Introduction to Molecular Thermodynamics
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Lecture - 14
Fundamentals of Statistical Mechanics

Welcome back to the last part of our discussion on how to identify and count the possible number of microstates of a system in equilibrium. So, the first thing that I would like to mention here is that we are looking at the microstates of N identical non-interacting particles.

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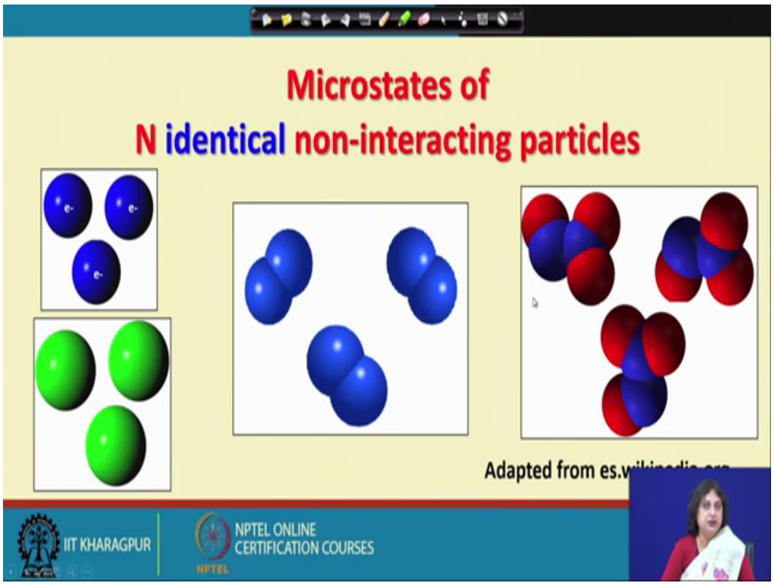

Whereas this particles can be a cluster of electrons or a cluster of atoms or it may be some gas molecule comprised of say a diatomic molecule and it may so, happen that we are looking at a liquid or a solid which is comprised of much more complicated multi-atomic molecules.

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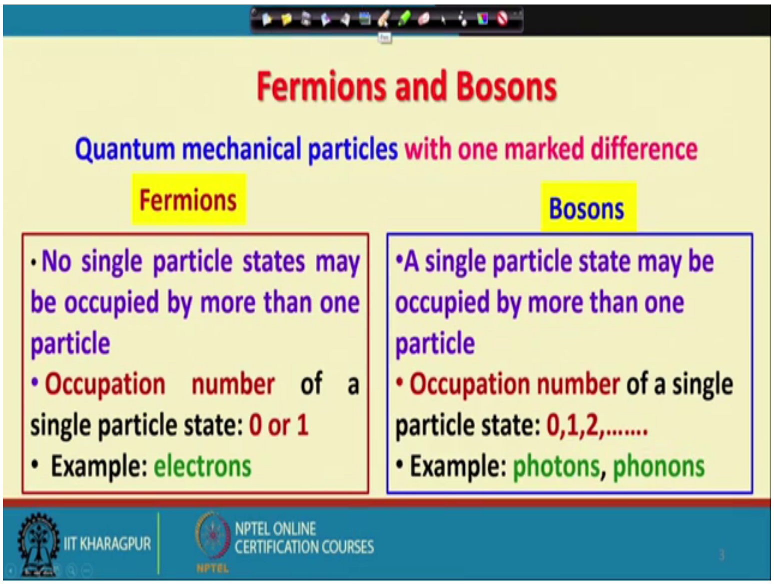

And the question that we are we have been asking in the last class, was that is it possible to identify some of this quantum particles in terms of the fermions and bosons. So, what is the difference between the fermions and bosons, the fermions are the ones where no single particle state can be occupied by more than 1 particle. And this means that the occupation number of every single particle state can be either 0 or 1, and we have also demonstrated that electrons are the examples of such fermions.

The other class of particles that we were talking about were bosons, where unlike the fermions there is no restriction on the occupation number of a single particle state and therefore, this occupation number may vary from 0 1 2 and so on and so forth. And the examples that we consider are photons or the light the quantum of energy for electromagnetic radiation with bright, and phonons that is the quantized vibrational modes of solids.

Now, with this background in mind today what we are going to do is we are going to talk about counting of the numbers of microscopic states of systems that are comprised of N non-interacting identical particles ok.

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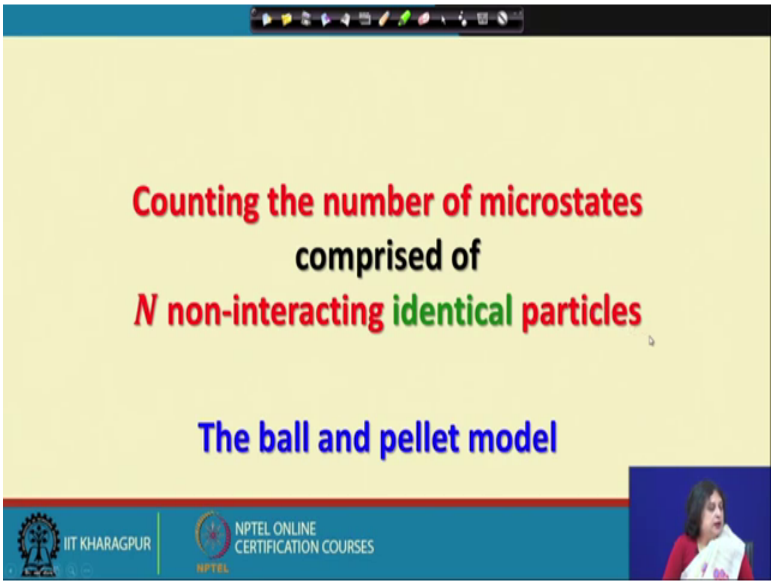

So, the let us try to address this problem of the counting of microscopic states by using what we mean by a ball and pellet model.

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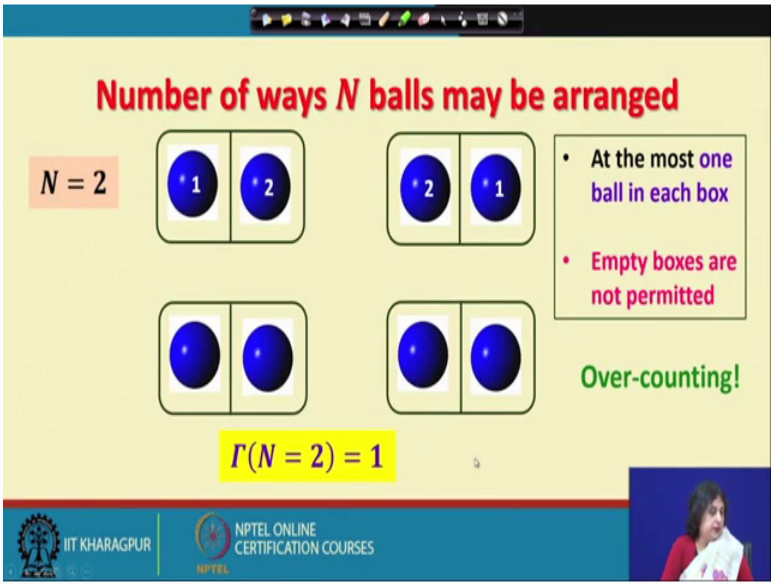

So, let us try and understand the number of ways, in which N balls may be arranged. Now for the sake of simplicity I will be taking N is equal to two. So, I just have 2 balls and there are some rules of this game, the rules are as follows at the most. So, I have a single box in which I am going to arrange this balls and at the most 1 ball can be placed in each box and empty boxes are not permitted.

So, now what I have here is I have this big box in which there are 2 compartments, and in these 2 compartments I can put only 1 ball each. So, that is the rule of the game I cannot leave any of this sub- compartments in my box empty. Now I have numbered here my balls as number 1 and number 2 then; obviously, you will be able to say that well these are the 2 ways in which I can arrange the balls, and what are these ways.

The first 1 has ball number 1 in the left side compartment, and ball number 2 in the right side compartment, in the second arrangement I have in the left side compartment ball number 2 which was in this case in the right side compartment I will have ball number 1 in the other 1. So, it is understood that for capital N equal to under the rules of these rules of the game these are the two ways in which the balls can be arranged.

And if I now remove the identifying number on the balls, now what do I see under the same rule of the game that I can put 1 box in each of these compartments, and no empty boxes permitted I see that these 2 states, now go over to these 2 states. Now can you distinguish by looking at these 2 states whether they are the same or different; obviously, your answer would be if you cannot distinguish between the individual particles given the situation, and given the rule of the game. If I say that I am having 2 different ways I shall be over counting, and why am I over counting that is simply because the 2 balls are identical and here therefore, the correct number of ways in which these 2 identical balls can be arranged in the box comprised of 2 compartments following these rules of the game is 2 is 1.

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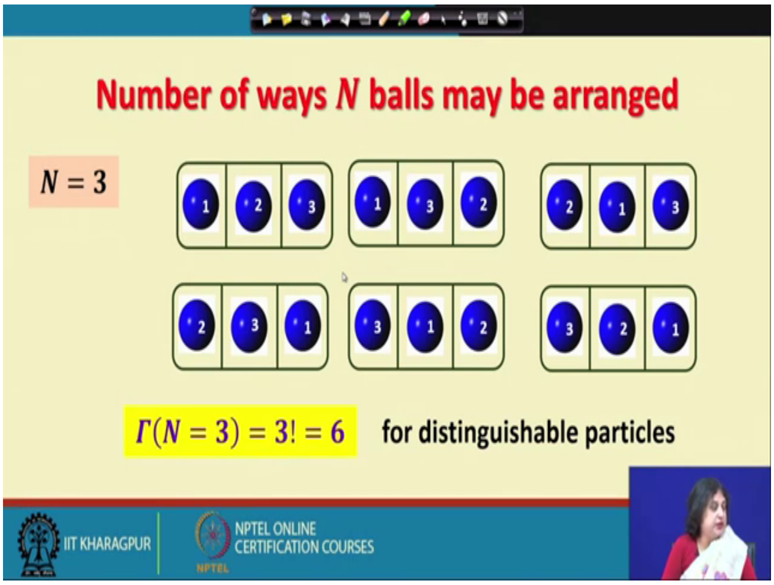

Now, let us now have the other case where I have 3 balls to be arranged, in 1 box which has 3 compartments. And the rules of the game remain the same now in this case once again so, this is my first case this is my big box which has 3 equivalent sub compartments.

I was supposed to put in the balls numbered as 1 2 3 in them in all possible ways so; obviously, it is very easy you can play around and find out the number of ways, in which you can arrange this balls which are labelled as 1 2 3; obviously, there are 6 possible ways and therefore, if you look at this kind of picture you will say that if I have 3 such distinguishable particles, then the total number of ways in which these 3 particles can be arranged is 3 factorial which is the number 6. And these are the 6 possible arrangements that I have shown to you.

Now, once again let me remind you that we are dealing with identical particles therefore, what I would like to do is I would like to have a look at these states, these ways of arranging the balls when I remove the identifying number and this is what happens.

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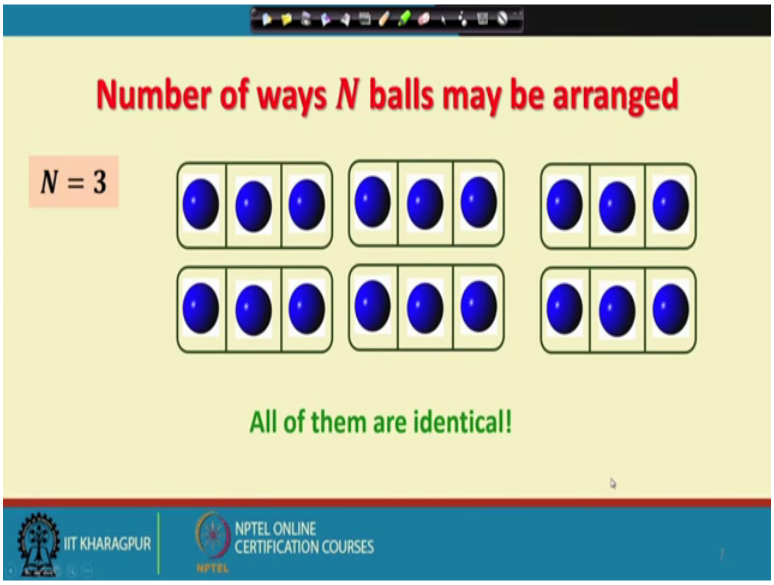

So, once again I find that the different arrangements without the numbers are absolutely the same, therefore if you now say that that there are six different ways of arranging these 3 balls in that box comprised of 3 compartments. Once again you are over counting and therefore, I would say that all of them are identical.

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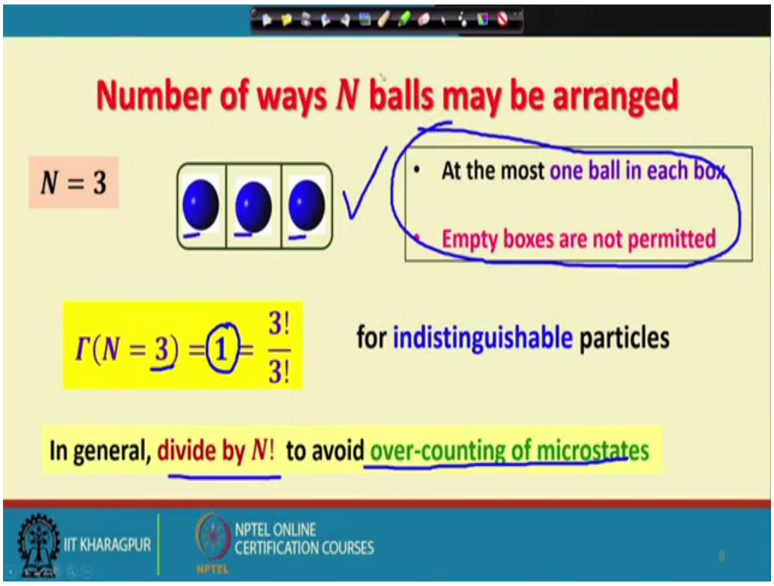

And then what I must be doing is following these rules of the game I must understand that there is only 1 unique way by which I can arrange these 3 balls. That is 1 ball in each compartment. So, what is the number of ways in which these N balls may be arranged, so you see that this number turns out to be 1. Now the question is it possible that I find out what would be this number corresponding to this particular value of N, I understand that this number can be written as 3 factorial divided by 3 factorial, because 3 factorial is the total number of ways in which this particles if I could label them as distinguishable then they would have arranged ok.

So, instead of 1 I would have got 6 distinguishable ways therefore, in general a prescription is followed that if you have your rules of the game are something like this. Then you must say that in general you construct as many microscopic states of the different ways in which these balls can be arranged, but you divide by N factorial to avoid the over counting of microscopic states.

We are going to use this concept later on, but there are 2 ingredients that you must be aware of that we are using here. First of all as it follows from our previous discussion that we must be concerned about first the box that is 1 energy state at the microscopic level, where I am putting the particles to construct the actual representation of the microscopic state of the system.

Therefore the number of microscopic states will definitely depend on, the number of sub-compartments that this big energy box has, it also would depend on the number of particles that I have in my system, which I assumed to be not interacting with each other. They are identical and then I must also remind you that there is a rule of the game. And the rule of the game is decided for example, I have shown you 1 rule of the game the other 2 rules of the games are corresponding to how you can populate fermions and bosons in their respective single particle states.

So, let us now go back and have a look at the different ways in which fermions and bosons can be arranged.

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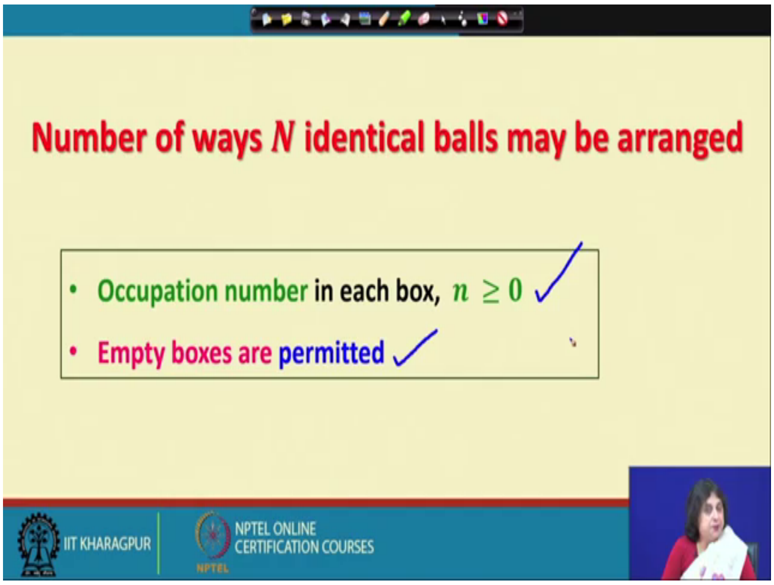

So, once again let me highlight the fact that whenever we are dealing with fermions and bosons, then I must remember that the occupation number in each of the some compartments in the box must be greater than or equal to 0 and in this case just, because 0 appears the rule of mind game includes empty boxes means the sub-compartment if I have a given box 1 of the sub- compartment of the box may be empty; that means, the occupation number of that box that sub-compartment may be equal to 1.

Now, with rule in mind let us go back, and now check out what happens when we talk about say 2 particles and 1 single particle state.

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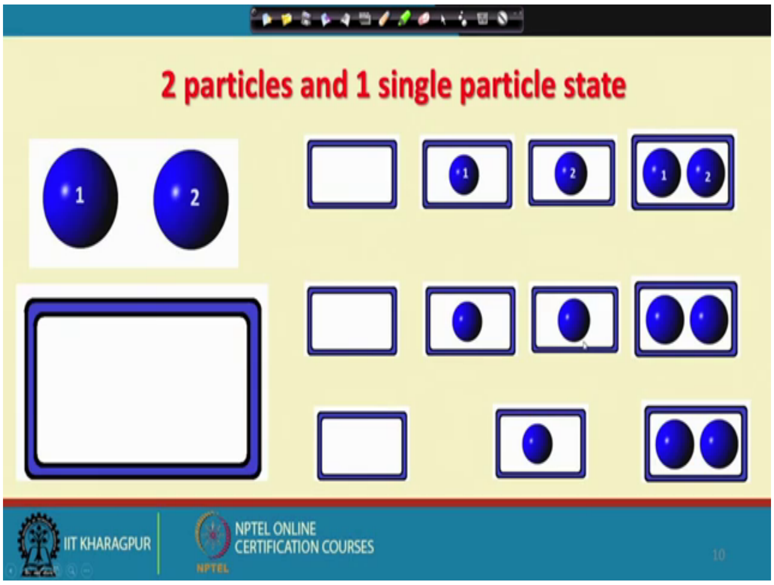

So, once again just like before I am going to use the balls to represent my particles; obviously, this is an approximate representation and is being used for the sake of our understanding.

Now, to start with I have labelled this balls as 1 and 2, and the task is I have to put them in 1 single particle state, which means that I have 1 such box and there is no sub-compartment in this box. So, this is; obviously, 1 of the ways in which you can put the 2 particles in this box this is the first case where the box is empty you have not put any of the balls here so, here N is equal to 0.

The next thing that you have here is the other situation, where you have taken only wall number 1 and put it in the box so, this must be N equal to 1. There is another option for getting that N equal to 1 that is instead of the wall number 1 you put the ball number 2. And just because they have these numbers associated with them you understand that this state is different, from this state even if they have hold the same occupation number.

Now, let us have a look at the third option where I have shown you the only possible state with the occupation number N equal to 2. Now here as you see that both the particle 1 and particle 2 have input simultaneously in the box. Now as I understand that here what I am doing is I am putting no restriction on how many particles can be there populating this single particle state.

Therefore it is obvious that these are different arrangements without any restriction for 2 particles in 1 particle state; 1 single particle state. Now if I remove these numbers this is exactly what you get. So, what you find is; obviously, this remains the same this also remains the same, but now I have this problem that both these states are absolutely identical.

So, therefore I must understand that whenever I am using these 2 particles and they are identical to each other, then I must be having instead of the 4 possible states that I have shown here only 3 states because you cannot distinguish whether you have put in particle number 1 or 2 in this box. And therefore these 2 states with occupation number they are equivalent and therefore, you can see that the microscopic state of these identical particles can be completely characterised by saying what is the occupation number of that given single particle state.

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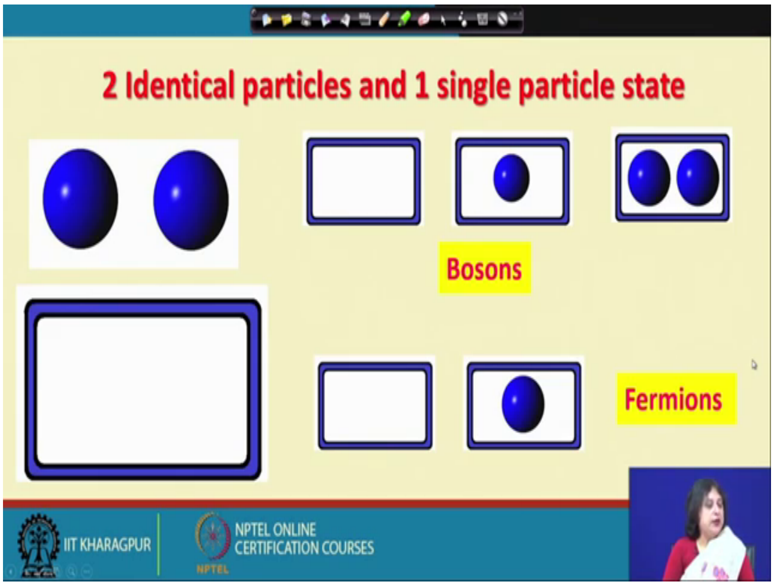

Let us now look into a little different rule of the game, where I am going to use different conditions for the values of N, and when did we see this different rules in the case of bosons and fermions. So, let us first have a look at what are the possible ways in which you can represent the microscopic states of bosons so; obviously, in the case of bosons N is going to be greater than or equal to 2 for 2 identical to bosons.

And therefore, the permitted microscopic states are the 1 with N equal to 0, the 1 with N equal to 1, and the 1 with N equal to 2 right. Now, if I think about the fermions now what is the rule of the game of fermions in the case of fermions no single particle state can have more than 1 particle. So, in this case for the case of fermions the occupation number N must be either 0 or 1. So, correspondingly I must be having this kind of allowed microscopic states for the fermions.

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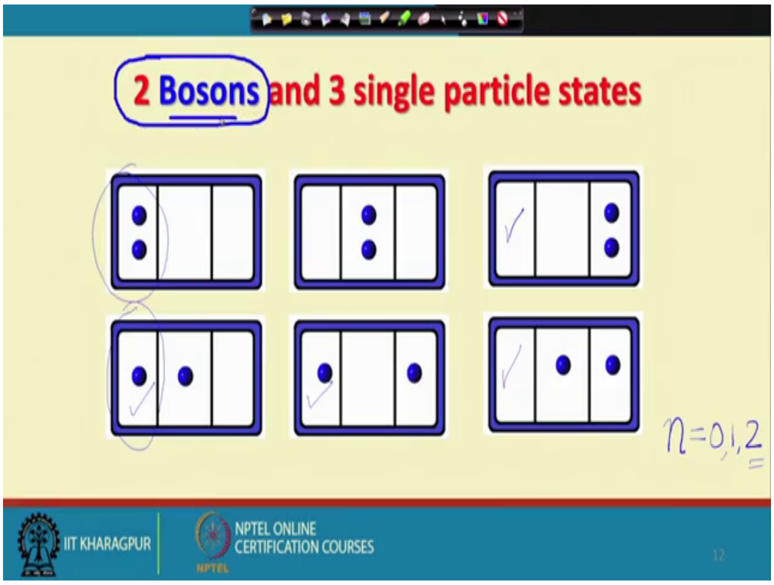

Now this way we can go ahead and try and understand what happens for example, if I have 2 bosons, but 3 single particle states now these are the possibilities. So, what I have is I have this given box which corresponds to a constant energy of that single particle state. And this single particle state is triply degenerate, which means there are 3 compartments which are equivalent to each other. And we are required to distribute 2 bosons in these 3 compartments, and then I would say that well these are bosons and therefore, in this case what is going to be my occupation states; my occupation states, are going to have values like 0, 1 or 2 for every single particle state.

Now, in this case why do I stop at 2 because that is the maximum number of bosonic particles that I have in this example. So, can you identify amongst all these in which the leftmost compartment has an occupation number equal to 0; obviously, this structure this microscopic state are the ones where this leftmost sub-compartment is having an occupation number equal to 0.

Now, can I find out the microscopic states of the bosons where the occupation number is equal to 1, in the left most state; obviously, this microscopic state and this microscopic state has n equal to 1 form this left most sub-compartment and; obviously, if I am looking for those states where n is equal to 2 for the left most compartment, this; obviously, is the case where the left most compartment is having both the bosons associated with it.

So, now this tells us that if I have a specific rule of the game whether it is a boson or it is a fermion, and I have a given number of single particle states is possible for me to just play around with this balls and given the number different compartments in which I place them, and provided this compartments are equivalent to each other in the sense, that all of them belong to the same single particle state I can generate the different microscopic states of the system. Now, let us next look at what happens to the fermions.

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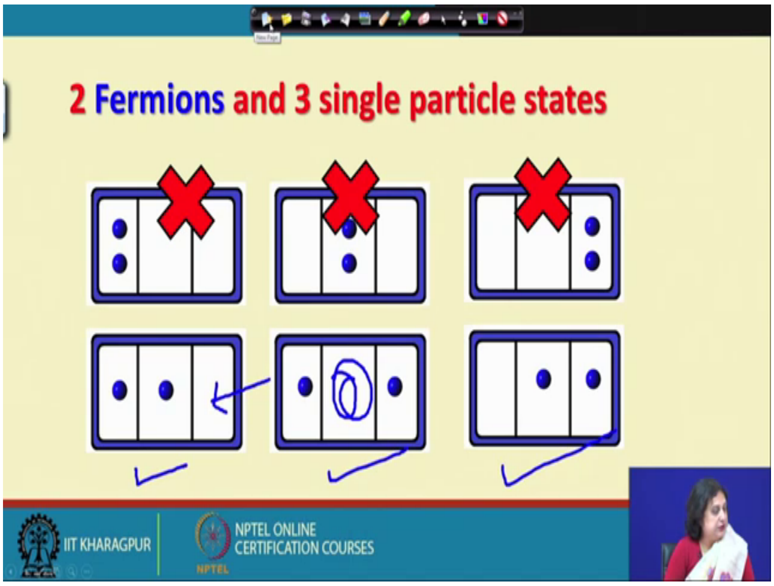

So, now I have 2 fermions and 3 single particle states. Now in the case of 2 fermions I already know that my n value that can be only equal to 1. Now let us have a look at what happens if I have 2 fermions and 3 single particle states, now for the fermions you; obviously, know that for any compartment so, let us now consider the case where I have 2 fermions and 3 single particle states. Now in this case what happens as you understand that so, let us now consider a system where there are 3 single particle states and I have 2 fermions to be put in it. Now this is why I have the picture showing you that there are there is 1 big box which signifies at the total energy of the system is constant.

And for this constant total energy there are 3 single particle states as given by this 3 sub-compartments, and following the rule of game for the fermions I am going to allot 2 fermions to each of these compartments, and in this case I realise that I must be having occupation number of each sub-compartment either equal to 0 or equal to 1 right.

So; obviously, if I have to follow this rule I understand that some of the states that I have shown here are not possible can you tell me what they are; obviously, I can very easily show that the first 3 states, where you have in each of the sub-compartments the occupation number of 2 are not possible for the fermions. So, for the fermions the possible microscopic states are these 1 2 and 3.

Now, can you identify the microscopic state that is having N equal to 0 for the central compartment of course, this is the 1 where there is no particle in the central box. So, this is the microscopic state for which N is equal to 0 at this central compartment. Now think about the microscopic state of these 2 fermions system where the right most state is empty so; obviously, this is a microscopic state which has the right most state right most box empty.

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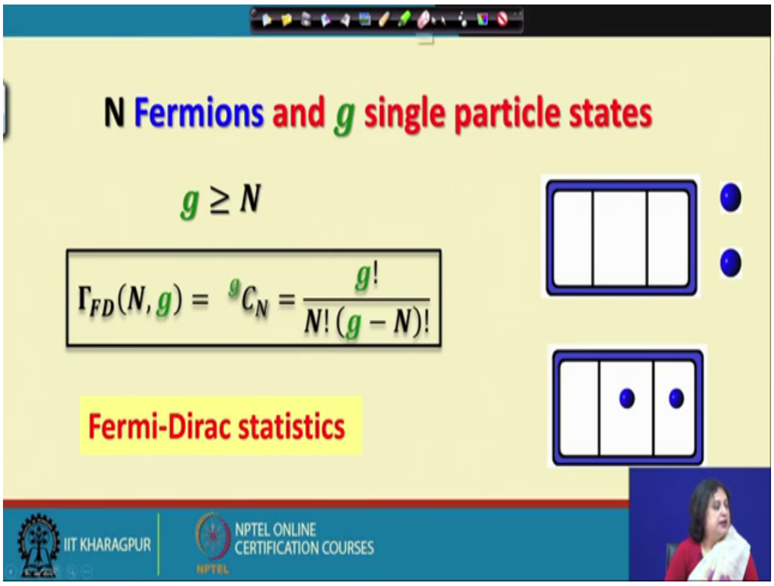

So, now the question is these are actually very simple systems where I have been using accountable problem, in the sense that I have some 2 fermions 3 single particle states and so, on and so, forth. But actually the problem comes when you have a very large number of particles, we have repeatedly seen in this course that we are going to talk about a very large number of particles. And equivalently there may be a very large number of single particle states available to them, where we are going to populate these particles to construct the single particle states.

So, let us now have go and have a look at what happens if I have capital N fermions to be distributed to small g single particle states to generate the different microscopic states of the system. And therefore, the task right now is I have this big box where I have 1, 2, 3 such a single particle states, and I say that I am going to allot these let us say 2 balls into these compartments, this is the specific case where capital N is equal to 2 and small g is equal to 3.

And I also know that typical microscopic state of the system may be generated like this, where I have assigned 1 ball each to these compartments leaving the left most empty, but at this point we are asking the question under the condition that the number of single particle states is greater than or equal to the total number of fermions available. Can I get the general number where I can say that well if you have g single particle states, and you have N fermions to be distributed over them what is the number of microscopic states that you will be generating and this; obviously, is the answer as you see that you basically have 2 choose the number of ways in which you can distribute capital N particles in small g boxes. So, this is g C N. and if I write down the explicit expression; that means, g factorial divided by N factorial in to g minus N factorial, and appearance of this term actually justifies the fact that I must be having this condition fulfilled. Now, let us check if these numbers give me the right kind of answer, when I have capital N is equal to 2 and g equal to 3.

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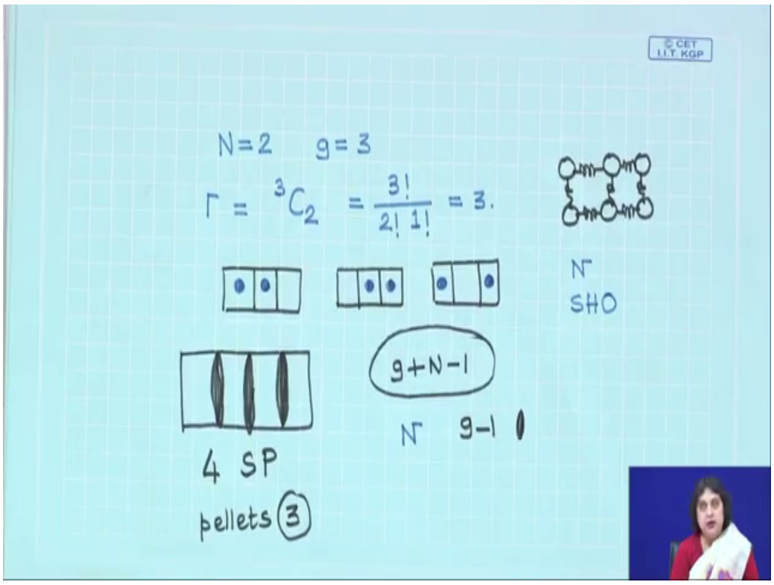

So, when I have capital N equal to 2 and g equal to 3, then the number of micro-states that are possible is given by 3 C 2 right, and this is nothing, but 3 factorial divided by 2 factorial into 1 factorial and this is equal to 3. And we have already seen that these 3 states are like these so, this is the microstate number 1, this is the microstate number 2, and this is the microstate number 3.

So, the basic idea here is I am going to use this kind of ball and box representation to generate the different microscopic states possible for this system. Now let me go back and then mention that this kind of counting of the number of microscopic states is attributed to what is known as Fermi-Dirac statistics, Fermi and Dirac both are highly celebrated name in the world of physics, and this particular equation is the elementary starting point in which they started dealing with the properties of fermionic systems.

The next question that I have is can we have a similar counting prescription for the bosons.

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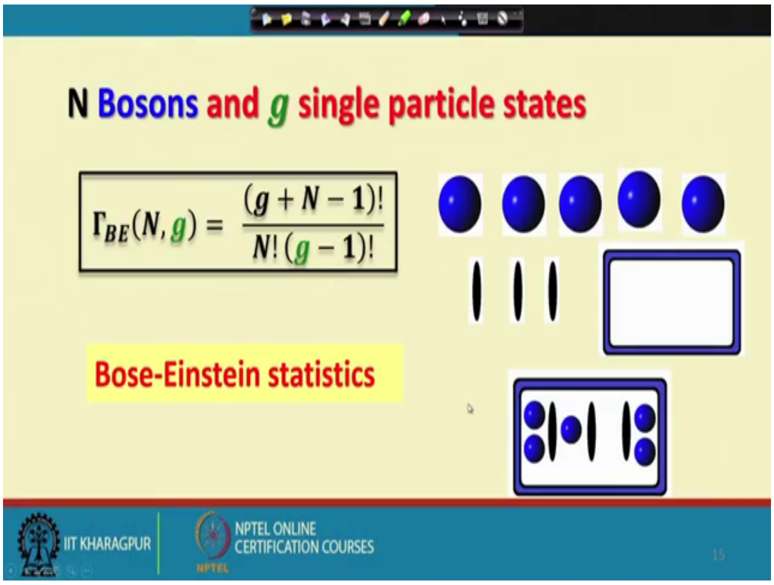

So, in the case of N bosons and g single particle states, now I have let us say that these are the balls the blue balls represent some this bosons, and in this case I am using 1 2 3 4 5, five an identical blue balls to represent the bosons here. The g single particle states I am going to represent using g minus 1 pellets. So, this is pellet 1 2 and 3 and I am going to use this big box once again which tells me that the total energy of the system is concerned, and then how am I supposed to construct a typical microscopic state of this system using these balls and these pellets in this box. So, this is how I generate the different microscopic states.

So, as you see that I have subdivided this big box into 1 2 3 4 four compartments. And so, 3 pellets give me 4 compartments, and then this reminds you of the kind of situation that we had to start with that I have this big box, and then I am placing separators here in the form of the pellets. So, if I have 4 single particle states what is the number of pellets that, I will have the number of pellets that I will have is equal to 3 ok

Now, I have put an of these 5 balls in these different sub-compartments created by the pellets. Now as you understand that these are bosons and therefore, you do not have any restriction on the number of balls that you can put in any of this compartments therefore, the problem now is you have been given g single particle states. And this g single particle states are separated from each other using g minus 1 pellets, and then you will have to have capital N balls.

So, a total number of g plus N minus 1 symbols are available to you and you are going to play around with all possible permutations of the symbols, but you must realise out of them capital N are your blue balls and g minus 1 these are your pellets therefore, what is the number of distinct microscopic states for a given system like this and this; obviously, is given by g plus N minus 1, whole factorial divided by N factorial into g minus 1 factorial.

And this is the starting result for counting the number of microscopic states for the celebrated Bose Einstein statistics named after the famous Indian physicist Satyendra nath Bose and the world-renowned physicist Albert Einstein. So, but you have seen this results before do you remember where you have seen this result before.

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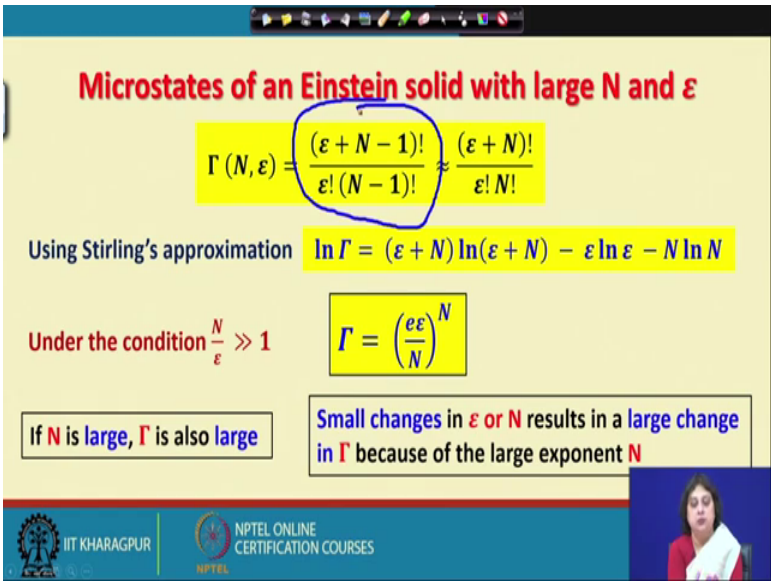

You have seen it where we have been counting the number of micro-states of an Einstein solid. And here as you see that we are basically using the same counting procedure because in an Einstein solid you would remember that what you the way you represent the solid is a collection of simple harmonic oscillators where the atoms are present at different lattice positions connected by springs.

And you say that these springs vibrate in such a way that the net vibrational pattern of the solid can represented as a total N simple harmonic oscillators which are independent of each other. So, we are talking about N bosons, and the collective vibrational pattern, that you get the number of microscopic states that you get are those of the quantized vibrational modes. And therefore, you can use the Bose Einstein statistics to find out the number of micro-states possible.

So, that concludes our discussion on the counting of number of microscopic states in a system comprised of non-interacting identical particles. We will now go over and discuss the fundamentals of statistical mechanics that relies crucially on whatever concept we have learned so far.

Thank you.