Introduction to Molecular Thermodynamics
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Lecture – 34
Application of Molecular Thermodynamics

Welcome back. we will continue our discussion on the application of molecular thermodynamics principles to the understanding of specific heat of solids and this is the second part of our discussion.

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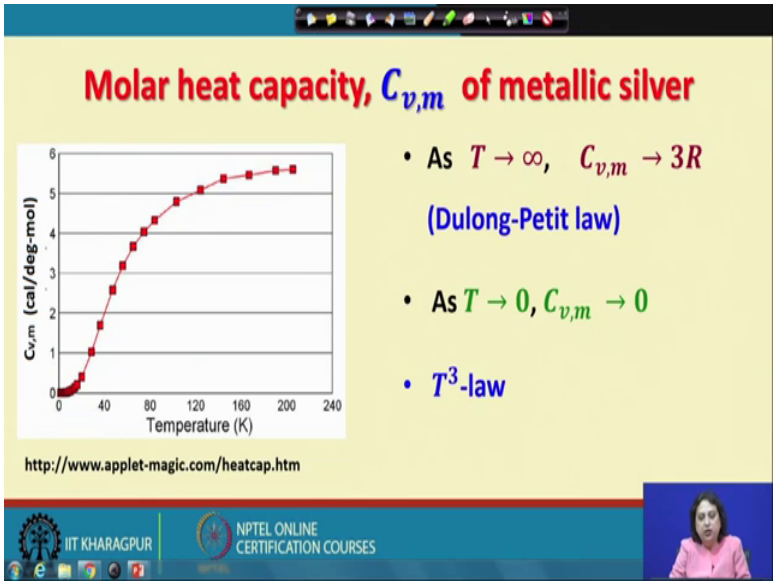

We have already seen that the molar heat capacity of an atomic solid is a function of temperature and it goes to a constant value as we move to high temperatures and it goes to 0 as we go to very low temperatures and the value of C v falls to 0 as t cubed and this is known as the t cubed law.

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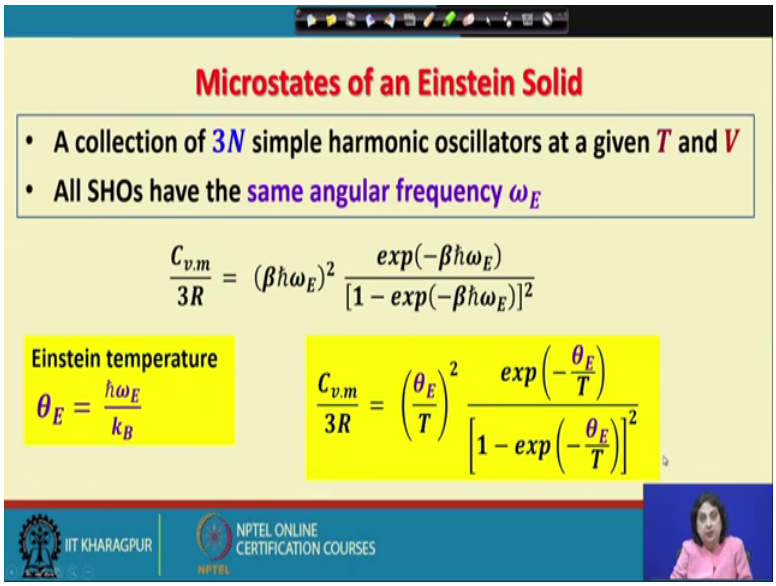

We have also seen that if UI use the Einstein model to represent the microstates of the solid, then I would talk about this model as the solid as a collection of 3 and simple harmonic oscillators which are present at a given temperature and t and volume v and each of these oscillators will have an intrinsic angular frequency omega and all the values of omega are the same. So, accordingly we used the Einstein model and use the principles of canonical ensemble and found this expression for C v.

Now, introducing the Einstein temperature what we found is C v can be written entirely in terms of 3 r the Einstein temperature theta E at a given temperature t. So, the question was this is an enormous triumph of the basic formulation, but does it work.

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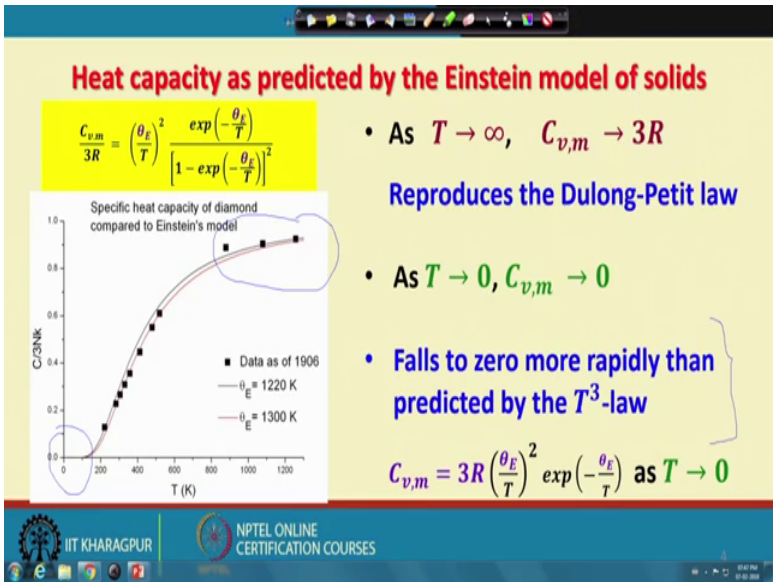

So, one went back and compared the predictions of Einstein model to the experimental data and it was found that yes the Einstein model, the very simple model of representing the solid is a collection of 3 and simple harmonic oscillators they correctly it correctly gives you the high temperature behavior that C v should become a constant as t tends to infinity. It also correctly predicts that C v should go to 0 as temperature goes to 0, but there was one shortcoming over here and that is the fall of C v to 0 at low temperatures that was much faster than that would have been predicted by the t cube law. So, this is a common problem that is faced by the scientists all throughout the day.

You basically try to understand why should the solid have a heat capacity which is a function of temperature and you basically wanted to understand it simply in the way we understood the heat capacity of ideal gases and we compared even the effect of structure from monatomic to diatomic ideal gases, but what we find here that the simplest model does not work so; obviously, what one has to do is, one requires a lot more introspection into the problem especially in the light of the fact that now we have solids and solids as you are well aware that these systems exhibit the strongest correlation and strongest interaction between their constituent particles.

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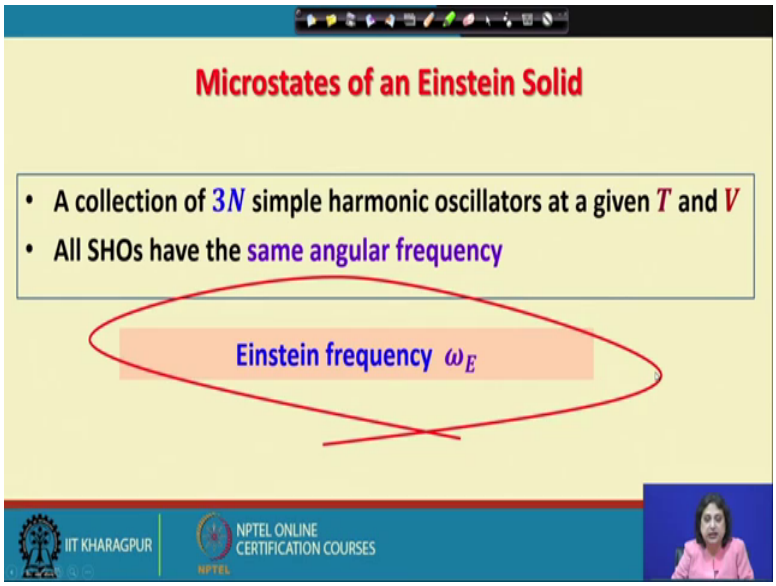

So, if we look back at the Einstein model, then we see that there are 2 points that we would like to investigate. First can I really express the vibrational frequencies or the complex vibrational frequencies of a solid has collection of 3N independent simple harmonic oscillators and even if we can there is a more serious second point that can I really assume that all these simple harmonic oscillators will have the same angular frequency.

So, basically in the first part of my lecture today we will still assume that yes, the vibrational pattern of the solid can indeed be represented by a collection of 3N independent simple harmonic oscillators. I will take up this problem in the second half, but let us first try and look at the problem with the basic assumption that all the simple harmonic oscillators have the same frequency which is your Einstein frequency.

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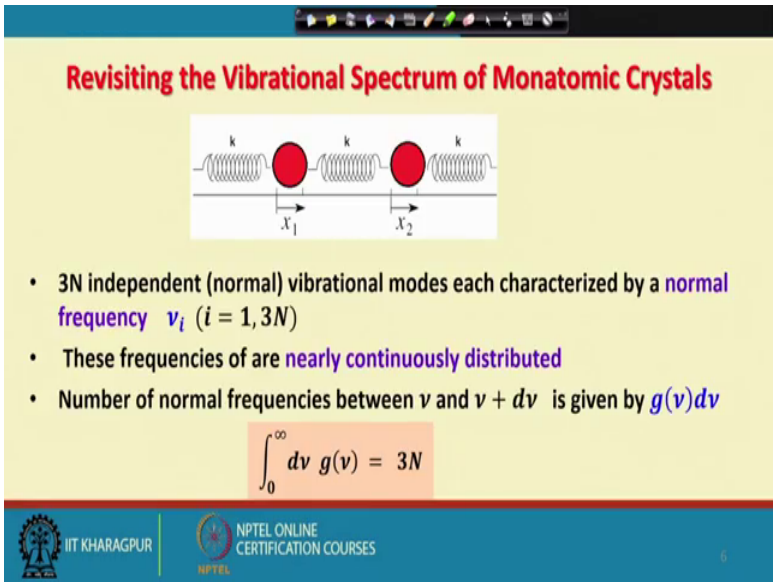

So, if I look at the vibrational spectrum of a monatomic crystal, typically in each dimension I would represent the an constituent atoms by connecting them in a direction using a simple harmonic spring and I would say that if there are 3N independent vibrational modes. They are going to be represented by this kind of a ball and spring representation and let me replace that single Einstein frequency by a normal frequency nu I for each of the 3N modes present in the system.

Now, as you see that N is a number which is a very large number typically the Avogadro number. So, we have a very large number of frequencies that are possible and this frequencies are nearly continuously distributed expected to be nearly continuously distributed and the there will be, but there will be a finite number of normal frequencies between say nu and nu plus d nu and let us say that this number is given by g nu d nu. So, then what is g nu? g nu is a term which is called the density of states. So, in this case the density of vibrational states.

Now, even if there are a large number of frequencies and they are. So, close to each other that you can eventually think that they are nearly continuously distributed. You must realize that the frequencies of oscillation of all these 3N simple harmonic oscillators are quantized because we have seen that the quantum of lattice vibration is known as the photons and that is the basic assumption in the quantum theory of solids that the lattice vibrations are quantized and then we will call them as a phonons. So, what we are trying

to say here is that even under that restriction, I have a very large number of frequencies possible, for which it may be more useful to talk in terms of a density of states, but with 1 restriction and that restriction is, I if I sum over all possible values of nu, I must get back the total number of vibrational modes that I started with.

So, now, with this concept in mind in instead of the Einstein model, now I have capital 3 into capital N, these many simple harmonic oscillators which are independent of each other. I have not as yet identified what these simple harmonic oscillators are, but I am assuming that these the vibrational pattern of the solid can still be represented by the vibrational patterns of these 3N simple harmonic oscillators, which are oscillating independent of each other.

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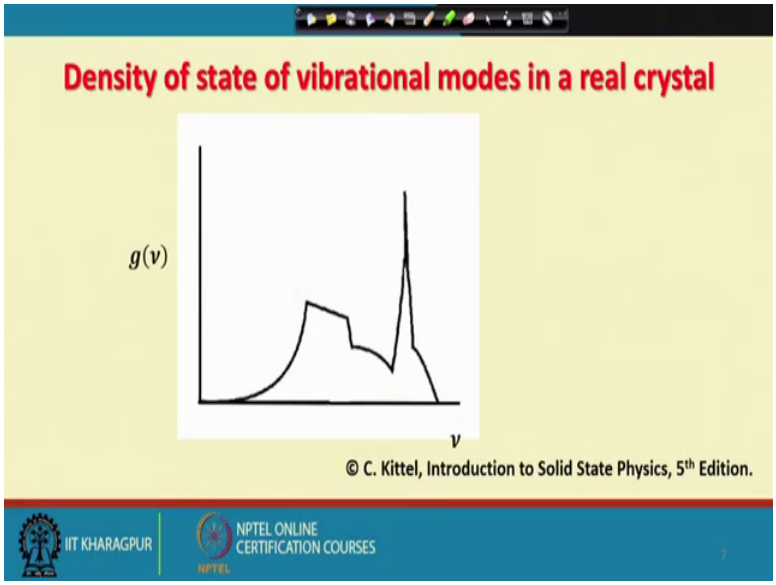

And unlike the Einstein theory now I have assumed that these oscillators each is having a distinct frequency nu I ok. With this idea one looks back at typically is there anything like g nu that can be determined from experiments. So, this is typically a density of state of vibrational modes in a real crystal which says that the density of states of the vibrational frequencies this actually is a non trivial this has a non trivial dependence on the allowed values of nu.

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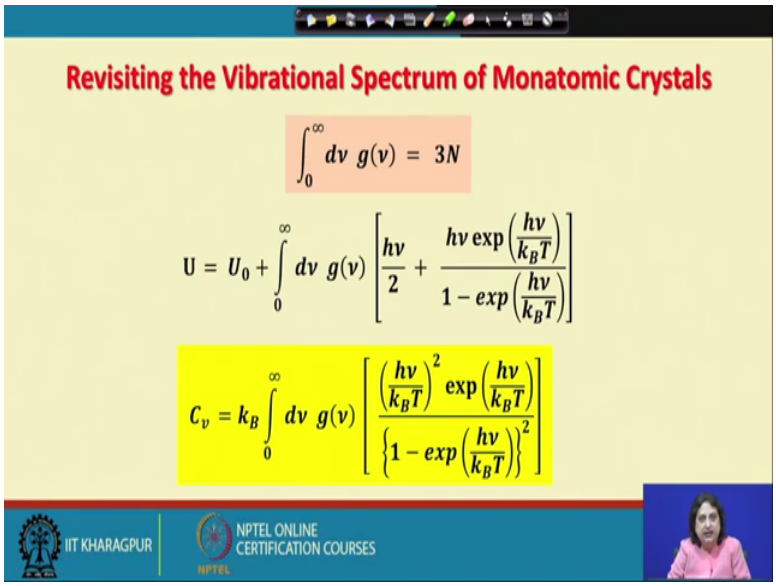

So, let us now revisit the vibrational spectrum of a monatomic crystal and try to use the concept of the density of states. So, if I use this density of states now the expression for internal energy of my system is going to be given by an expression like this and of course, you can calculate the specific heat of the solid by taking a temperature derivative on both sides of this expression and this is a resultant expression which follows. You may care to check the calculation yourself or you can just try to understand, why an expression like this appears doing the mathematical exercise here is not mandatory.

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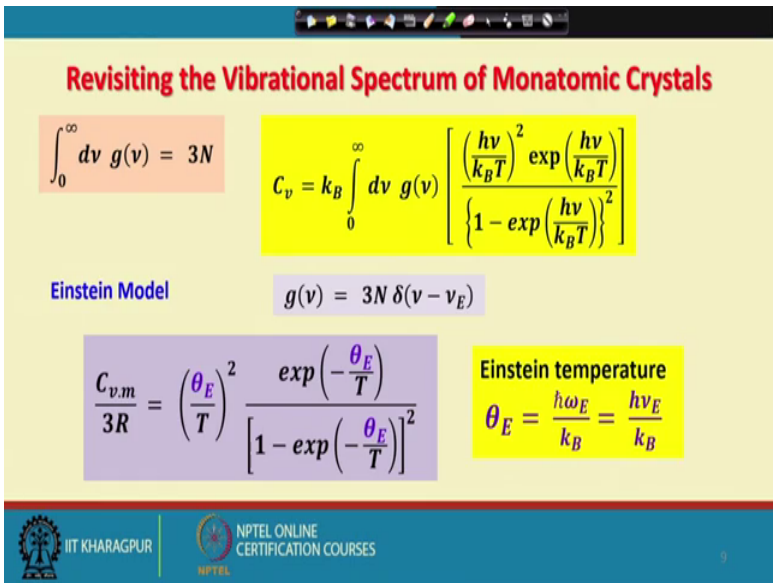

So, now that I know that C v can be represented in terms of this term h nu by KT and the density of states g nu in the Einstein model it was approximated that g nu is 3N into a Dirac delta function, which gives you a peak at nu equal to nu E or the Einstein frequency nu E.

So, correspondingly if you use the properties of Dirac delta function you put it back in here, this is the expression that you will get which is the same expression that we have seen in our previous lecture. So, basically what we are trying to say is that right now if I assume that the density of states gives you a nonzero peak only at nu equal to nu E, I retrieve the results that I have got from Einstein model within the present formulation.

Now, let us go ead and try and see how we can improve this because we have already seen that this is not good enough especially at low temperature. So, what we do next is we introduce to you the Debye model of heat capacity of crystalline solids.

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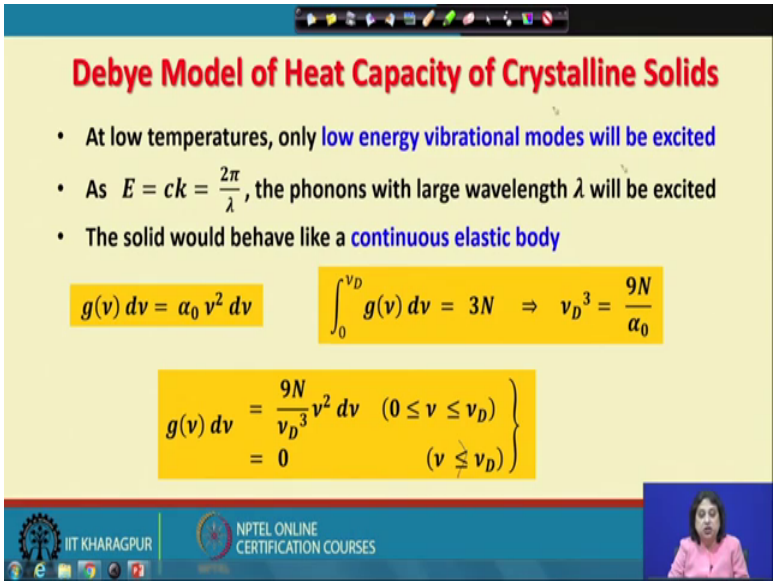

So, here there were a few more considerations that turned out to be crucial in analyzing the low temperature behavior of heat capacity of these solids. At low temperatures you understand that the available thermal energy to the system is very small as a result of which only low energy vibrational modes will be excited. Now, we know that the energy is inversely related to the wavelength of the excited modes and therefore, at low temperature it is expected that phonons with large wavelength will be excited and therefore, I would say that at the low temperature the solid would behave like a

continuous elastic body. Now, the study of vibrational patterns in a continuous elastic body is a very well studied and well investigated field of physics and there you find that under such condition g nu d nu can be given by an expression like this. So, this is where I am using the result from known literature of vibrational patterns in a continuous elastic body and correspondingly Debye introduced this relationship where he said it must be so, that there will be an upper limit to the integration such that when upon this integration you get back the finite number of vibrational modes equal to 3N.

So; obviously, if you plug back this expression that is alpha naught v square into d nu, nu square into d nu in this expression you can find out what nu d is. Now,when you do this then what happens is you can eventually write the write the expression for g nu d nu as this is something into nu square d nu, when the frequency of the vibrational modes are less than or equal to the Debye frequency and it is equal to 0 for all frequencies, sorry this must be greater than nu d. When that happens then one can actually go ead and with this expression of g nu d nu we can find out what the expression for C v is.

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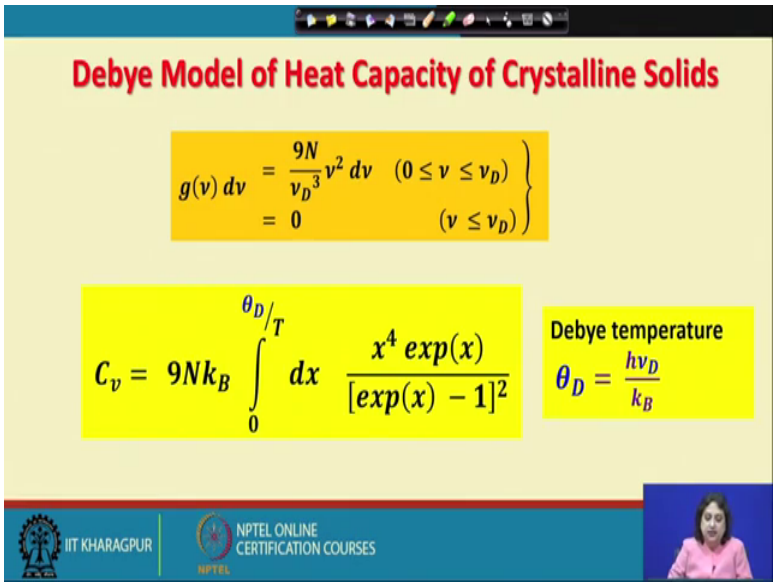

And this is the expression for C v which of course, can be evaluated in certain limits using special integrals, but I am not asking you to do that. One can also evaluate this function C v as a function of temperature by carrying out this integration numerically, but here what I would like you to note is that here I have introduced the concept of Debye temperature just like the Einstein temperature and now my C v is dependent on

this theta d because this theta d appears in the upper limit of the integration and which is a rather complicated integration. Now, what have we learned from here? We learnt that if I want to give some input about the density of states of the allowed vibrational frequencies of the solid which would mimic something like the real cases that we see, then it is indeed possible to obtain an expression for C v that is expected to do a little better than what the results we had for the Einstein solid.

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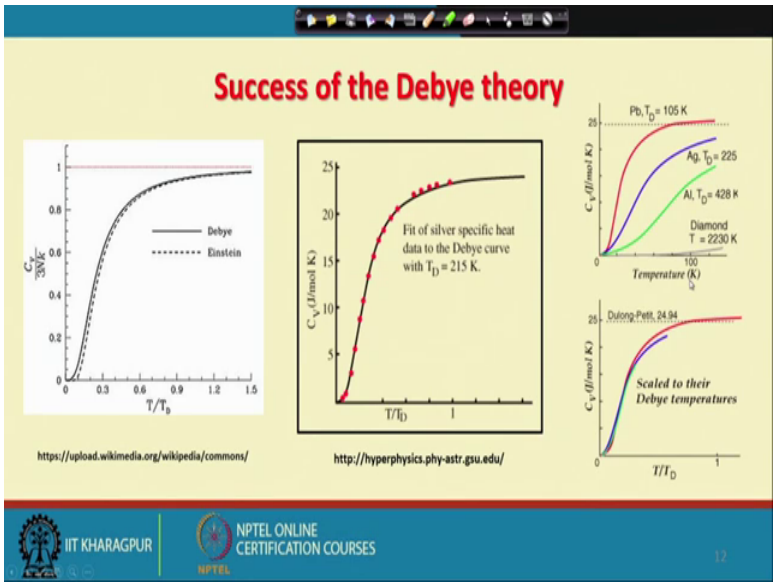

So, let us next check if the Debye theory was successful. It was found that the Debye theory correctly predicted the approach of specific heat to 0 at low temperatures and it was applicable for a wide range of systems and if you plot the plot the low temperature behavior as a function of t cubed, you do get a linear behavior. Now, in the light of this. So, there are 2 lessons that we have learnt.

The first lesson is we assume that the solid can still be represented as a collection of 3N simple harmonic oscillators and then we said that for a realistic solid it is not only 1 frequency that matters, but there may be a range of frequencies starting from 0 and going up to a certain cutoff and upper limit, that is required to describe the vibrational pattern of a solid. So, that I will say that these are the vibrational modes that will be excited when I supply thermal energy to the solid and this is a reason why this excitation of these vibrational modes is a reason why the thermal the specific heat of the solid will exhibit a temperature dependent behavior.

Now, let us go back and look at the mass and spring model of the crystalline solid in a little closer.

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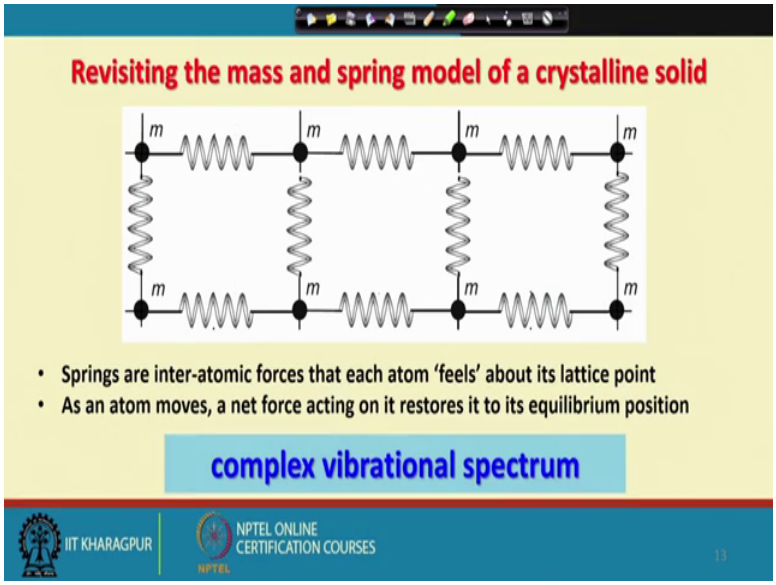

So, this is how I am representing the mass m of an atom in a crystalline solid at the lattice positions and these are strongly interacting with their neighbors as a result each pair of neighbor is connected by a harmonic spring. So, as you see that these are the neighbors that I am talking about for this particular atom.

So, it has two neighbors in this direction and if I go in this direction as I have shown in this figure there is another one connected to it as a spring. Now, in this model what we understand is that the springs are the inter atomic forces that each atom feels when it is sitting at its lattice point and therefore, as it moves if any of these atoms they want to move, then there will be a net force acting on it that will restore this atom to its equilibrium position ok.

So, when you supply thermal energy to the system these atoms have some excess thermal energy at their disposal which they are going to use to execute this motion, but the moment they start moving there is a restoring force acting on it putting it back to its original position. So, basically then what we are looking at is this jumble of springs connected to each other will give you a very complex vibrational pattern and therefore, the amount of energy that would be required to heat up this system to a certain extent will be guided by the underlying complex vibrational pattern.

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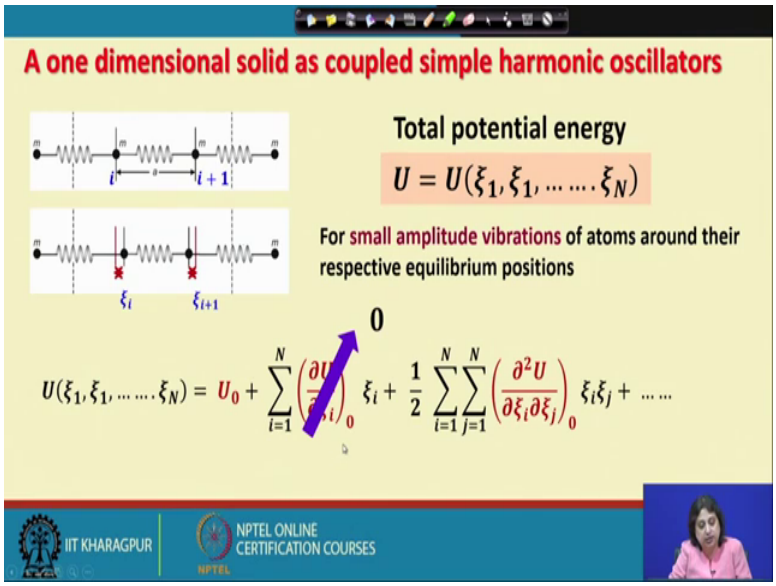

So, let us have a look as to what we can say about this kind of connected ball and spring model of the solid. So, as you see this is the picture where I have shown the equilibrium position of the atoms at the lattice points. So, this is where the ith atom is located at rest, this is where the I plus oneth atom is located at rest and this is the spacing lattice spacing between them and their strong interaction is represented by this harmonic spring connecting them to each other.

Now, if it so happens that from its equilibrium position the ith atom undergoes a displacement which is says psi I, then since this is connected to this it may so happen that this will undergo a displacement like this. So, this is the displacement of the I plus oneth atom in the lattice and let me denote it as psi of I plus 1.

So, what I understand is because of the connected nature of the movement of the atoms the total potential energy as the as the atoms move about, they are it is going to be a function of psi 1, psi 2 etcetera upto psi n. So, this quantity is actually psi 2. So, now, what happens is in the next phase, I can very easily say that well if I have a solid a stable solid then the atoms will be able to execute only small amplitude vibrational motion around their respective equilibrium position.

So, I can expand this potential energy about the equilibrium, mean equilibrium position with respect to each of the atoms constituting it. So, that this is the potential energy when all the atoms are at their mean equilibrium position. This is the term which is del U del

psi 0, that is the first derivative term which has the first order displacement at each of the lattice sides psi I and then this is the term which tells me that this is quadratic in the displacements and this is the second order derivative of u with respect to psi I and psi j. So, this is standard Taylor expansion.

Now, what I understand is since the system is going to exhibit most stable configuration at equilibrium, where all the atoms are present at their respective lattice points, therefore, these derivatives evaluated are evaluated at those equilibrium positions and since the potential energy must be having a minimum this first derivative must go to zero.

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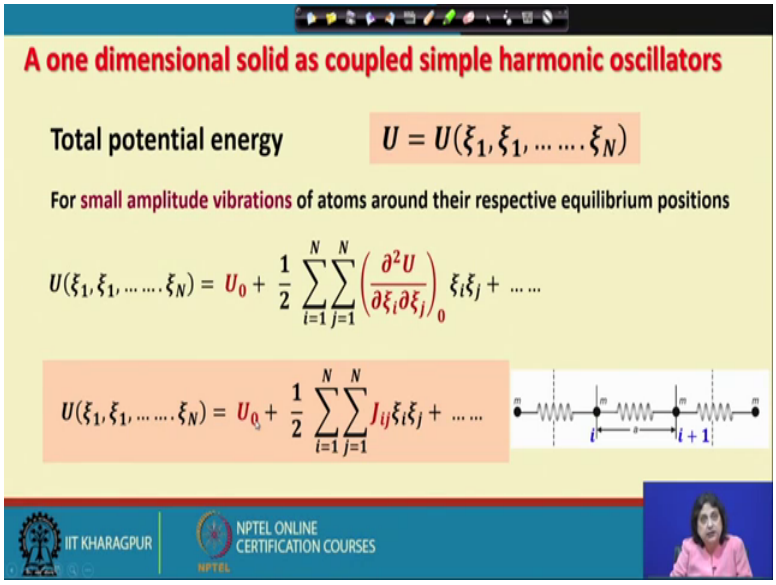

So, that basically tells me that under such condition, I should be able to write the total potential energy of the solid as a constant term plus a term that is quadratic in the displacements or in other words I can introduce a spring constants Jij representing the coupling of the displacement psi i and psi j and I would say that u is a u represents the potential energy of a system of coupled simple harmonic oscillators, but that does not help us we do not know how to solve the Schrodinger equation or for this kind of system even for a smaller number of particles.

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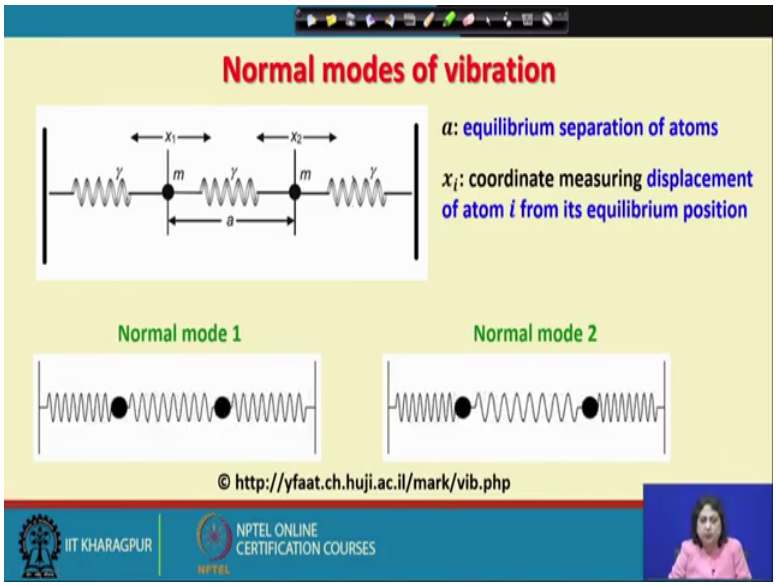

And therefore, what one does is, one tries to figure out those combinations where I can treat these coupled vibrations as normal vibrations, which are a collection of vibrational modes which are executed independent of each other. So, in this particular case as you see I am highlighting over here 1 normal mode when the 2 atoms are moving in phase and there is another one which are moving not in phase, but out of phase to each other. So, if I take this as oscillator 1 and if I take this as oscillator 2, then these 2 represent the vibrational pattern of these 2 coupled simple harmonic oscillators effectively.

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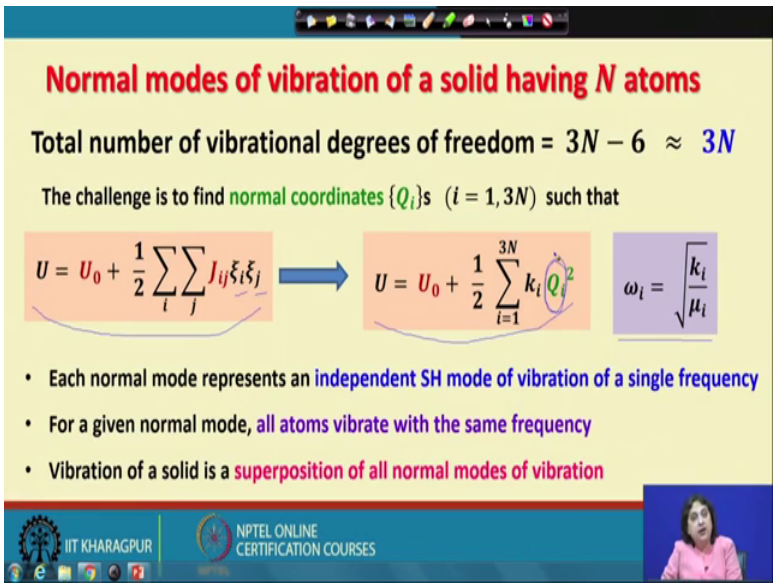

So, this is the role of the normal modes of vibration. So, what is it that a normal mode of vibration will give me? Let us say that I start with a solid having capital N atoms. Then the total number of degrees of freedom is 3N minus 6, but for N equal to Avogadro number this is practically equal to 3N. So, what basically we are trying to do is, we are trying to replace this representation by this representation and it is indeed a challenge to find out this normal coordinates qi s which will have these intrinsic angular frequencies omega is such that the total potential energy, now can be represented in terms of 3N independent simple harmonic oscillators.

Now, please try to understand that here these are the atomic displacements which are coupled to each other in the solid and here qis are some functions of these psi is and psi js which are so defined such that this combinations q 1, q 2, q 3 this behave these vibrational modes they behave independent of each other. So, we can say that the conclusion from this exercise is that each normal mode represents an independent simple harmonic mode of vibration having a single frequency. For a given normal mode or atoms vibrate with the same frequency and the vibration of a solid is a superposition of all normal modes of vibration and now this tells us that if I want to visualize the normal modes in simple real cases.

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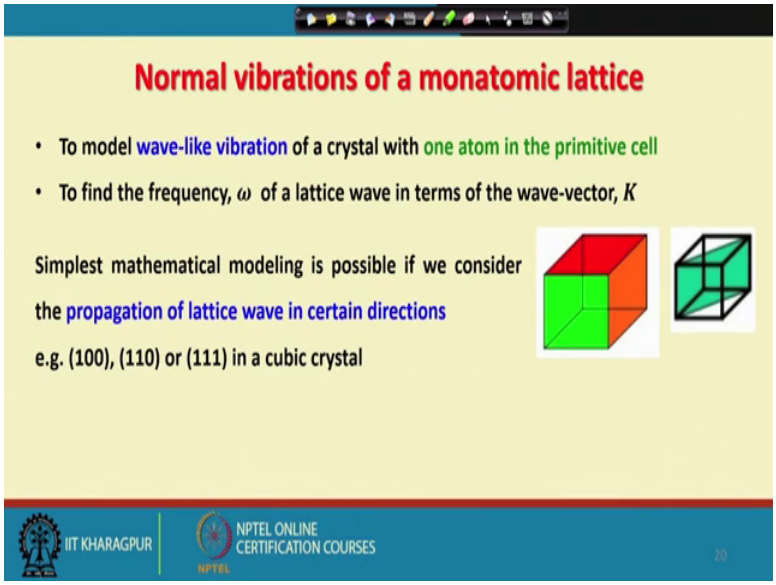

Then let us take up the normal vibrations in a monatomic solid, where let us try to think about the wave like vibrations of the crystal that has only 1 atom in the primitive cell and

basically here description of the wave like vibration is essentially correlating the frequency omega of the lattice wave in terms of the wave vector k and the simplest mathematical modeling that is possible here is, if I consider the propagation of the lattice wave in certain directions like as you see this is the 100 direction of the cubic crystal or this is 111 direction of the cubic crystal. So, what I am talking about is the monitoring the propagation of the lattice wave along these directions.

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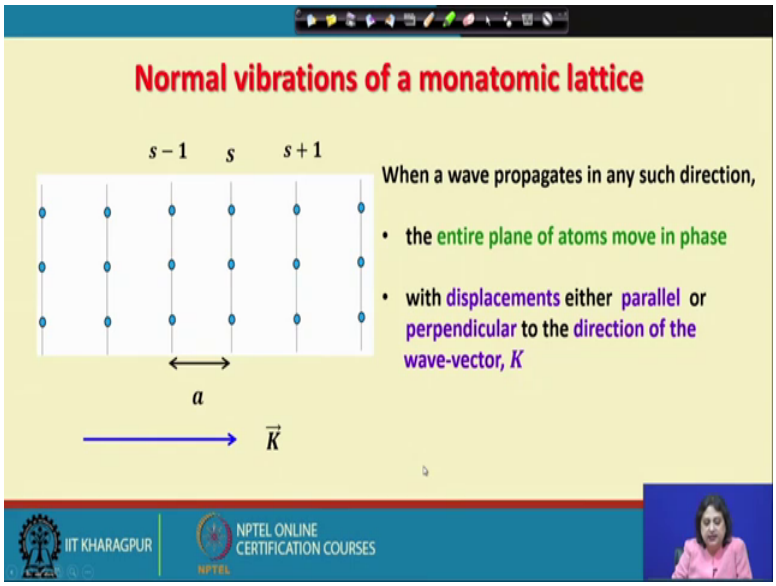

Now, when we talk about these. So, along these directions and along the planes that I have shown in the previous slide, let us say these are the regular arrangement of atoms and if when a wave propagates in any such direction then what will happen this all these planes of atoms will move in phase with displacements either parallel or perpendicular to the direction of the wave vector K.

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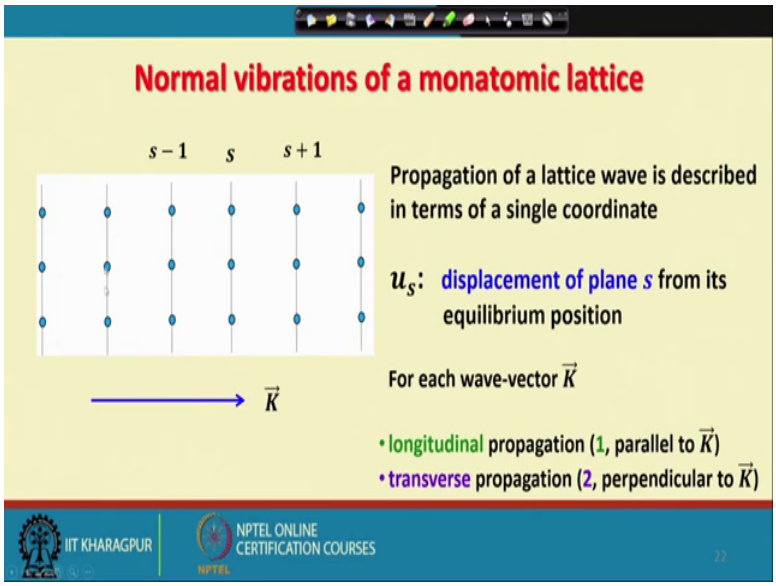

Now, let us try and understand this by taking the actual example of what will happen when this equilibrium picture of a particular direction of propagation this is the direction of propagation of the wave vector K and I have linear arrays of the atoms in this direction arranged in this direction and then what is I am saying is by choosing to represent the situation in this direction, I can describe the propagation of the lattice wave in terms of a single coordinate which is shown here as Us.

So, if this is my sth plane, this is a neighboring plane which is s minus oneth plane and this is a neighboring plane s plus oneth plane ok. If this plane undergoes a displacement when a lattice wave passes through this direction, then I would say that I am looking at the displacement of the place plane s from its equilibrium position as the lattice wave progresses. Now, as you understand for each wave vector, there can be 3, directions there can be a longitudinal propagation which is the movement of this displacement of this plane parallel to the direction of K and the there can be other displacements like 1 is perpendicular to the direction of K in the plane of the board and the other one must be perpendicular to the plane of the board.

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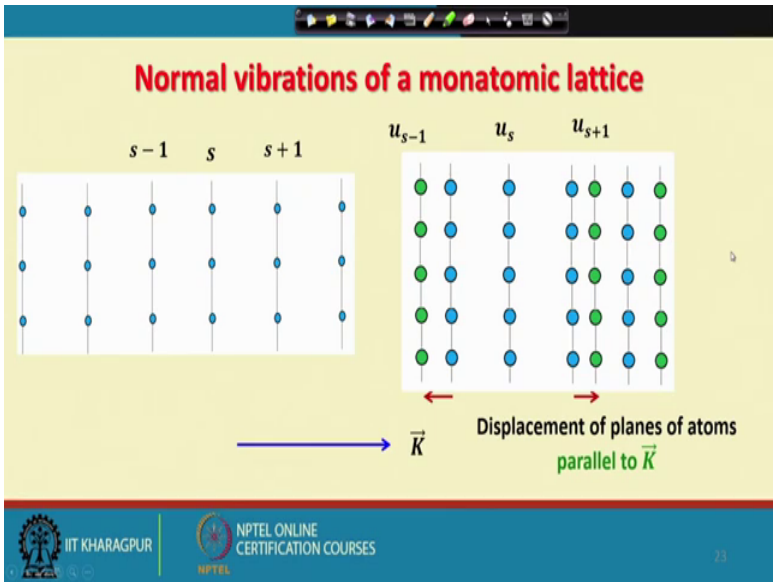

Now, let us have a look at what these displacements might look like. So, this is the representation. So, if this is the equilibrium distribution in the plane of our choice in the direction of the propagation of the wave vector K. So, I see that U s minus 1 has moved here. U s has stayed here, but Us plus 1 has moved here. So, I am looking at displacement of these planes of atoms parallel to the direction of K, either in the plus K direction or minus K direction.

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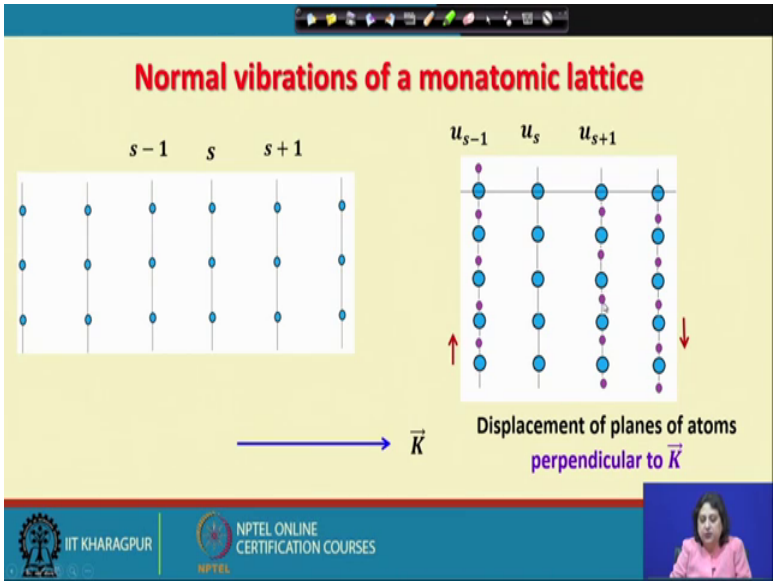

We can also think of displacement of the planes of atom perpendicular to K. So, if you compare these 2 pictures as you see Us remain the same, but this plane has moved in this direction perpendicular to the direction of Kand this plane has moved downward where each atom has moved downward in a direction perpendicular to K.

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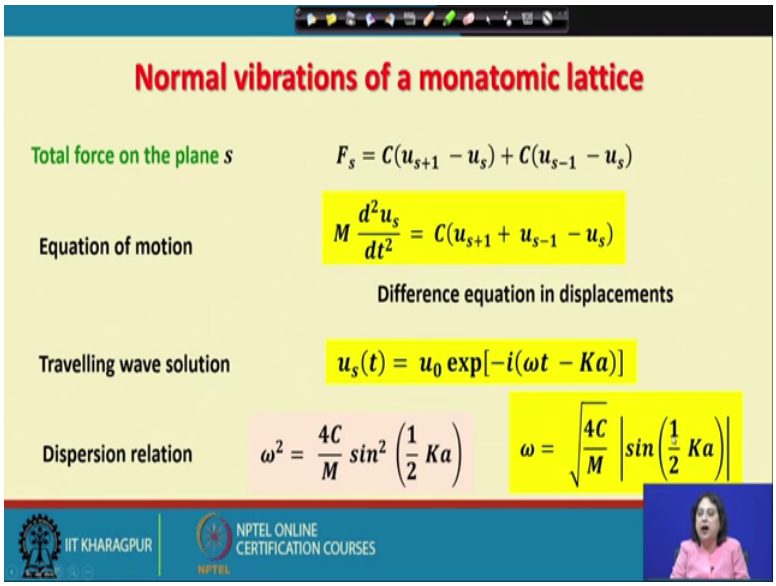

So, basically then, one can write down the total force on the plane in terms of the displacement or the force acting on it because of its coupling to its nearest neighbor. So, s will be coupled to the atom, then the s plane will be coupled to atoms on the s plus oneth plane and s minus oneth plane. So, the equation of motion of each atom on the sth plane will be given by an equation like this which is a difference equation in displacements and it has a solution which is known as a traveling wave solution and it is given by this.

So, what happens here is that the specific way this wave is going to propagate, now will depend on the relationship between omega that is a intrinsic angular frequency and the wave vector K and this dispersion relation in a monatomic lattice can be obtained from by solving these equations and you find that omega is proportional to sin of half Ka.

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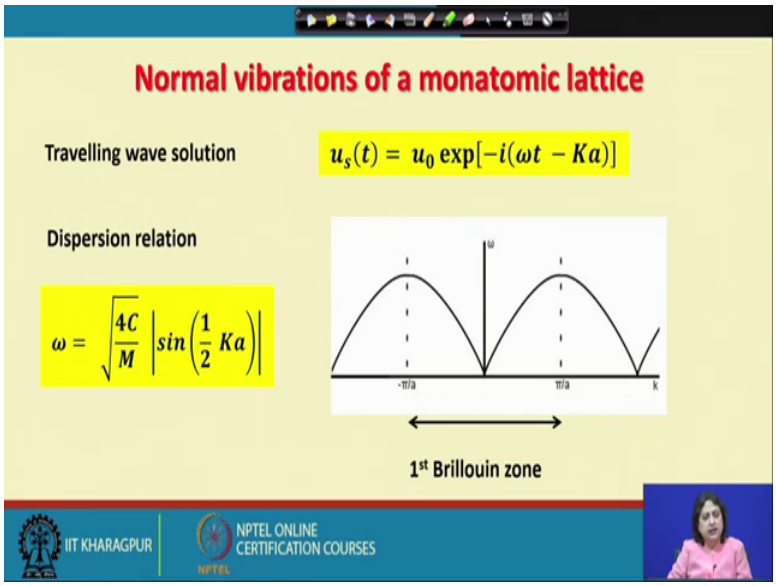

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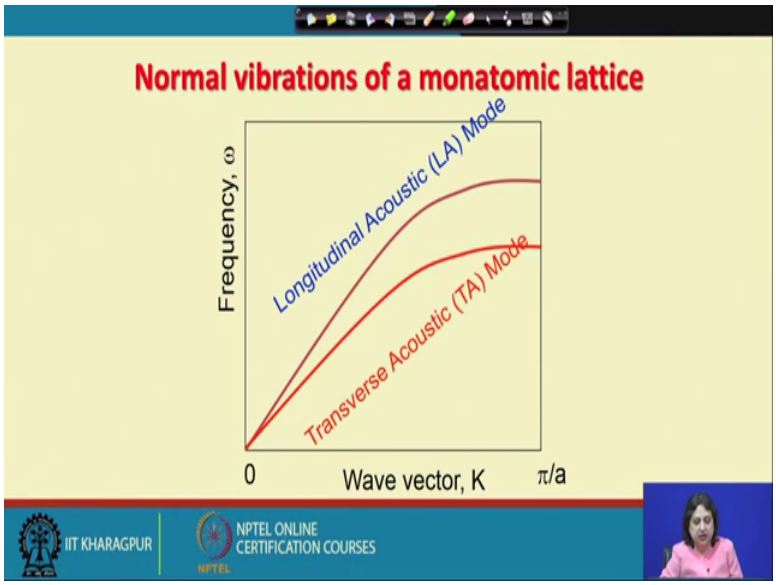

Now, these are the dispersion relations that are usually plotted and measured in experiments. So, this is typically what is known as the dispersion relation in a monatomic lattice and as you see as K goes to 0,

the omega is nearly linear and if you look at the overall different modes like the longitudinal modes and transverse modes you see that there are 1 longitudinal and 2 transverse modes, but as you see here I am calling them acoustic modes, that is simply because in the limit where omega is proportional to K, you see essentially the sound

waves propagating through the medium because of the because of the vibrations that are excited. So, if I go back and have a look at what is happening at K going to 0, I find that here I have phonons with frequency which goes to 0.

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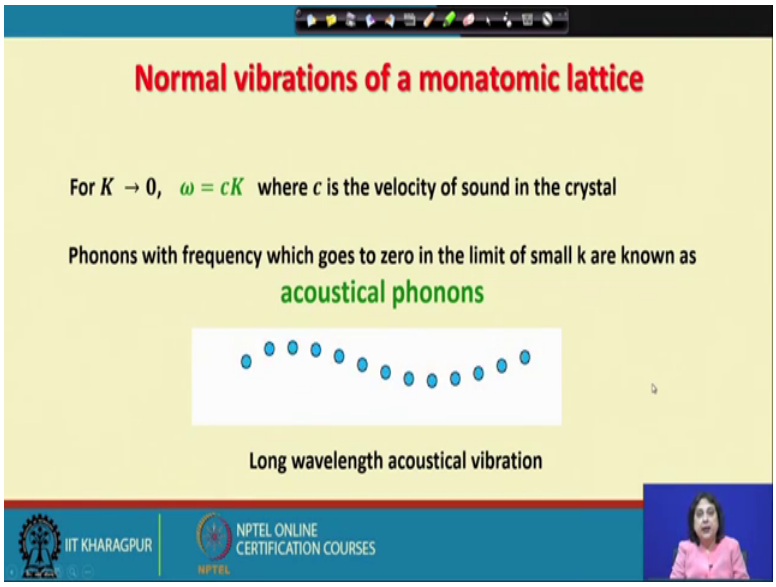

In the limit of small k and these are known as acoustical phonons and this is how they look like and what I am showing to you is the long wavelength acoustical vibration that will correspond to the transverse acoustical, one of the transverse acoustical modes. So, these are representations of the typical normal modes of vibration in a real solid.

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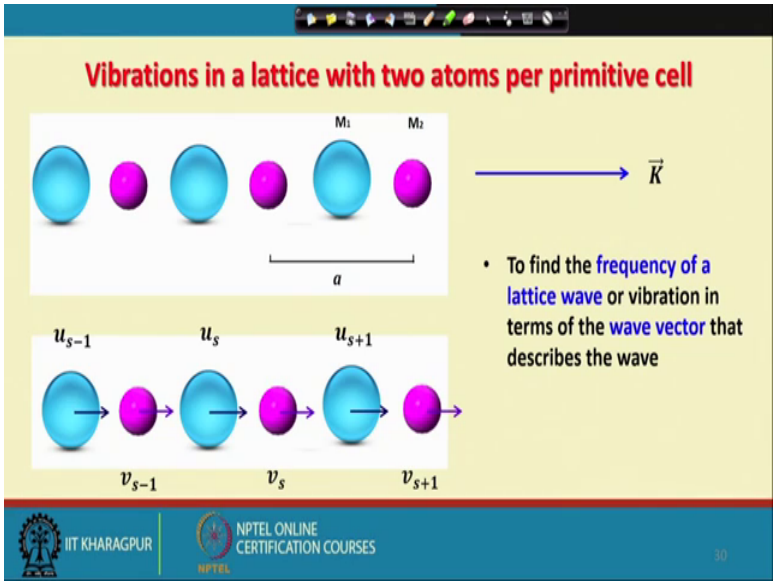

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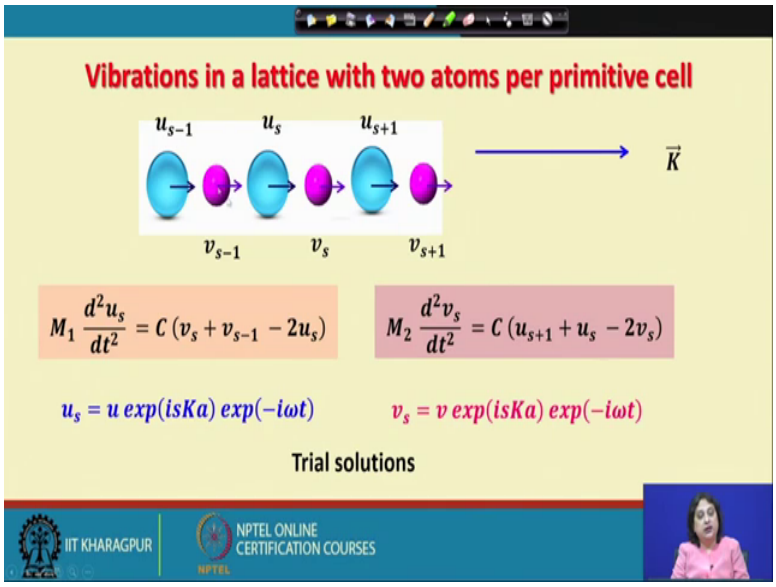

You can have representations of these systems in a more complicated situation where I have a lattice with 2 atoms per primitive cell and here once again, one can write down the equations of motion of the sth plane, but now you have 2 types of planes, one is associated with the blue atom another one is associated with the purple atom.

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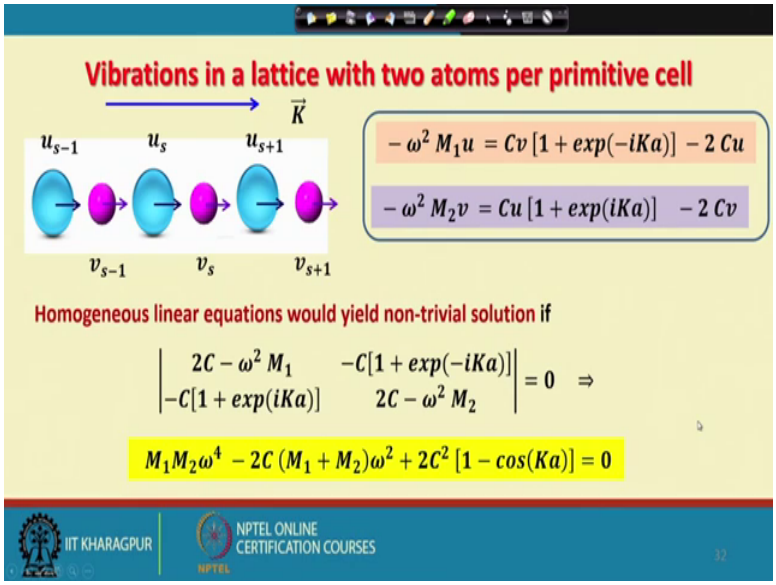

And once again if you solve you find that this is the equation that you need to understand in to need to solve in order to understand what frequencies are possible for the propagation of vibrational waves through a lattices like this.

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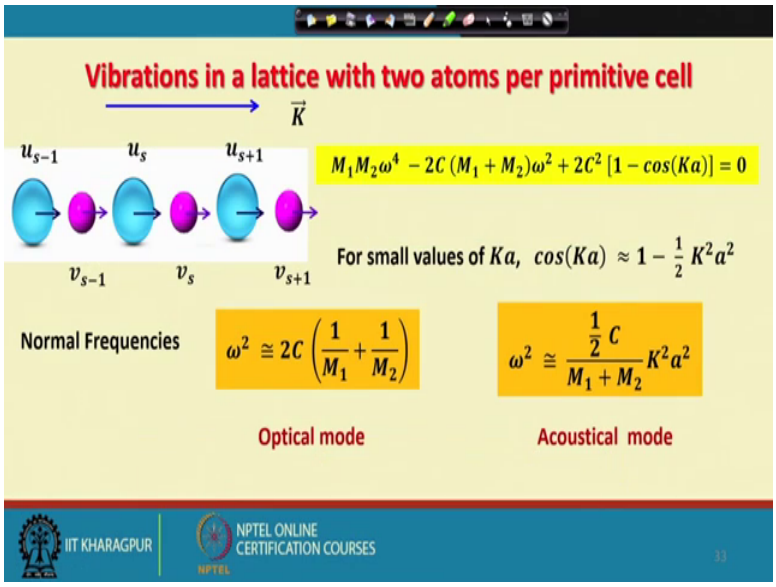

And then you find that there are 2 possible for small values of k, there are 2 possible solutions. For, one set of solutions you have the acoustical modes as before which goes to 0 as k goes to 0, but now you see because of the underlined change in the structure of the solid, you have an additional value of omega and this is known as the optical mode.

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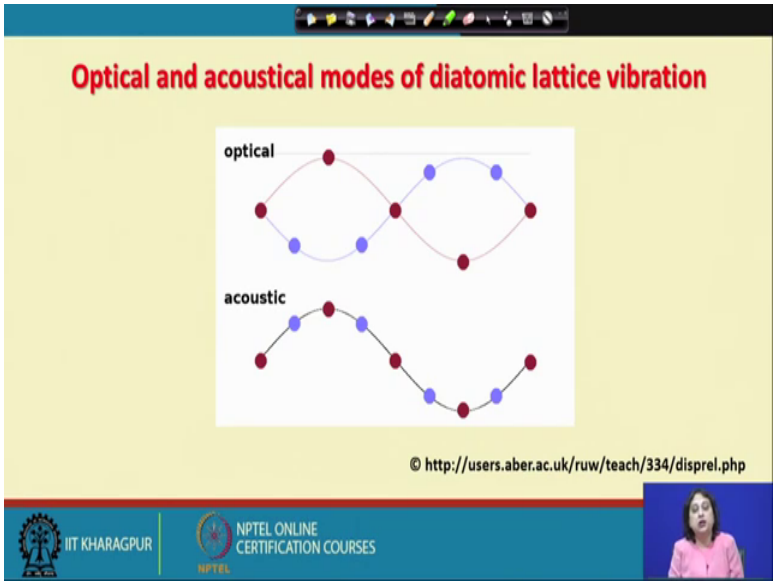

I will explain to you what these 2 modes look like. So, as you see in the acoustic modes both type of atoms move in phase with each other and they go and their frequencies go to 0 as k goes to 0, but when I have the optical modes, you see that the brown atoms are moving out of phase with the blue atoms that atom of type 2 and if it so, happened that they carried charges. So, this had a positive charge and this has had a negative charge, this kind of vibrational patterns will generate a charge separation which then will be able to couple to incoming light, that is the only way a photon can come interact with impinging light in the system and that is the reason why this type of vibrational modes are called optical modes.

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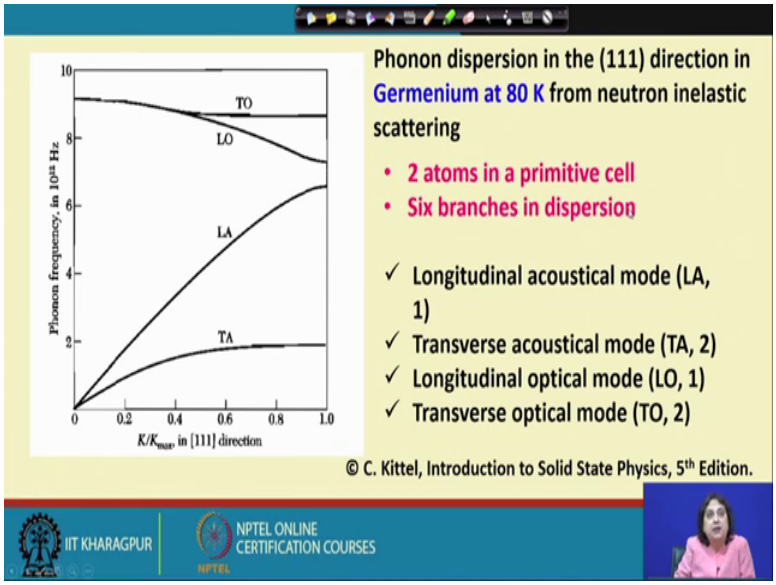

And if you go out and look at the actual experimental data, you will find that for example, as I have shown here for germanium and 80 Kelvin, you can actually find out all the different types of longitudinal acoustic modes, a transverse acoustic modes or longitudinal optical mode or transverse optical mode.

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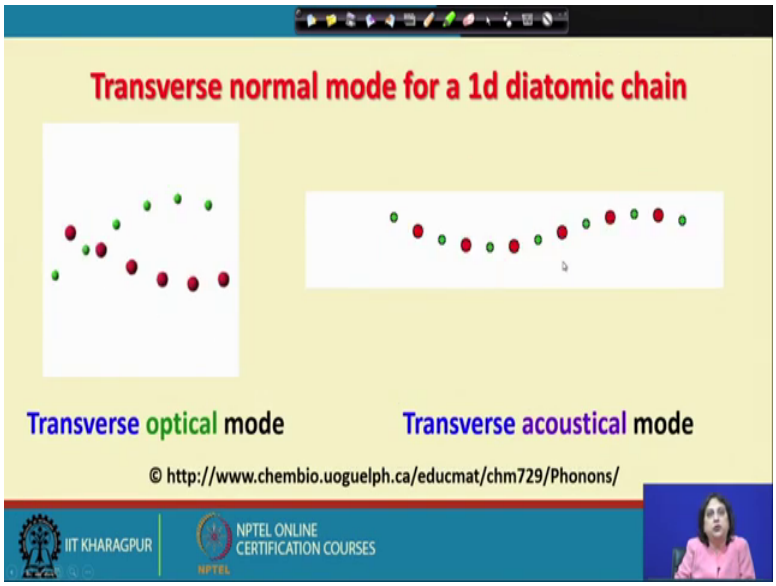

So, these are the typical representations of these normal modes in this kind of 1 dimensional diatomic chain and the take home message over here is that each of these vibrational modes behave as if they are independent simple harmonic oscillators in this given solid.

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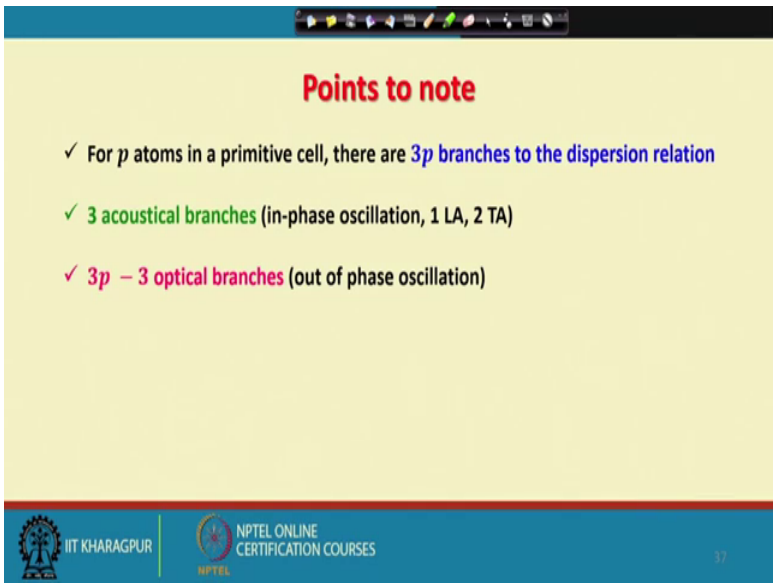

Therefore I would say that the for if I have a very complicated solid, say there are 3N atoms or 3p atoms in the p atoms in the primitive cells in the 3 dimension, there are 3p branches to their dispersion relation and this tells me that you still will have a very large

number of frequencies to talk about and you will have to look at what these different acoustical branches are and what the optical branches are and interpret the density of states of the vibrational frequencies accordingly.

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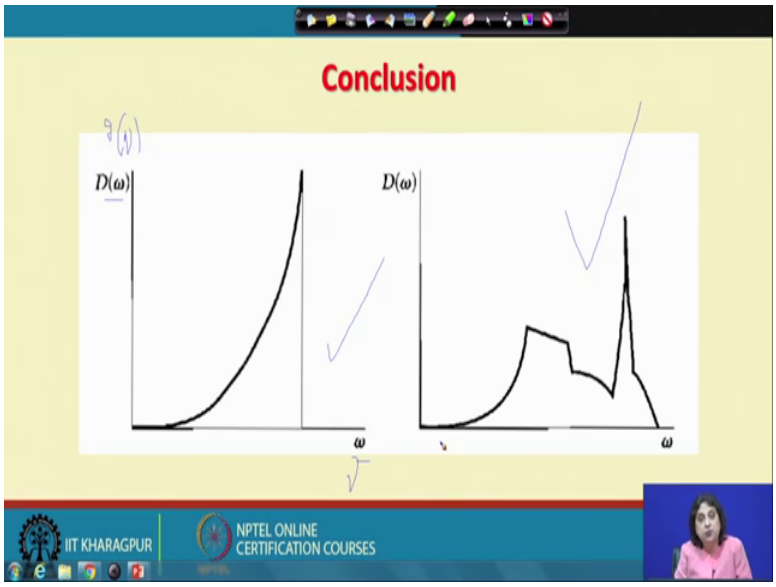

What went right for Debye theory? In the Debye theory, this is the approximation that is being used to represent the density of states, I. have written d omega as a function of omega which is equivalent to representing g nu as a function of nu ok. Now, as you see that this actually gives me nu as a function of nu square, g nu as a function of nu square.

And if you compare it to the case where you have the phonon spectrum for a real solid you see that this is valid for low frequency behavior of the density of states and these modes are excited at low temperature. So, what went right for Debye theory was that Debye could propose the correct form of the density of states at low temperatures and therefore, that is the reason why the Debye theory could successfully predict the low temperature behavior of a given solid.

I must leave with this last warning. I have used a lot of concepts from solid state physics today. You are not required to go back and look up the entire syllabus of a solid state physics, which is covered typically in undergraduate physics course. The message I want you to have is in order to understand what is happening in an experiment you really have to probe deep and try to understand the behavior of a given system not only in terms of a

simple model that is useful to you, but borrow the language from other systems, other limiting behavior of the same type of systems and use them to construct a better model.

Thank you.