Introduction to Molecular Thermodynamics
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Lecture – 19
Canonical Ensemble Part II

Welcome back, we will continue our discussion on the canonical ensembles today by considering the three important relationships.

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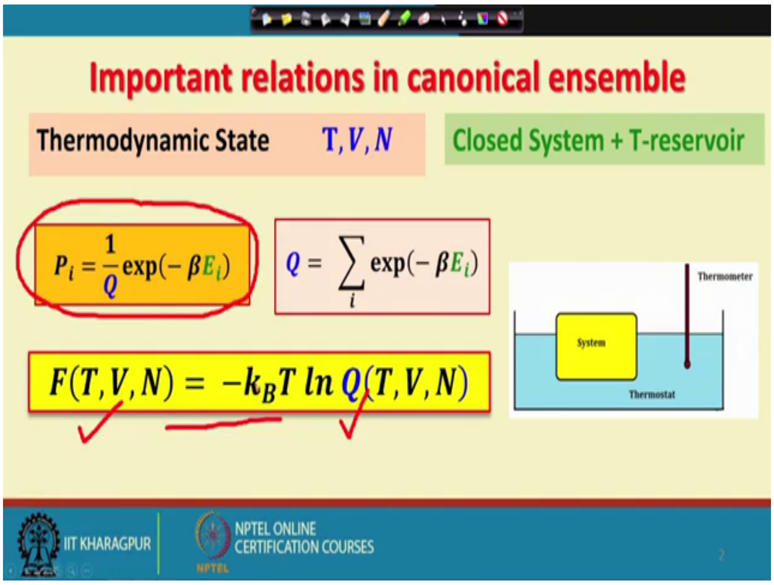

Important relations in canonical ensemble

Thermodynamic State T, V, N

Closed System + T-reservoir

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

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

$$F(T,V,N) = -k_B T \ln Q(T,V,N)$$

That we have already discussed about today I am going to first look at the importance of this particular relationship, and show you that once you have a model you will be able to find out the partition function Q from there calculate the Helmholtz free energy F, and do what calculate whatever thermodynamic quantity you would like starting from a microscopic model. In the second part of this lecture we will look at the properties of this probability P i and the practical significance that this relationship has. So, first let us have a look at how to model the thermodynamics of a system starting from the partition function.

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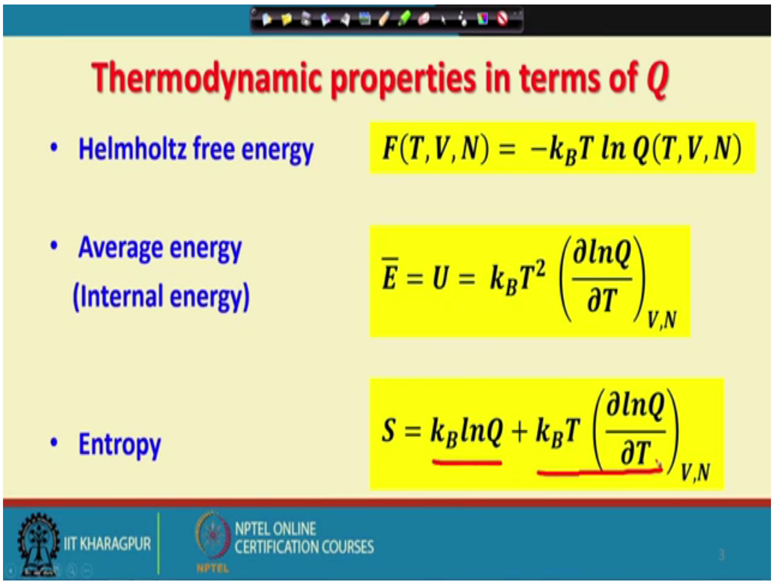

Thermodynamic properties in terms of Q

- Helmholtz free energy $F(T,V,N) = -k_BT\ln Q(T,V,N)$
- Average energy (Internal energy) $\bar{E} = U = k_BT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{V,N}$
- Entropy $S = \underline{k_B\ln Q} + \underline{k_BT\left(\frac{\partial \ln Q}{\partial T}\right)}_{V,N}$

So, this is the relationship that we already know from the derivation, that I present it in the earlier lecture. So, we know that the Helmholtz free energy, which is a natural variable of the parameters T, V and N that is related to the natural logarithm of the partition function capital Q, and here this capital Q contains all the informations regarding the microscopic states of the system.

Now, let us think about another thermodynamic property like the internal energy. Now if I want to find out the internal energy, I have made it very clear by now that the internal energy is nothing, but the average energy in this canonical ensemble. So, how do I find out the average energy?

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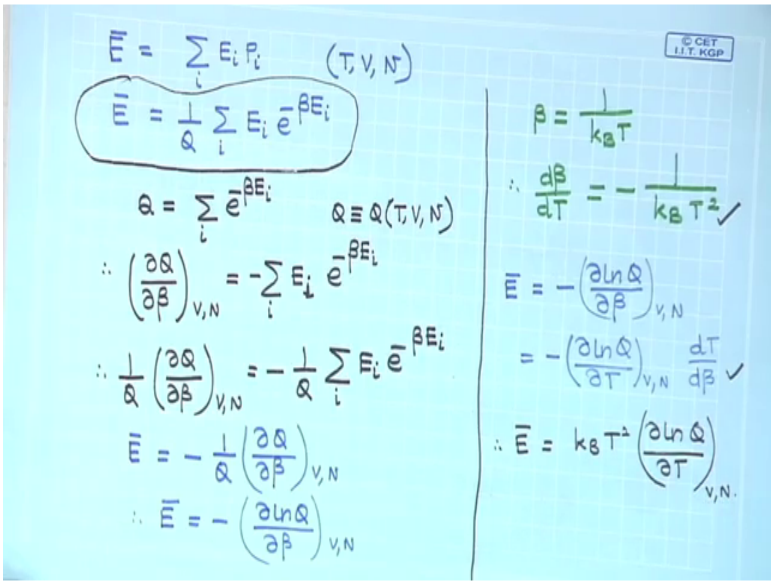

$$\bar{E} = \sum_i E_i P_i \qquad (T, V, N)$$

$$\boxed{\bar{E} = \frac{1}{Q}\sum_i E_i e^{-\beta E_i}}$$

$$Q = \sum_i e^{-\beta E_i} \qquad Q \equiv Q(T, V, N)$$

$$\therefore \left(\frac{\partial Q}{\partial \beta}\right)_{V,N} = -\sum_i E_i e^{-\beta E_i}$$

$$\therefore \frac{1}{Q}\left(\frac{\partial Q}{\partial \beta}\right)_{V,N} = -\frac{1}{Q}\sum_i E_i e^{-\beta E_i}$$

$$\bar{E} = -\frac{1}{Q}\left(\frac{\partial Q}{\partial \beta}\right)_{V,N}$$

$$\therefore \bar{E} = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{V,N}$$

$$\beta = \frac{1}{k_B T}$$

$$\therefore \frac{d\beta}{dT} = -\frac{1}{k_B T^2} \checkmark$$

$$\bar{E} = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{V,N}$$

$$= -\left(\frac{\partial \ln Q}{\partial T}\right)_{V,N} \frac{dT}{d\beta} \checkmark$$

$$\therefore \bar{E} = k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{V,N}.$$

Of course, by definition this average energy is given by summation over i E i P i right. So, E i for the i-th microscopic state E i is a solution of the Schrodinger equation. So, this is the i-th energy eigen state, and P i is the probability that the system resides in this i-th microscopic state, under the given condition of temperature, volume, and number of particles.

Now if I write down explicitly what P i is I can very easily show that this must be something like E i e to the power of minus beta E i by definition of P i. So, this is my e bar. Now is it possible to simplify this expression to a more useable form for that, what I am going to do is, I am going to write down the definition of Q. So, by the definition of Q I have to sum over all possible values of i of this exponential function, what I do next please remember that Q is a function of T, V and N therefore, or I can take a derivative of Q with respect to either T or V or N.

What I decide to do here, is I am going to take a derivative of Q with respect to beta keeping V and N constant. Now very simple mathematical treatment tells you that you can do this derivative within the summation, and what you will be left with is on the right hand side that is E i e to the power of minus beta E i. Now i divide both sides with respect to capital Q giving me this as minus 1 by Q summation over i E i e to the power of minus beta E I, now does this look familiar of course, this is nothing, but this expression that I have written down here, and therefore I should be able to say that E bar is equal to minus 1 by Q del Q del beta keeping volume and number of particles constant, but as you see that this can be further simplified I can very easily write down that E bar is equal to minus del l n Q del beta keeping V and N constant. Now somebody may argue that well the actually we would like to see the derivative with respect to temperature rather than beta.

So, that is pretty simple once again, what we can do is we start from the definition of beta, beta is equal to 1 by k T therefore, what is d beta d T it is a function of temperature k B being a universal constant that is 1 by k B T square. Now can I write down what E bar is in terms of taking a derivative with respect to temperature, I know that E bar is del l n Q del beta keeping V and N constant.

And this I am going to write as del l n Q del t keeping V and N constant into dT d beta therefore, if I just check this expression and this expression, and combine them what do I get, I get E bar that is equal to k B T square del l n Q del T, V N. So, this is trivial algebra and one can have a look at the expression for internal energy, that I have put in over here, and that is nothing, but k B T square into del l n Q del T keeping volume and number of particles constant.

Now once you have the Helmholtz free energy, and the internal energy in that case it is very easy to find out what the entropy of the system is, now can you guess because that is only be a one more algebraic step and that can be carried out as follows. So, I am looking for an expression for entropy.

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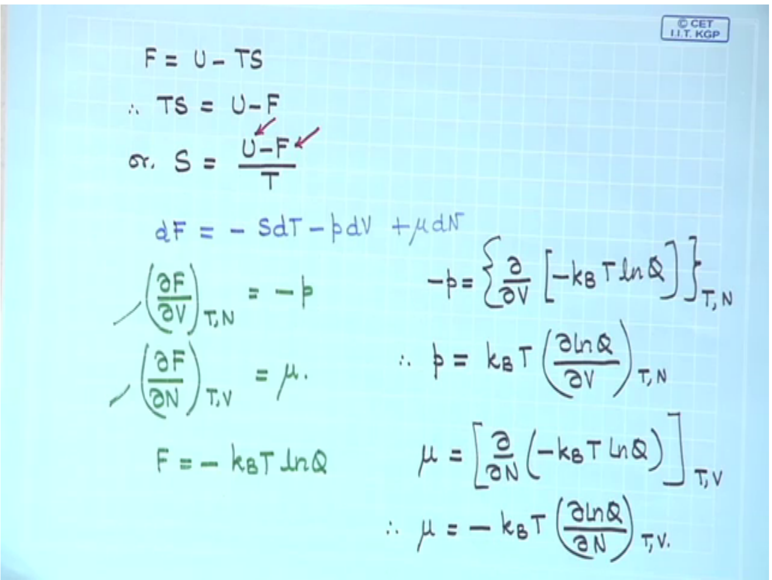

$$F = U - TS$$

$$\therefore\ TS = U - F$$

$$\text{or, } S = \frac{U-F}{T}$$

$$dF = -SdT - pdV + \mu dN$$

$$\checkmark \left(\frac{\partial F}{\partial V}\right)_{T,N} = -p \qquad -p = \left\{\frac{\partial}{\partial V}\left[-k_B T \ln Q\right]\right\}_{T,N}$$

$$\checkmark \left(\frac{\partial F}{\partial N}\right)_{T,V} = \mu. \qquad \therefore\ p = k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_{T,N}$$

$$F = -k_B T \ln Q \qquad \mu = \left[\frac{\partial}{\partial N}\left(-k_B T \ln Q\right)\right]_{T,V}$$

$$\therefore\ \mu = -k_B T \left(\frac{\partial \ln Q}{\partial N}\right)_{T,V}.$$

Now, I know that F is equal to U minus T S right therefore, I can write down that T S is equal to U minus F or S is equal to U F divided by T, I know at present U in terms of l n Q, I know F in terms of l n Q therefore, if I plug these expressions in what should I get, this is the expression that I am going to get can you identify the different contributions that are coming in to this expression of course, this part comes from the Helmholtz free energy part, and this part comes from the internal energy part.

So, as you see that if you have a model for which you can determine the partition function, Q you will be able to calculate not only the Helmholtz free energy, and the internal energy, but also the entropy of the system of course, there are other quantities which are very very important as far as our understanding of any working thermodynamic system is concerned.

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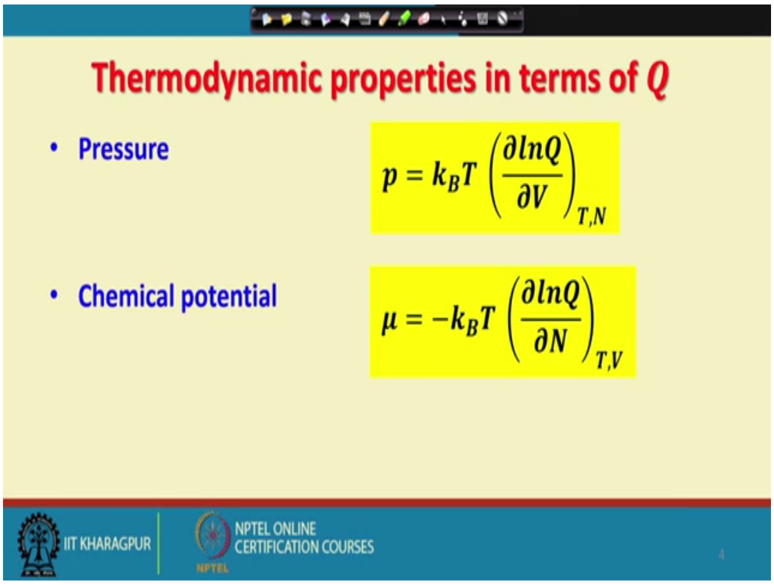

Thermodynamic properties in terms of Q

- Pressure $p = k_BT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N}$
- Chemical potential $\mu = -k_BT\left(\frac{\partial \ln Q}{\partial N}\right)_{T,V}$

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So, let us have a look as to how we can calculate a pressure from l n Q. So, in order to do that you must realize that I can write down d F as minus S d T minus p d V plus mu d N in general so, when I have a closed system d N is 0. So, this term will not be there, but if I have an open system, where N is allowed to fluctuate the last term on the right hand side will be present.

So, from here I can immediately write down that del F del V, T N what is that quantity that is equal to minus p, and del F del N, T, V that is equal to mu. So, if I now explore the fact that F is equal to minus k B T l n Q, I note that in both the cases I am keeping temperature constant therefore, I should be able to write that minus p is equal to del del V of minus k B t l n Q, and this derivative is being done, under the condition of constant temperature and number of particles.

And therefore, i will be able to write that p is equal to k B t del l n Q del V T, N. So, that is exactly what we have noted down here, that pressure is equal to k T multiplied by a derivative of natural logarithm of Q with respect to volume keeping temperature and number of particles constant.

Now, similarly it is very easy to show that the chemical potential, now is given by mu is equal to del del N of minus k B T L n Q, but now the constancy is maintained for both temperature and volume, under such condition I can take out the k T from the derivative and write that this is del l n Q del N, T, V. So, even if in general it is not a closed system, but an open 1 in that case you can find out the chemical potential starting from Q.

Now, let me take a very simple example, where I have a highly idealized system where there is only 1 particle.

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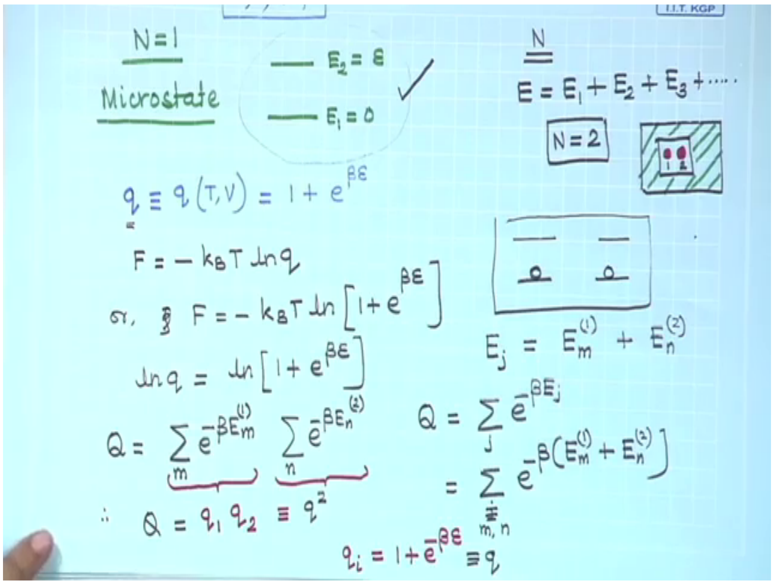

N=1

Microstate

$E_2 = \varepsilon$

$E_1 = 0$

✓

$$q \equiv q(T,V) = 1 + e^{\beta\varepsilon}$$

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

or, $F = -k_B T \ln\left[1 + e^{\beta\varepsilon}\right]$

$$\ln q = \ln\left[1 + e^{\beta\varepsilon}\right]$$

$$Q = \underbrace{\sum_m e^{-\beta E_m^{(1)}}}\ \underbrace{\sum_n e^{-\beta E_n^{(2)}}}$$

$$\therefore\ Q = q_1 q_2 \equiv q^2$$

$$q_i = 1 + e^{-\beta\varepsilon} \equiv q$$

N

$$E = E_1 + E_2 + E_3 + \cdots$$

N = 2

$$E_j = E_m^{(1)} + E_n^{(2)}$$

$$Q = \sum_j e^{-\beta E_j} = \sum_{m,n} e^{-\beta\left(E_m^{(1)} + E_n^{(2)}\right)}$$

That is N is equal to 1 and the model the microstate of the system is given in terms of this 2 state model. So, it has E 1 equal to 0 only 2 energy states are possible, and E 2 is equal to epsilon, then the question is can I do, can I set up the partition function of this system. We have already seen that by definition for this system, if it is present at a given temperature volume with N equal to 1 where for each with this single particle, this is the definition of the microstate, then the corresponding canonical partition function.

This is going to be a function of temperature, and volume and this is given by 1 plus e to the power of beta epsilon. So, if that happens then I can very easily write down, what is I am writing this small q instead of capital Q, because I have a single particle system. Now what is the Helmholtz free energy for this system? That is; obviously, going to be minus k B T l n Q or F is going to be equal to minus k B T l n 1 plus e to the power of beta epsilon. Now since I know things like l n q of course, I can find out all other thermodynamic properties because that, can be obtained as a derivative with respect to this l n q is that correct yes. Now the question is if I have a collection of N particles that are not interacting with each other, and that distinguishable from each other, in that case the total energy of the system will be written as say something like E 1 plus E 2 plus E 3 and so, on and so forth. So, maybe let me take a simpler system like capital N is equal to 2.

So, I have a 2 particle system for each particle the microstate is given like this, I have taken these 2 particles in the set up of a canonical ensemble that is I my system is comprised of 2 such particles whose microstates are given by this 2 state system, this is particle 1, and this is particle 2, they are present in a system and in equilibrium with the thermal reservoir.

Now my question is in this case as I as you understand that there may be many different states for in general; so, in this case what are the different states 1 of the typical state would be particle 1 in the lower energy state, and particle 2 also in the lower energy state may be an so, this is the lowest energy microstate for the system . So, this way I can see that the j-th energy state, will correspond to the say m-th energy state of particle 1, plus m-th energy state of particle 2.

So, what is the total partition function of the system then that is going to be summed over all j e to the power of minus beta E j. Now this I am going to write down as summed over all j e to the power of minus beta, but e j is something like this E 1 plus E n 2, which means that instead of j i will now have to sum over m and n. So, in practice what I have now is 2 terms e to the sum over m e to the power of minus beta E m, and summed over n e to the power of minus beta E n right.

This is for particle 1 and this is for particle 2, but as I said both the particles have the same underlying structure microscopic state and therefore, I can say that this is the single particle partition function for this 2 states system. So, I will be able to write that capital Q that is equal to this is small q 1 multiplied by this is corresponding to the particle 2 small q 2, but basically if they are underlying microstates are the same, and they are not interacting with each other therefore, replacing these 1 2 things I can write down any of these q is nothing, but 1 plus e to the power of minus beta epsilon.

As a result 1 plus this as a result capital Q is now becoming, if I put this as small q in general small q square.

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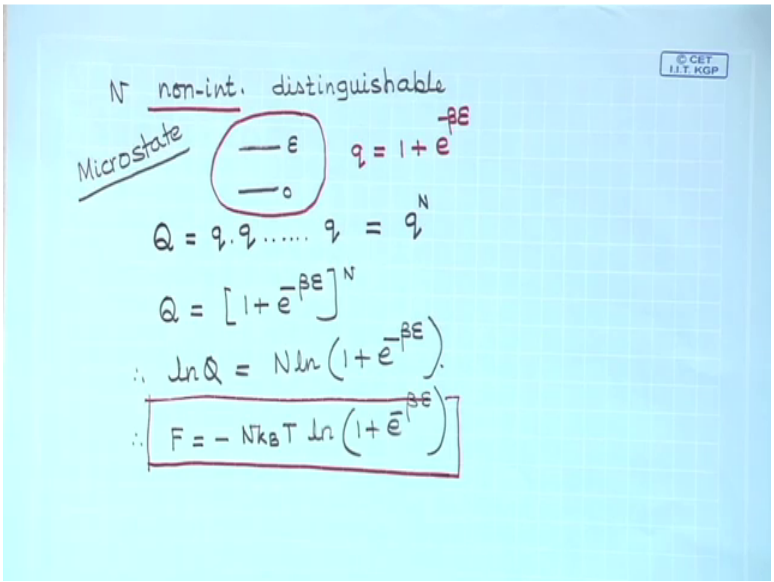

N non-int. distinguishable

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

$Q = q.q \ldots\ldots q = q^N$

$Q = \left[1 + e^{-\beta\varepsilon}\right]^N$

$\therefore \ln Q = N \ln\left(1 + e^{-\beta\varepsilon}\right)$

$\therefore \boxed{F = -N k_B T \ln\left(1 + e^{-\beta\varepsilon}\right)}$

So, once again let us recapitulate if I have capital N particles that are non-interacting that are distinguishable otherwise in terms of the label that they carry like particle 1 2 etcetera, but if their microstate they have the same microstate does not matter which particle, you are talking about I said that they have the same microstate like this.

Then each of these particles is characterized by a single particle partition function which is 1 plus e to the power of beta minus beta epsilon, and then if these are non-interacting and therefore, I should be able to write that the net partition function for this N particle assembly is going to be small q for the first particle, small q for the second particle, and so on and so, forth up to the n-th particle and that must be equal to small q to the power of n.

So, if I have capital n non interacting distinguishable 2 state particles present under canonical ensemble, then what is going to be the form of capital Q; capital Q, is going to be given by 1 plus e to the power of minus beta epsilon whole to the power of N. So, what is l n capital Q, that is going to be N l n 1 plus e to the power of minus beta epsilon and of course, I can write down that the free energy is minus N k T l n 1 plus e to the power of minus beta epsilon.

Now, from this result you see what we started with was very simple I had a microscopic model of my particles, these numbers were obtained from the solution of the Schrodinger equation for this kind of particle. And we found that there are only 2 energy Eigen states possible 1 is 0, and other is having some energy value epsilon.

And then we ask this question that what is the free energy of this system, the microscopic model mind you give you a model at the microscopic level, or the atomic level, or the molecular level. And the free energy is where you have 10 to the power of 23 particles together for the sake of simplicity, we have assumed that they are non-interacting and as a result you see that I have been able to obtain an usable form of expression for the Helmholtz free energy.

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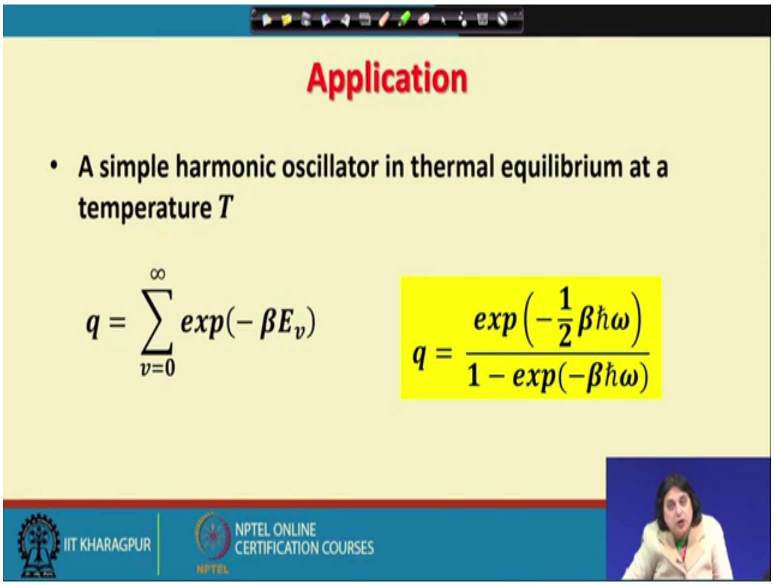

Application

- A simple harmonic oscillator in thermal equilibrium at a temperature T

$$q = \sum_{v=0}^{\infty} exp(-\beta E_v)$$

$$q = \frac{exp\left(-\frac{1}{2}\beta\hbar\omega\right)}{1 - exp(-\beta\hbar\omega)}$$

Now if I go a little further you will see that it is possible to talk in terms of the thermodynamics of a simple harmonic oscillator. So, let us say that I have a volume V, and there is a; this constant volume box it has only 1 simple harmonic oscillator in it, and this box is surrounded by a rigid impermeable ball it is placed in contact with a thermal reservoir so, that it attains thermal equilibrium with the reservoir at a temperature T. Then my question is; what is the canonical partition function for this single simple harmonic oscillator?

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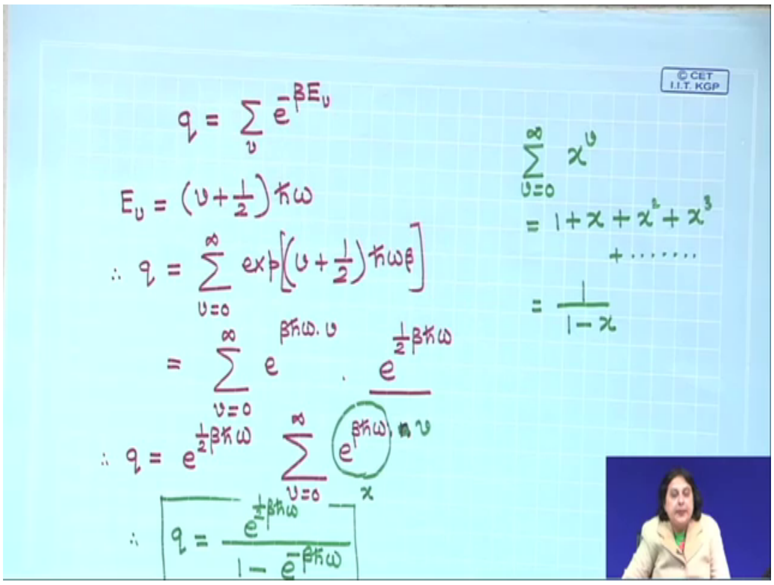

$$q = \sum_{v} e^{-\beta E_v}$$

$$E_v = \left(v+\frac{1}{2}\right)\hbar\omega$$

$$\therefore q = \sum_{v=0}^{\infty} \exp\left[\left(v+\frac{1}{2}\right)\hbar\omega\beta\right]$$

$$= \sum_{v=0}^{\infty} e^{\beta\hbar\omega . v} . \underline{e^{\frac{1}{2}\beta\hbar\omega}}$$

$$\therefore q = e^{\frac{1}{2}\beta\hbar\omega} \sum_{v=0}^{\infty} \underset{x}{\left(e^{\beta\hbar\omega}\right)}^{v}$$

$$\therefore \boxed{q = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}}$$

$$\sum_{v=0}^{\infty} x^{v}$$

$$= 1 + x + x^2 + x^3 + \ldots\ldots\ldots$$

$$= \frac{1}{1-x}$$

The answer is q must be equal to summation over all possible microstates of this oscillator e to the power of minus beta E V. Now for a given simple harmonic oscillator do I know what E V is the solution of Schrodinger equation tells me that, possible values of E V are V plus half h cross omega. So, I can directly put it in there.

So, I will say that q is equal to summation over V going from 0 to infinity because those are the allowed values of the vibrational quantum number, then exponential V plus half h cross omega multiplied by beta. Now I see that there are 2 portions in this within the summation. So, 1 portion is e to the power of beta h cross omega into V another portion is e to the power of half beta h cross omega; obviously, this term does not depend on the summation I take it out of the summation and therefore, I find that small q is equal to e to the power of half beta h cross omega into this infinite summation.

And the moment you have some infinite summation you should be aware that this is something that you need to evaluate if possible for this expression to be practically useful. So, in order to do that what I will do is I am going to represent this, sorry not N this is V this number as x. So, what does this summation look like then, I have V equal to 0 to infinity x to the power of V, and this I can write down as 1 plus x plus x square plus x cube and so on and so forth. But this infinite series does look familiar and it does have an analytical result, and that is given by 1 by 1 minus x. So, if I put it back over here what I find is q is equal to e to the power of half beta h cross omega divided by 1 minus x which is this quantity e to the power of minus beta h cross omega.

So, this is what we have written down over here. So, now you see that for this system if since I can evaluate the partition function it is very easy to work out the thermodynamics from here.

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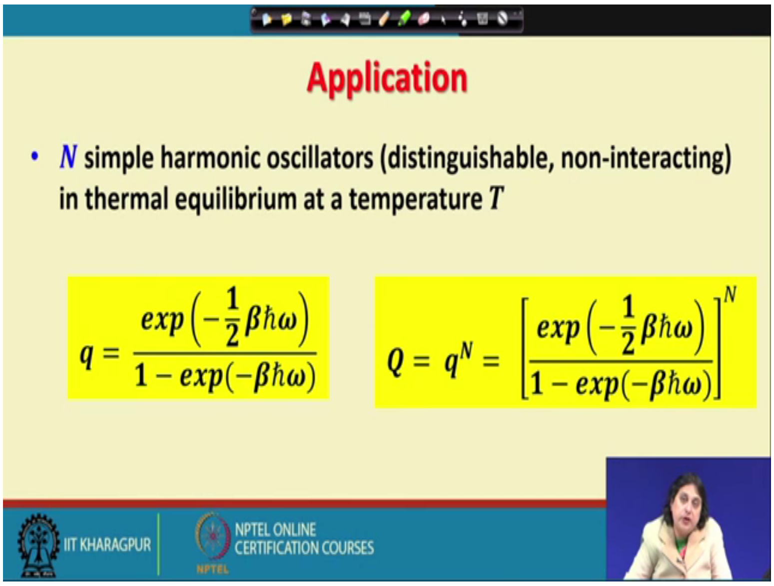

Application

- N simple harmonic oscillators (distinguishable, non-interacting) in thermal equilibrium at a temperature T

$$q = \frac{exp\left(-\frac{1}{2}\beta\hbar\omega\right)}{1 - exp(-\beta\hbar\omega)}$$

$$Q = q^N = \left[\frac{exp\left(-\frac{1}{2}\beta\hbar\omega\right)}{1 - exp(-\beta\hbar\omega)}\right]^N$$

Similarly when I have capital N such simple harmonic oscillators all having the same angular frequency; in that case if they are distinguishable and non-interacting, and if they are present in a constant volume V at a constant temperature T, I can very easily write down that for each of the simple harmonic oscillators, I can have an analytical expression for the canonical partition function. And then the canonical partition function for the N particle system is going to be given like this. Now once you know capital q you can very easily find out the natural logarithm of this quantity and connected to the thermodynamics.

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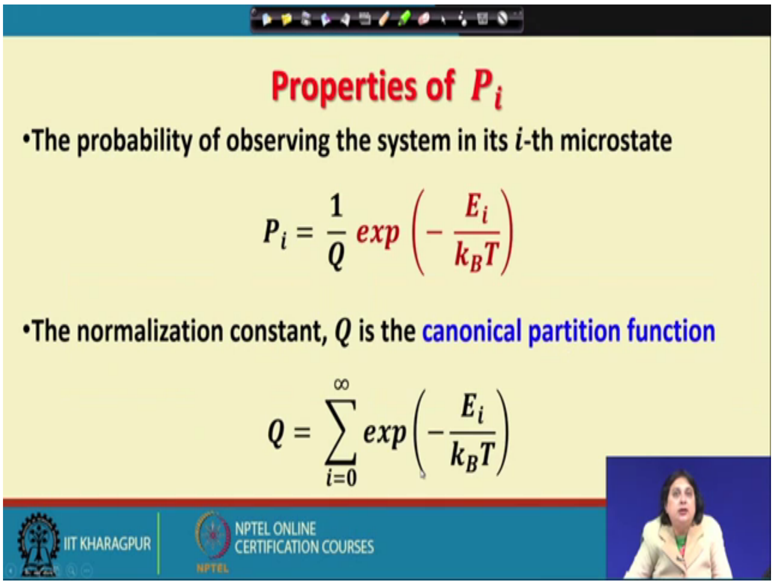

Properties of P_i

- The probability of observing the system in its i-th microstate

$$P_i = \frac{1}{Q} exp\left(-\frac{E_i}{k_B T}\right)$$

- The normalization constant, Q is the canonical partition function

$$Q = \sum_{i=0}^{\infty} exp\left(-\frac{E_i}{k_B T}\right)$$

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So, in the next lecture we will see some of these very interesting applications, but before I go finish this lecture, I would quickly like to highlight the other end of what of the 3 relationships that we have learnt in this class.

So, we have learnt what P i is. So, P i by definition is related to capital Q and E i where, capital Q is the canonical partition function which you have already seen.

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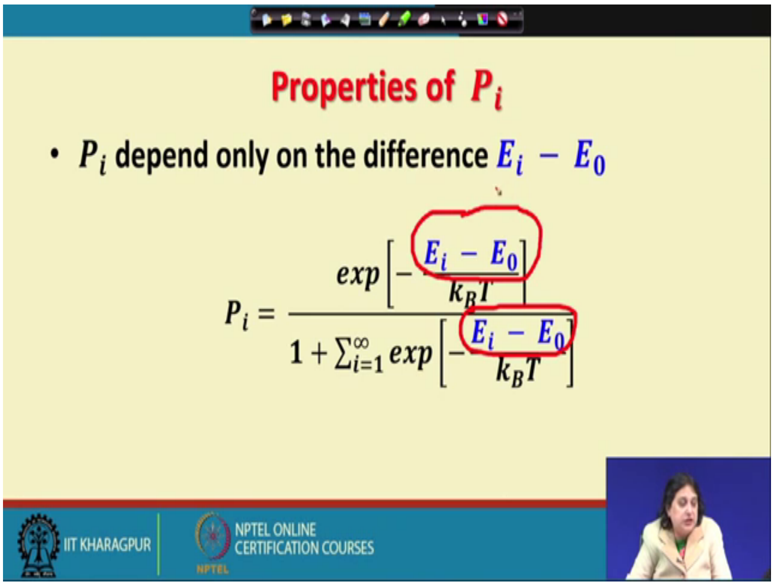

Properties of P_i

- P_i depend only on the difference $E_i - E_0$

$$P_i = \frac{exp\left[-\frac{\boxed{E_i - E_0}}{k_B T}\right]}{1 + \sum_{i=1}^{\infty} exp\left[-\frac{\boxed{E_i - E_0}}{k_B T}\right]}$$

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Now let me go a little further and say that did you notice that p i depends only on the difference E i minus E naught that is simply, because we can set the 0 of energy to the lowest energy state, and count the difference in energy from there. So, accordingly we will see that the p of i can be written down using this kind of expression, where p i is having functional dependence on E i minus E naught, and you are setting e not equal to 0 in your energy scale; sow, if I go a little further and try to understand the consequence of this.

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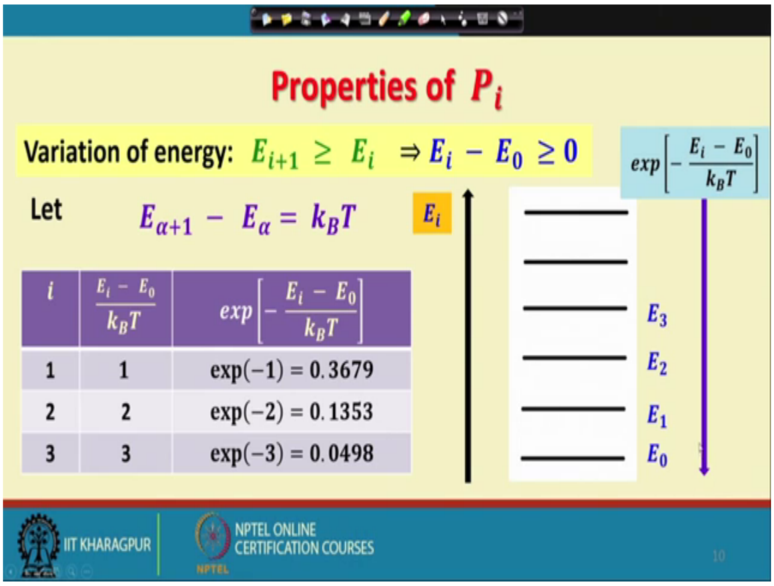

Properties of P_i

Variation of energy: $E_{i+1} \geq E_i \Rightarrow E_i - E_0 \geq 0$

$\exp\left[-\frac{E_i - E_0}{k_B T}\right]$

Let $E_{\alpha+1} - E_\alpha = k_B T$

i	$\frac{E_i - E_0}{k_B T}$	$\exp\left[-\frac{E_i - E_0}{k_B T}\right]$
1	1	$\exp(-1) = 0.3679$
2	2	$\exp(-2) = 0.1353$
3	3	$\exp(-3) = 0.0498$

We understand that in general from the solution of the Schrodinger equation for simple systems, we always find that E i plus 1 is greater than or equal to E I, assuming that i is the quantum number that we are talking about, and this would imply that E i minus e naught will always be greater than or equal to 0.

So, this typically is the way we assign the energy states the lowest energy state E not that is the 0 of the energy state, and as I go from E naught E 1, E 2, E 3 and so on and so forth, the energy value E i that increases.

Now, for the sake of simplicity let me assume that this particular energy level the difference in the energy level this gap its uniform for all the energy states, and this is equal to k T. Once we do that it is possible for us to have a simpler expression for this quantity E i minus E naught by k T. So, what happens if I go from i equal to 1 2 to 3, this quantity E i minus E naught by k T that also increases as 1 2 and 3, and correspondingly what I can say is if I look at this quantity which controls the probability P i, that now is a number less than 1. And if it is a number less than 1, as I go from i equal to 1, to i equal to 3, I find that this exponential factor it goes from about 0.4 to about 0.5. So, this number decreases. Now this is what has been shown pictorially over here, then this value it increases as you go down in energy, and it decreases as you go up in energy.

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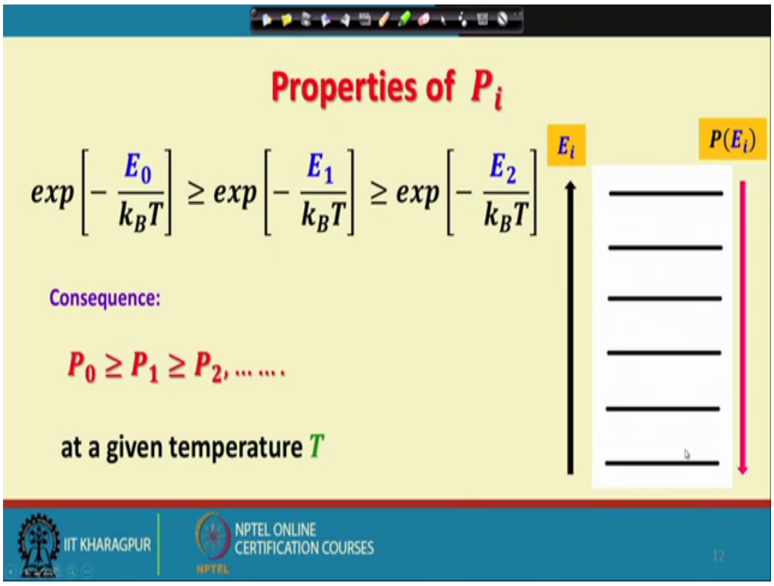

Properties of P_i

$$\exp\left[-\frac{E_0}{k_BT}\right] \geq \exp\left[-\frac{E_1}{k_BT}\right] \geq \exp\left[-\frac{E_2}{k_BT}\right]$$

Consequence:

$P_0 \geq P_1 \geq P_2, \ldots\ldots.$

at a given temperature T

Now the result of all these things is that, I can very easily write down that e to the power of minus E naught by k T will always be greater than or equal to e to the power of minus E 1 by k T and higher and higher energies, and the consequence is that if I follow the definition of probability, then what will happen is if energy increases, in this direction the probability of observing that particular state, or the probability of a particle of occupying that particular state at a given temperature decreases.

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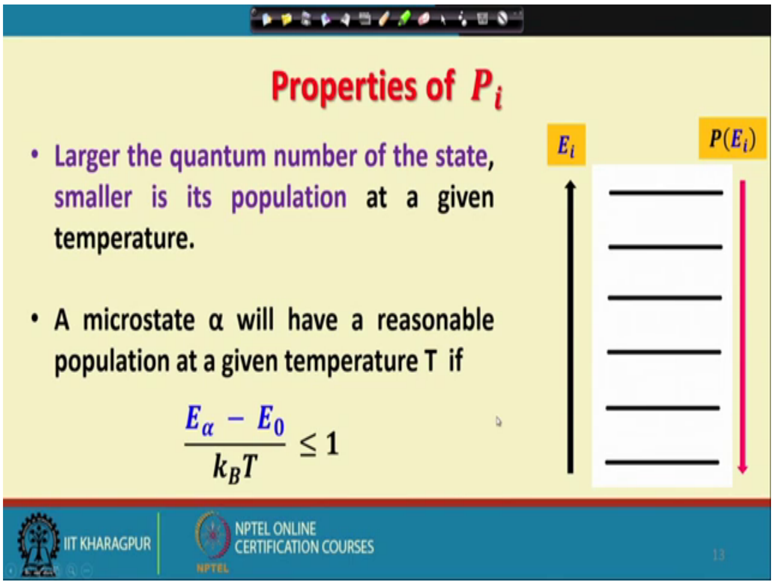

Properties of P_i

- Larger the quantum number of the state, smaller is its population at a given temperature.
- A microstate α will have a reasonable population at a given temperature T if

$$\frac{E_\alpha - E_0}{k_B T} \leq 1$$

Now, so basically what we are concluding is larger the quantum numbers of the state smaller is its population at a given temperature therefore, if you are trying to understand that you have a very large number of particles in your system, and whether a substantial fraction of it will be present in a microstate some kind of an alpha, all you have to do is look at what this number is if E alpha minus E naught by k T is much less than is less than or equal to 1, there will be a reasonable fraction of the population present in that microstate alpha.

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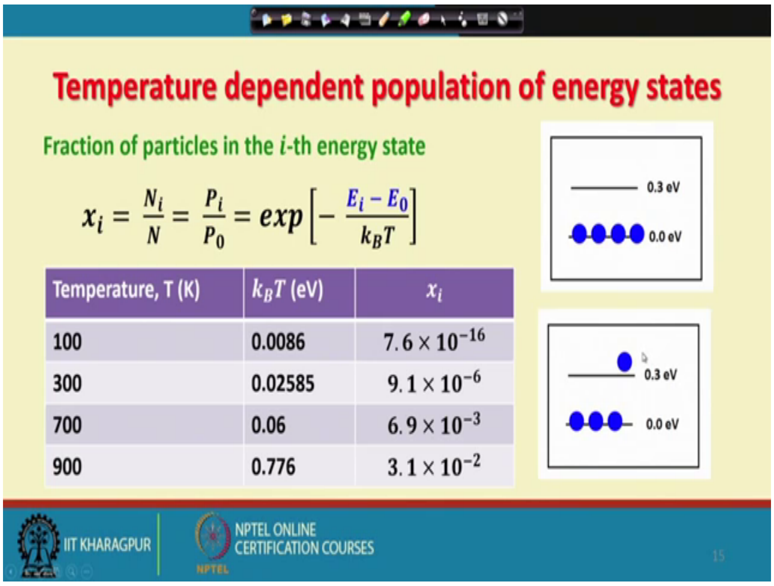

Temperature dependent population of energy states

Fraction of particles in the i-th energy state

$$x_i = \frac{N_i}{N} = \frac{P_i}{P_0} = exp\left[-\frac{E_i - E_0}{k_B T}\right]$$

Temperature, T (K)	$k_B T$ (eV)	x_i
100	0.0086	7.6×10^{-16}
300	0.02585	9.1×10^{-6}
700	0.06	6.9×10^{-3}
900	0.776	3.1×10^{-2}

So, that brings us to this very interesting concept of how you alter the population of energy states with temperature. So, as you understand the fraction of particles in the i-th energy state is nothing, but N i by N where N is a number of particles present in the i-th energy state in an assembly of a total of capital N particles. And now I can write this as P i by P naught. What is P i? P i is the probability that the system resides in the i-th microscopic state, and P naught is the probability that the system is present in the microstate having the energy E naught, and we already know that this is related to this exponential function.

Now, as I increase temperature as you see at hundred kelvin for a simple system like this, where the energy difference is about 0.3 electron volt initially at low temperature, the fraction of molecules present in the higher energy state is virtually 0, but if you look at higher temperatures you see about 3 percent of the population has been transferred to the upper energy state.

And this tells me that typically, this is the representation of the microstate dominant microstate at low temperature while this is the domain 1 of the more probable microstates having a particle occupying the higher energy state, but please remembers out of the many particles present only three percent will be going for this model to the higher energy state.

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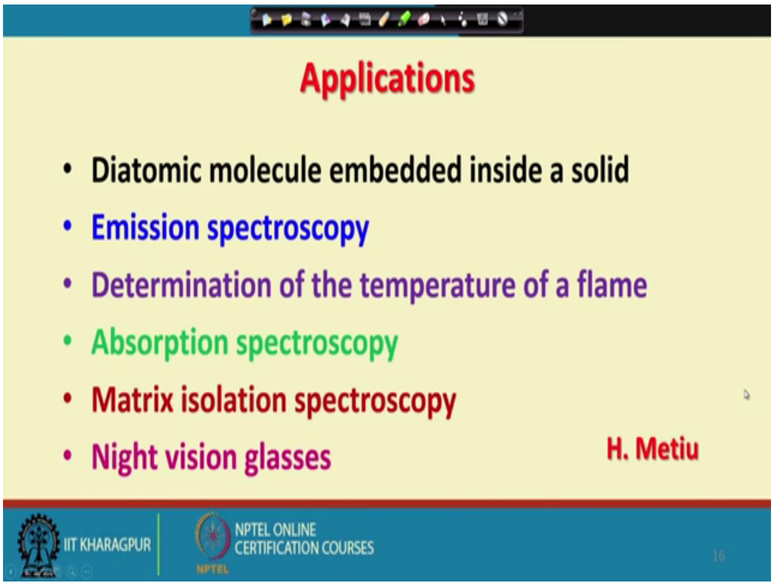

Applications

- Diatomic molecule embedded inside a solid
- Emission spectroscopy
- Determination of the temperature of a flame
- Absorption spectroscopy
- Matrix isolation spectroscopy
- Night vision glasses

H. Metiu

And the applications of such very simple ideas about the temperature dependent population of the energy states, in a canonical ensemble, and these ideas have been discussed very nicely by Horia Metiu in his book on statistical mechanics, and I would encourage you to go back, and read a little bit like how 1 can find out the temperature of a flame or the emissions interpret emission spectroscopy, and absorption spectroscopy as a function of temperature or even design things like night vision glasses, which are rather exotic, but has this principle at the at the core.

So, thank you and we will discuss the applications of whatever we have learnt in part 1 and part 2 for the canonical ensemble in the next lecture.