Introduction to Molecular Thermodynamics
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Lecture - 21
Ideal Gas

Welcome back. So, today we are going to start the second part of our course, where we are going to use the language that we have developed so far in this course into explaining the properties of some very simple systems. And today, the topic of our lecture is, statistical thermodynamics of ideal gases.

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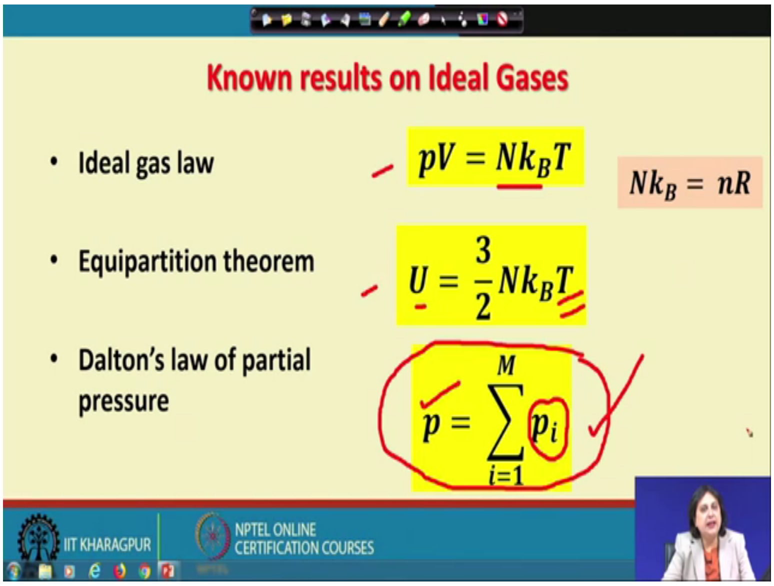

Known results on Ideal Gases

- Ideal gas law $pV = Nk_BT$ $\quad Nk_B = nR$
- Equipartition theorem $U = \frac{3}{2}Nk_BT$
- Dalton's law of partial pressure $p = \sum_{i=1}^{M} p_i$

Of course, ever since you started studying science, you have come across a large number of chapters dedicated to the ideal gases. The very first law that you would have studied in your school days is the ideal gas law. So, what is the ideal gas law? If you take a wide

Range of gases and you make a measurement on their pressure, volume at a given temperature or volume and temperature at a given pressure and so on. You can play around with it. Then a functional relationship can be return down that says, that the pressure of a gas is proportional to the temperature of the gas and inversely proportional to the volume of the gas under the given experimental conditions. So, this is what is known as the ideal gas law.

Now, in the ideal gas law then, p represents the pressure, V represents the volume occupied by the gas and T is the temperature at which the gas has been kept. So, p V divided by T is equal to N into k B. Now, what is capital N? Capital N is the number of the gas particles present in the system. So, in a macroscopic system it is typically one Avogadro number. So, that is 1 mole. Now, k B is a universal constant and here we are probably more familiar with the use of the universal gas constant where the small n represents the number of moles.

So, the small n into capital R that is the universal gas constant is nothing but in an alternative representation, if I am using the number of gas particles rather than the number of moles then the universal gas constant is written in terms of the Boltzmann constant. So, once again this is also a universal constant, but now it is not per mole, but it is per molecule or per particle, that is constituting the gas that you are interested in.

The other very well-known result that we have come across is the equipartition theorem. You must have studied equipartition theorem when you studied the kinetic theory of ideal gases and it basically says that the internal energy of an ideal gas, that is a function of temperature and temperature only. Now, please remember that in this particular discussion we are restricting ourselves to a constant value of n. Therefore, we have close systems and in all the observations I have shown here n is a constant.

So, as you see that in both these expressions what I have is p V by T is a constant in a closed system, similarly you for a close system depends only on temperature at which the gas is present. The there are other several other observations I would like to highlight one more of them which is rightly known as Daltons law of partial pressure. Now while these 2 are applicable to a single component system having only one type of gas particles present in the system this is applicable to a mixture of let us say capital M different types of gases each of which is maintained under the same condition of temperature and total pressure p. Then the Daltons law of partial pressure says that if small pi is the partial pressure of the ith component in this mixture, in this gaseous mixture, in that case if I add up all these partial pressures I will get back the total pressure p.

So, the aim of today’s lecture is keeping ourselves focused on a one component ideal gas. And try to understand if starting from a microscopic model; if I can derive this experimental observation of ideal gas law or the result that we have arrived at from the kinetic theory of gases. So, let us go ahead and try and understand how to do the statistical thermodynamics of an ideal gas system.

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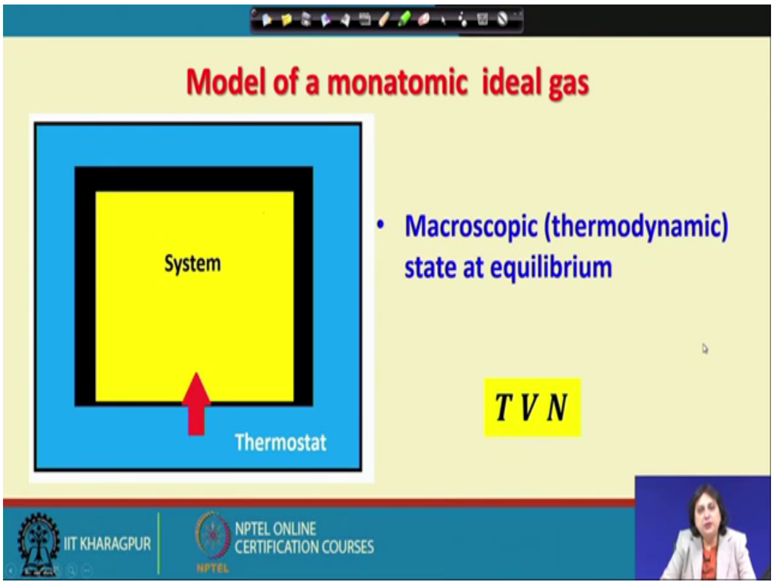

Model of a monatomic ideal gas

- Macroscopic (thermodynamic) state at equilibrium

T V N

So, the moment I say I am doing statistical thermodynamics, you understand that I will have to first express; what is a thermodynamic state of the system, if the system is in equilibrium. So, here is a picture that you can see that I am having the system which is shown in this yellow box this is surrounded by black wall on 3 sides which is rigid in permeable and insulated, but on one side of the wall it still rigid and impermeable, but I have made it diathermal so that when pleased in contact with the thermostat this blue region is the thermostat then the system can exchange thermal energy and attain an equilibrium which is the thermal equilibrium with respect to the thermostat.

In this case the equilibrium state of the system we have already discussed at length is going to be given by specifying the value of temperature at which the equilibrium has been established, the volume of this enclosing box in which my system is contained and the number of particles that are present in this system which cannot escape from the yellow region shown. Now, this is at the microscopic level and what happens to the microscopic level? So, in statistical thermodynamics, the other range length scale that we are talking about is a microscopic length scale where the language that we use to describe the microscopic state is quantum mechanics.

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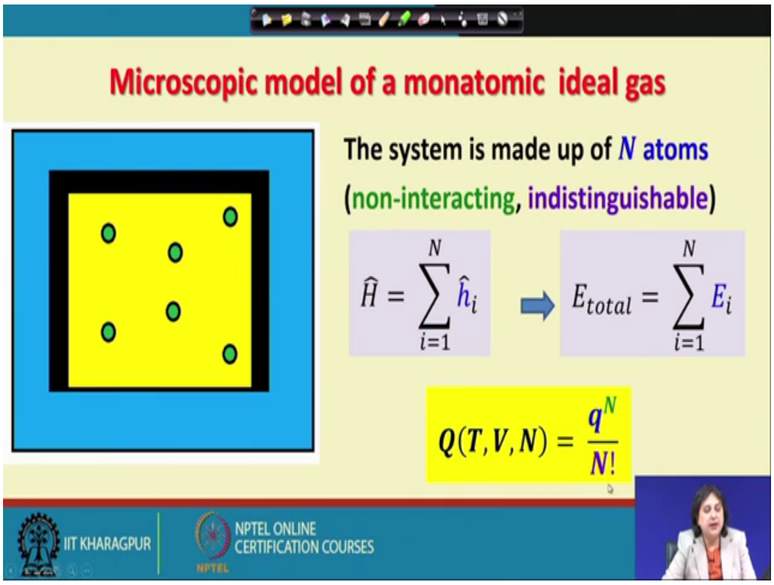

Microscopic model of a monatomic ideal gas

The system is made up of N atoms

(non-interacting, indistinguishable)

$$\hat{H} = \sum_{i=1}^{N} \hat{h}_i \Rightarrow E_{total} = \sum_{i=1}^{N} E_i$$

$$Q(T,V,N) = \frac{q^N}{N!}$$

So, if I look at the system now and zoom on what I have here in this within this box, if I can see the constituent particles they may be atoms or molecules, but to start with for the simplest case, we are going to talk about an monatomic ideal gas. So, these are one atom that are present at the microscopic level of this system. These atoms are constrained to move within this volume V they cannot escape from within this box to the outside. And when I want to study the microscopic model, I am going to solve the Schrodinger equation and I have already discussed that the Schrodinger equation while solving the Schrodinger equation you assume that it is an isolated system.

So, the total energy is constant. So, the microscopic model that I am going to use here is applicable when these particles are contend within a constant volume and their numbers do not vary and their total energy is a given constant. If I do that, then I can very easily say, that there are certain things that I must understand that this system is made up of capital N atoms in this picture 1, 2, 3 ,4 ,5, 6, N is equal to 6, but are these atoms different from each other? The answer is no.

The answer is no that is because if you take one mole of say organ gas is there any way you can distinguish atom1 from atom2; obviously, all of them are identical. So, we are dealing with capital N identical particles at the microscopic level. And now since it is a ideal gas I would say that this particle does not know that this other particle exists and as a result, I would say that I have capital N atoms and these atoms are indistinguishable and they are non-interacting.

So, when I set up this problem like this. Then the next question that I ask is, in order to be able to use the formulation of quantum mechanics, I must be able to write down the Hamiltonian operator of this system. So, the Hamiltonian operator in this particular case happens to be given by an expression like this. Here, I have used this notation for the Hamiltonian operator for this entire system that is made up of capital N atoms.

Now simply because all these atoms are non-interacting therefore, I can very easily say that this total Hamiltonian is now a sum of the Hamiltonians corresponding to each of the non-interacting particles present in the system. If they were interacting I would have some terms or some operators corresponding to the interaction between the ith and jth particle, but here there is no inter particle interaction or no inter atomic interaction.

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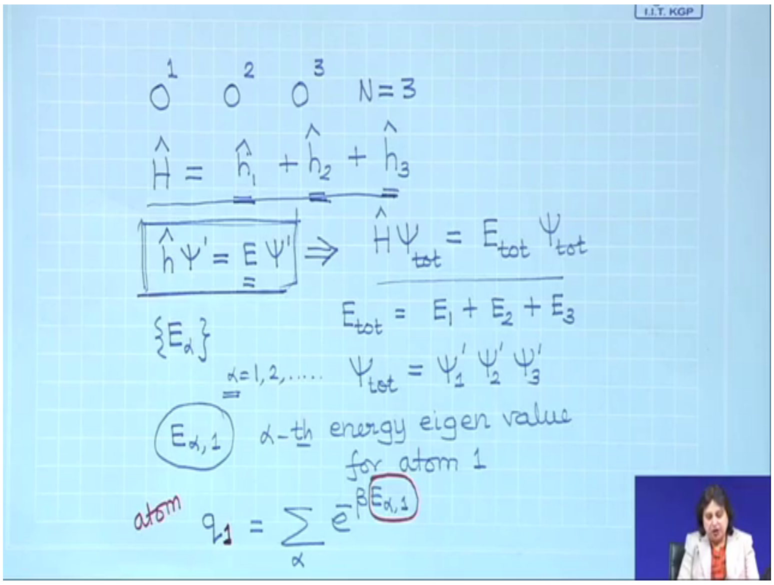

$$\overset{1}{O} \quad \overset{2}{O} \quad \overset{3}{O} \qquad N=3$$

$$\hat{H} = \hat{h}_1 + \hat{h}_2 + \hat{h}_3$$

$$\boxed{\hat{h}\Psi' = E\Psi'} \Rightarrow \hat{H}\Psi_{tot} = E_{tot}\Psi_{tot}$$

$$\{E_\alpha\} \qquad E_{tot} = E_1 + E_2 + E_3$$

$$\alpha = 1, 2, \ldots\ldots \qquad \Psi_{tot} = \Psi_1' \Psi_2' \Psi_3'$$

$E_{\alpha,1}$ α-th energy eigen value for atom 1

atom $q_1 = \sum_\alpha e^{-\beta E_{\alpha,1}}$

As a result, for example if I have atom 1, atom 2 and atom 3 which means if I had capital N is equal to 3, their total Hamiltonian of the system would have written as small h1 cap plus small h2 cap plus small h3 cap.

So, this is the single particle Hamiltonian for the first atom, this is the single particle Hamiltonian for the second atom and this is the single particle Hamiltonian of the third atom. And since all of them are the same therefore, you understand that this is essentially I am taking the same Hamiltonian 3 times.

Now, in order to understand what this small h is for a given atom then this particular I should be able to say that this h operating on the single atom refunction will give me energy of the single atom as the energy Eigen value multiplied by the refunction. As a result, and this would be mean that having these separable terms in the original Hamiltonian which operates on the total refunction of the system and this should give me E total as a energy Eigen state multiplied by the total refunction.

Now, this is true. I know that this can be written as a sum of these 3 individual operators and therefore, I must have the 2 following solutions I must be having that for a given total energy of the system that must be equal to E1 plus E2 plus E3.

Whether it is responds to one of the energy Eigen states of particle1 or atom1. This is an another energy Eigen state of atom 2 and this the energy Eigen state of atom 3. And obviously, you understand that this solution is possible if I can write that psi this is psi1, psi2 and psi3 maybe I will use some kind of different notation for the different way functions. So, these are the single particle way functions psi1 prime, psi2 prime, psi3 prime correspond to the single particle way function which is obtained as a solution of this single particle Schrodinger equation.

Once you are able to write this therefore, I can always go back and say that in consequence to having these non-interacting particles I must be I must have this kind of simplification that the total energy of the system for an N particle system is actually, the sum of all the individual energy Eigen values. So, this has actually a very big consequence. So, let us say that I have these single particle equations and then they give me energy value E alpha for each particle, right?

So, alpha can be the 1, 2, 3 and so on and so forth. So, the different microscopic states are generated by these notations this indices alpha. So, E alpha 1 would correspond to the alpha th energy Eigen state, energy Eigen value for atom 1. Then for atom 1 if I want to write down the single particle partition function then it turns out to be q1 and that is given by summation over all possible values of alpha e to the power of minus beta E alpha 1.

So, what is this 1 corresponding to this corresponds to the atom number, right? So, this is my atom number and when I write this I am writing down the different possible solutions of the Schrodinger equation for this atom 1 and E alpha is the alpha th energy I can value for this atom 1.

So, in general if I do not use any index for the particle

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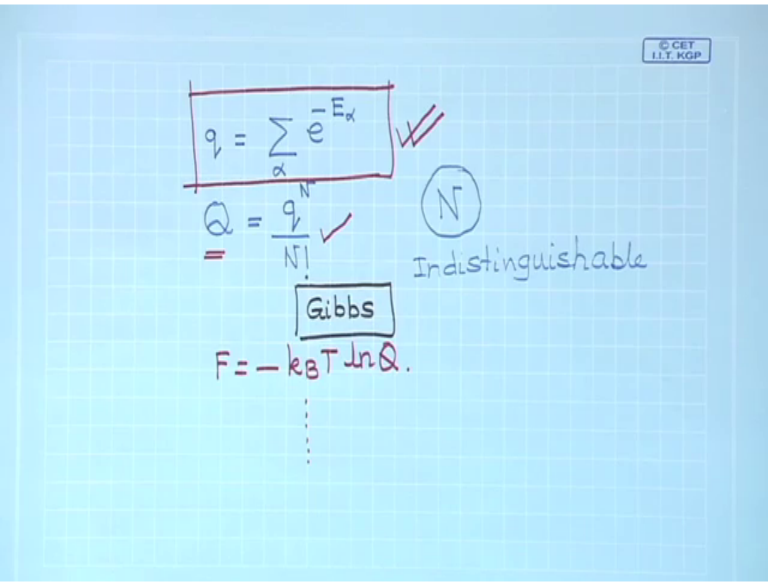

I can write down that for a single particle system the canonical partition function is going to be summation over alpha e to the power of minus beta E alpha. Now what I have here is capital Q. Now capital Q is the total partition function for this capital N particle system which are not interacting with each other and therefore, if they are distinguishable I will write that capital Q is equal to small q to the power of N.

We have already discussed this, but in addition to this, I have all these atoms indistinguishable and therefore, if I go on counting the same thing again and again, I will be having over counting problem. So, how did we overcome this over counting problem? If you had capital N indistinguishable particles, then while writing it down one can divide the small q to the power of N by N factorial. Now this was the prescription of the famous scientist Gibbs and we will see if I do not use this factor I will not be able to reproduce the fundamental property of in shop b like it is extensivity property.

So, I will start with this expression that I have now system made up of N non-interacting and indistinguishable atoms, where the total Hamiltonian of the system can be summed over all the individual identical contributions coming from each of the atoms. So, that the energy is now a sum over all the individual energies and of the atoms and the total partition function is given by the single particle partition function raise to the power of N divided by capital N factorial. Now once we know this, then let us focus on the single particle partition function small q.

Now, as I said for a given atom, if I want to find out small q

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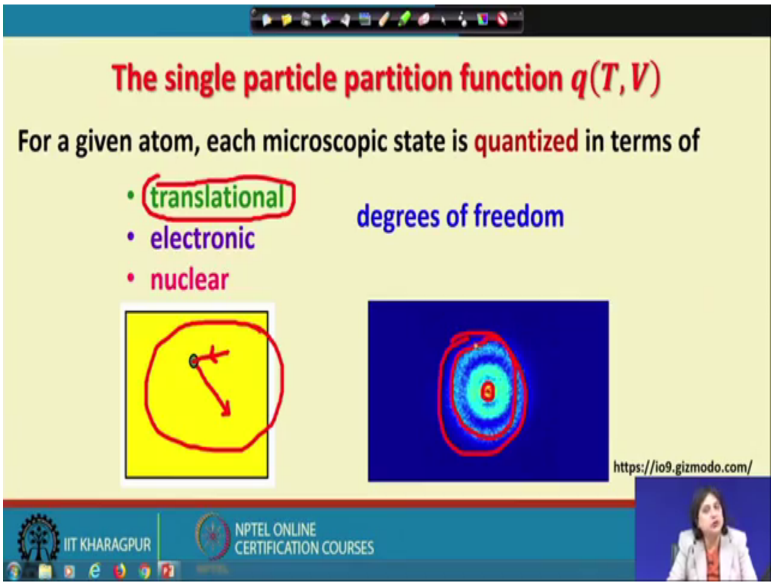

The single particle partition function $q(T, V)$

For a given atom, each microscopic state is quantized in terms of

- translational
- electronic
- nuclear

degrees of freedom

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I will have to estimate this quantity that is my small q, if I know small q and for a given N, I can find out capital Q. If I can find out capital Q, I can find out all the thermodynamic quantities by knowing that F is equal to minus k BT l n Q, and from here I can find out all other thermodynamic quantities and therefore, I am going to know focus on evaluation of the small q for the model that we have proposed here and in that model the first thing that I tried to understand is what these microscopic states are. Now for every for a given atom, each microscopic state is quantized in terms of several degrees of freedom.

So, in the case of an atom what are the different degrees of freedom that I should take care to describe the microscopic system? The first one you should talk about is a translational degree of freedom, the atom itself is a small ball like this which can move about in the box in which the gas is a confined so it has translational motion, right? Now in the next face part, I should understand that this atom is a quantum particle and it has electronic as well as nuclear degrees of freedom and therefore, a summation over all possible microscopic states means that I should take into account the quantisation in terms of the translational degree of freedom, all the microscopic states that are being generated by quantization of the translational degree of freedom, all the microscopic states generated by the electronic degrees of freedom, as well as nuclear degrees of freedom.

So, this means that I am now going to have to think about this entire problem in terms of 2 different perspectives; one is you have this entire box where you are looking at the translational motion of this particle.

So, that is the part which talks about the translational motion. It does not talk about if there is any structure or microscopic structure associated with this green particle, but as quantum mechanics tells us the atom has a specific structure, specific microscopic structure and what is that structure? So, instead of this entire box, if we zoom into the atom itself what do we see? What we see is there is a nucleus at the center and there is a an electronic cloud around it.

So, that is the well-established kind of picture that we have regarding the microscopic structure of an atom. So, the question is, is it possible to describe these microscopic states not only in terms of a particle moving or translating throughout the box as a whole, but also in terms of the underlined microscopic structure of the particle itself being an atom i am talking about the contribution of the atomic structure to the single particle partition function.

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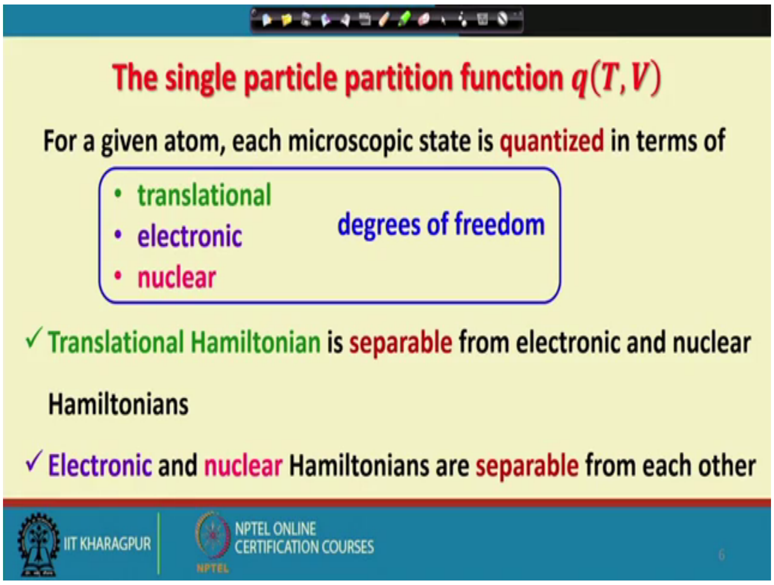

The single particle partition function $q(T, V)$

For a given atom, each microscopic state is quantized in terms of

- translational
- electronic
- nuclear

degrees of freedom

✓ Translational Hamiltonian is separable from electronic and nuclear Hamiltonians

✓ Electronic and nuclear Hamiltonians are separable from each other

So, let us start by understanding that the translational Hamiltonian is separable from the electronic and nuclear Hamiltonians and similarly the electronic and nuclear Hamiltonians are separable from each other and this is possible, if the energy scales of each of the degrees of freedom and the times scales when we in which this changes along this degrees of freedom are widely different from each other.

An of course, that is what is a good of very good approximation for one single atom moving about in a huge box So, we are going to assume the seperability of translational motion from the electronic or nuclear degrees of freedom and we are also going to understand that the since electrons move at a time skill much smaller than the nuclear motion, then for all practical purposes i can assume the nucleus to be essentially fixed in one of it is nuclear energy states while the electron moves about it.

So, what is the consequences of this kind of approximation? The consequences is that we can know go back and write that even the single particle Hamiltonian operator can be separated into 3 independent contributions.

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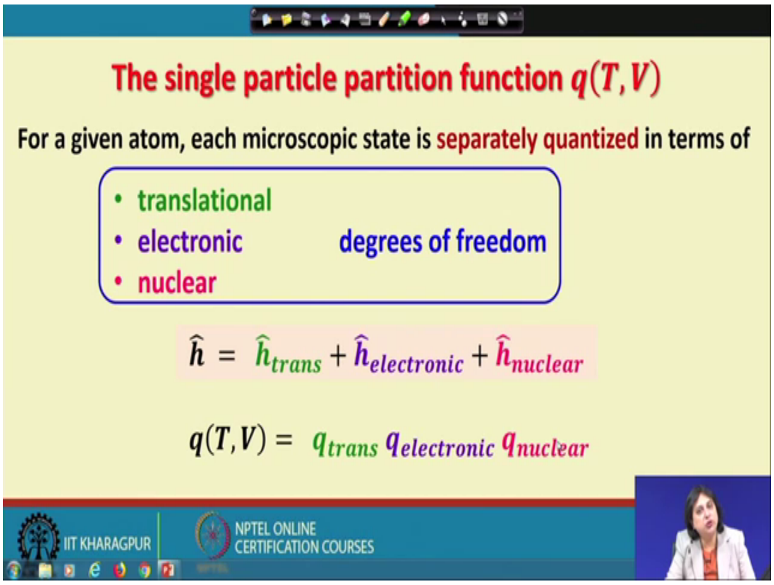

The single particle partition function $q(T,V)$

For a given atom, each microscopic state is separately quantized in terms of

- translational
- electronic
- nuclear

degrees of freedom

$$\hat{h} = \hat{h}_{trans} + \hat{h}_{electronic} + \hat{h}_{nuclear}$$

$$q(T,V) = q_{trans}\, q_{electronic}\, q_{nuclear}$$

The first one is the operator corresponding to the translational degree of freedom. So, and this is the operator contributing to the electronic degree of freedom and this is the operator contributing to the nuclear degree of freedom. If that happens then, we understand the consequence will be that at the level of the single particle partition

Function, this term will contribute to q Trans, this term will contribute to q electronic and the nuclear the existence of the independent nuclear term in the Hamiltonian operator for each particle will contribute this q nuclear. So, if that has happened then we understand that at present evaluation of this small q requires us to model q small q trans, small q electronics as well as small q nuclear.

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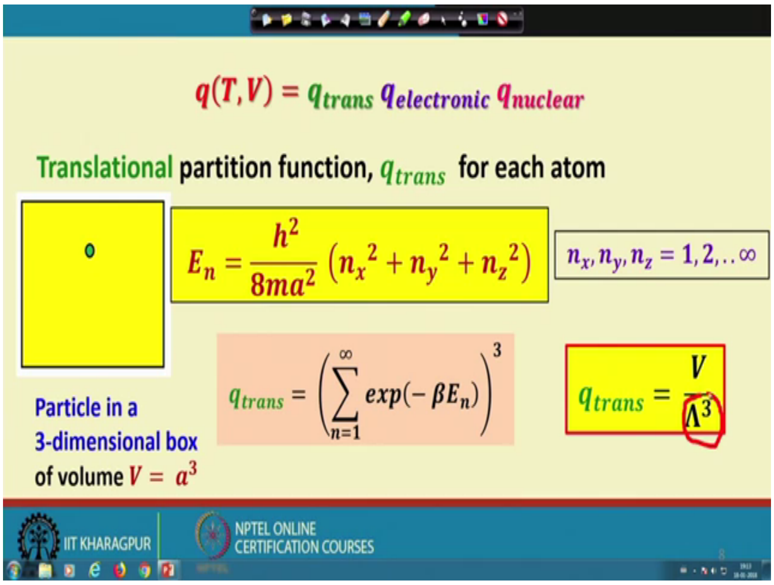

$q(T,V) = q_{trans}\, q_{electronic}\, q_{nuclear}$

Translational partition function, q_{trans} for each atom

$E_n = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)$

$n_x, n_y, n_z = 1, 2, .. \infty$

$q_{trans} = \left(\sum_{n=1}^{\infty} \exp(-\beta E_n)\right)^3$

$q_{trans} = \frac{V}{\Lambda^3}$

Particle in a 3-dimensional box of volume $V = a^3$

Now, in order to evaluate them each of these partition functions i am going to use some of the results that we have already developed in the course that we have here. So, the first part that we are being looking for is the translational partition function. Now how do I find this out? So, once again look at the degree at the degree of freedom we are come focusing on. It is the motion of this particle in a 3-dimensional box and you have already seen how to solve the Schrodinger equation for a particle in a 3-dimensional box.

Let me choose the volume of the box as a cubed so, it is a cubic box and i know the solution of the Schrodinger equation which is given in terms of 3 quantum numbers n x, n y and n z and here m is the mass of this particle and a is the dimension in each direction of the box. So, the different energy states of this atom will be generated by this number n which is nothing but combinations of these stray quantum numbers n x, n y and n z each of which can vary from 1 to infinity. So, we have already seen that for a 1-dimensional box if I have a particle in a 1-dimensional box.

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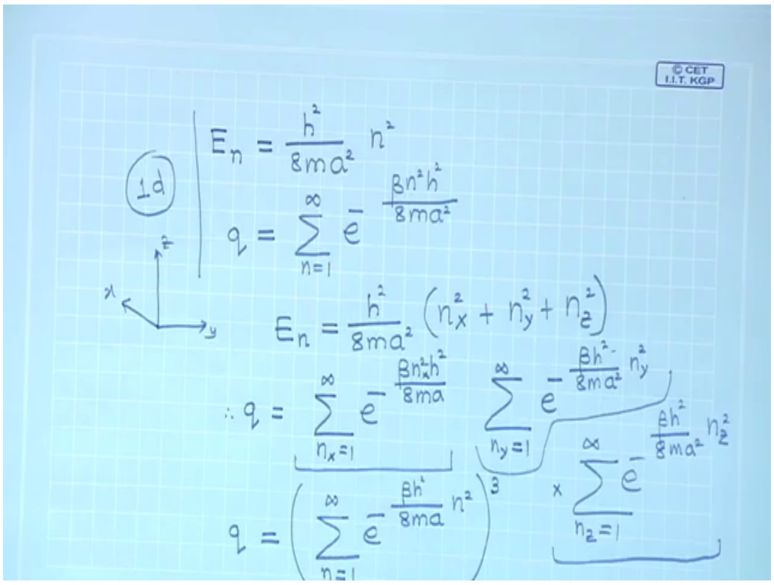

$$E_n = \frac{h^2}{8ma^2} n^2$$

$$q = \sum_{n=1}^{\infty} e^{-\frac{\beta n^2 h^2}{8ma^2}}$$

$$E_n = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

$$\therefore q = \underbrace{\sum_{n_x=1}^{\infty} e^{-\frac{\beta n_x^2 h^2}{8ma}}}\ \underbrace{\sum_{n_y=1}^{\infty} e^{-\frac{\beta h^2}{8ma^2} n_y^2}} \times \underbrace{\sum_{n_z=1}^{\infty} e^{-\frac{\beta h^2}{8ma^2} n_z^2}}$$

$$q = \left(\sum_{n=1}^{\infty} e^{-\frac{\beta h^2}{8ma} n^2}\right)^3$$

Then E n is given by h square by 8 m a square into n square. In that case small q is given by summation over n going from 1 to infinity into the power of minus beta n square h square divided by 8 m a square.

Now, this is for a particle in a one-dimensional box. Now I have 3 dimensional boxes, but please remember in this 3-dimensional box the x, y and the z directions are independent of each other, and therefore i would say that well my E n is nothing but h square by 8 m a square into n x square plus n y square plus n z square. So, by definition small q now can be written as n x going from 1 to infinity e the power of minus beta n square h square by this pre-factor by this n x square similarly, same thing for the n y term for the y direction.

So, beta h square by 8 m a square and then n y square multiplied by summation over n z equal to 1 to infinity e to the power of minus beta h square this quantity now what is the difference between this term this term and this term? All of them are the same apart from the dummy index n x, n y and n z therefore, i can very easily write that this q trans is going to be something like small q to the power of summation over n going from 1 to infinity e to the power of minus beta h square divided by 8 m a multiplied by n square, this summation multiplied with each other and therefore there is a cubic term.

And we have already seen how to evaluate this single particle partition function and therefore, we know the q trans as a function of volume which is a cubed and also in terms of this lambda cubed. And do you know what lambda is this depends on the mass of the particle, it depends on the temperature at which the system is present. So, we will continue our discussion next with the determination of q electronic and q nuclear I will see how to get the total partition function of the system.