Introduction to Molecular Thermodynamics
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Lecture – 17
Canonical Ensemble Part I

Welcome back. Today we are going to talk about the last part of the language of molecular thermodynamics. And today we are talking about the canonical ensembles. So, let us try and see what these 2 terms mean first, ensembles. So, when we talk about ensembles, we are actually thinking about the collection of microscopic states that possible for a given system. And when I say it is canonical, it means that there is a general set of rules which all the microstates in the ensemble follow.

So, of course, we have seen microcanonical ensembles. There also there was a specific rule which all micro states were following, and that rule was a constant energy constant volume and constant number of particles. Now in canonical ensemble, we are thinking about a system, which is comprised of once again a very large number of particles, which is present at a given volume. But now unlike the system in a micro canonical ensemble, we have a different experimental situation. Now let us see what we mean by the macroscopic state or the experimental situation under which we are studying the properties of a system in canonical ensemble.

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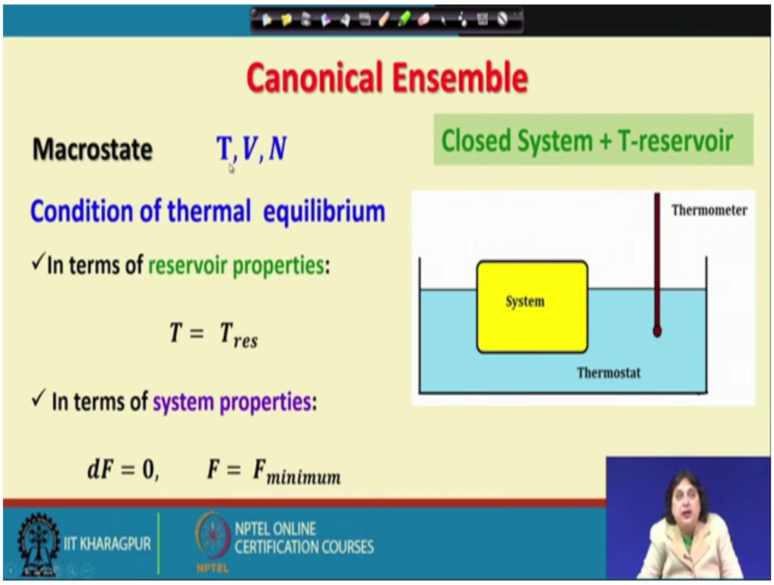

Canonical Ensemble

Macrostate T, V, N

Closed System + T-reservoir

Condition of thermal equilibrium

✓In terms of reservoir properties:

$$T = T_{res}$$

✓ In terms of system properties:

$$dF = 0, \quad F = F_{minimum}$$

So, this is the experimental picture that I have in mind, when I talk about canonical ensembles. So, as you see that I have a system marked here using this yellow box ok. Now this system is surrounded by a rigid wall which is impermeable to whatever substance is there within it. And the system has been equilibrated with respect by placing it in a thermostat. So, which means that the walls which are in contact with a thermostat they are capable of exchanging thermal energy from within the system to the reservoir and vice versa.

Now how do I know that the system is in equilibrium? I will measure the temperature using a thermometer as shown here, and when the temperature of the system becomes independent of time, I would say that the measurable property of the system temperature is now independent of time, indicating that this system is now in thermal equilibrium with the reservoir. So, under such condition we have already seen that the macro state of the system is now given by specifying the value of temperature, the value of volume. And the number of particles contained within the system of interest which is shown in this yellow box.

So, basically, we are talking about in an canonical ensemble a closed system, which is in equilibrium with a thermal reservoir. Now of course, we already have seen the condition of thermal equilibrium, and in terms of reservoir properties, the condition is I must be having temperature of the system is equal to temperature of the reservoir. And therefore, I am saying that the temperature of the this yellow box, this is going to be the same as the temperature of this blue region. So, that is the measurable condition which involves the reservoir property to establish the condition of thermal equilibrium.

Now, we have also described that if I want to know, what is the condition of thermal equilibrium in terms of system properties only, then we have seen that this is given in terms of the associated thermo dynamic potential. Now when you have this kind of macroscopic state given by temperature volume and the number of particles, we have already seen that here the thermodynamic potential is given by the Helmholtz free energy. And therefore, in terms of system properties alone, establishment of a new equilibrium state is guided by the fact that the Helmholtz free energy should be minimized under the given condition.

So, this is what we know about the macro state of the system.

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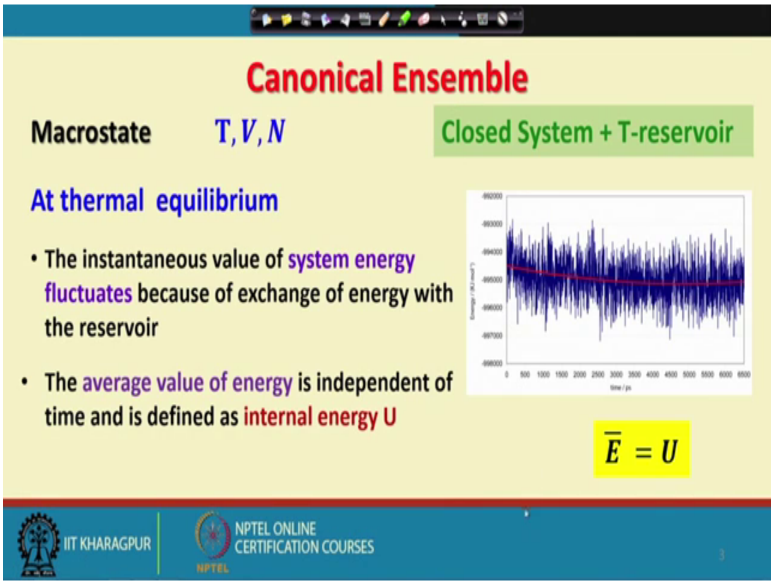

Canonical Ensemble

Macrostate T, V, N Closed System + T-reservoir

At thermal equilibrium

- The instantaneous value of system energy fluctuates because of exchange of energy with the reservoir
- The average value of energy is independent of time and is defined as internal energy U

$\bar{E} = U$

Now let us go and try and have a look at the net energy content of the system a little more closely Now just because the system is exchanging thermal energy with the reservoir, then I cannot say that if I had the means to measure the energy of the system, it must be fluctuating in time. So, this is a typical plot that has been shown over here as you see to start with the system started with some value of energy which is shown here. After some time, it is value reached here. And then after sometime it is value decreased here.

Now, why is that happening so. That is happening because, when you have kept the system in contact with the thermal reservoir; obviously, there will be some influx of heat, and heat will flow also out of the system. Now when heat comes into the system, the net energy content of the system increases, and if the net energy content of the system increases, then that is shown here by an increase in the instantaneous value of the energy. Now the moment the energy goes on increasing, it is expected that a hotter body has as a higher energy content; which means that by putting in extra energy into my system, I am heating the system up. But the temperature needs to be maintained constant. So, at this point the system would like to lose some energy. And the way it does it it releases energy through the die thermal walls to the surrounding reservoir.

As a result, the energy value comes down. So, this way by through the exchange of energy between the system and the surrounding, the constant temperature condition is maintained. But this also tells me that this must be having some confusing concept associated. And that is we have always talked about a constant energy condition, when we were discussing the micro canonical ensemble. And now I am saying that even if the system is at equilibrium, the instantaneous value of energy is not a constant. If I had some means of measuring the instantaneous value of energy, it is varying with time. So, isn't that a contradiction, how do I say that the system is still in equilibrium? I will answer this question.

But before that let us have a look at what happens at thermal equilibrium. Now at thermal equilibrium, the instantaneous value of the system energy goes on fluctuating as shown in this figure as I have mentioned right now. But as you see, if I take the average within certain time interval, initially it was varying with time, that average as shown by this red line over here. That is initially varying, and then it becomes nearly independent of time. So, it is this average value that would be measured in experiments ah, if we could measure energy ok.

So, we would say that at equilibrium, then the average value of this fluctuating quantity becomes independent of time. And this average value is nothing but the internal energy u as we encounter in the equilibrium thermal equilibrium system. So, this is a extremely interesting concept, that we must remember that although energy is fluctuating about an average value. This average value is independent of time, when the thermal equilibrium has been achieved between the system and the surrounding.

Now, what is the consequence of this observation? When I look at the consequence I would like to remind you, that the value of energy of the system directly affects the number of microstates accessible to the system we have discussed this topic in detail.

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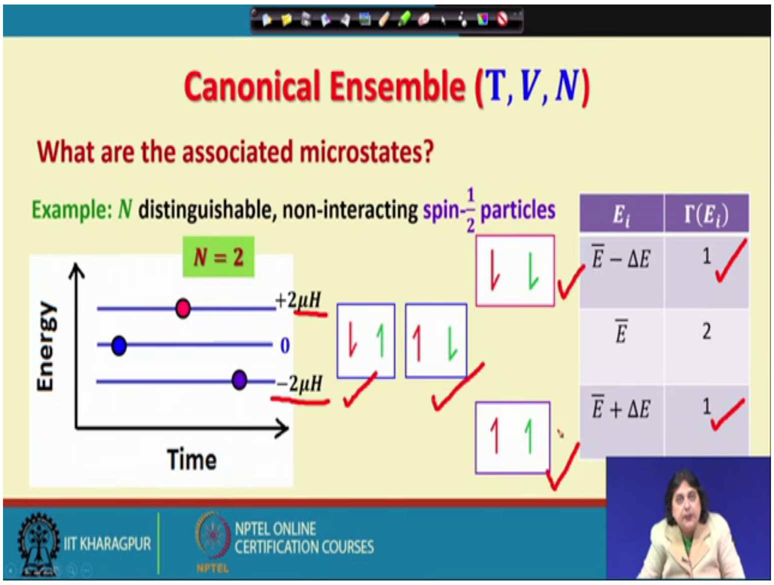

Canonical Ensemble (T, V, N)

What are the associated microstates?

Example: N distinguishable, non-interacting spin-$\frac{1}{2}$ particles

$N = 2$

E_i	$\Gamma(E_i)$
$\bar{E} - \Delta E$	1 ✓
$\bar{E}$	2
$\bar{E} + \Delta E$	1 ✓

So, let us next ask the question, when the total energy is fluctuating about a time independent average value. What happens to the associated microscopic states? So, if I look a little closely, in terms of a simple example, let us go back revisit the example of n distinguishable non-interacting spin half particles present at a given temperature T V and number of number of particles is fixed.

Now, let me take this very simple example of 2 such particles. Now for each such spin half particle, I am see I would say that well the system energy can be [vocalized-noise]. These 3 values and this follows from the solution of the Schrodinger equation for 2 distinguishable non-interacting spin half particles. Now here I have not explicitly shown the field in which this spins, half particles are present. But it is presence is indicated by the by this term H multiplied by the magnetic moment mu.

Now, let us say that I start with one microscopic state of the system with this energy 0 ok. Now for this 0 energy, I would say, what are the associated microstates by now; you must be able to show very easily, that these are the 2 possible microscopic states, when the total energy of the system is equal to 0 in the scale. Now if it so happens, that I have the system in this higher energy state. So, what happens? What are the typical microstates associated with the system residing at the higher energy state. We understand that this must be the case, when both the spins are oriented anti-parallel to the applied field.

Similarly, if we could have the system in the lower energy state, then what would have happened is there would be only one microscopic state possible, and that is the one where both the spins are oriented parallel to the applied magnetic field. Now what is this what is the outcome of this example, we conclude that here; let us say that this is my average energy of the system E bar equal to 0. So, how many microstates are there? There are 2 such microstates which I have put in here. Now think about the higher and the lower microscopic energy states. So, when I have a lower energy that is E minus delta E, where delta E is equal to 2 mu H. I see that I have one microstate accessible and when I am looking at some E plus delta E state.

I have another microstate accessible to the system. Therefore, the conclusion that I get from here is this. Like, if I could fix the energy at E bar, then the property of the system will be controlled by only these 2 microscopic states which are associated with the energy E bar equal to 0. But if I allow fluctuations in the value of energy, the fluctuation such that it can take up values like E bar minus delta E or E bar plus delta E, I see that additional microscopic states like this or this become accessible to the system[noise].

Now, let us go and take a little more complicated example and that is as follows.

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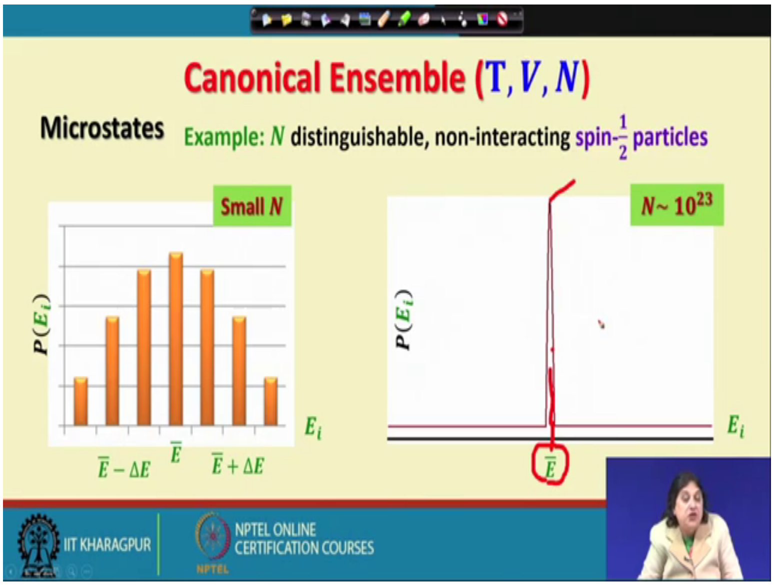

Canonical Ensemble (T, V, N)

Microstates Example: N distinguishable, non-interacting spin-$\frac{1}{2}$ particles

So, next let us choose a small n something like n equal to 6 or so. Then what we find is that, if I look at the possible values of the total energy of the system, and I plot along the y axis, the associated probability of observing the system at these energy values in contact with a thermal reservoir of course, then this is the kind of distribution that I will get. So, once again you get a peak the maximum number of microscopic states, is associated with the average value, but as you can see that there are substantial number of energy states associated with the energy values such as E plus delta E and E minus delta E.

But the interesting point is all these microscopic states are accessible provided the amount of energy that you are supplying to the system through it is interaction with the reservoir is big enough to cover say delta E to delta E or 3 delta E similarly, minus delta E minus 2 delta E and so on and so forth. So, what we understand here is ok, we are still in the small n case. Now let me think about the case where I have n of the order of 10 to the power of 23 a very large number. We have already seen that under such condition, the probability distribution will take the shape of a Gaussian distribution. And this Gaussian distribution is going to be very sharply peaked at around the average energy E bar ok.

So, E bar is associated with the maximum number of microscopic states ok. The system is most probable to exist in those microscopic states that are having a total energy of E bar. But think about E bar minus delta E. Please remember here delta E is a very small number compared to the total range of E I values available, and then if I go from this the position of the peak, I see that there are other microscopic states also possible which are very close in energy to the E bar and there is a substantial number of them.

So now that we have understood that what is going to happen to the system, when it is capable of taking up energy and releasing energy to the thermal reservoir? We understand that at thermal equilibrium the system will evolve towards the average energy state, which is associated with a maximum number of microscopic states, but there will be other microscopic states associated with accessible values of energy like, say E plus delta E or E minus delta E. So, what is the conclusion from this discussion? The conclusion is like this. The number of microstates instantaneously so, the conclusion from this analysis is summarized here if we think about the microstates of a canonical ensemble, where the system macroscopically is being maintained at a given temperature volume and number of particles.

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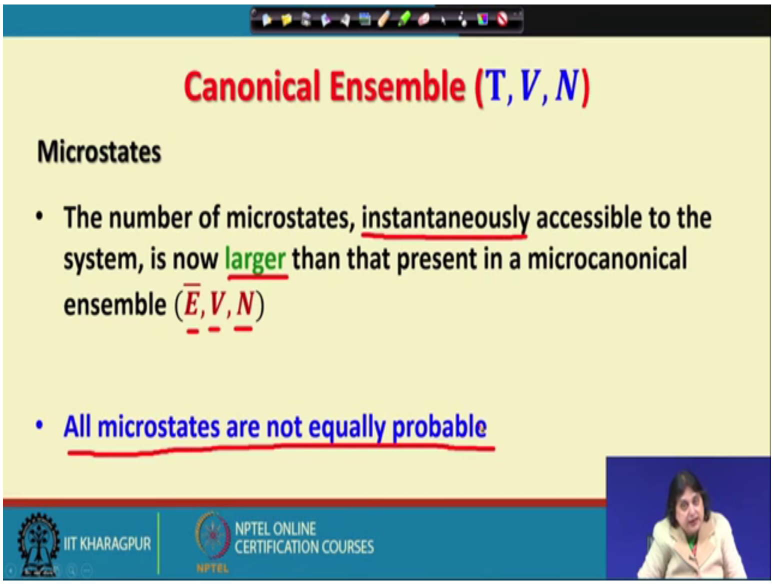

Canonical Ensemble (T, V, N)

Microstates

- The number of microstates, instantaneously accessible to the system, is now larger than that present in a microcanonical ensemble $(\bar{E}, V, N)$
- All microstates are not equally probable

The number of microstates that is instantaneously accessible to the system is larger than that present in a microcanonical ensemble, where you have an energy of total energy value equal to E bar volume v and the total number of particles N. And this is exactly what we have demonstrated to you by showing that if I fix those to spin half particle system to E bar equal to 0 the number of microstates of accessible would be only 2. But if I allowed the fluctuation of energy about E bar such that E bar plus delta E and E bar minus delta E are also accessible. Then the total number of microstates would be equal to 2 plus 1 plus 1 equal to 4.

The other important conclusion that we have got from here is under the condition that the total energy is varying instantaneously; all microstates are not equally probable. For a given value of energy S whatever microstates possible corresponding to that value of the energy are equally probable, but when many such values of energy are accessible to the system, the different bunches of microscopic states, that are associated with these range of values make the accessible microstates to the system unequal in their probability of occurrence. So, then the question comes, if I know ok I have a collection of microscopic states for a given system at thermal equilibrium. May I ask, what is the probability of observing this system, in a given microscopic state I? And this is the question that we are going to answer next.

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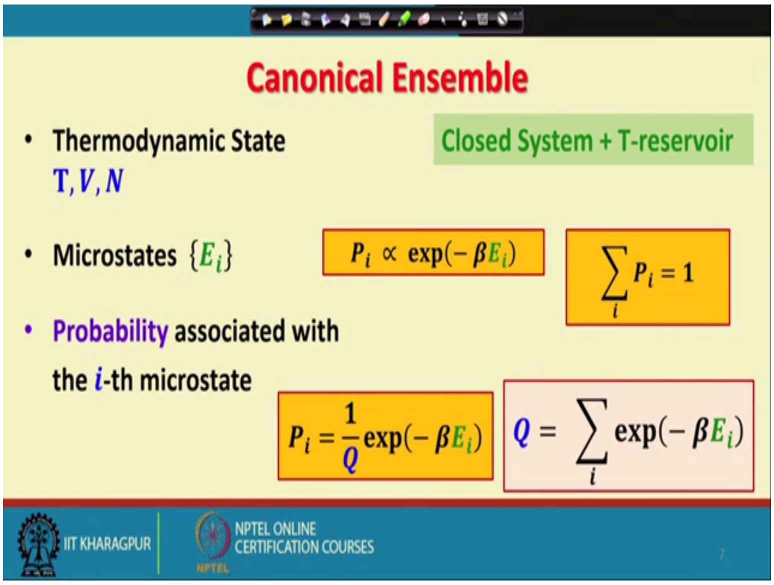

Canonical Ensemble

- Thermodynamic State T, V, N

Closed System + T-reservoir

- Microstates $\{E_i\}$

$P_i \propto \exp(-\beta E_i)$

$\sum_i P_i = 1$

- Probability associated with the i-th microstate

$P_i = \frac{1}{Q}\exp(-\beta E_i)$

$Q = \sum_i \exp(-\beta E_i)$

So, if I quickly go through the concepts, then we have said that for a closed system in contact with a thermal reservoir, I have all the micro states characterized by the different accessible values of E I. Then I am asking the question, what is the probability associated with the I ith microscopic state, that has an energy Eigen value of E I. The answer is this probability is going to be proportional to exponential of minus beta E I. In this discussion, I am going to use this definition again and again.

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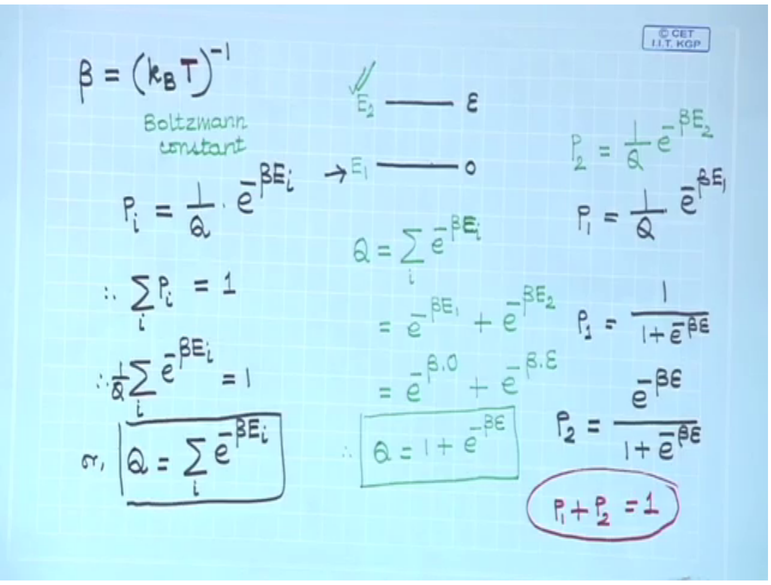

$\beta = (k_B T)^{-1}$

Boltzmann constant

$P_i = \frac{1}{Q} \cdot e^{-\beta E_i}$

$\therefore \sum_i P_i = 1$

$\therefore \frac{1}{Q}\sum_i e^{-\beta E_i} = 1$

or, $\boxed{Q = \sum_i e^{-\beta E_i}}$

E_2 —— ε

E_1 —— 0

$Q = \sum_i e^{-\beta E_i}$

$= e^{-\beta E_1} + e^{-\beta E_2}$

$= e^{-\beta . 0} + e^{-\beta . \varepsilon}$

$\therefore \boxed{Q = 1 + e^{-\beta \varepsilon}}$

$P_2 = \frac{1}{Q} e^{-\beta E_2}$

$P_1 = \frac{1}{Q} e^{-\beta E_1}$

$P_1 = \frac{1}{1+e^{-\beta \varepsilon}}$

$P_2 = \frac{e^{-\beta \varepsilon}}{1+e^{-\beta \varepsilon}}$

$P_1 + P_2 = 1$

So, beta is equal to KBT whole inverse if I define the macroscopic state of the system in terms of this temperature t.

In that case we can define this quantity, KB which is a universal constant and known as the Boltzmann constant. And so, KBT together give us idea about the thermal energy of available at a temperature T. Then beta is inverse of this thermal energy. Now if I look back, then I find that the probability associated with the I yath microscopic state is exponential of minus beta E I, where I is the I yath energy Eigen state obtained for this particular system. Now of course, if you talk about probability, as you have seen that there is a proportionality sign here.

Now, I know that under the normalization condition, I must be having that summation over I P I equal to 1. So, let me now write down that ok let me say that P I is equal to some normalization constant Q 1 by Q multiplied by E to the power of minus beta E I. Therefore, if I sum over all possible microstates I and sum over P I I must be having one. Therefore, doing a very simple algebra, we can say that this must be equal to 1. Or in other words I identify as the normalization constant Q, summation over I E to the power of minus beta E I, is that clear, ok? So, if I know the different energy eigenstates possible for a given system, then I can find out the normalization constant Q and accordingly I can completely write down what is the probability that this system resides in the I th energy Eigen state.

For example, if I have this classic 2 state system where this is the lower energy state is having an energy 0, and the upper energy state is having an energy equal to epsilon. In this case, do I know how to write down capital Q? Of course, I understand that capital Q is equal to summation over I E to the power of minus beta beta E I. How many microstates are there? How many energy Eigen states are possible? 1 2. Therefore, I would say that this can be written as beta E 1 plus E to the power of minus beta E 2. So, what is E 1? E 1 is equal to 0.

So, I would write that is equal to minus beta into 0. What is E 2? E 2 is this energy value, and E 2 by the definition of the problem is given by this number epsilon. Therefore, if I simplify I find that for this simple system, capital Q is equal to E to the power of minus beta epsilon. So, this is perfectly simple. Then if I ask the question, what is the probability that, this system presides in the upper energy state E 2 at a given temperature t/. So, then the probability that the system occupies the upper energy state characterized by the energy E 2, will be given by 1 by Q into E to the power of minus beta into E 2, right.

So, if that is so, then I can very quickly write down that P 2 is going to be equal to E to the power of minus beta epsilon divided by 1 plus E to the power of minus beta epsilon. Now what is P 1? P 1 is the probability that the system occupies the lower energy state, that is this one ok. By definition P 1 is equal to 1 by Q into E to the power of minus beta E 1. If I put all the values back, what should I get, I get this is equal to 1 plus E to the power of minus beta epsilon, right. Now you can very easily check that P 1 plus P 2, that is equal to 1 ok.

So, what I have achieved over here is as follows. I have achieved here the probability associated with the I th microstate in terms of not only the energy Eigenvalue, but also in terms of a normalization constant, which sums over all possible micro states of the system.

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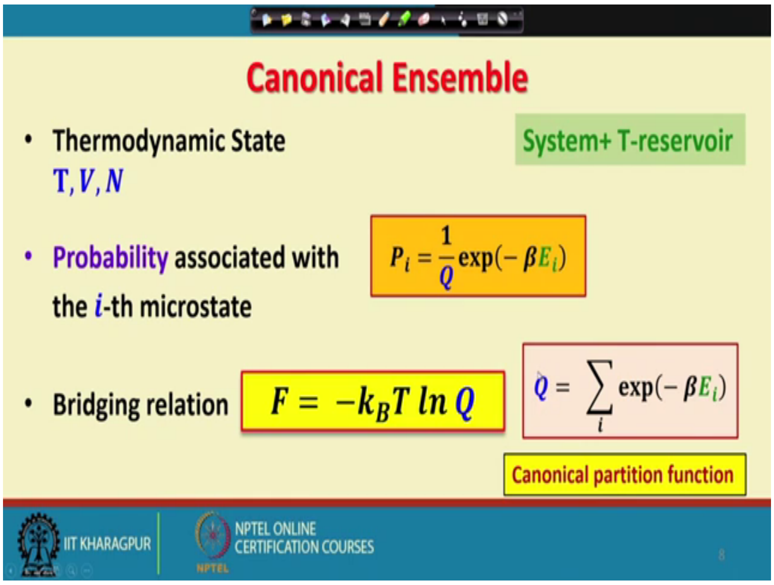

Canonical Ensemble

- Thermodynamic State
  T, V, N

System+ T-reservoir

- Probability associated with the i-th microstate

$$P_i = \frac{1}{Q}\exp(-\beta E_i)$$

- Bridging relation $F = -k_B T \ln Q$

$$Q = \sum_i \exp(-\beta E_i)$$

Canonical partition function

With this knowledge then the results of molecular thermodynamics gives us something which is very, very important. And that is a bridging relationship. Have you seen a bridging relationship before? Yes, you have, you have seen that in a micro canonical ensemble.

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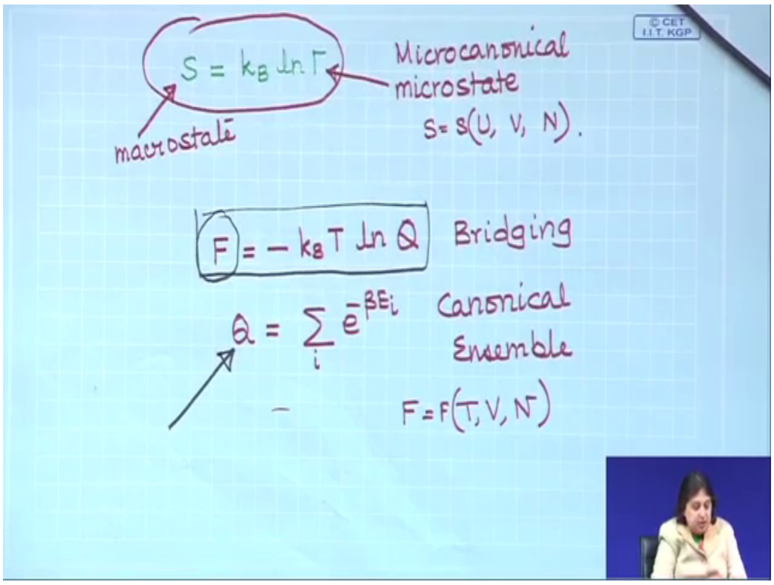

$S = k_B \ln \Gamma$

macrostate

Microcanonical

microstate

$S = S(U, V, N)$.

$F = -k_B T \ln Q$ Bridging

$Q = \sum_i e^{-\beta E_i}$ Canonical Ensemble

$F = F(T, V, N)$

We could write down this famous Boltzmann hypothesis, that S is equal to KB l n gamma ok.

Now, all the information regarding the micro states is contained within this factor gamma, and all information regarding the macro state is contained within the entropy S; which means that this gave us a bridging relationship between the macro and the microscopic length scales. In the canonical ensemble, we also have a similar relationship, which is which can be derived from the Boltzmann hypothesis. And this relationship is F is equal to minus k t l n Q. So now, let us have a look at what we have achieved over here. F is equal to minus KB T l n Q. Now what is Q Q is equal to summation over I E to the power of minus beta E I.

So, as you see that all the microscopic information that you can ask from a given system, they are contained within this normalization constant Q. And if you look at the original expression, then what do I have on this side? I have the Helmholtz free energy F and this Helmholtz free energy F is the representative property of the macroscopic length scale. And therefore, this particular relationship is the all important bridging relation in the canonical ensemble ok.

So, as you understand in the canonical ensemble the thermodynamics is being described in terms of a given temperature volume and number of particles. We know that F is a thermodynamic potential under such condition, which is a natural variable of these these

3 parameters and this appears in this bridging relationship. On the other hand, when you had the micro canonical ensemble, there I know that I can describe the system in terms of U V N. These 3 parameters and the entropy can be described in terms of these 3 parameters as functions of natural variables of these 3 parameters. So, side by side just like the starting from the hypothesis of Boltzmann in the micro canonical ensemble, it can be shown in the canonical ensemble that the bridging relationship gives you a connection between the Helmholtz free energy and the canonical partition function. Now I have introduced this terminology the canonical partition function.

And this describes the normalization constant Q, the normalization constant Q tells us how the different energy states the total available energy is distributed or partitioned amongst the different accessible energy states. And that is the reason why it is called a partition function.

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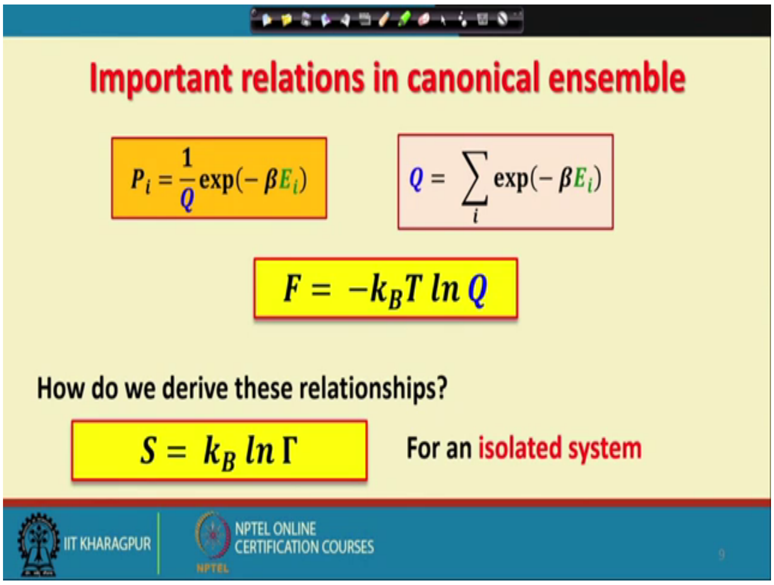

Important relations in canonical ensemble

$$P_i = \frac{1}{Q}\exp(-\beta E_i)$$

$$Q = \sum_i \exp(-\beta E_i)$$

$$F = -k_B T \ln Q$$

How do we derive these relationships?

$$S = k_B \ln \Gamma$$

For an isolated system

So, the at the in conclusion, I would say that we have now come across 3 very important relationships as far as the description of canonical ensembles is concerned, we can think about now what is the probability of the I th microstate in this system in terms of temperature, in terms of the energy Eigenstates that we are talking about, and the canonical partition function Q. And knowing this at the microscopic level, we can calculate all possible thermodynamic properties using this bridging relationship; obviously, you would be asking the question, how do I derive such a relationship. As I have said it is possible to derive these relationships from the Boltzmann hypothesis for an isolated system. In the next lecture, we will show you how to do so.

Thank you.