Introduction to Molecular Thermodynamics
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Lecture – 16
Microstates of a System

Welcome. Today we are going to start on the last part of the grammar of introduction to molecular thermodynamics. And in this connection, today we are going to talk about ensembles. If you look at what an ensemble means, it means a collection. And what kind of collection are we talking about? We are talking about a system which is comprised of a very large number of particles, which may be atoms, molecules very complicated molecules or something else that I am not specifying right now.

But I have a very large number of particles in the system under some given thermodynamic condition. And we have already seen in this course, at under such condition it is possible to show that the number of microstates is a very, very large number. So, when I talk about an ensemble in this case, I am talking about or a collection of all those microstates that are possible under a given thermodynamic condition.

And in today's lecture I am going to introduce to you the microcanonical ensemble. Although, this in this section we are going to look at two kinds of ensembles. The first one is the microcanonical ensemble, and the second one is the canonical ensemble. But todays focus is going to be the microcanonical ensemble, and in the next lecture, we will talk about the canonical ensemble.

So, let us go and try and see what is the advantage of talking in terms of this ensembles.

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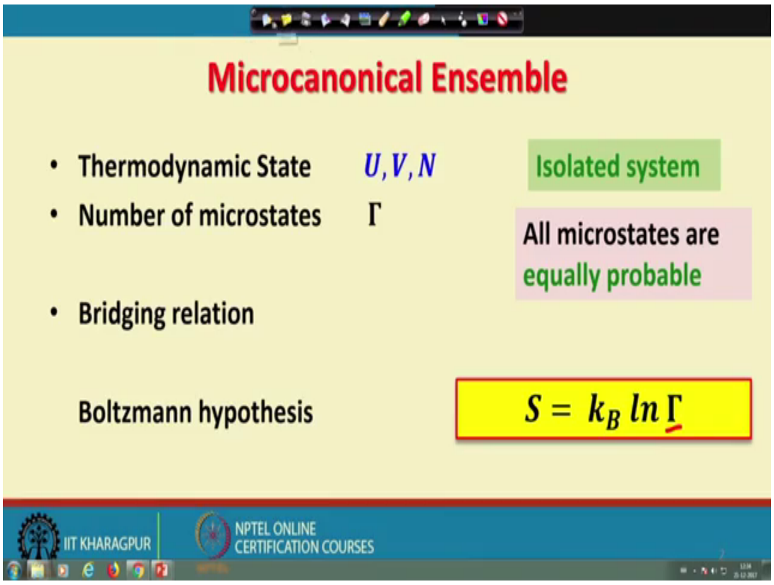

Microcanonical Ensemble

- Thermodynamic State U, V, N
- Number of microstates Γ
- Bridging relation

Isolated system

All microstates are equally probable

Boltzmann hypothesis $\boxed{S = k_B \ln \Gamma}$

So, as I said today's topic is micro canonical ensemble, and how do I define a microcanonical ensemble? As I have said that the moment I try to define a any ensemble, I will have to talk about one condition that is obeyed by all the microscopic states present in the system. In our case we are going to use the language of thermodynamics to describe this generic condition.

So, when I am talking about a microcanonical ensemble I am basically defining the thermodynamic state in terms of the internal energy, volume and the number of particles. Now that probably tells you that we are talking about an isolated system. At equilibrium this isolated system has a specific value of energy which is u that is a total internal energy. The and therefore, the system is not exchanging any energy with the surroundings, and that is the reason why I would say that the system is surrounded by an adiabatic wall.

Now, if the system is surrounded by a rigid wall; in that case it is micro state will be characterized by a given value of volume V, which is a volume of a box if all the or a bounding or the space contained within the bounding walls of the system. And finally, if the walls of the system are impermeable to the particles inside, then the number of particles in the system are also going to be a constant. So, this is typically an example of an isolated system at equilibrium; where it is equilibrium state is characterized by the internal energy volume and the number of particles.

So, for a condition micro state like this we have already seen, how to define the corresponding microstates as given by the solution of Schrodinger equation? And we have also seen how to calculate the number of such possible microstates for a given value of the total energy of the system. So, as before let me designate this number as gamma.

So, what is gamma? Gamma is the number of microstates which conforms to this particular thermodynamic micro state condition. And in this case, I would use the fundamental hypothesis of statistical mechanics saying that each and every one of these gamma microstates are equally probable.

Now, as you understand that, this particular limit is the description of the system in the macroscopic limit and whenever I am talking about the microscopic limit, then I am characterizing them in terms of quantum numbers and counting the number of microstates. All of which obey this particular number, now the we have already seen what the bridging relationship is between these 2 limits and that is the Boltzmann hypothesis.

So, do you remember what the Boltzmann hypothesis is? Yes, the Boltzmann hypothesis gives you the entropy which is a thermodynamic quantity in terms of this number of microstates gamma. So, this fundamental equation once again is a hypothesis. We can justify the existence of an equation like this.

But as I have discussed before, it cannot be proved. It required the genius of Boltzmann to come up with an equation like this. In today's class we are going to look at how we can use the Boltzmann hypothesis within the framework of a microcanonical ensemble to obtain the thermodynamic property of a system for which we know the underlying solution of the Schrodinger equation.

So, let us go and see what we can do with this very simple set of equations to achieve our goal.

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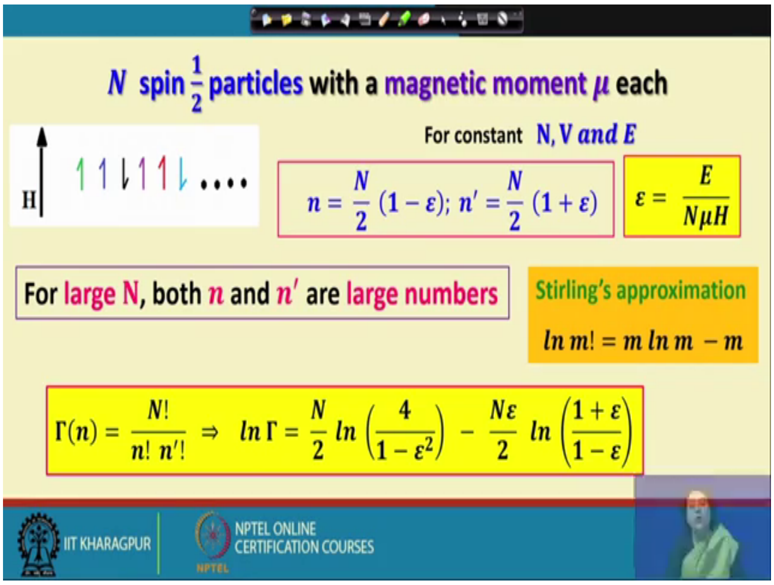

N spin $\frac{1}{2}$ particles with a magnetic moment μ each

For constant N, V and E

$$n = \frac{N}{2}(1-\varepsilon);\; n' = \frac{N}{2}(1+\varepsilon)$$

$$\varepsilon = \frac{E}{N\mu H}$$

For large N, both n and n' are large numbers

Stirling's approximation

$$\ln m! = m \ln m - m$$

$$\Gamma(n) = \frac{N!}{n!\, n'!} \Rightarrow \ln\Gamma = \frac{N}{2}\ln\left(\frac{4}{1-\varepsilon^2}\right) - \frac{N\varepsilon}{2}\ln\left(\frac{1+\varepsilon}{1-\varepsilon}\right)$$

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As you may remember, we have already seen this system of N non-interacting spin half particles which is present in an isolated condition, but it is immersed in a field of strength H. In that case this is a typical microscopic state of the system, and we have already seen that how the different microscopic states of the system can be characterized in terms of this number. Small n which indicates the number of up spins in a given microscopic state.

And obviously, small n is a function of the total number of particles, as well as the quantity epsilon which is related to the total energy of the system. So, for a given value of epsilon and for a given system where you have a specific magnetic moment. You understand that epsilon can have specific values, and we have been able to show that if N is a very large number, then we can use a sterling's approximation and calculate the number of microscopic states as a function of N which using the sterling's approximation simplifies to this expression.

This derivation we have already done while we were counting the number of microscopic states for a system like this. But I never explained to you why I am doing this? Why I am counting the number of microscopic states. So, this will now become evident to you when I say that I can now use the Boltzmann hypothesis.

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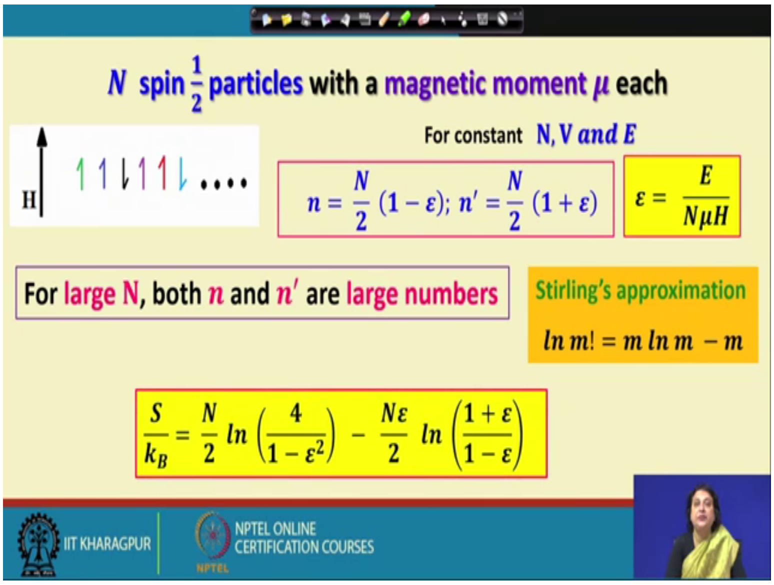

N spin $\frac{1}{2}$ particles with a magnetic moment μ each

For constant N, V and E

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For large N, both n and n' are large numbers

Stirling's approximation

$\ln m! = m \ln m - m$

$$\frac{S}{k_B} = \frac{N}{2} \ln\left(\frac{4}{1-\varepsilon^2}\right) - \frac{N\varepsilon}{2} \ln\left(\frac{1+\varepsilon}{1-\varepsilon}\right)$$

And find out the entropy of a system like this. So, the entropy is obtained by replacing l N gamma by this quantity S by k b.

So, what is S by k b? That is nothing but l N gamma. So, that is what exactly we have obtained from our previous studies. So, this tells me that yes, starting from the Hamiltonian of a spin half particle. I could build up a molecular a model for which a typical microscopic state is like this, and then starting from that molecular model I am now able to predict a thermodynamic property.

And I am asking, I am proposing here that the entropy of the system is going to be given by an expression like this. So now, you understand that this is a big advancement thanks to Boltzmann hypothesis, and here embedded in everything that we have done is the hypothesis that all the microscopic states that I have used here they are equally probable for a given energy volume, and number of particles.

Now, in the next part of this lecture we are going to generalize this discussion to a 2-state system; obviously, you understand a spin half particle is indeed one example of a 2-state system. So, it means that a solution of the Schrodinger equation of the microscopic states of the system yields only 2 energy eigen states. So, let us next go and have a look at how we can work out within the scope of microcanonical ensemble the thermodynamics of a 2-state system.

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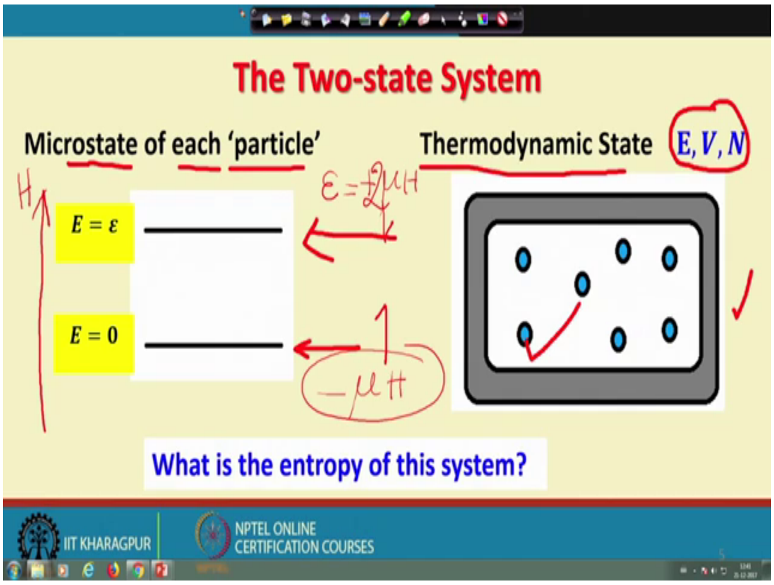

The Two-state System

Microstate of each 'particle'

Thermodynamic State E, V, N

$E = \varepsilon$

$E = 0$

What is the entropy of this system?

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So, let me introduce this 2-state system as follows. First of all, I must be having for the ensemble a definition of the thermodynamic state. So, I have the thermodynamic states specified as some given value of the total energy of the system, some volume of the system and a total number of particles. So, in this picture I show typically what I mean by this. So, my system has a fixed volume, it is surrounded by a rigid adiabatic impermeable wall and I have these particles in the system which I have shown here.

Now, each of these particles have been subjected to be investigated using the Schrodinger equation. And then I can use the solution of the Schrodinger equation to define the microstate of each of these particles. And by my choice that, I we find we define that there will be 2 such solutions possible. The lowest energy eigen state is the one which has been characterized by an energy value of 0. In certain scale and there is only one more energy state possible and that is energy equal to epsilon.

Now, as you see that for the spin half system, what did we have? What would be the energy E equal to 0 state? If I placed a field H like this, then the E equal to 0 state will have the spin up direction, and the higher energy level would have the spin down direction, and in that case, I would have E equal to epsilon would be equal to plus mu H, and actually plus 2 mu H. Because I am taking minus mu H as the 0 of scale of my energy.

And therefore, the question that I ask for this generalized system is can I do the thermodynamics of a system like this, where the system is comprised of a very large number typically the Avogadro number of particles. And I maintain the system under the condition of isolated experimental situation, and I ask the question what is the entropy of the system, or any other thermodynamic property of the system for that matter.

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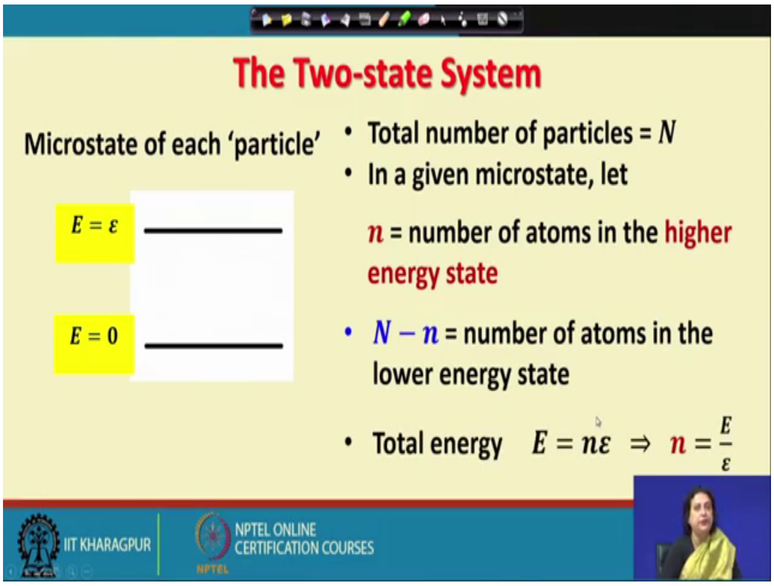

The Two-state System

Microstate of each 'particle'

- Total number of particles = N
- In a given microstate, let

  n = number of atoms in the higher energy state

- $N - n$ = number of atoms in the lower energy state
- Total energy $E = n\varepsilon \Rightarrow n = \frac{E}{\varepsilon}$

In order to do that, what we are going to do is, we have talked about the microstate of each particle, and we know that the total number of particles is equal to N. Now in a given microstate let me indicate by this number small n, the number of atoms in the higher energy state.

And since the total number of particles is constant in the system therefore, I must be having if small n is the number of atoms in the higher energy state, what is the number of atoms in the lower energy state? That must be capital N minus small n the rest of the atoms or particles present in the system. There is something else that comes out from this particular treatment. I have already said that the number of particles is constant in this system, and also the total energy of the system is constant, right.

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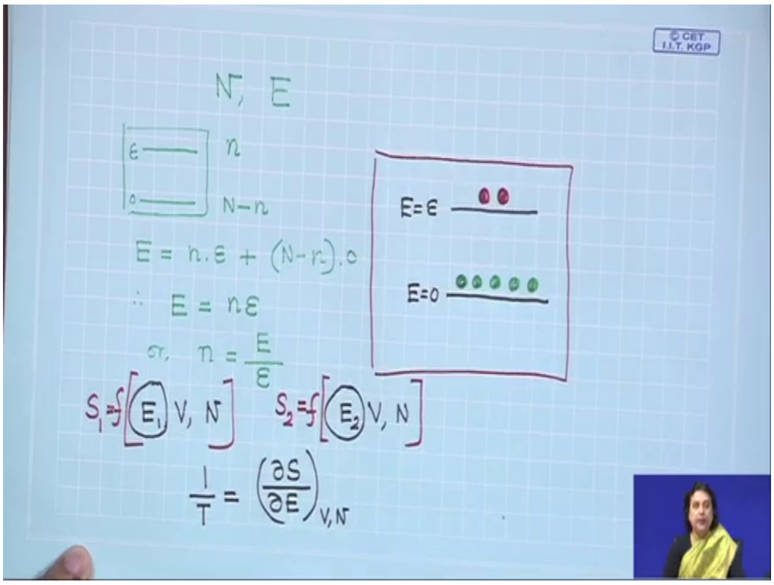

N, E

$E = n.\varepsilon + (N-n).0$

$\therefore\ E = n\varepsilon$

or, $n = \frac{E}{\varepsilon}$

$S_1 = f\left[\boxed{E_1} V, N\right]$ $S_2 = f\left[\boxed{E_2} V, N\right]$

$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}$

Now, I have the situation in a given microstate, I have N particles residing in the upper energy state having energy epsilon, and capital N minus small n particle residing in the lower energy state having energy 0. So, for any such microscopic state what is the energy of the system? That must be small n into epsilon plus capital N minus small n into 0.

And therefore, I can very easily say that capital E that is the total energy of the system is given by small n into epsilon. Or in other words small n that is the occupation number of the higher energy state, that uniquely decides the describes the different microstates of the system, this is related to the total energy E and epsilon. So, this is exactly what we have shown here.

So, we say that if I have this information regarding the microstate of the system, telling me that there is only one parameter of the microstate which is epsilon. And in the micro state I have the total number of particles N, and the total energy E. Then I can characterized all possible microscopic states of the system in terms of this independent parameter which in this case acts as a does the role of a quantum number which is given by a ratio of this E by epsilon.

Now, once we know this then let us see and go ahead, and try to see how the system now looks like.

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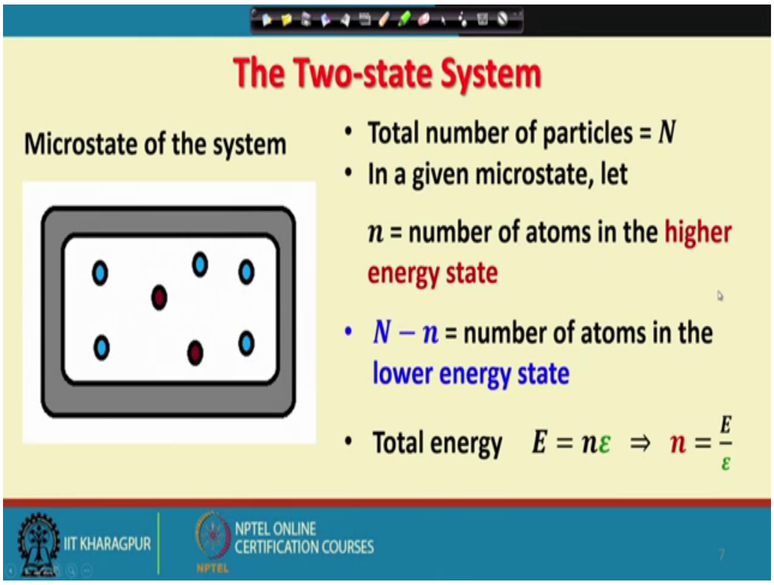

The Two-state System

Microstate of the system

- Total number of particles = N
- In a given microstate, let

  n = number of atoms in the higher energy state

- $N - n$ = number of atoms in the lower energy state
- Total energy $E = n\varepsilon \Rightarrow n = \frac{E}{\varepsilon}$

So, this is a typical representation of the microstate of the system, where as I have shown using colour codes small n corresponds to the number of particles or atoms in the higher energy states. So, in this system I have 1, 2, 3, 4, 5, 6, 7 atoms. Out of these I have only 2 of them residing in the higher energy state. And the rest that is rest 5 particles 1, 2, 3, 4, 5, they will be residing in the lower energy state.

A typical way of representing this kind of microstate using the energy diagram is like this. So, this is E equal to 0, and this is E equal to epsilon. And according to this picture, I have how many in the lower energy state? 1, 2, 3, 4, 5 particles in the lower energy states, and only 2 particle in the upper energy state. So, this is the energy state representation of what I have shown pictorially in this picture.

Now, once we have clarified the setting up of the model system, let us next concentrate on what we can say about the thermodynamics of this 2-state system.

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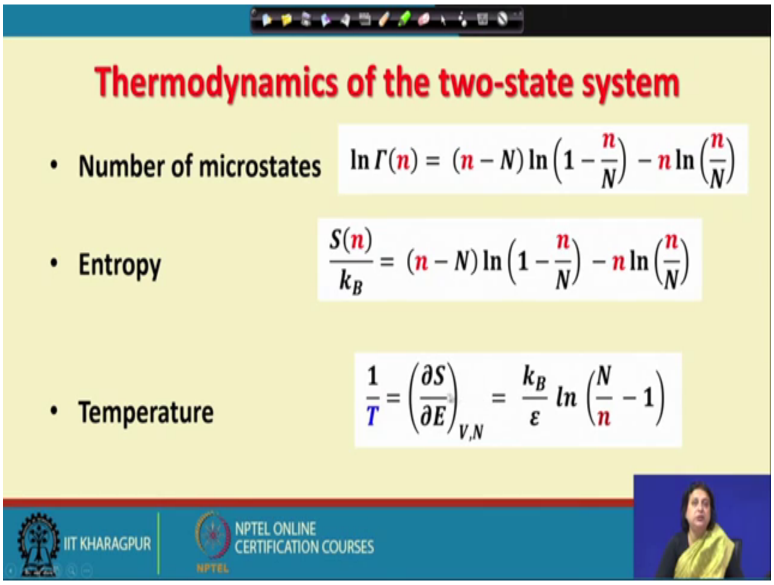

Thermodynamics of the two-state system

- Number of microstates $\ln \Gamma(n) = (n-N)\ln\left(1-\frac{n}{N}\right) - n\ln\left(\frac{n}{N}\right)$
- Entropy $\frac{S(n)}{k_B} = (n-N)\ln\left(1-\frac{n}{N}\right) - n\ln\left(\frac{n}{N}\right)$
- Temperature $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{k_B}{\varepsilon}\ln\left(\frac{N}{n}-1\right)$

So, I know the number of microstates you can very easily find out, that this is going to be the number of microstates of the system consistent with a given value of capital N, that is the total number of particles and the total energy E.

Now, as you see that gamma N has contributions both from small n minus capital N and only small independent terms. And I will leave this expression to be derived by you by looking at the a model system. Because I have already worked out this for the spin half particles.

Now, once you know this number of microstates, then what is the entropy, I am going to use the Boltzmann distribution, and directly write down the entropy S as a function of n. But here on the left-hand side, I have written S by k B, because this is the term which is equal to this log of gamma term. As a result, as you see that the right-hand side is identical. The only thing that I have changed is the left-hand side.

Now once you know entropy then the information that you have is as follows. You have an isolated system, in that isolated system many, many states are micro states are possible. And these microstates are uniquely described by a single parameter which depends on the total energy and the number of particles.

Now, I am going to go a little beyond what happens to the system, if I introduce a concept of temperature. Now in an isolated system you must be very, very careful. If you are use studying an isolated system, it is not interacting with the surrounding in any way. So, it is not exchanging energy with it is surrounding.

But if it so happens that, I allow the system to undergo a change in it is energy like by bringing it into equilibrium with some other thermostat. Then upon equilibration with the thermostat, the energy value will change why will it change because the system will then exchange thermal energy between itself.

And it is surrounding, and then I once again isolated and make it another isolated system at equilibrium; such that it has some other value of the total energy. And if I have not allowed the change in a volume and number of particles so, basically what I have with me is the first state where I had E 1 V N and the second state, where now I have E 2 V N. So, which is a quantity that has changed between these are the same isolated system. I find that the 2 isolated systems are different in terms of the amount of total energy that it has. So, in this case we can start talking about what is the temperature.

Now, you understand that the entropy of the system in the first case, that is going to be a function of this. So, it is value is going to be dependent on what E 1 is. And in the second equilibrium state this is going to be dependent on the value of E 2. And then we can measure the rate of change of entropy as the total energy changes. And this definition is given by 1 by T that is del S del E V N. So, this is the result that I am going to use next, and try to see what the value of temperature is. Now if I know S, then I know that I am going to use the definition del S del E V N.

Now, look at the expression of S that we have, we now know S as a function of n.

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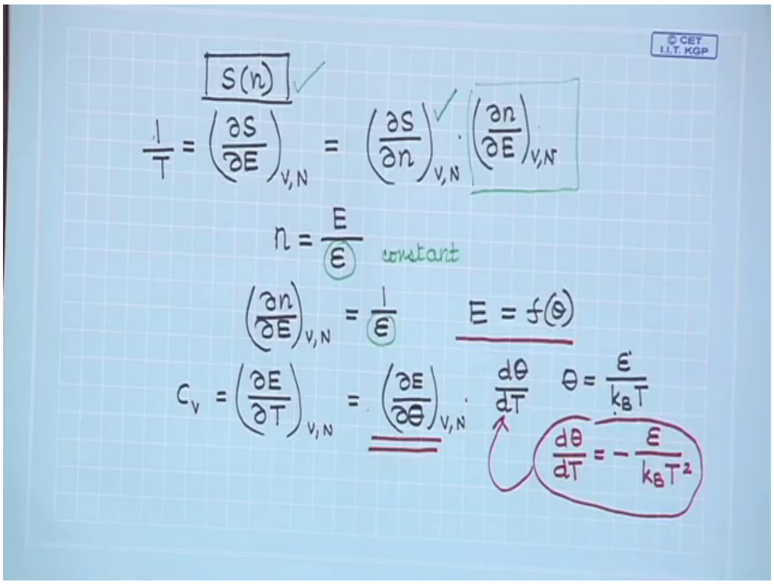

$$\boxed{S(n)}\ \checkmark$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} = \left(\frac{\partial S}{\partial n}\right)_{V,N}^{\checkmark} \cdot \boxed{\left(\frac{\partial n}{\partial E}\right)_{V,N}}$$

$$n = \frac{E}{\varepsilon} \quad \text{constant}$$

$$\left(\frac{\partial n}{\partial E}\right)_{V,N} = \frac{1}{\varepsilon} \qquad \underline{E = f(\theta)}$$

$$C_v = \left(\frac{\partial E}{\partial T}\right)_{V,N} = \underline{\underline{\left(\frac{\partial E}{\partial \theta}\right)_{V,N}}} \cdot \frac{d\theta}{dT} \qquad \theta = \frac{\varepsilon}{k_B T}$$

$$\frac{d\theta}{dT} = -\frac{\varepsilon}{k_B T^2}$$

Now, in order to obtain temperature, we would require del S del E V N. But what I have here is S as a function of N. Therefore, I am going to use a chain rule and say that I am going to evaluate del S del N under the condition of constant volume and number of particles.

But now I would also require del N del E under the same conditions. But do you know what E is of course, we know that small n is related to capital E. So, that is capital E by epsilon. Now please try to understand that for a given system this epsilon is a constant. It is a characteristic constant of the system that I am starting. Therefore, I can very easily say what is del N, del E if I keep everything else constant. That must be equal to 1 by epsilon; where epsilon is once again a constant.

If I now just look back I know S as a function of N. Therefore, I can find out this derivative. And I already know that this particular derivative is equal to 1 by epsilon. And therefore, the result that we get is what is shown here, and this is given by k B by epsilon then logarithm of this fraction minus 1.

So now you have actually achieved a lot. You have started from the solution of the Schrodinger equation for a given system; which gave you only 2 solutions 2 energy eigen states, corresponding to the 0 energy and some excess energy epsilon. And we have been able to obtain the entropy as well as how this entropy would change if I allowed the change in energy of the system.

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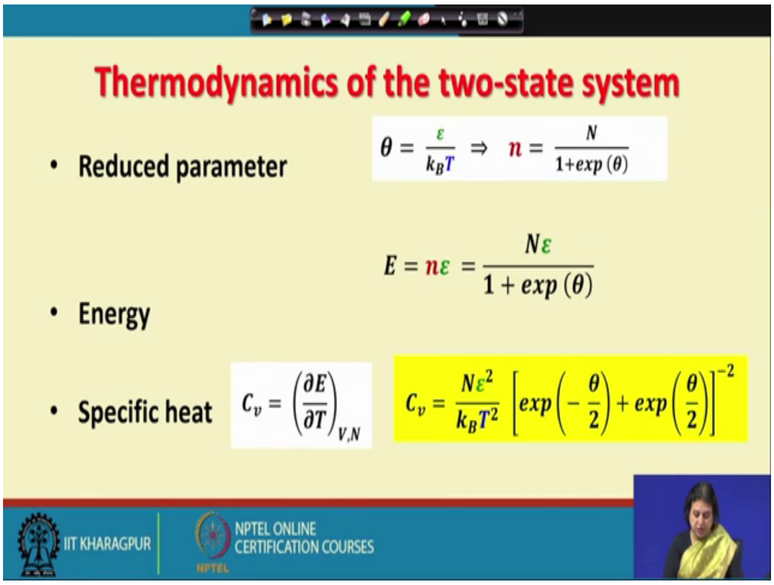

Thermodynamics of the two-state system

- Reduced parameter $\theta = \frac{\varepsilon}{k_B T} \Rightarrow n = \frac{N}{1+\exp(\theta)}$
- Energy $E = n\varepsilon = \frac{N\varepsilon}{1+\exp(\theta)}$
- Specific heat $C_v = \left(\frac{\partial E}{\partial T}\right)_{V,N}$ $C_v = \frac{N\varepsilon^2}{k_B T^2}\left[\exp\left(-\frac{\theta}{2}\right)+\exp\left(\frac{\theta}{2}\right)\right]^{-2}$

So, in the next slide we go a little further in the thermodynamics of the 2-state system and introduce what we call as a reduced parameter. So, this reduced parameter is defined as theta. So, what is theta? Theta is a in this particular case a ratio of this energy epsilon which is a parameter from my microscopic model. And k B T that is the thermal energy at a temperature T.

Now, epsilon has a dimension of energy k B T has also has a dimension of energy. So, what is the dimension of theta? The dimension of theta is 1, which means it is a dimensionless quantity. And that is the reason why I all it a reduced parameter. Now if I write down the number N as a function of this reduced parameter, then this is the expression that I am going to get. You see that small n is equal to capital N divided by 1 plus exponential of theta.

Now, if that is so, then it is possible to go ahead and simplify the expression for the total energy of the system, because the total energy of the system is N epsilon. And I know what small n is as a function of theta. So, I just plug it back over here, and that gives me the total energy of the system.

So far so good. But if this is not exactly a measurable quantity, what is it that we measure in experiments when we are trying to understand the thermodynamic properties of the system? One typical quantity is it is specific heat. And the definition of specific heat is that if you know the total energy of the system, and if you can measure this measure the response of the system how the energy changes as you vary the temperature of the system under isochoric and constant particle conditions then this ratio will give you the specific heat under isochoric condition in a closed system.

So now, I have an expression of E in terms of my microscopic parameters epsilon, and theta which includes not only the microscopic parameter epsilon, but also the temperature T. And therefore, it is possible for me to derive an algebraic expression for C v. So, all I have done is I know E, I have taken a derivative of E with respect to temperature.

So, once again you need to find out C v that is equal to del E del T V N. Now you already know E as a function of theta. Isn't it? Therefore, you will find it useful to derive this as del E del theta V N multiplied by d theta d T. Because by definition theta depends only on temperature as a variable epsilon and k B both are constants.

So now all you need to do is, you can find out what d theta d T is. So, what is d theta d T? D theta d T is now going to be given by minus epsilon by k B T square. I can use this expression put it back in here, and I since I know E as a function of theta. I can find out this particular derivative. So, by in doing a little bit of algebra over here you will be able to show that this is what the specific heat is.

Now, having an analytical expression is actually extremely useful when you interpret the experimental data.

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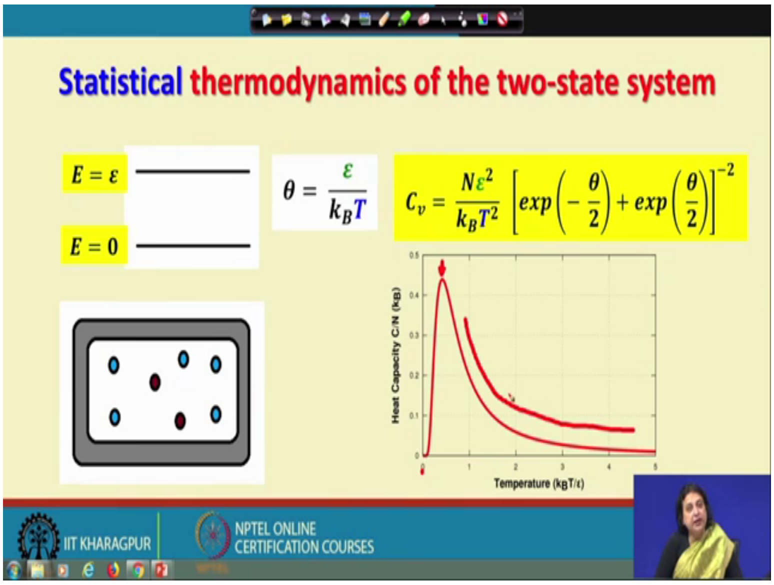

Statistical thermodynamics of the two-state system

$E = \varepsilon$

$E = 0$

$\theta = \frac{\varepsilon}{k_B T}$

$C_v = \frac{N\varepsilon^2}{k_B T^2}\left[exp\left(-\frac{\theta}{2}\right) + exp\left(\frac{\theta}{2}\right)\right]^{-2}$

So, that is what we are going to show right now. So, if you carry out experiments by measuring the heat capacity of some given substance, and you and for this you measure the heat capacity at different temperatures, then sometimes your experimental result might show a variation like this. So, initially your heat capacity is small, then it goes up and then it turn goes down. And this maximum appears somewhere around a near about 0.5, value of this k B T by epsilon, that is a 1 by theta.

Now, this behaviour you must realize is not a common behaviour for example, for the solids. Because you have learnt from de long petit law that at very high temperatures I must be having a constant value of heat capacity in a system. And therefore, if you have any such observation, you actually say that well I do have an anomalous behaviour. And this particular behaviour is known as typical of a system, where it has 2 energy states which are very close to each other. And all other energy states are much, much higher compared to these 2.

In that case, yours heat capacity upon measurement at different temperatures will show a behaviour like this. And the appearance of this maximum is known as a Schottky hump.

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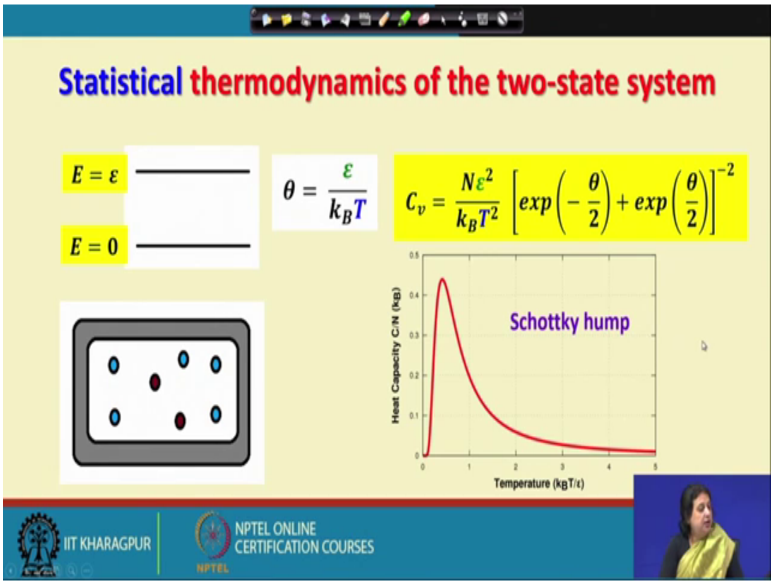

Statistical thermodynamics of the two-state system

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So, as far as experimentalists are concerned, what they will say is well, I have done a measurement. I have taken a measurement of the heat capacity of the system, and I have repeated my experiments at different temperatures, and I have come up with the Schottky hump.

Then they will construct the microscopic model of the system by saying that, there are 2 lowest energy eigen states of this system live very close to each other.

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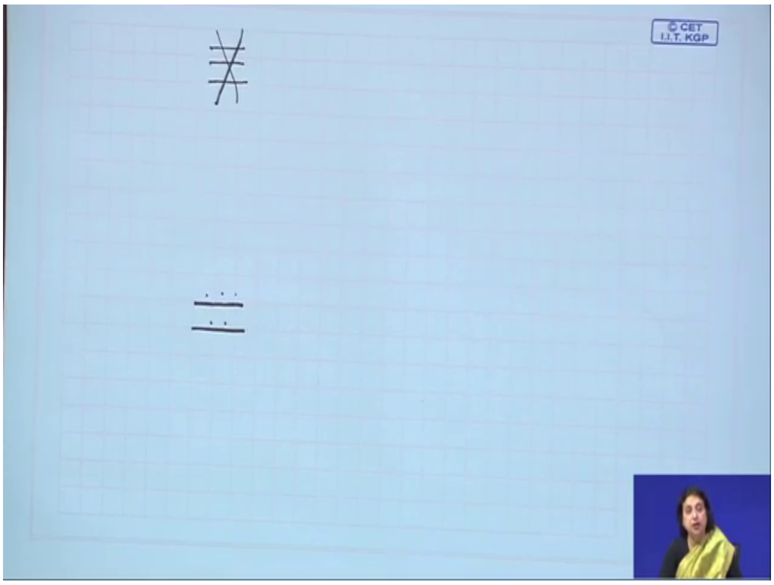

And the others are probably much, much higher up. Therefore, at normal temperatures the system populates only these 2 energy states and not these ones. And it is only under that condition that you will observe a Schottky hump in your experiment.

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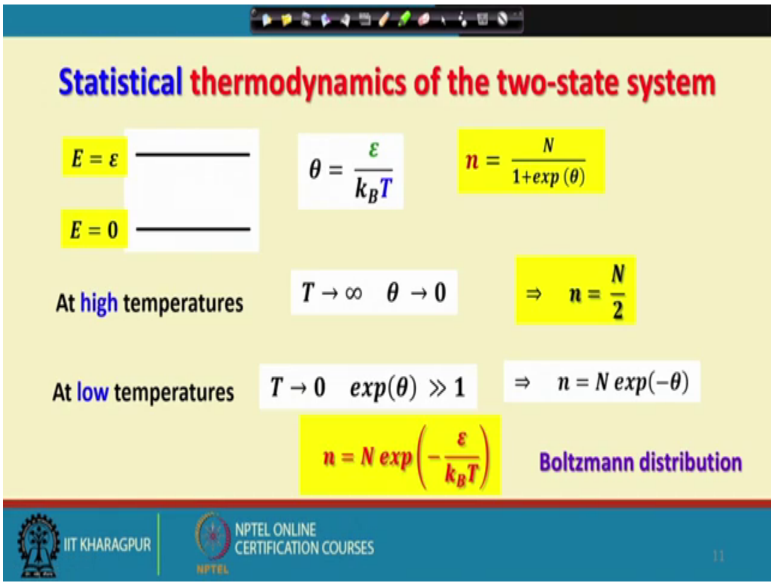

Statistical thermodynamics of the two-state system

$E = \varepsilon$

$E = 0$

$\theta = \frac{\varepsilon}{k_B T}$

$n = \frac{N}{1+exp(\theta)}$

At high temperatures $T \to \infty \quad \theta \to 0$ $\Rightarrow \quad n = \frac{N}{2}$

At low temperatures $T \to 0 \quad exp(\theta) \gg 1$ $\Rightarrow \quad n = N\,exp(-\theta)$

$n = N\,exp\left(-\frac{\varepsilon}{k_B T}\right)$ **Boltzmann distribution**

And one last thing that I would like to mention over here is that we have already seen the value of N as a function of theta.

Now, let me ask this question. At high temperature when the temperature goes to infinity, in that limiting case theta must go to 0. So, in that case what happens is, I retrieved the value that small n must be capital N by 2. So, what does it mean? It means at very high temperature, if I have a 2-state system then the population will be equally distributed between the lower and the higher states.

Now, if I am at a very low temperature. In that case T goes to 0; which means that exponential theta that is much, much greater than 1. So, I can neglect this term one in the denominator. And write down N as capital N; that is, the total number of a particles multiplied by exponential minus theta. Now let me put back the expression for theta, and that is nothing but the well-known result that we have come across previously as the Boltzmann distribution.

So, this is where I am going to stop. I have shown to you the strength of statistical thermodynamics or molecule of thermodynamics, where we start from a very simple model of the particles atoms or molecules comprising the system, where they are present in under a given thermodynamic state. And how we can interpret important experimental results using this very simple models. In the next class we are going to discuss the canonical ensembles which correspond to a much more realistic system where the system has been put in contact with a thermal reservoir. Goodbye.