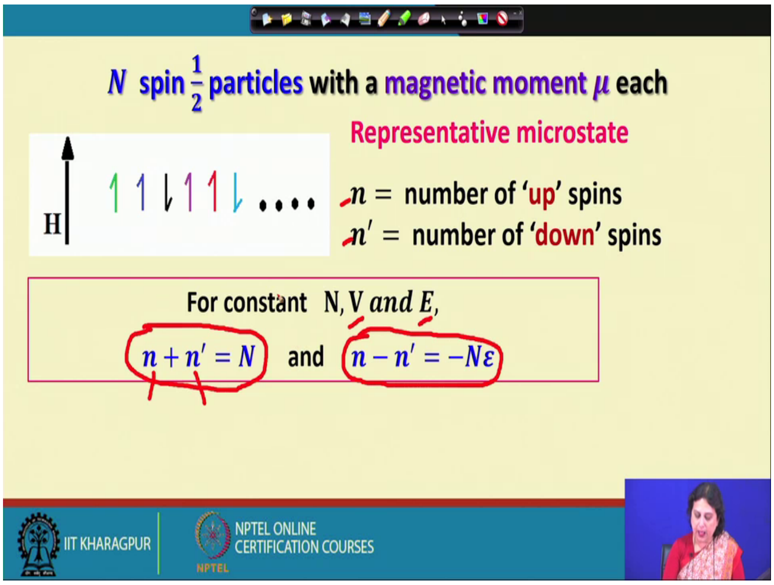

So, here this is a representative microscopic state as you can see here. So, this is the direction of the applied field, this white region defines the total volume v that is available to this spins for occupation and here a particle 1 is pointing up, particle 2 is pointing up, but particle 3 is pointing down. And the other spins are also taking up respective orientation.

So, this is one typical microscopic state depending on how all these spins are arranged up or down, I would say that many such microstates are possible. So, how do I express or how do I define one such microscopic state. I will define it in terms of 2 numbers and what are these numbers? These numbers are as follows; first I will say that I have for any even such microstate small n is a number of up spins.

So, if I have these many spins, how many up spins do I have 1 2 3 4. So, small n would be equal to 4 and n prime is equal to the number of down spins. So, in this picture I will have n prime equal to 2. And therefore, if I have capital N equal to 6, for this microstate it is completely described in terms of the small n equal to for up spins and small n prime equal to 2 down spins. So, let us not really bother about what exactly the values of n n prime are, but instead what we will see is there are 2 constraints on this system. If I hold the total number of particles present in the system constant, if they are present in a constant volume v, and if the total energy of the system is fixed, then there are 2 equations that must be a satisfied by the numbers n and n prime. Does not matter which microscopic state I am looking at I must have n plus n prime is equal to capital N.

So, whatever microscopic state I construct by varying I n and n prime these 2 numbers must always add up to capital N. And also I must know that the total energy of the system imposes certain restriction on the number n and n prime.

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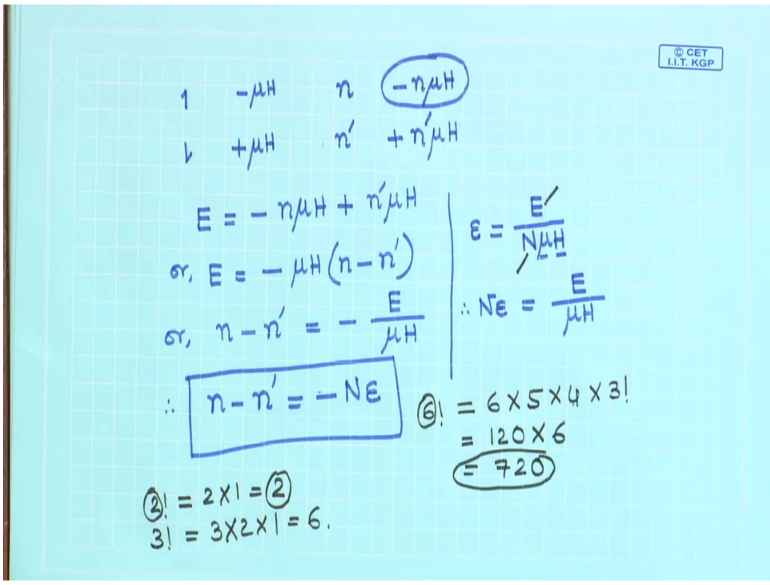

And this is because I know that for one up spin, the energy contribution is minus mu H . So, when I have small n such up spins, then what is the total contribution to the energy minus n into mu H.

Similarly, if I have one down spin, then the contribution to the energy of the system is plus mu H. So, if I have n prime such down spins, then the total contribution to the energy would be n plus n prime mu H. Now I have already mentioned that the total energy of the system is constant. So, then I must be having E is equal to whatever contribution I have got from this small n the up spins that is minus n mu H. And then whatever contribution I have got from this n prime down spins that is n prime mu H or I can write that E is equal to minus mu H into n minus n prime or I can say that n minus n prime is nothing but minus E by mu H.

Now, let me introduce this quantity which I have already done in yesterdays class, that epsilon is equal to capital E divided by capital N mu H. Therefore, if you fix the macroscopic state of the system by specifying the value of E and value then the value of capital N, and by the design of the system mu is also a given constant, H is also given therefore, epsilon is also a function of E and capital N and therefore, I can very easily write that n epsilon that is equal to E by mu H. Therefore, this equation turns out to be small n minus n prime that is equal to minus n epsilon.

So, this is exactly what the relation that we have obtained by looking at the conservation of the total number of particles, present in the system as well as this equation is the consequence of the fact that the total energy of the system is fixed. Therefore, I the question that we are asking here is what is the number of microstates that are possible when you have fixed the total number of particles volume and the total energy of the system that is what we are going to calculate next.

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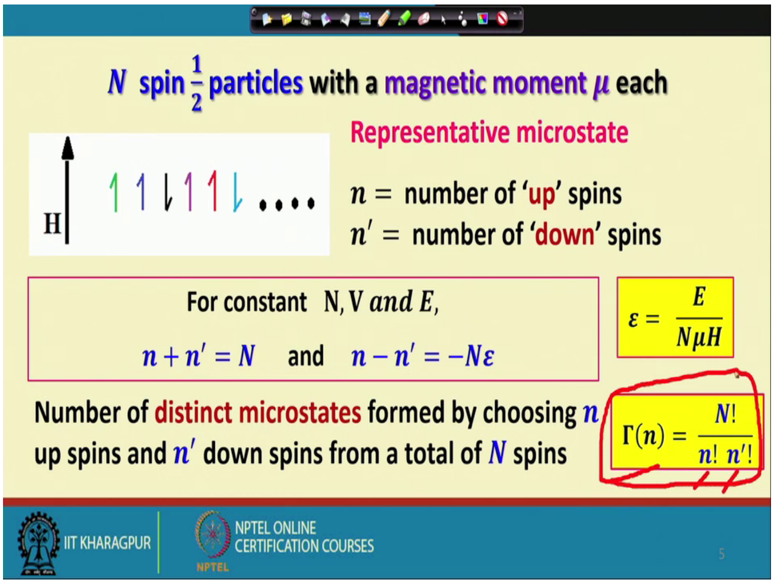

Now, in this case please remember, that we have put in this definition that epsilon is equal to the total energy E which is a given constant, then capital N mu H. So, in this particular case the other reminder that I have for you is that the number of distinct microstates are formed by choosing these numbers small n and n prime, from a total of capital N spins. So, smaller n of them we will have up spins. So, automatically n prime that is capital N minus small n will have down spins. So, the question is the number of micro distinct microstates is equal to the number of ways in which you can choose small n up spins from a total of capital N spins and therefore, I must be having gamma corresponding to such choice is capital N factorial divided by small n factorial by small n prime factorial.

So, this is the number of ways in which you can choose from an assembly of capital N spins, small n spins with up spin and the rest of the spins that that are n prime numbers with down spin.

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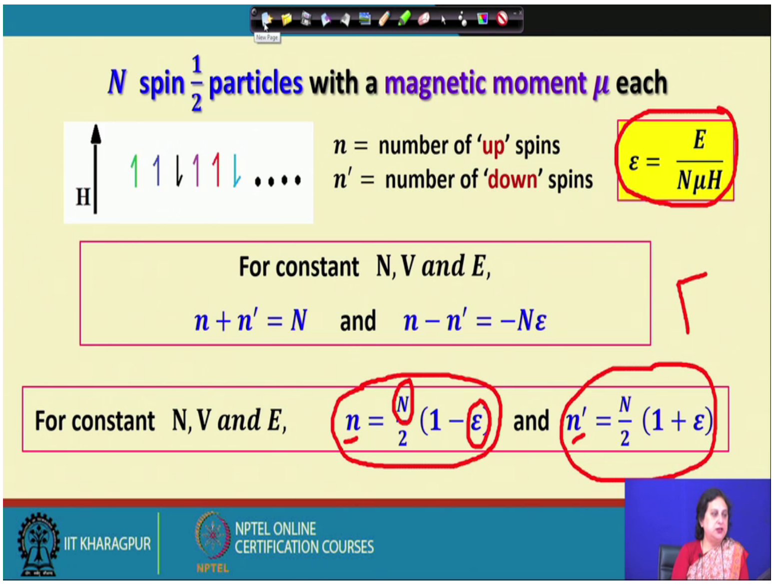

While this is actually understandable, let us now have a look at what happens if I want to express this small n and n prime in terms of the given constants capital N V and capital E these 2 algebraic equations can be solved very easily. And you we will find that small n is given by an expression like this. And n prime is given by an expression like this.

Therefore, previously we had expressed the number of microscopic states in terms of n and n prime and here I find that n and n prime they are decided by the values of capital N and epsilon and what does epsilon depend on? By the definition of epsilon I find that it depends on the way we have defined the macro state of the system. And therefore, I understand that the number of distinct microscopic states, here is going to be equal to gamma n where small n is itself a function of E V and N.

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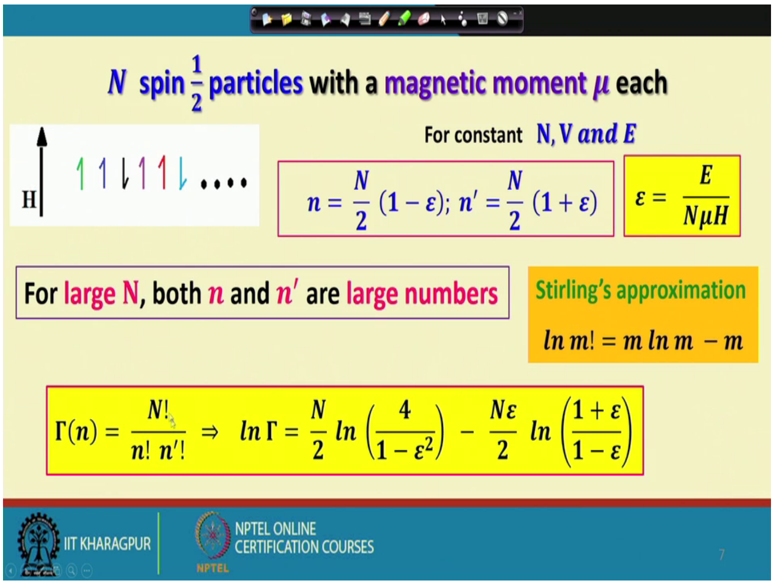

So, if I go back and then try and try to answer this question, that given the formats of small n and n prime, what happens for realistic systems in realistic systems? I have a very large value of capital N. Now what is small n and n prime? These add up to capital N and therefore I must be having both n and in prime as very large numbers. Now what is the consequence of having both small n and n prime as large numbers and this is as follows.

As I see that there is an extremely useful mathematical tool that is known as stirlings approximation, which allows us to evaluate factorial of a number in terms of its logarithm. So, if n is a very large number in that case natural logarithm of n factorial its can be very easily approximated as m multiplied by the natural logarithm of m minus m. So, as you see that if you use your calculator and try to calculate the factorial of a number, this number becomes increasingly large. So, if I want to find out what is factorial 2?

Factorial 2 is 2 into 1 that is equal to 2, factorial 3 that is equal to 3 into 2 into 1 that is equal to 6, this way if you use your calculator let us say what is factorial 6; 6 into 5 into 4 into factorial 3. So, what you have is 5 fours are 20. So, 120 multiplied by 6. So, that is equal to 720. So, by going from this number 2 to 6, I can say that the value of the factorial has increased from 2 to a large number 720 and if you use your calculator you will be able to see that you cannot find out the factorial of a given number, beyond certain integers.

I will ask you to go back and check this using whatever calculator you use. So, basically then whenever you are counting the number of microscopic states, it becomes a problem when you are trying to estimate the number of microscopic states in terms of capital N factorial and small n factorial and n prime factorial. Here capital N small n and n prime all of them are very large numbers. Now if I can use the stirlings approximation in that case as you see, all I will have to do is I will have to take a natural logarithm on both sides and evaluate if I do that in that case what happens is I know that gamma is equal to I know that gamma is equal to.

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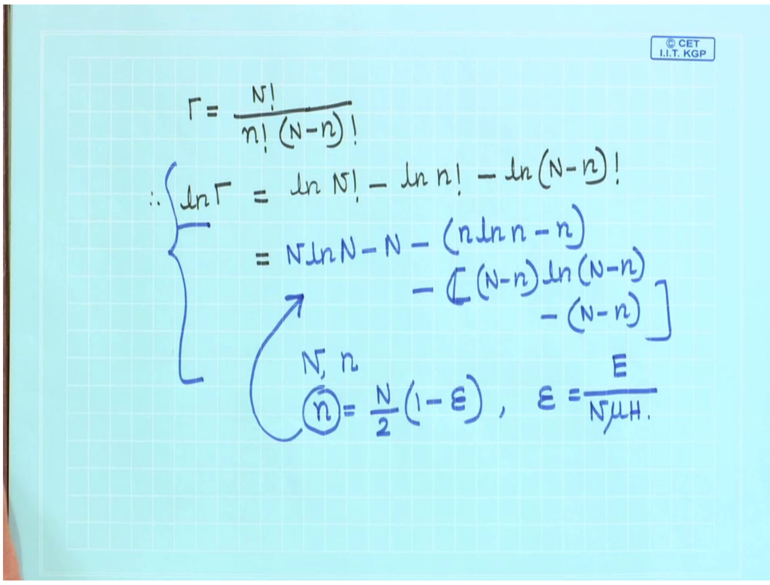

Capital N factorial divided by small n factorial into capital N minus small n factorial. So, what is l n gamma? L n gamma is equal to l n capital N factorial minus l n, small n factorial then minus l n, capital N minus small n factorial. Now I am going to use the stirling approximation. If I use the stirling approximation in that case what I find is the first term turns out to be n l n n minus n, minus this term is small n l n n minus small n and then this term turns out to be capital N minus n l n capital N minus n minus capital N minus small n.

Now you can do the algebra here very easily and we will be able to see that you can write down l n gamma in terms of a very simple algebraic relationship involving capital

N and small n, but you do not know what small n is. Small n is given by capital N by 2 1 minus epsilon. Where epsilon is equal to capital E divided by capital N mu H and you can put this expression of n back into this expression and what you get is a very nice expressions giving us what l n gamma is in terms of capital N and epsilon. So, let us have a look at this particular equation. So, what is it that we have achieved? We have achieved the estimation of the number of microscopic states possible for a given system with a constant value E V and N.

And this expression tells me how many microscopic states are possible if I the try to represent the system in terms of a collection of up and down spins. Now when we do this we are going to have a look at this particular mathematical expression and focus on what it means.

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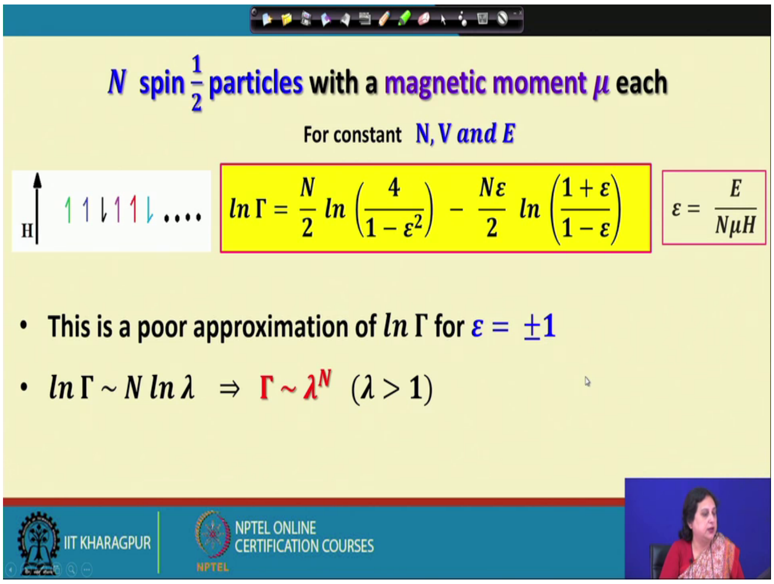

It means something very simple; although it looks a bit cumbersome and you might think that what uses this, and also you see that there is some problem as far as a mathematical property of this equation is concerned. This must be a very poor approximation for the total number of microscopic states, in the case when epsilon is equal to plus minus 1.

So, of course, this relationship is valid when epsilon has a value, which is other than plus 1 or minus 1. Now when I look at this expression for values of epsilon other than plus minus 1, I understand that I can take capital N out and recast the rest of the terms as l n of in lambda, where lambda is a number that is greater than 1. So, basically I can rewrite the equation shown above as natural logarithm of gamma that is a number of microstates, actually would go something like capital N the number of particles present in the system multiplied by the natural logarithm of a number lambda, where lambda is greater than one. So, what does it mean? It means that the number gamma I itself can be given by lambda to the power of N where n is greater where lambda is greater than 1.

Now as you see that just because lambda is greater than 1, it brings us to a very very important conclusion.

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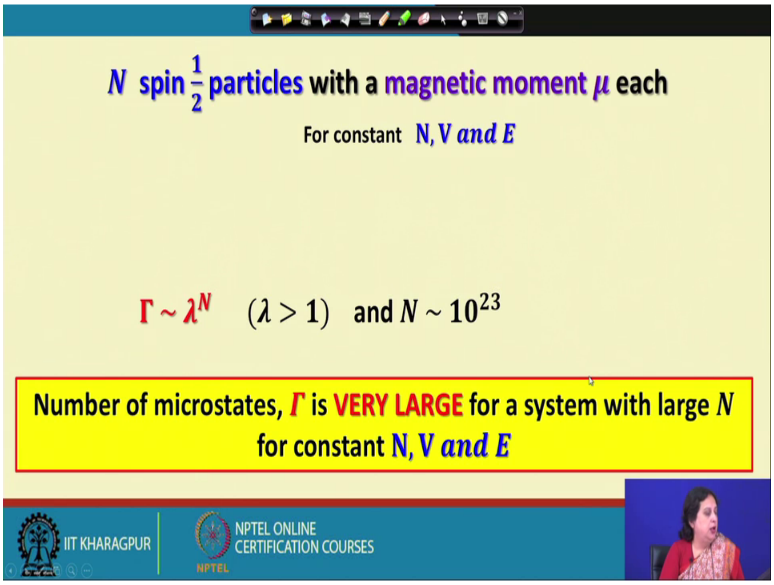

And the conclusion is the number of microstates gamma is very very large for a system, if a very large number of particles is present in the system and a constant value of energy is available to it. So, and since we are in the real system, we are interested in typical values of n which is of the order of the Avogadro number, you understand that whatever we have said till now is actually valid and therefore, we would conclude here by saying that we have considered a very simple case where each particle has only 2 microscopic states either it is spin up or it is spin down.

So, if I have a very large number of such particles, which do not interact with each other and if they can carry a label distinguishing each of them from others, in that case we have been able to calculate the number of microscopic states, that is possible if you fix the total energy E volume V and the total number of particles. And we have been able to show that under this given macroscopic state, a very very large number of microscopic states is possible.

In the next lecture, we will take up the case of simple harmonic oscillators and show you how such similar conclusions may be arrived at using the same considerations.

Thank you.