Introduction to Molecular Thermodynamics
Prof. Srabani Taraphder
Department of Chemistry
Indian Institute of Technology, Kharagpur

Lecture – 33
Specific Heat of Solids

Welcome. In this part of ah the lectures, we are going to use the principles of molecular thermodynamics that we have learnt in this course so far and see the applications through different systems. And in today’s lecture, we are going to consider the specific heat of crystalline solids.

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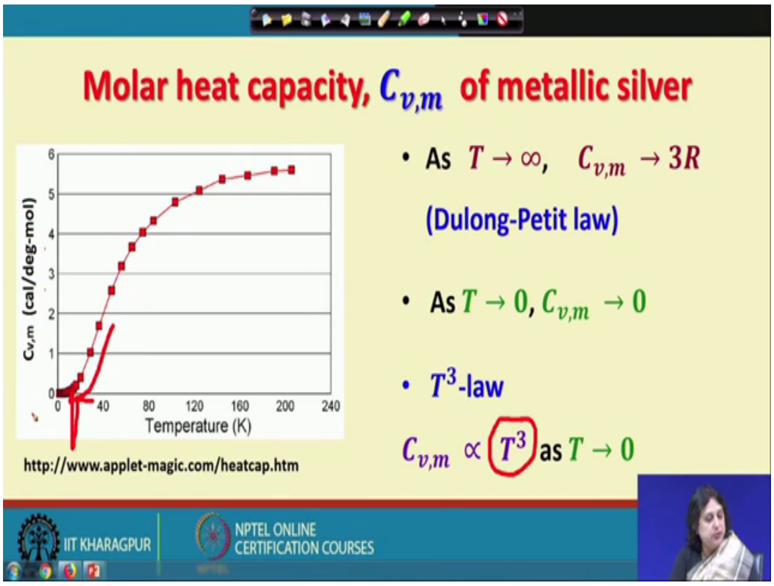

Molar heat capacity, $C_{v,m}$ of metallic silver

http://www.applet-magic.com/heatcap.htm

- As $T \to \infty$, $C_{v,m} \to 3R$ (Dulong-Petit law)
- As $T \to 0$, $C_{v,m} \to 0$
- T^3-law

$C_{v,m} \propto \boxed{T^3}$ as $T \to 0$

Now, if we look at the experimental data on the ah molar heat capacity ah metallic silver, what we find that this actually exhibits a ah non-monotonic increase as temperature is increased from very small values very close to 0 Kelvin to the higher temperatures like say 300 Kelvin. So, what we find is here initially the values are very close to 0 then there is an increase and what happens near the top is it is attaining some constant value. Actually these ah this particular behavior is not ah ah specific for ah the kind of [vocalized-noise] ah system for which I am showing the experimental data rather this is representative of the typically what you observe as you the measure the specific heat of the solid. When you are at a very high temperature, then it is found that all the ah solids exhibit a constant value of the heat capacity.

You must have studied ah this observation in your high school days in the form of Dulong-Petit law. It is one of the most well-known experimental observations in the studies of property of solids therefore, all the solids generally when present at a very high temperature in that case we would find that they exhibit a constant value ah of specific heat ah equal to 3 R, where R is the universal gas constant.

Now, what happens if I go down to lower temperatures? When I go to very low temperature what I find is as T goes to 0 from this constant value the C v rapidly drops down to 0, and at absolute value of ah ah 0, its ah term which is expected to be very very small and nearly 0. Now, the way it approaches zero at very low temperatures has been the subject the subject of investigation in the very large number of studies and in this case there was a law which has been formulated based on the generic behavior found for a very wide range of solids and this is known as the T cube law.

So, what does the T cube law say, the T cube law says that as the system goes from a lower temperature to a very low temperature then it rapidly falls down. And this fall is having a temperature dependence in the sense that in this region C v varies as T cube as one goes from a low temperature to even lower near zero temperatures. Therefore, it is very clear that if any microscopic modeling of this particular system like a solid a crystalline solid is ah needed, it has to reproduce this kind of the set of three different limiting behavior of specific heat. So, but before we go into that let us review a few more experimental cases where this T cube law has been observed.

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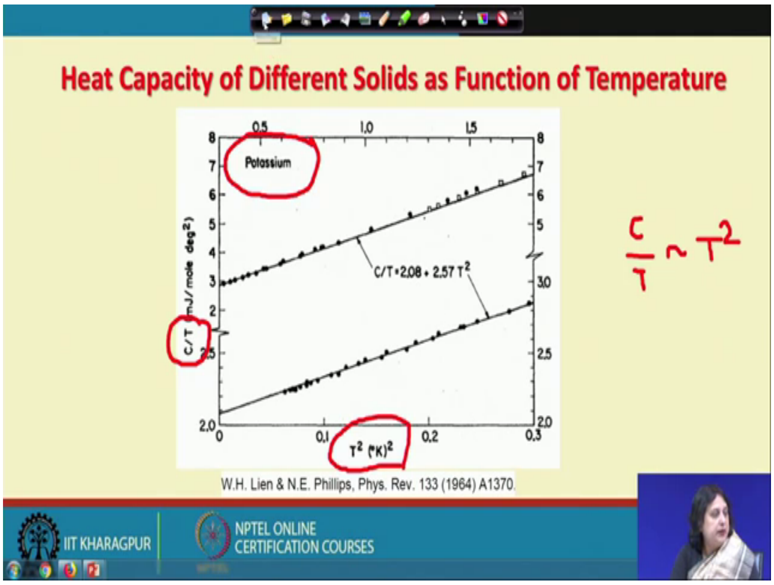

Heat Capacity of Different Solids as Function of Temperature

$\frac{C}{T} \sim T^2$

W.H. Lien & N.E. Phillips, Phys. Rev. 133 (1964) A1370.

So, what is found is this is a measurement of the heat capacity of different solids at ah ah function of temperature at very low temperature, and this is the measurement for potassium. And here you can see that along the y-axis [vocalized-noise] x-axis, we are plotting T square; and here on the y-axis, we are plotting C by T. Therefore, it is found that C by T goes as T square [noise] for these plots for this system which means that C at low temperatures employed here, they vary as T cube.

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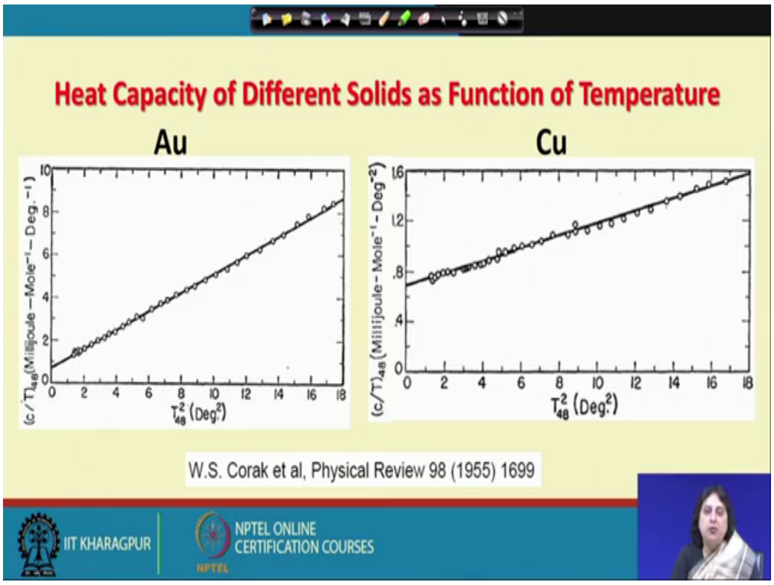

Heat Capacity of Different Solids as Function of Temperature

W.S. Corak et al, Physical Review 98 (1955) 1699

Similar trend is observed when you consider systems like gold or copper. So, once again at very low temperatures if you look at the kind of low temperature that is accessed by ah these kinds of these experiments you find that the T cube law that is C varying as T cube is valid. So, then the question is all the ah relationships that I am showing to you applies to mono atomic solids I have done that ah actually to keep the treatment and understandings of the systems very simple. But this kind of behavior ah can also been seen for much more complicated solids as well, but for the purpose of today's lecture I am not going to cover them.

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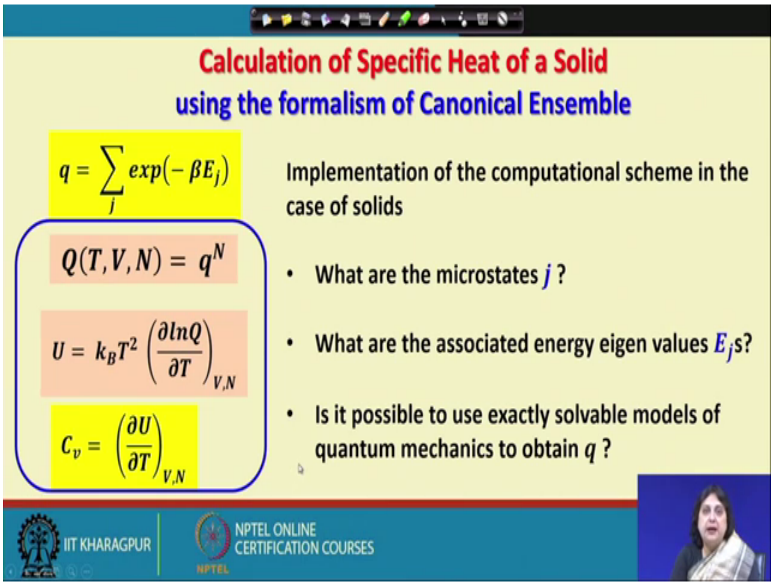

Calculation of Specific Heat of a Solid
using the formalism of Canonical Ensemble

$$q = \sum_j exp(-\beta E_j)$$

$$Q(T,V,N) = q^N$$

$$U = k_B T^2 \left(\frac{\partial lnQ}{\partial T}\right)_{V,N}$$

$$C_v = \left(\frac{\partial U}{\partial T}\right)_{V,N}$$

Implementation of the computational scheme in the case of solids

- What are the microstates j ?
- What are the associated energy eigen values E_js?
- Is it possible to use exactly solvable models of quantum mechanics to obtain q ?

So, now going back the task is for a given mono atomic solid which is crystalline in nature. So, I need to find out or calculate the specific heat of that crystalline solid. And for this purpose, I am going to use the formalism of canonical ensemble. So, the prescription by now must be very clear to you. You first find out the single particle partition function for the given ah system then you calculate the canonical partition function for the entire system provided. You can represent the constituent particles of the system as capital N independent non-interacting single particles. Now, obviously, once you can calculate capital Q, you can follow the prescription of molecular thermodynamics, and calculate internal energy U and then take a temperature derivative ah to ah of ah U to find out the specific heat.

So, now, how do I implement this computational scheme when I am talking about a system like ah [vocalized-noise] silver solid or copper solid or gold solid and so on and so forth ok. So, for that I realize that this part is fairly standard by now we have now tested the predictions of this prescription for many different systems that are exactly solvable given quantum mechanics. So, we know what ah E js are what js are. So, we could calculate small q and follow this prescription to ah get the thermodynamics properties.

But when I have a solid at hand what I understand is here the information that I must provide are as follows. So, what are these microstates [vocalized-noise] that I ah [vocalized-noise] represent using the index j [noise]. And if I know these microstates what would be the associated energy value eigen values of E j. Now, in a solid as you understand that uh they are constituent particles. So, if in I have a mono atomic solid in that case the constituent uh constituent particles are atoms, and these atoms are strongly interacting with each other. And therefore, you cannot exactly solve the quantum mechanical ah equations namely the Schrodinger equation for a system, for a system like this which is comprised of a very large number of strongly interacting atoms.

So, the next question that we ask is, is it possible to describe the microstates in such a way that I can still use the exactly solvable models of quantum mechanics to model the single particle canonical partition functions small q. So, this is exactly what I am going to do step by step in the next few slides that I discuss here.

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Microscopic view of the crystalline Solid

Eur. J. Phys. 35 (2014) 055021

http://cellnexx.co.uk/

So, let us first look at the established microscopic view of a crystalline solid. So, typically you may have studied in solid state chemistry that if you can generate ah a mathematical array of points which is described in terms of lattice, you can put in the atom the [vocalized-noise] atomic solid at these lattice point. And for example, here I have shown you some ah ah different ways in which you can create two-dimensional lattices by varying the spacing between the lattice points, the angle through which is connect ah connecting vectors um are related to each other and so on and so forth. And basically then what happens is once you have a basic ah ah pattern defined in the unit cell in that case what you can do is you can then go on repeating it in one direction or the other. For example, here in this case, the basic unit is a hexagonal ah unit this is been definitely repeated periodically ah in the x and the y direction and that gives you a ah ah crystalline two-dimensional face.

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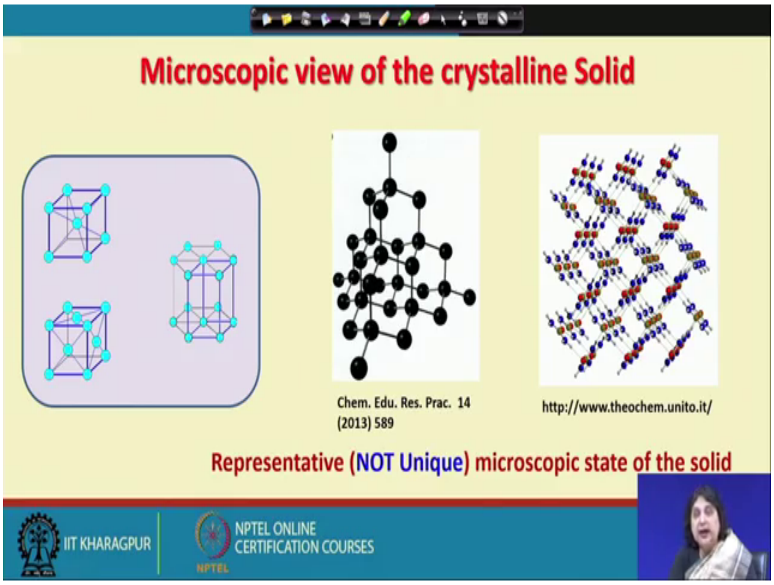

Microscopic view of the crystalline Solid

Chem. Edu. Res. Prac. 14 (2013) 589

http://www.theochem.unito.it/

Representative (NOT Unique) microscopic state of the solid

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Now, of course, most of the solid systems that we encounter are based on three-dimensional ah crystal structures, where the unit cells contain the atoms arranged in a specific manner in the [vocalized-noise] lattice giving rise to rather exotic three-dimensional structures [vocalized-noise] such as a one of dimension here or this is a very complicated structure of a molecular solid. But as chemists we always think about the structure as a unique structure, unique microscopic view of the crystalline solid. And this is the ah this of course is the unique repeating unit as you see here or here or here that will build up the structure.

But what we most of the time do not realize is that this is not the only structure possible [vocalized-noise] for the microscopic state of the solid. So, [vocalized-noise] what I show you here is a representative microscopic state of the solid which would be obtained by taking one unit like this and repeating it if a three dimensions periodically and indefinitely in the x, y and z reduction. So, you will get a big ah cage like structure. And we would say that well this is a unit structure of the solid at the microscopic level. And now I am going to show you that of course, at finite temperature this is not going to be the unique structure of the solid, and there are many many other possibilities.

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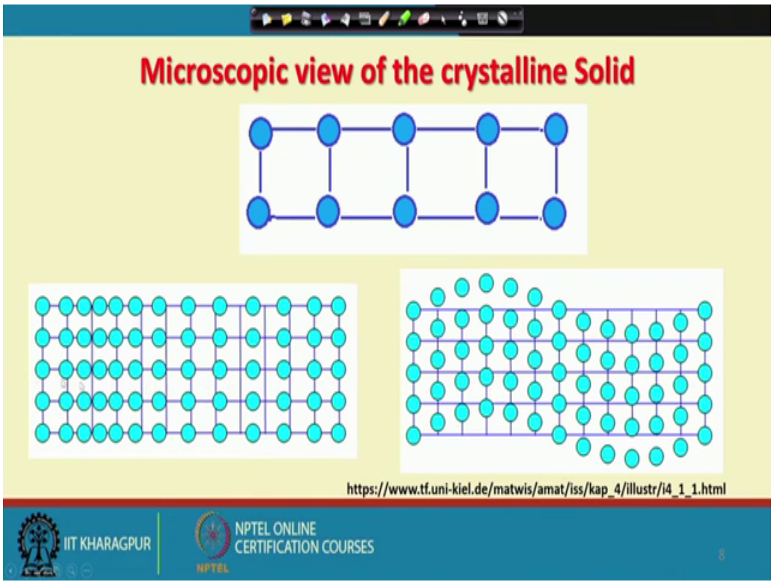

Microscopic view of the crystalline Solid

https://www.tf.uni-kiel.de/matwis/amat/iss/kap_4/illustr/i4_1_1.html

So, let us see why I say this [noise]. So, first of all to keep the things simple I am taking a two-dimensional ah system where these atoms have been placed at the ah corners of a ah [vocalized-noise] corners of this square creating a regular pattern in the x y direction. Actually, I have not shown you the regular pattern in the y, I am highlighting only this portion ok. So, now, it so happens that at finite temperature these atoms I want to have some amount of thermal energy given by Boltzmann constant multiplied by the temperature in absolute units.

Now what will happen there simply because these atoms belong to ah solid they are strongly correlated to the neighboring particles that are present on the neighboring sites of the lattice, therefore, these atoms can actually have only very limited options to use up the available thermal energy at a given temperature. So, this is how they can use it up. So, if you have a closer look at this picture, you see that this atom is more or less present at its equilibrium position at the lattice point. But look at this, this atom which is originally present at the center with its lattice point has moved in this direction. And this atom [vocalized-noise] from its ah equilibrium lattice point has moved away, so that the distance between this is larger why because of the movement of these two atoms, this distance becomes smaller than the lattice spacing.

So, basically what we are looking at are the possible changes associated with the thermal motion of the atoms at and around the lattice points. So, it may so happen here I have been highlighting their displacement along the x-axis, but if it so happens that they are displaced along the y-axis. So, this is a perfect arrangement of all the atoms along the y-axis, and this is where all the atoms have undergone a positive displacement to higher values of y. And this is an arrangement where each atom at the lattice point in this region is undergoing a negative displacement in the sense that they move towards the negative direction in the y-axis. And what is the net conclusion here we find that there is some zones of higher density of particles compared to this, and this a low density region. And here very clearly we see a wave like pattern forming because of the motion of the individual atoms.

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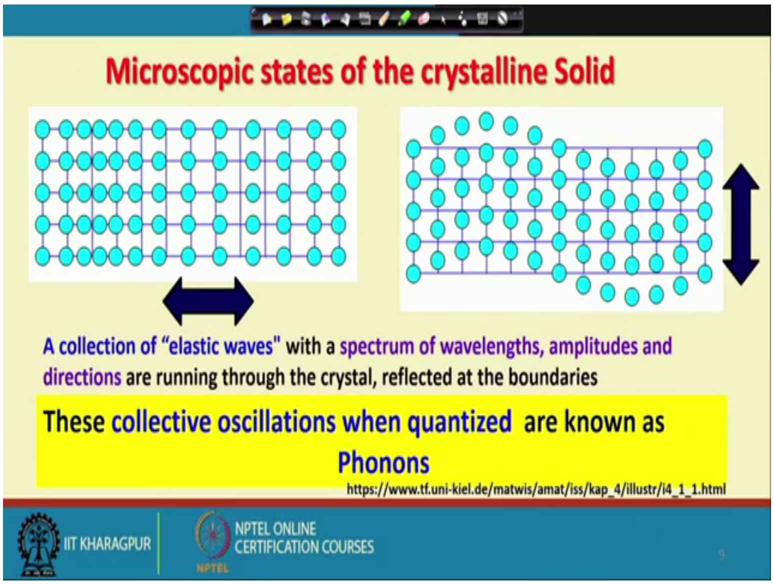

Microscopic states of the crystalline Solid

A collection of "elastic waves" with a spectrum of wavelengths, amplitudes and directions are running through the crystal, reflected at the boundaries

These collective oscillations when quantized are known as Phonons

https://www.tf.uni-kiel.de/matwis/amat/iss/kap_4/illustr/i4_1_1.html

Now what are these motions? So, if we have a look at the combination of the motion of the atoms around the lattice position either in the x direction or in the y direction, so the net result would be a collection of elastic waves with a spectrum of wavelength, amplitudes and directions running through the crystals. So, I have several atoms strongly correlated to each other present in the system, and they are collectively undergoing displacement at along the two degrees of freedom available to them x and y. And simply because these are solid atoms, they can only execute a small amplitude vibrational motion about their mean equilibrium position which is at the lattice points. Now, in the literature these collective oscillations resulting from the displacement or the vibration of this atom about their mean lattice position ah these collective oscillations when quantized I have given the name phonons.

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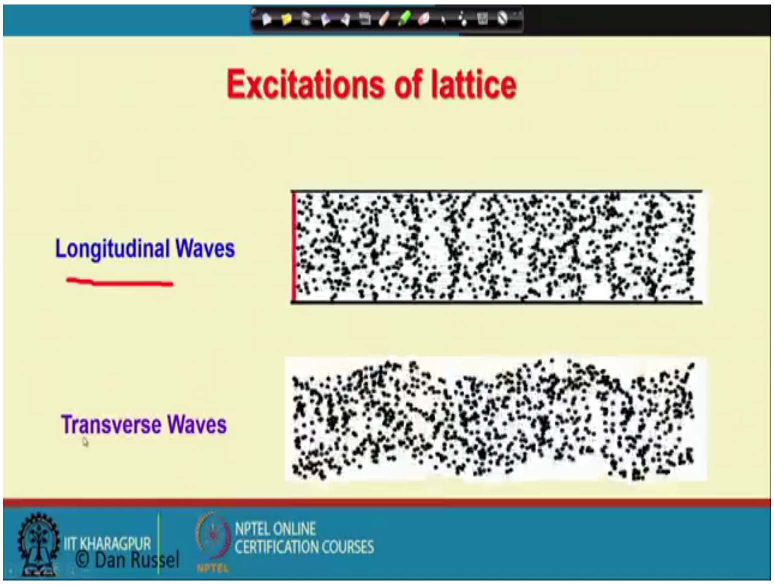

Excitations of lattice

Longitudinal Waves

Transverse Waves

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Now, let us have a ah visual ah look at the kind of different kinds of ah ways in which ah the atoms ah the molecules or the particles in a lattice can use up the available thermal energy. The first one that I show here is a longitudinal wave. And as you see that in this case, you [vocalized-noise] in a entire wave front is moving in this direction. On the other hand, when I have a transverse wave, then the way the wave travels through the system is pretty different.

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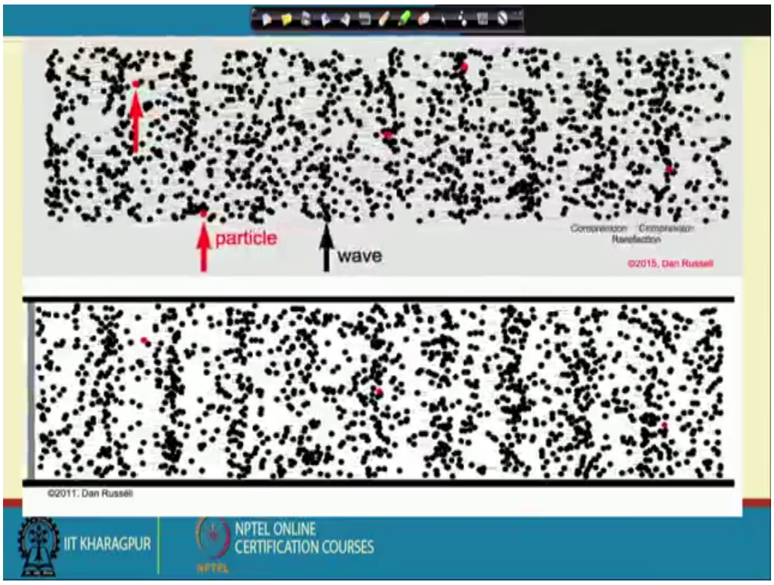

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So, now, if I go [vocalized-noise] back and look at what is happening to each of the particles in the medium due to whose displacement these different types of waves are coming into the picture. If you focus your attention to a particle here, you see that it is basically oscillating in the x direction. On the other hand, if I look at and [vocalized-noise] it is because of the oscillation periodic oscillation of similar particles, I get the wave front moving in along the x direction, which is the longitudinal direction in this case. Similarly, if we look at the motion of this particle, this is ah this you can ah [vocalized-noise] follow and see that how it is moving it is remaining in this phase, but how two different particles are moving through the medium through their displacement.

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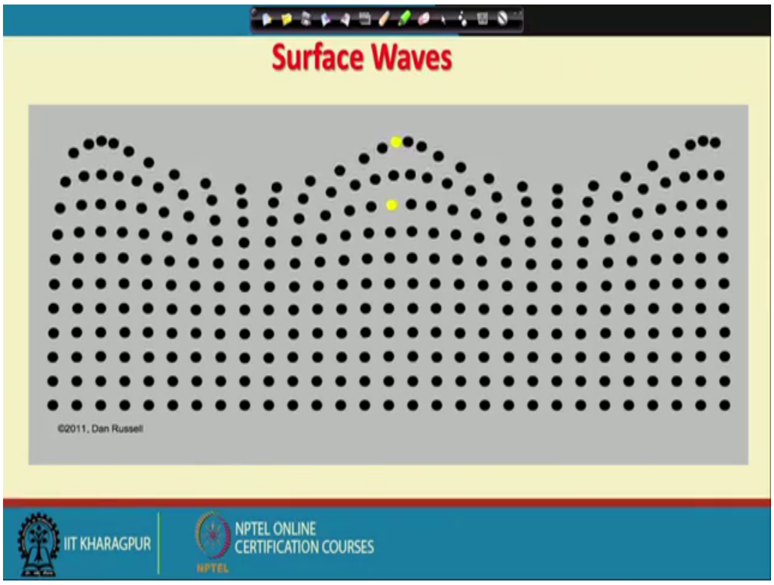
Surface Waves

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Now, if you are looking at the surface of the solid; obviously, the pattern of vibration the collective vibration is going to be different. So, these are ah what are known as the surface waves ok.

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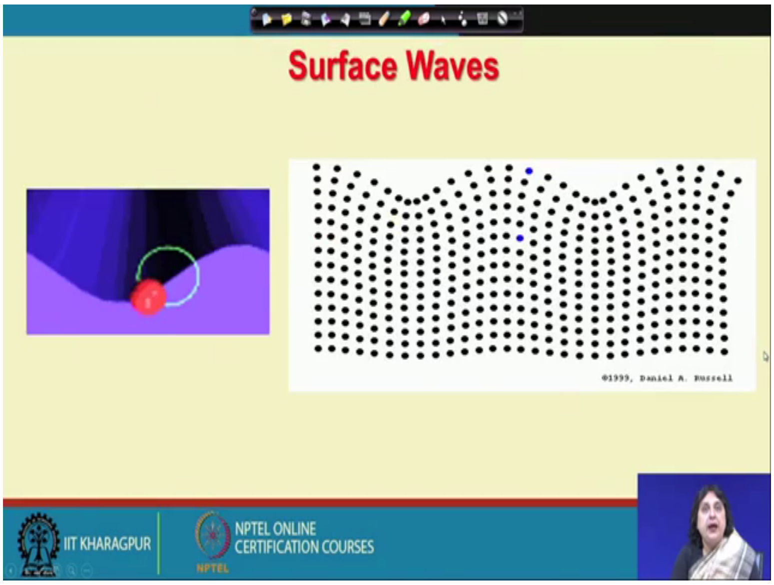

Surface Waves

And if actually if you look at a single particle on the surface you find that this particle actually is executing a very interesting circular motion and that is given rise to and when all the particles on the surface do so together the collective motion that we see that ah seen shown in terms of this wave. And these are known as surface waves.

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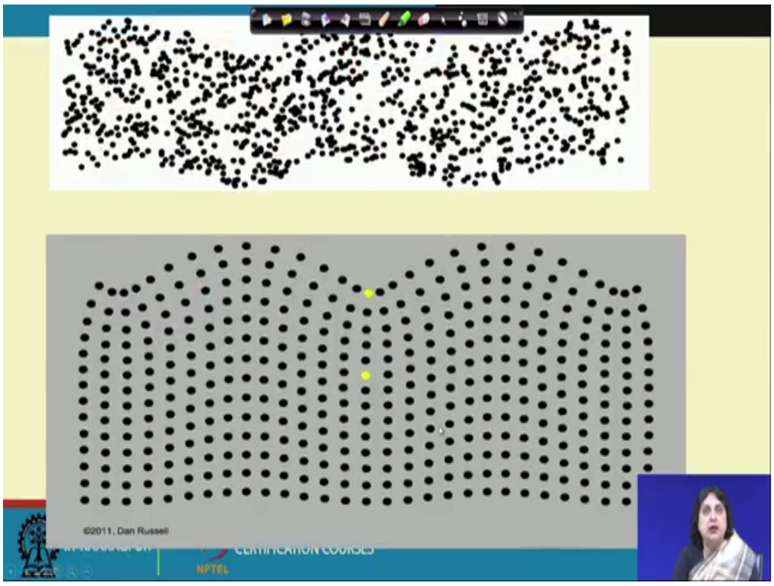

So, having these different types of ah structural fluctuations available to us then the question is ah well what are going to be then the different microscopic states when we are considering the crystalline solid.

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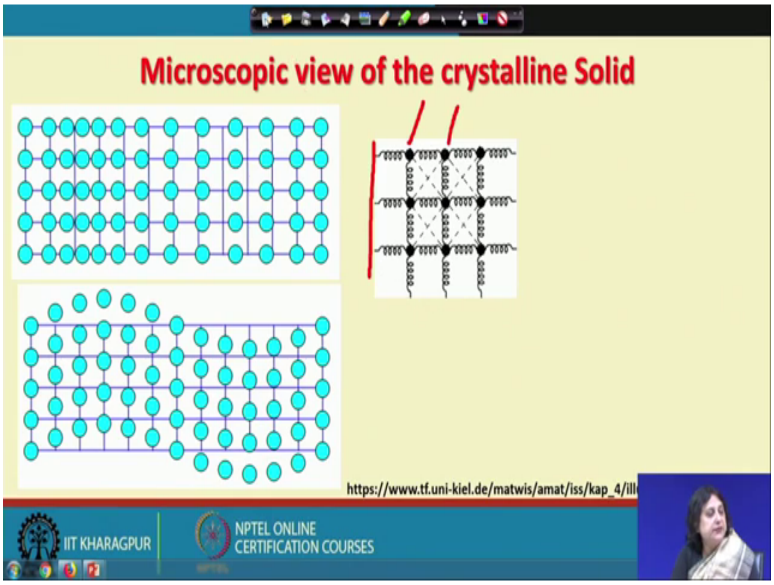

Microscopic view of the crystalline Solid

https://www.tf.uni-kiel.de/matwis/amat/iss/kap_4/ill

So, one way of doing it is; obviously, use the ball and spring model. So, you place a ball at every point on the lattice and then you represent the strong correlation between the position of this atom and this atom in the solid by placing a tight spring between them. So, in that case a two-dimensional solid can be schematically represented like this.

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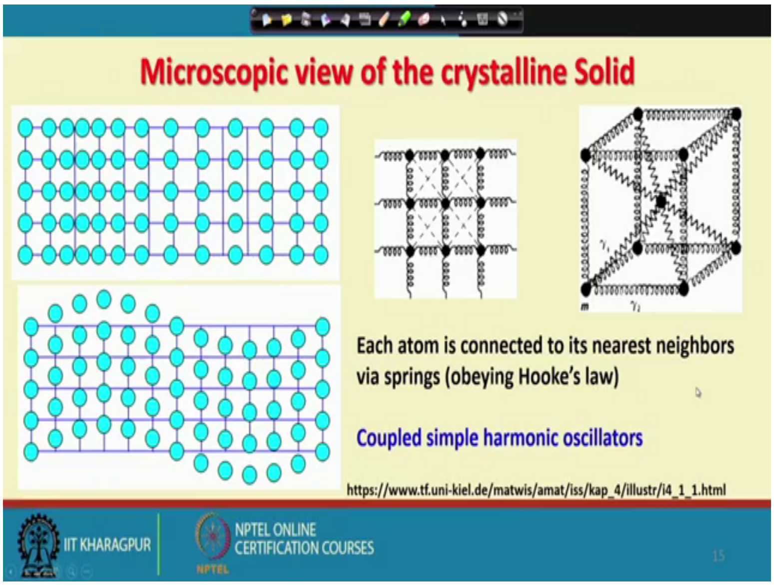

Microscopic view of the crystalline Solid

Each atom is connected to its nearest neighbors via springs (obeying Hooke's law)

Coupled simple harmonic oscillators

https://www.tf.uni-kiel.de/matwis/amat/iss/kap_4/illustr/i4_1_1.html

Again, we can have the similar representation of a three-dimensional ah unit cell of a solid by connecting the corners of a cube with respect to ah ah with the help of a spring. So, basically what we are seeing here is if I want to know what this complicated vibrational patterns are, what do I have to do. I will have to say that well I assume that ah [vocalized-noise] each atom is connected to its nearest neighbor via some springs which obey the Hook's law. In that case, what I have is either in two dimension or in three dimension, I have a the [vocalized-noise] net vibrational pattern generated by a set of coupled simple harmonic oscillators.

Now, if you ah think about classical mechanics or ah or mathematical problems of ah [vocalized-noise] solutions of partial differential equations, the solutions of this kind of ah problem is known regarding how to represent the coupled ah oscillation of ah um number of ah ah couple simple harmonic oscillator in terms of an equal number of independent simple harmonic oscillators.

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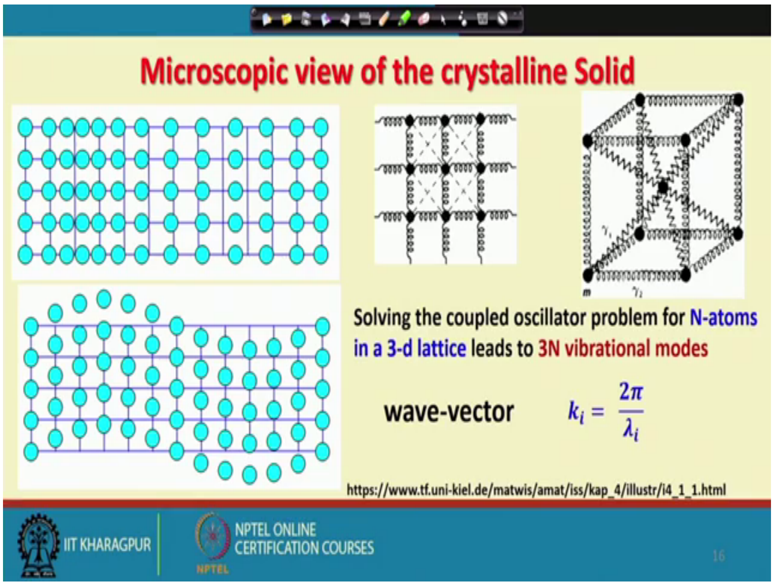

Microscopic view of the crystalline Solid

Solving the coupled oscillator problem for N-atoms in a 3-d lattice leads to 3N vibrational modes

wave-vector $k_i = \frac{2\pi}{\lambda_i}$

https://www.tf.uni-kiel.de/matwis/amat/iss/kap_4/illustr/i4_1_1.html

So, this is something that is known and I am not going to show you the solution rather tell you qualitatively that [noise] when you solve these coupled oscillation oscillator problem for N-atoms in a three-dimensional lattice we get 3N vibrational modes. So, basically what you say is each of these vibrational modes now behave as if as if they are a simple harmonic oscillator and they are associated with some kind of a wave factor and [noise] each wave factor of this 3N vibrational modes have a characteristic wavelength. And therefore, as you see that you can then say that this particular ah um solid its microscopic states can be described in terms of 3N simple harmonic oscillators which are independent of each other that is something that is achieved by the mathematical solution of the problem of coupled ah ah harmonic oscillators. And each of these ah [vocalized-noise] simple harmonic oscillators are characterized by a wave factor k i ah that is ah related inversely to the wave length of the underlying vibrational pattern like the [vocalized-noise] underlying ah ah simple harmonic oscillator representing the particular vibrational pattern.

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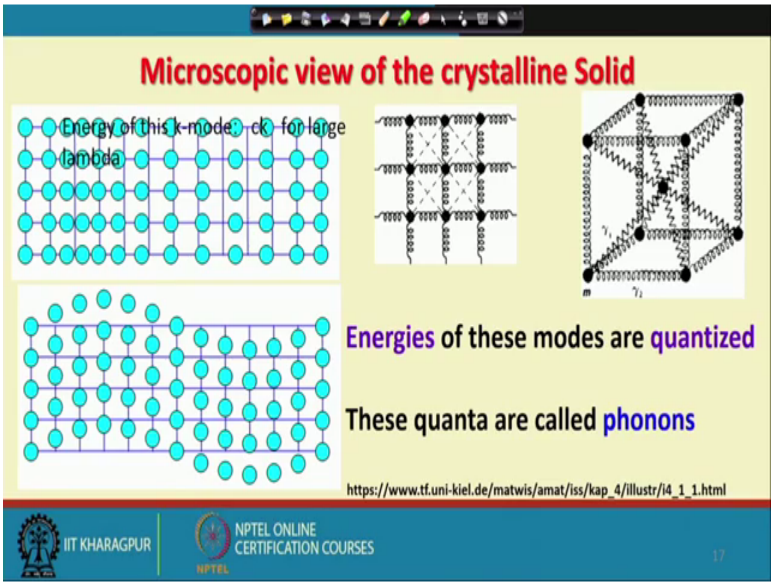

Microscopic view of the crystalline Solid

Energy of this k-mode: ck for large lambda

Energies of these modes are **quantized**

These quanta are called **phonons**

https://www.tf.uni-kiel.de/matwis/amat/iss/kap_4/illustr/i4_1_1.html

Now, here energies of these collective modes, collective vibrational modes according to quantum mechanics at the microscopic level these are quantized. So, these quantized ah energies of the vibrational modes are called phonons. So, the different microscopic states of the crystalline solids are described in the [vocalized-noise] terms of these phonons and we understand that there is a large number of phonons present that describe the accessible microscopic states of the crystalline solids.

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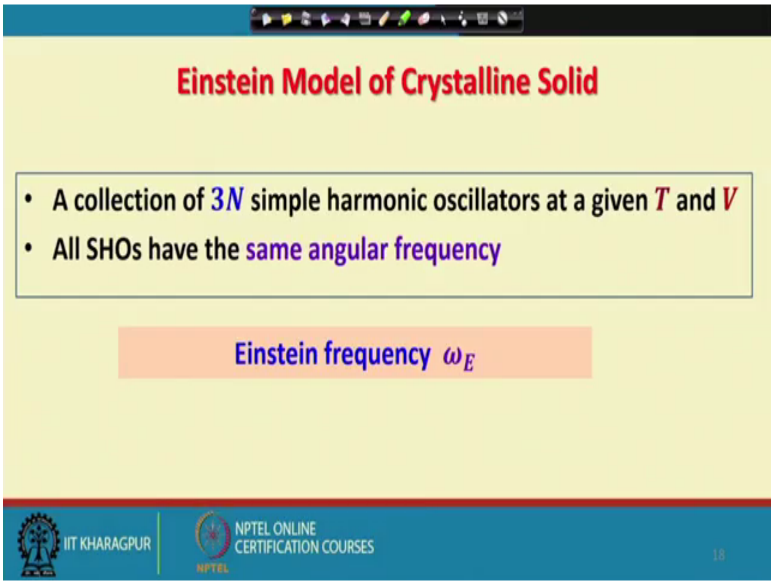

Einstein Model of Crystalline Solid

- A collection of $3N$ simple harmonic oscillators at a given T and V
- All SHOs have the same angular frequency

Einstein frequency ω_E

So, at this stage, we can revisit the Einstein model of ah solids and say that well here I am going to describe the ah vibrational ah motion of atoms in terms of a collection of 3N simple harmonic oscillators at a given temperature and volume. And let us also assume that all these simple harmonic oscillators have the same angular frequency. And this frequency is given this name Einstein frequency.

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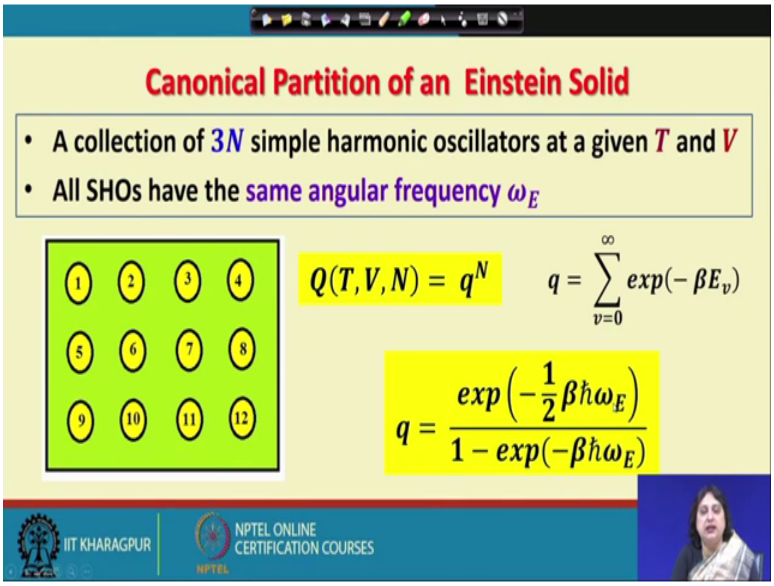

Canonical Partition of an Einstein Solid

- A collection of $3N$ simple harmonic oscillators at a given T and V
- All SHOs have the same angular frequency ω_E

$$Q(T,V,N) = q^N$$

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

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

If that happens then from the prescription of ah ah molecular thermodynamics, we can very easily say that for these collections of 3N simple harmonic oscillators, I can always write down what the single particle canonical [vocalized-noise] partition function is. And I understand here instead of any intrinsic frequency, I am using the same frequency omega E for each of the oscillators present in the system.

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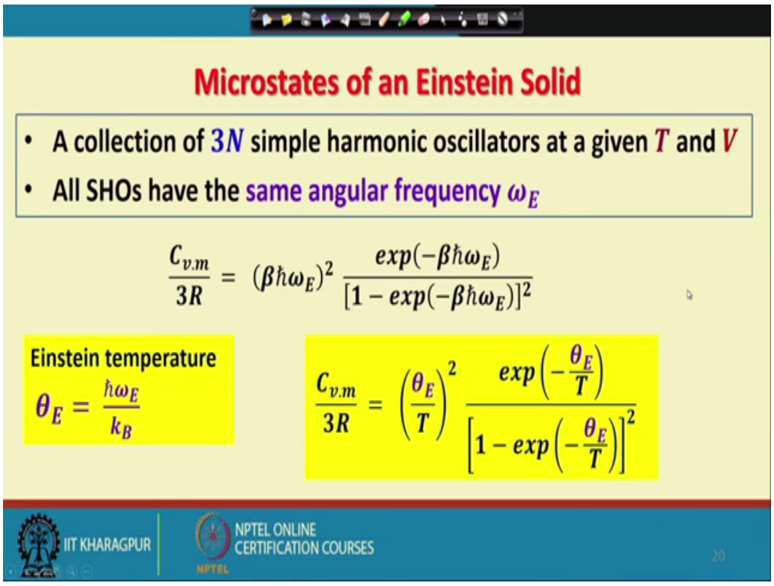

Microstates of an Einstein Solid

- A collection of $3N$ simple harmonic oscillators at a given T and V
- All SHOs have the same angular frequency ω_E

$$\frac{C_{v,m}}{3R} = (\beta\hbar\omega_E)^2 \frac{exp(-\beta\hbar\omega_E)}{[1-exp(-\beta\hbar\omega_E)]^2}$$

Einstein temperature

$$\theta_E = \frac{\hbar\omega_E}{k_B}$$

$$\frac{C_{v,m}}{3R} = \left(\frac{\theta_E}{T}\right)^2 \frac{exp\left(-\frac{\theta_E}{T}\right)}{\left[1-exp\left(-\frac{\theta_E}{T}\right)\right]^2}$$

Now, in this way, once I know small q following the prescription of molecular thermodynamics I can very easily go and derive this algebraic expression for C v. Actually, it is more customary to introduce the Einstein temperature which is nothing but the Einstein frequency multiplied by h cross divided by the Boltzmann constant and in terms of Einstein temperature then the specific heat turns out to be an expression like this.

So, as you see that by having the microscopic model of the solid in terms of the ah different ah vibrational collective vibrational motions, we have been able to express the specific heat as a function of temperature because temperature appears over here. And the characteristic properties of the system in terms of its [vocalized-noise] microscopic parameters appeared here in terms of this Einstein temperature. So, for given values if you can measure the values of Einstein temperature then you should be able to ah find out how C v varies with respect to temperature that is exactly what one does next.

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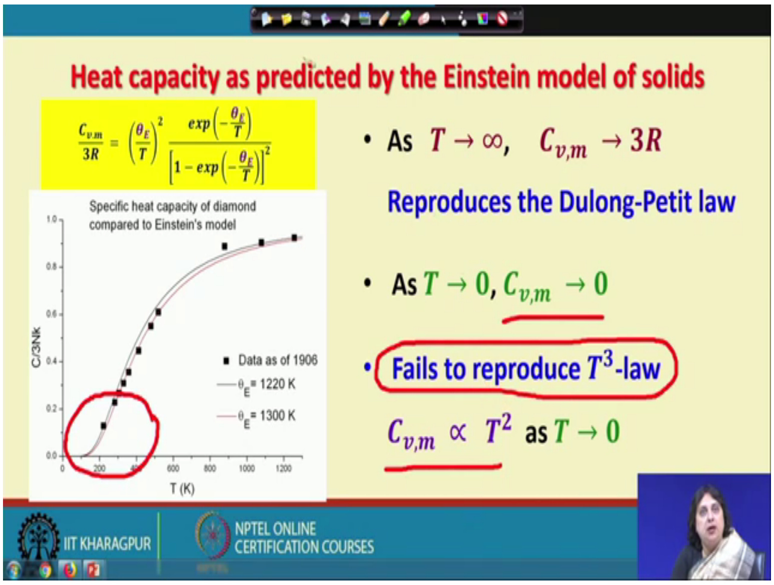

Heat capacity as predicted by the Einstein model of solids

$$\frac{C_{v,m}}{3R} = \left(\frac{\theta_E}{T}\right)^2 \frac{exp\left(-\frac{\theta_E}{T}\right)}{\left[1 - exp\left(-\frac{\theta_E}{T}\right)\right]^2}$$

- As $T \to \infty$, $C_{v,m} \to 3R$

  Reproduces the Dulong-Petit law

- As $T \to 0$, $C_{v,m} \to 0$
- Fails to reproduce T^3-law

  $C_{v,m} \propto T^2$ as $T \to 0$

So, [vocalized-noise] what [vocalized-noise] I have shown here in this picture is what will be the calculated value of C v at a different temperatures and the solid lines are giving you the variations of C v calculated first at theta E equal 1220 Kelvin and then theta E at 1300 Kelvin. And this square boxes are the initial measurement of the ah specific heat values of the solid which is diamond. So, now, one has this unique opportunity to look at the ah the fact that there is clearly a discrepancy between the theoretical prediction and the observed variations in the ah ah in the specific ah value values at very low temperature.

So, the question is how good is the Einstein model? In order to understand this as I said the experimental data is interpreted I ah by looking at limiting ah ah limiting behavior at high temperature, low temperature, and what happens in between. So, at very high temperature, if you look at the expression for ah C v as predicted by the Einstein model, you will find that this quantity actually would go to 1. Whatever appears here in the on the right hand side, this will go to 1 ok, because I have 1 by T here, so as T goes to infinity these goes to 1. And if I expand them what I have on the right hand side is one minus E to the power of minus theta E by T and this I can write as 1 minus 1 plus theta E by T.

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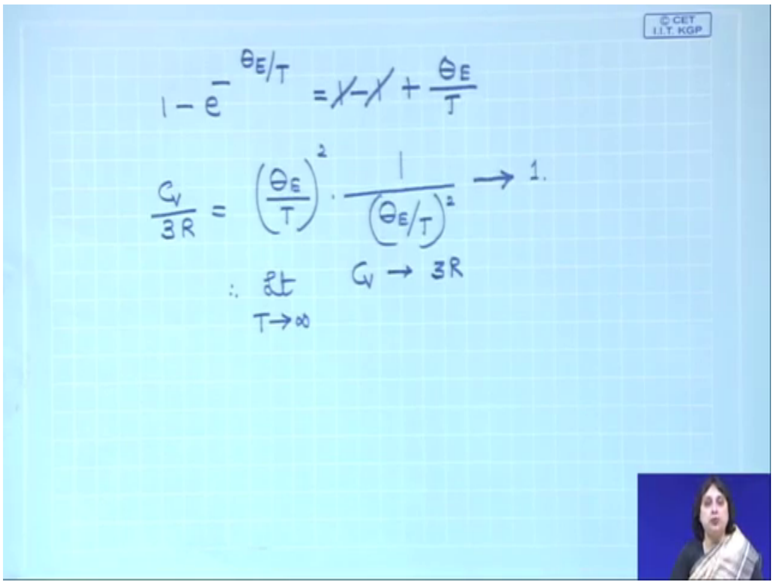

$$1 - e^{-\theta_E/T} = \cancel{1} - \cancel{1} + \frac{\theta_E}{T}$$

$$\frac{C_V}{3R} = \left(\frac{\theta_E}{T}\right)^2 \cdot \frac{1}{\left(\theta_E/T\right)^2} \to 1.$$

$$\therefore \lim_{T\to\infty} \quad C_V \to 3R$$

So, in the expression for C v by 3 R, now I have theta E by T whole square into 1 divided by theta E by T whole square. And therefore, in the limit where T is very high this term goes to 1 which means in the limit T tending to infinity I must be having C v tending to 3 R now that is a successful reproduction of the Dulong-Petit law. Now, let us have a look at what happens when T goes to 0. When T goes to 0, I have the entire expression if you use the L-Hospital's law, you will be able to show it very easily that C v will also go to 0.

Now, here comes the most important observation that tells us that not everything is well with Einstein model of solids. So, what I find is here if I plot the low temperature behavior of the of C v in the measured data, I find that it eh it follows the T cube law. But if I once again look at the behavior of C v as a function of temperature for small values of T, I find that it will go as T square ok. So, this means that in this particular case I do have this problem that Einstein model although it could produce the high temperature behavior of the solid successfully, it was not able to explain the entire range of behavior of the solids, the specific heat of solids, and it failed especially in the low temperature region. So, in the next lecture we are going to examine the short comings associated with the assumptions present in the Einstein model, and then review the corrections and the improvements suggested by Debye and its subsequent study of the specific heat of solids.

Thank you.