Condensed Matter Physics
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Lecture - 12
The Concept of Phonons

So, until now we are being considering condense matter in particular crystalline solids has some kind of an assembling which is completely addressed, but we all know that the atoms and molecules even in a crystalline solid are not completely addressed at a any finite temperature at any finite temperature about absolute zero these atoms and molecules are in a state of thermal vibration about an equilibrium position in the crystalline solid. So, these thermal vibrations are usually treated as be in simple harmonic in other words the an harmonic neglected start with, and we considered this solid. Now from now on as on assembly of atoms and molecules, which are in a state of simple harmonic vibrations due to the thermal energy of this atoms and molecules there not to free to move around. And like the electron gas the electron in the electron gas, but they are fixed to regular lattice sites and they have an a equilibrium configuration and then they are free to vibrate execute simple harmonic vibrations are small amplitude about this equilibrium positions.

So, this is the concept of harmonics solid and this concept gives rise to the propagation of elastic are acoustic waves which are long-range inside the crystalline solid, this also through are liquids only in the difference is that there is long-range ordering in a crystalline solid while there is only short-range order in a liquid. So, these acoustic are electric waves propagate inside the crystalline in solid and as we already saw the atoms and molecules are not classical parts they are quantum particles. So, the concept regarding this vibrations regarding the propagation these elastic waves has to be in accordance with quantum laws.

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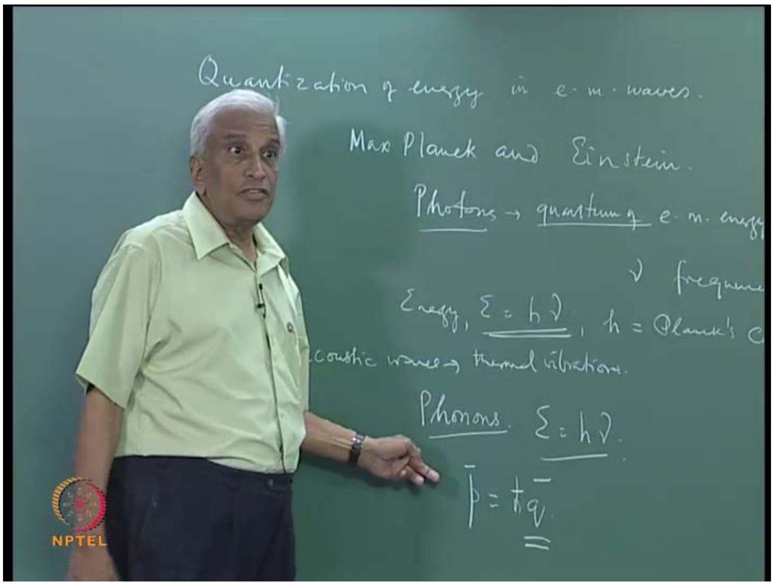

And we have already seen in the case of electromagnetic waves the quantum prescription the quantum nature of this system gives rise to what is called the quantization the concept of quantization of energy in electromagnetic waves. This was an idea which was originated by max planed and later put an firm bases by Einstein among others at the turn of the twenty th century, and this gale rise to the concept of four terms as the elementary excitation and this is a quantum of electromagnetic energy.

So, in the electromagnetic wave has a frequency nu the energy content of this energy quantum is given by the Einstein planks Einstein relationship energy e equals h nu, where h is planks constant. So, this idea is at the basis of all theoretical description of the propagation of electromagnetic base in quantum mechanical systems. So, the concept to the photon is a very well's establishment one now in the consider elastic or acoustic waves in a gain a quantum system. We are led by analogy with the photon we are led to the concept to the quantization energy in a elastic or acoustic waves, which arrives from thermal vibrations the quantize the excitation of these elastic or acoustic waves are known as phonons in analogy with the concept of photon's. So, the concept of phonons as quantize the excitation of the acoustic energy of waves in a long-range order crystalline solid is central to the idea of the description of a solid in thermal vibration a solid at any finite temperature.

So, from now on we will no longer regard this solid as an inner completely a system which is completely addressed we will start regarding this as a dynamical system which is in a state of vibration due to the thermal energy. And this state of vibration gives rise to propagation of questing waves are elastic wave who's quantize excitation are again given by e equal to h nu where u is the frequency as the acoustic wave. Now, just as the photon as on electromagnetic momentum associated this here also we have the momentum here.

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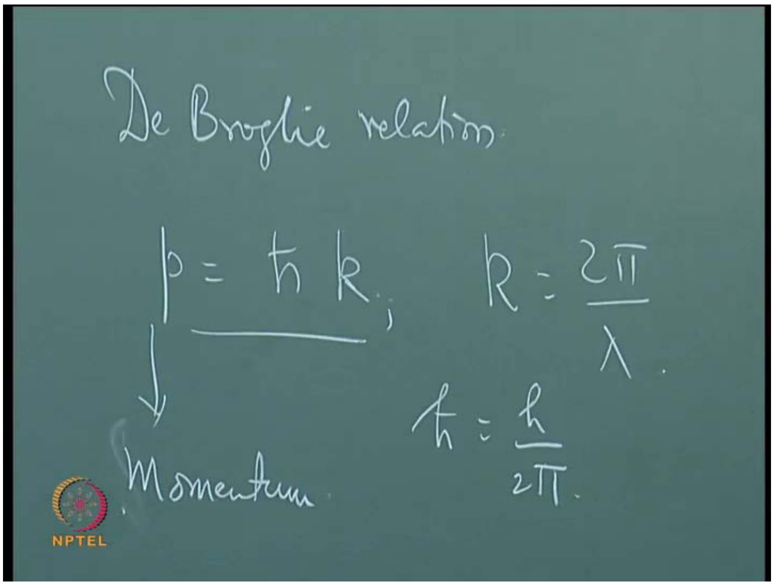

De Broglie relation.

$$p = \hbar k \,; \quad k = \frac{2\pi}{\lambda}.$$

$\downarrow$

Momentum.

$$\hbar = \frac{h}{2\pi}.$$

The momentum is given by the bedraggle relationship p equal to h cross k were k is the wave vector two pi by lambda h cross is h by two pi this is the momentum. So, the photon as not only an energy content, but also a moment term associated with these wave vector which intern defined by the wave line. So, there is an momentum wave number relationship, which is the really the bedraggle relationship in the same way. We also define the momentum here of phonons of h cross q in order to distinguish electromagnetic waves associated with propagation electrons are charged particles in order to distinguish the concept of elastic waves, which are associated with thermal are elastic vibration simple harmonic vibration of a of the atoms and molecules.

We use the wave number are inductor notation t equal to h cross q we use q as the wave vector when the refer to the phonons. So, when the use the lump symbol q we automatically know that we are talking about the phonon system and when you replied the wave vector k it is understood that we are dealing with the electrons are other charge particles which give rise to the propagation of electromagnetic base. So, now, we have the crystal the crystalline solid as from now on to be considered an assembly in which there are electrons in the form of electron gas. And then there are the associated ion are atom and molecule at the fixed lattices, which are again charge the ions are charged once the electron for... So, these are all charged excitation charge particles who's oscillation to vibrate gives rise to the propagation of photons which are quantize excitation of the associated electromagnetic field. And we also have thermal vibration are this atoms which are which give rise to simple mechanical or acoustic waves and this give rise to phonons. So, we have an equilibrium between the phonon at the electrons for example, so we we already talked in connection with resistivity are the electrical conductivity problem and other transport processes.

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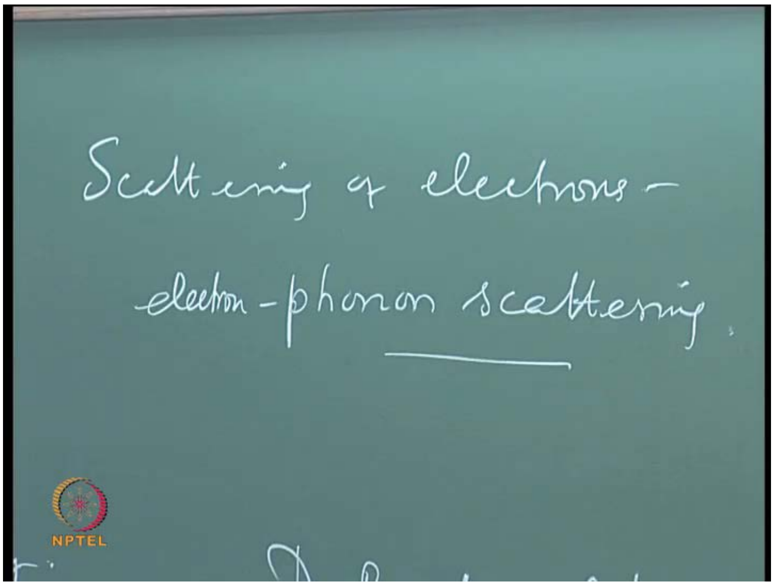

Scattering of electrons –

electron-phonon scattering.

We talked about the scattering of electrons among various scattering mechanism one other important mechanism is the electron phonon scattering. So, this is what give rise to the temperature dependent of the electrical resistivity of a metal. So, we will the origin of this temperature dependences in the electron phonons scattering processes. So, the concept to the phonon is of central important to our further description of the properties of condense matter.

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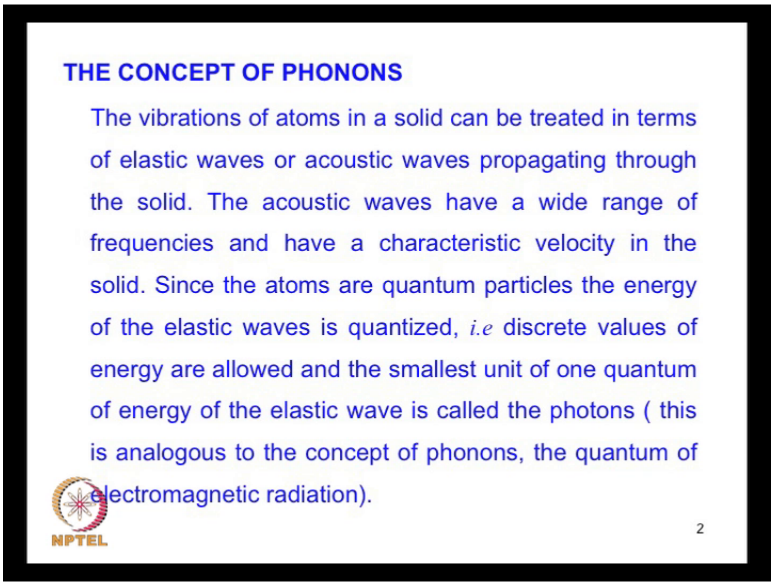

THE CONCEPT OF PHONONS

The vibrations of atoms in a solid can be treated in terms of elastic waves or acoustic waves propagating through the solid. The acoustic waves have a wide range of frequencies and have a characteristic velocity in the solid. Since the atoms are quantum particles the energy of the elastic waves is quantized, *i.e* discrete values of energy are allowed and the smallest unit of one quantum of energy of the elastic wave is called the photons (this is analogous to the concept of phonons, the quantum of electromagnetic radiation).

So, these phonon have discrete energy corresponding to different values of nu you have a discrete energy contents in the phonon. They gives the smallest quantum of energy, which is known as the phonon, which is analogous to the concept of the photon a solid is therefore, a system of a large number of phonons with a wide range of frequencies somewhat analogous to a black body which emits and absorb the large number of photons at all frequencies. So, at a given temperature this solid well have a certain equilibrium distribution of phonons of various energies, and as a temperature is change this distribution changes.

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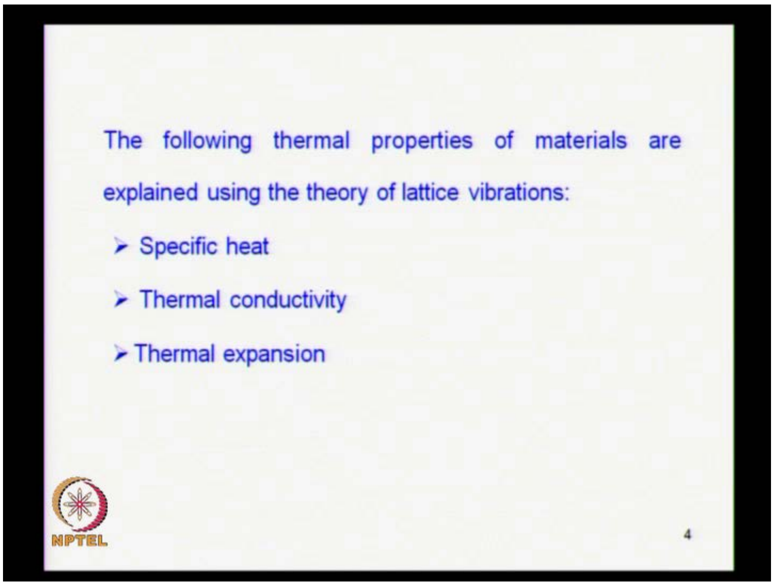

The following thermal properties of materials are explained using the theory of lattice vibrations:

- Specific heat
- Thermal conductivity
- Thermal expansion

So, this is the concept of phonons based on which we will be able to discuss thermal properties of materials.

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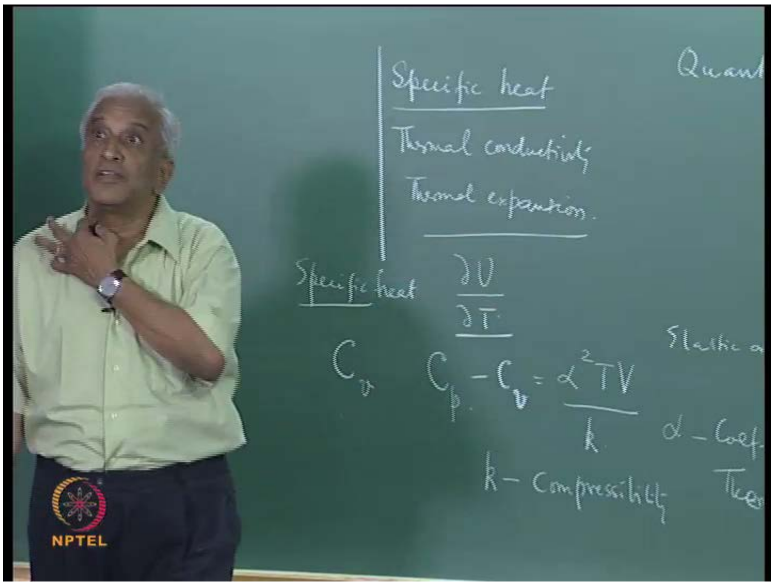

What happens? What are the terminal properties these are properties such as this specific heat thermal conductivity and thermal expansion we already considered specific heat and thermal conductivity of the electron gas. Now we are talking about this solid as a whole. So, the theory of lattice vibration vibration, such as lattice of atoms this theory of lattice vibration which gives rise to the concept the idea of phonons.

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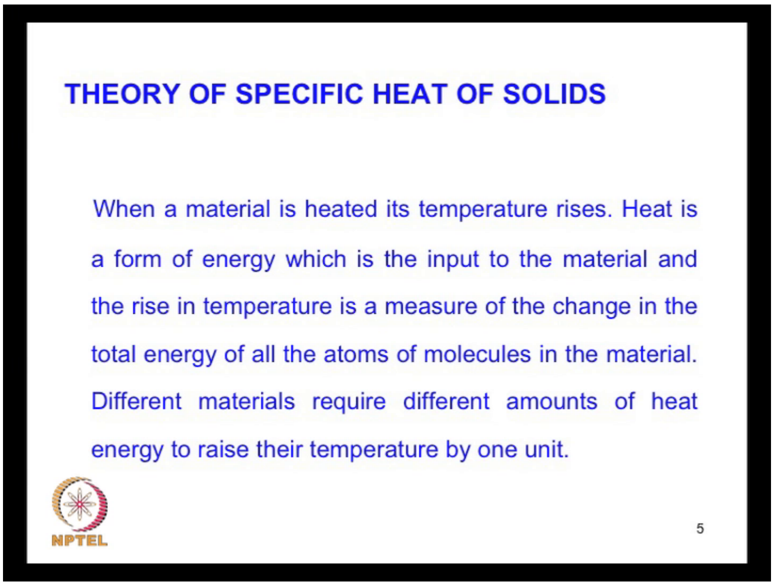

THEORY OF SPECIFIC HEAT OF SOLIDS

When a material is heated its temperature rises. Heat is a form of energy which is the input to the material and the rise in temperature is a measure of the change in the total energy of all the atoms of molecules in the material. Different materials require different amounts of heat energy to raise their temperature by one unit.

This is going to be the basis on the, which we will discuss this thermal properties such as this that will be the aim of this lecture we will start this discussion. So, again we will talk about the specific heat of a solid we all know about the concept of specific heat in a solid an a material is heated its temperature ices heat is a quantity of a energy which is given to the material and they raise and temperature is the response it is a measure of the change in the internal energy total internal energy of all the atom and molecule in this material. So, different materials depending on their various physical property required different amongst of heat energy to raise their temperature by say one degree kelvin.

So, this specific heat is defined as the derivative with respect to temperature of the internal energy. So, it defines the among of the thermal energy in joules, which is required to raise the temperature of one kilogram of the material through one degree celsius of a or one degree kelvin. So, the unity joule per kilogram per degree kelvin sometimes we also use the more are specifically instead of a kilogram, so in this case unities joule thermal per degree Kelvin.

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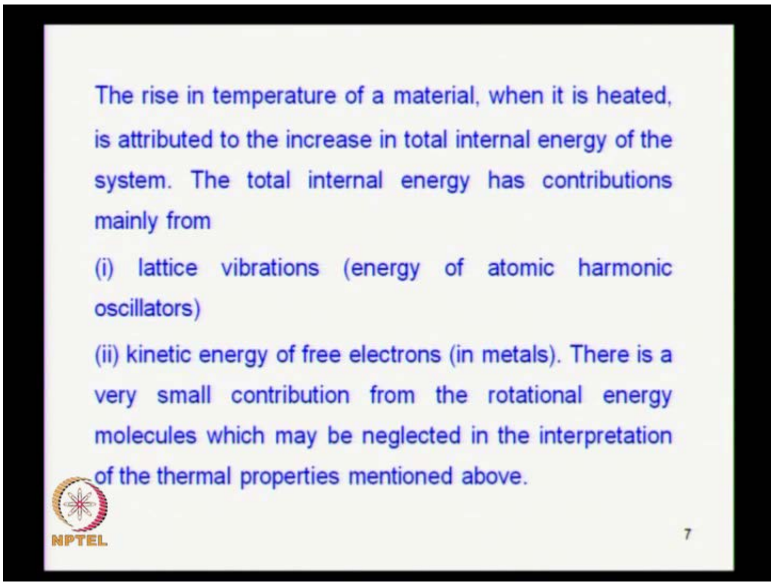

The rise in temperature of a material, when it is heated, is attributed to the increase in total internal energy of the system. The total internal energy has contributions mainly from

(i) lattice vibrations (energy of atomic harmonic oscillators)

(ii) kinetic energy of free electrons (in metals). There is a very small contribution from the rotational energy molecules which may be neglected in the interpretation of the thermal properties mentioned above.

So, rise in temperature is due to the increasing the internal energy and the total internal energy as different kinds of contribution one, and the main contribution is that arising from the vibration are the crystal lattice. These are the atomic harmonic oscillator their energy in addition, if you have for example, an electron which is in the form of a gas bound inside of metal. Then you have also the kinetic energy of these three electrons, you usually a relatively a small contribution compared to that from the lattice liberation. Then we have also a much smaller contribution in the rotational energy of molecules, this may be neglected in the interpretational these thermal problems for we will confine or attention to the contribution arising from the lattice vibration, we have already considered what happens when the electron gas is fitted.

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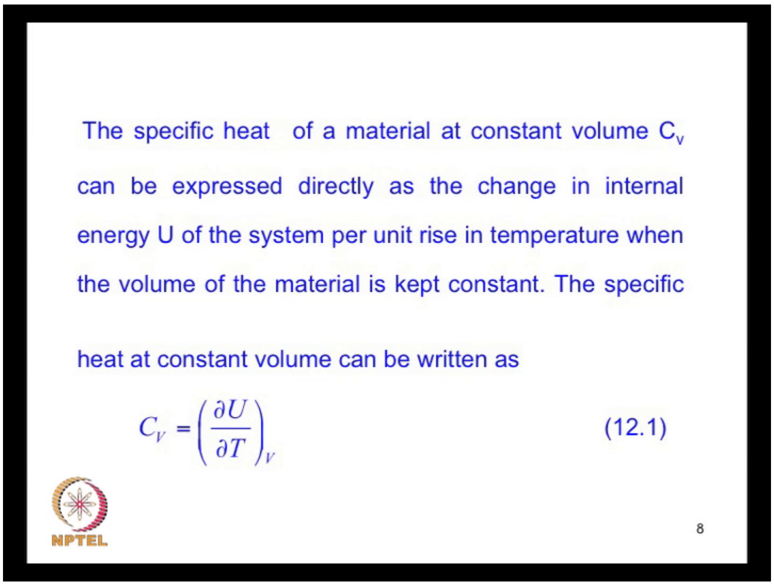

The specific heat of a material at constant volume C_V can be expressed directly as the change in internal energy U of the system per unit rise in temperature when the volume of the material is kept constant. The specific heat at constant volume can be written as

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad (12.1)$$

So, we will considered together d i. So, we will finally, now for in this stock we will confine our attention to the contribution to the specific heat arising in the vibration in the crystal lattice. Now in general we know from for gases, it is important to the distinguish between this specific heat at constant volume c v, and the specific eight at constant pressure because this to are very different quantities. In the case of a gas because whether it is the process that the heat change the input of heat is given a constant to keep this system volume constant or to keep this the system pressure constant are two different kinds of thermodynamic situation which gave rise to different amount of specific heat contributions. So, we have to use that the theoretical description usually gives you this specific heat at constant volume.

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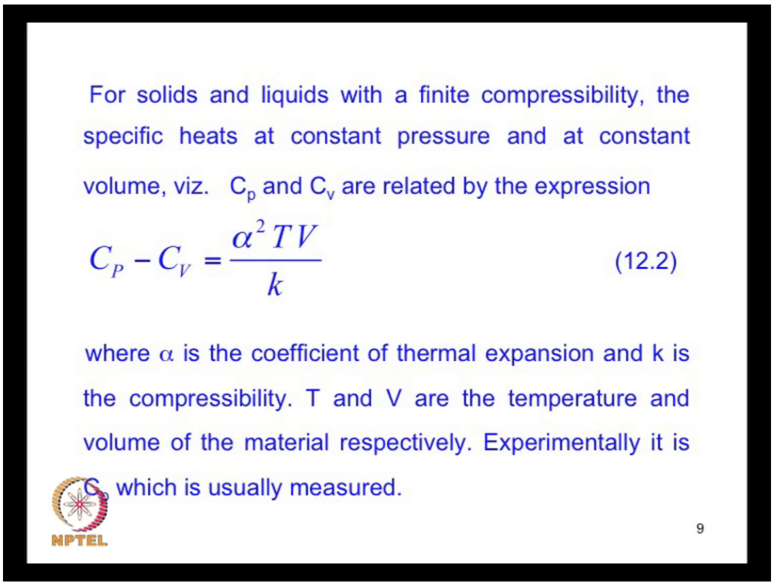

For solids and liquids with a finite compressibility, the specific heats at constant pressure and at constant volume, viz. C_p and C_v are related by the expression

$$C_P - C_V = \frac{\alpha^2 TV}{k} \qquad (12.2)$$

where α is the coefficient of thermal expansion and k is the compressibility. T and V are the temperature and volume of the material respectively. Experimentally it is C_p which is usually measured.

While this c p and c v differ considerably from each other in the case of a gas for solids and liquids which are not which have a finite compressibility they are relatively incompressible gases are very compressible, but solid and liquid have a finite compressibility. In this case we have relation between c p and c v given by alpha square t v by k. Now here alpha is a coefficient of thermal expansion k is the compressibility k compressibility alpha coefficient of thermal expansion p involve v r the temperature and volume with material respectively. So, once you know c p or c v, and if you know the compressibility and thermal expansion coefficient at a given temperature at volume you can easily calculate the other specific heat. So, c v is the one which is usually calculated theoretically.

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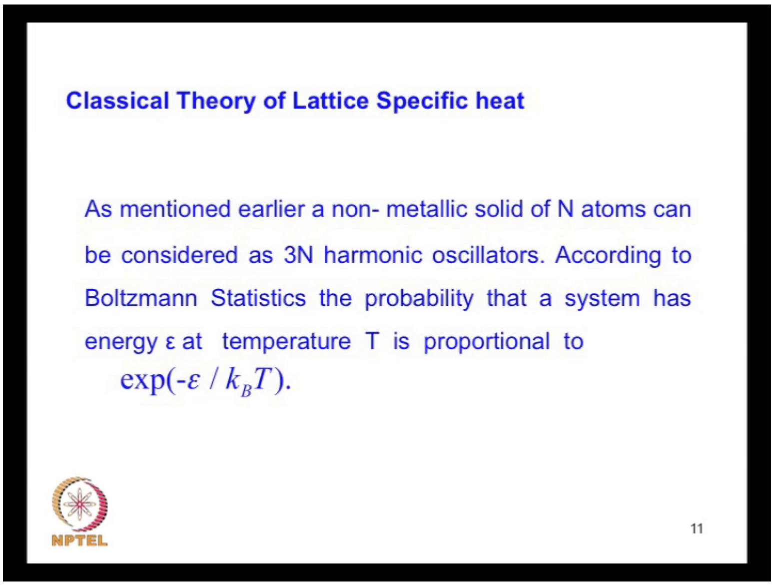

Classical Theory of Lattice Specific heat

As mentioned earlier a non- metallic solid of N atoms can be considered as 3N harmonic oscillators. According to Boltzmann Statistics the probability that a system has energy ε at temperature T is proportional to $\exp(-\varepsilon / k_B T)$.

In general the total contribution to you comes from the vibrations of the crystal lattice. So, let us consider this lattice vibration, and see how that results in a contribution to the specific heat the theories the concept of specific heat is a very old concept. So, there is a classical theory long before the advent of quantum theory people try to understand and how the specific heat can be calculated. If you consider a non metallic solid, we will add the electron gas contribution in the case of metallic solid later.

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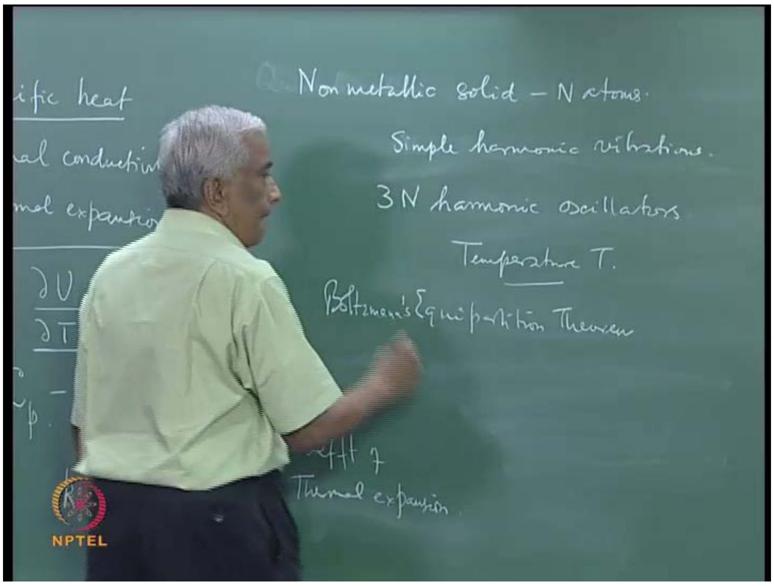

Non metallic solid – N atoms.

Simple harmonic vibrations.

3N harmonic oscillators

Temperature T.

Boltzmann's Equipartition Theorem

So, let us start with an nonmetallic solid containing n atoms. So, that is an assembly of n atoms and each of this atoms is in a state of thermal vibration which may be considered as simple harmonic vibrations which takes place in all the three degrees of freedom in all the three-dimensions x y and z in general. So, if there are three degrees of freedom associated with this vibrations for each atom. Then there are three n harmonic oscillators and what is the internal energy one harmonic oscillators, which is at a temperature t. Now has we all know the harmonic oscillators has a kinetic energy under potential energy. And each of this according to the equiv partition theorem due to blot man’s, which can be readily derived from the concept of Maxwell Boltzmann statistic the average internal energy contribution of associated with per degree of freedom is half k b t where k b is the Boltzmann concept.

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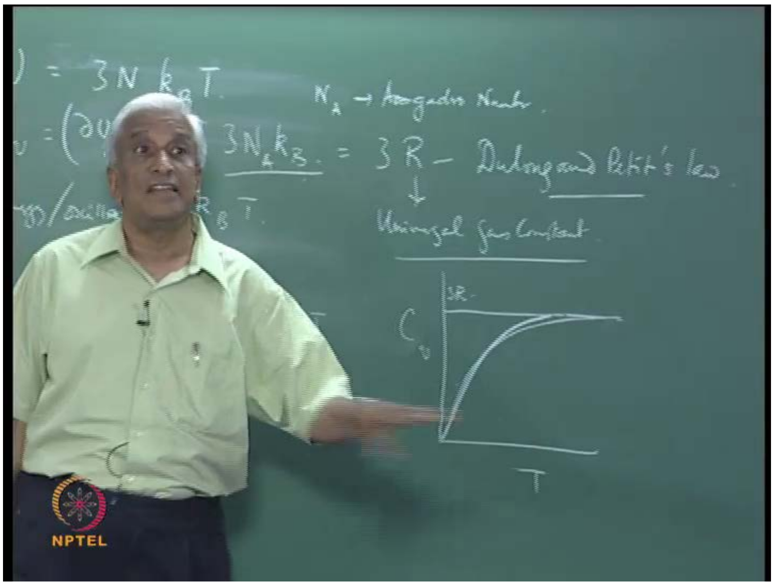

So, per degree of freedom. So, if if an oscillator we have kinetic and the potential energy. So, the total energy per oscillator average energy per oscillator is just k b t half k b t associated with the potential energy. And half k b t associated with the kinetic energy therefore, the total internal energy u of such a assembly of three and harmonic oscillator is just three n times k B t. Therefore, the specific k’th c v is just the u by d t at constant velue, which is three n k b, if it is the mauler specific, it we are considering we know that the number is the arrogant roll number. And therefore, these three n a k b is nothing, but three r where r is the gas constant universal gas constant. So, this is a constant in the specific heat according to classical theory of a crystal and solid is just three hour whether it is iron or whether it is a piece of stone.

If we neglect this regard the behavior dude the contribution due to the metallic behavior the presence of the free electrons. If you consider only the lattice vibration constant have a contribution then it is three hour the specific heat of a solid is independent as the temperatures. And the mauler specific heat of all materials is the same one more of any substance use you a contribution to the specific heat which is three hour this is lone this was known as the due long and petit is law due long, and petit proposed that the contribution from lattice vibrations to the internal energy.

And hence the mauler specific heat of a crest spine solid of any solid is just a constant three hour well this is not what we observe experimentally experimentally the mauler specific heat at for example, room temperature is different for different materials. If you look at the collapse stable for example, or any handbook of physics and chemistry, you will find the specific heat listed for different solid. And these are different for the different material and this specific heat of a given material is not independent of temperature as proposed by the videoing and interpreting law, but it increases with increasing temperature.

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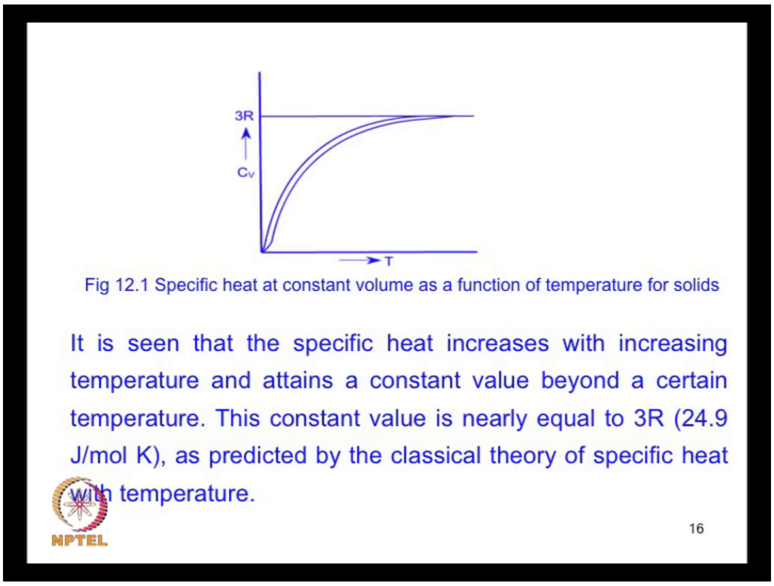

Fig 12.1 Specific heat at constant volume as a function of temperature for solids

It is seen that the specific heat increases with increasing temperature and attains a constant value beyond a certain temperature. This constant value is nearly equal to 3R (24.9 J/mol K), as predicted by the classical theory of specific heat with temperature.

And this behavior is shown in this figure; however, you will see also that this specific heat rises in general and goes and reaches any equilibrium and a constant value eventually at high-temperature at sufficiently high temperature and this value is three r different material will rise differently and they will do this at different temperature ranges.

So, these are different materials and you may have this specific heat values different and all these ranger and eventually I have temperature is reach and sufficiently high temperature they all attain this constant value. So, there is some substance in the classical theory, but it does not account for the temperature dependence, which is observed it only the classical theory only predicts the constants final value at a high-temperature value of this specific heat of materials.

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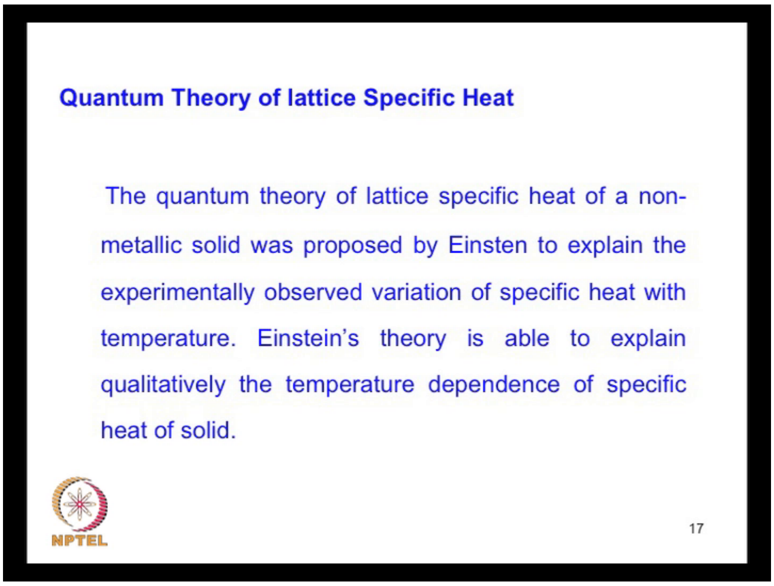

Quantum Theory of lattice Specific Heat

The quantum theory of lattice specific heat of a non-metallic solid was proposed by Einsten to explain the experimentally observed variation of specific heat with temperature. Einstein's theory is able to explain qualitatively the temperature dependence of specific heat of solid.

So, we know the theory which not only explains this constant value of about twenty-five calories per choose per mole k. So, the bond the theory which not only accounts for this constant values, but also accounts described the explains why? There is at this temperature dependents. And we all know that the main problem with this classical theory is that it is classical we need at one term theory of specific heats.

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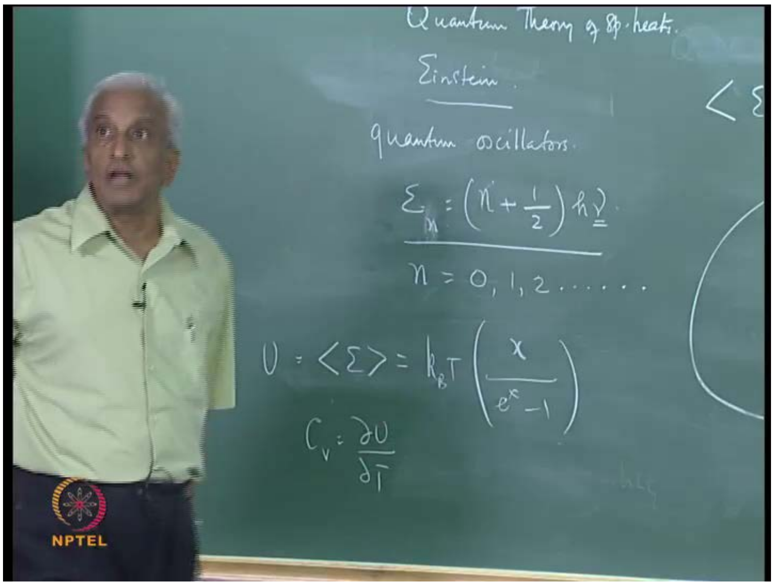

So, that is what we will discussed next and how do we go about it we again considered this harmonic oscillator solid, and this quantum theory again was first proposed by Einstein.

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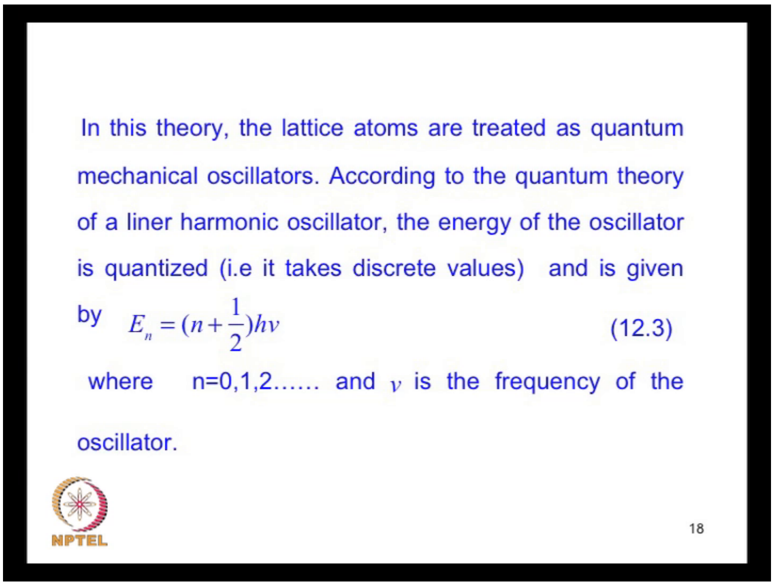
In this theory, the lattice atoms are treated as quantum mechanical oscillators. According to the quantum theory of a liner harmonic oscillator, the energy of the oscillator is quantized (i.e it takes discrete values) and is given by $E_n = (n+\frac{1}{2})h\nu$ (12.3)

where n=0,1,2...... and ν is the frequency of the oscillator.

The Einstein’s theory consists of the lattice atom as quanta mechanical oscillators. So, there are still simple harmonic oscillators, but they are not classical oscillator, but quantum simple or quantum oscillators. Now what is the difference between the classical theory of a linear harmonic oscillator, and the quantum theory of the linear harmonic oscillator I will not describe this I will not going to the detailed at this, but I will just assume this results from quantum mechanics. That the energy of such a quantum oscillator is given by the energy associated with the oscillator oscillating at a frequency nu is given by n plus half h nu where n is an integer 0, 1, 2, etcetera. So, a quantum harmonic oscillator of frequency nu can exist in various energy states e n various quantum states corresponding to n equal to zero n equal to one and n equal to two and so on and n can go up to infinity.

So, there are several quantum states if any zero the energy is just half h nu and that is what is known as the ground state of the harmonic oscillator even in the ground state the harmonic oscillator in a quantum harmonic oscillator I has what is known as a zero point energy which is just half h nu. And then there are excited states associated with n equal to one for example, which as three by two h nu when n is two it is five by two h nu and so on. So, you have a whole spectrum of energy Eigen values for the quantum harmonic oscillator.

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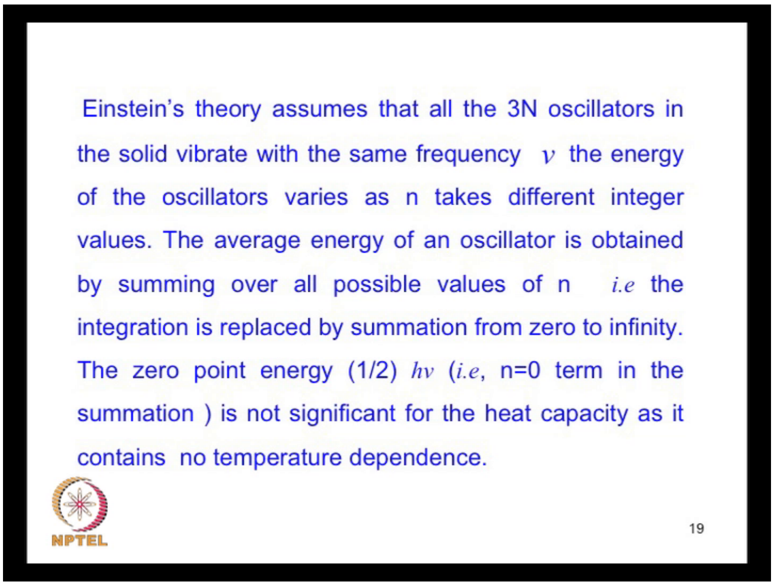

Einstein's theory assumes that all the 3N oscillators in the solid vibrate with the same frequency ν the energy of the oscillators varies as n takes different integer values. The average energy of an oscillator is obtained by summing over all possible values of n $i.e$ the integration is replaced by summation from zero to infinity. The zero point energy (1/2) $h\nu$ ($i.e$, n=0 term in the summation) is not significant for the heat capacity as it contains no temperature dependence.

So, this is the kind of statistical behavior of these three n harmonic oscillators quantum harmonic oscillators has to taking to account this set of a energy Eigen values of the quantum harmonic oscillator. So, again Einstein assumed that this frequency all the three in atoms in a solid vibrate with it with one frequency well again we know that this is not quite realistic. It is quite possible that different oscillator depending different atoms groups of atoms are molecules will vibrate at slightly different frequencies which can be picked up for example, by infra spectroscopy, but to start with we will go with this assumption. We will assume that nu is the same for all the three n atoms where n is of the order of the arrogate number it is ten to go 24. So, it is an astronomically large number of oscillators all vibrating in Unisom with one frequency that is the model of the Einstein solid which is not quite pleasurable, but we will just trap with it as an approximation. So, we have we have to calculate the average energy using this spectrum of energy Eigen values for this assembly of oscillators.

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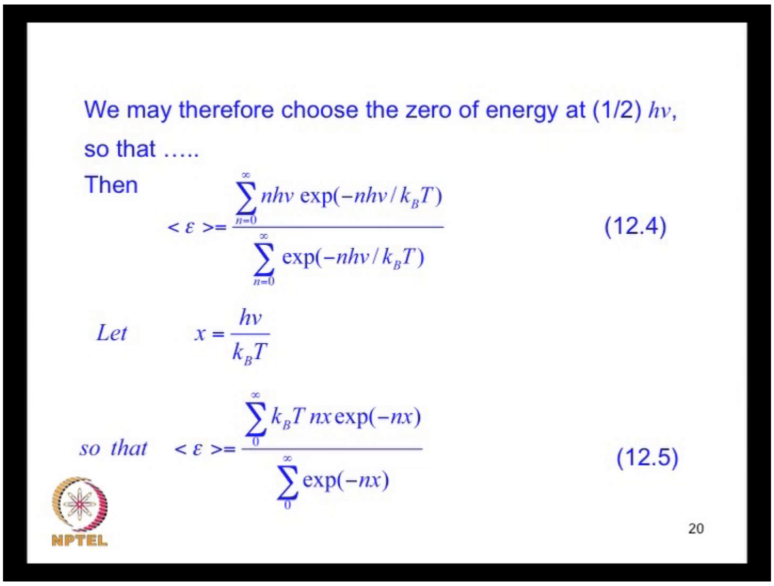

We may therefore choose the zero of energy at (1/2) $h\nu$, so that …..

Then

$$<\varepsilon>=\frac{\sum_{n=0}^{\infty} nh\nu \exp(-nh\nu/k_BT)}{\sum_{n=0}^{\infty}\exp(-nh\nu/k_BT)} \qquad (12.4)$$

Let $x=\dfrac{h\nu}{k_BT}$

so that

$$<\varepsilon>=\frac{\sum_{0}^{\infty} k_BT\, nx \exp(-nx)}{\sum_{0}^{\infty}\exp(-nx)} \qquad (12.5)$$

So, let us calculate this average energy therefore, we will find with the average energy is calculated usually only thing it is unlikely the classical solid. We do not have a continual a continuous distribution of energy, but we have a disc ream distribution we have a system, which can exist in a spectrum in a set of energy state which are all discrete corresponding to n equal to zero n equal to one n equal to 2, etcetera. So, we have two sum over all these energy state.

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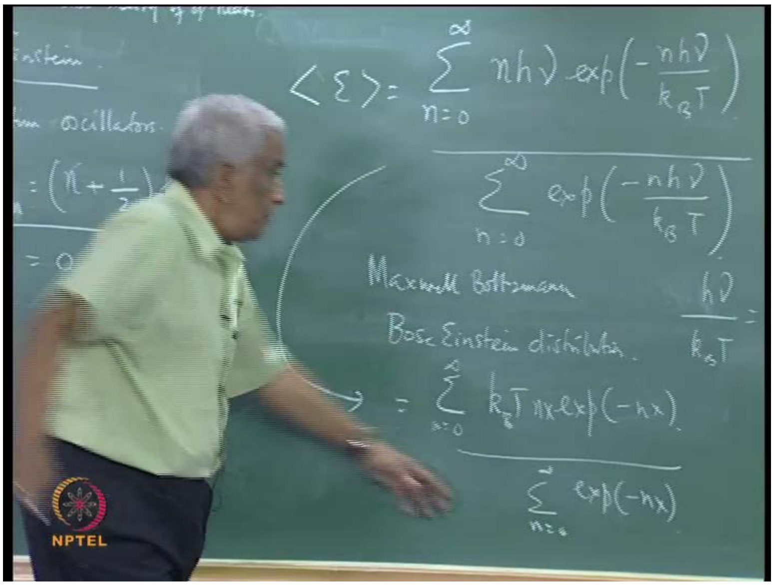

And the calculate the average energy as a summation over all the possible values of n time, and each of this as on energy content n h mu neglecting this zero point energy. Of course, and this will again have a Boltzman distribution by well strictly this distribution also has to be modified from Maxwell Boltzmann distribution prove, what is known as a bose Einstein distribution appropriate a quantum assembly just as we considered the fermi dirac distribution for the electron gas, which is subject to principal. We have to consider the Bose Einstein distribution which has a slightly different form, but for simplicity, we will assume that it is a classical system. And use the usual Boltzman distribution function in order to calculate this in order to go further we just take n h nu by k b t as x h nu by k b t. So, taking this we can rewrite this as sigma k b t times exponential minus n x by. So, that can be evaluated and this value once you it is a geometrical progression as you have for all the values of n from zero to infinity this would form a geometrical progression.

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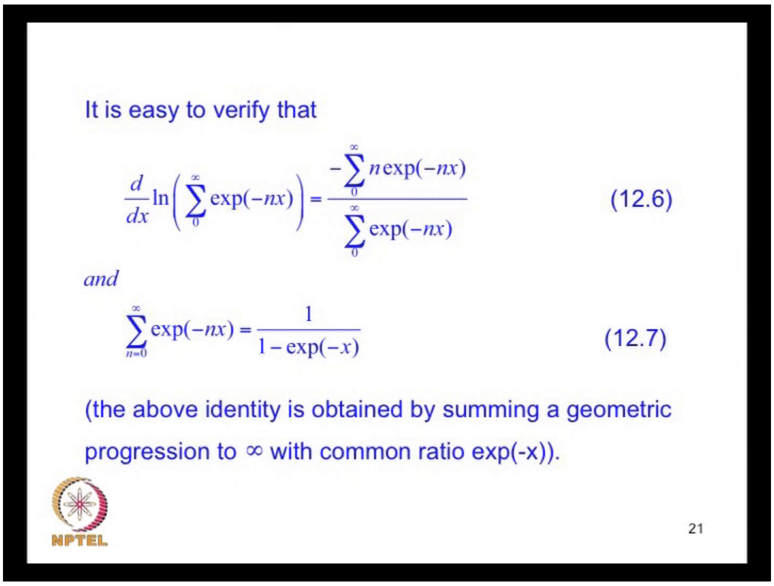

It is easy to verify that

$$\frac{d}{dx}\ln\left(\sum_0^\infty \exp(-nx)\right) = \frac{-\sum_0^\infty n\exp(-nx)}{\sum_0^\infty \exp(-nx)} \qquad (12.6)$$

and

$$\sum_{n=0}^\infty \exp(-nx) = \frac{1}{1-\exp(-x)} \qquad (12.7)$$

(the above identity is obtained by summing a geometric progression to ∞ with common ratio exp(-x)).

And when this is especially the denominator and this can be shown to be just the derivative d by d x of logarithm of the sigma exponential minus n x. And therefore, the summation over a exponential minus n x corresponds to a simple geometric progression.

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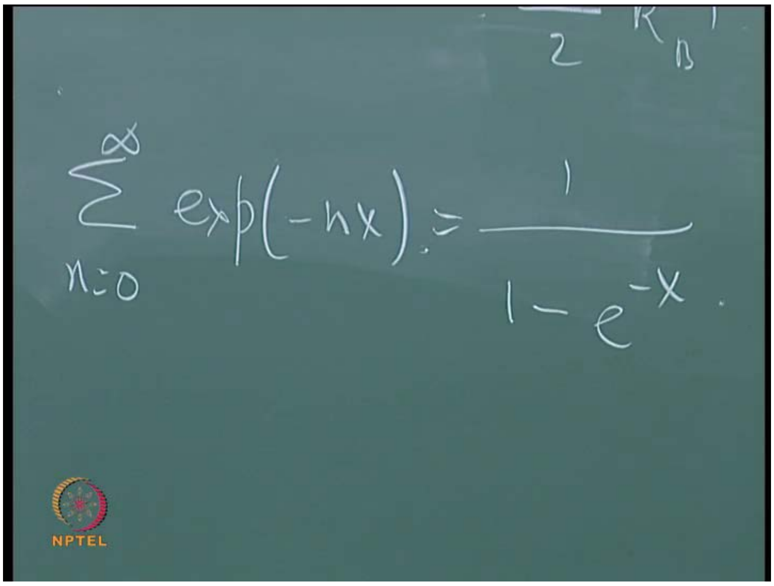

$$\sum_{n=0}^{\infty} \exp(-nx) = \frac{1}{1-e^{-x}}.$$

This is a geometric progression with all terms sum to infinity of this is one minus e to the power minus x, and this is nothing but of d by d x of log one by . So, how we can calculate this evaluate this in a close form. So, we get the final result is that this average energy turns out to be k b t times x by v power x minus one where x is of course, this.

So, this is the average energy which is the same as the internal energy. So, c v is just dot by d u by d t differentiating this quantity with respect to temperature.

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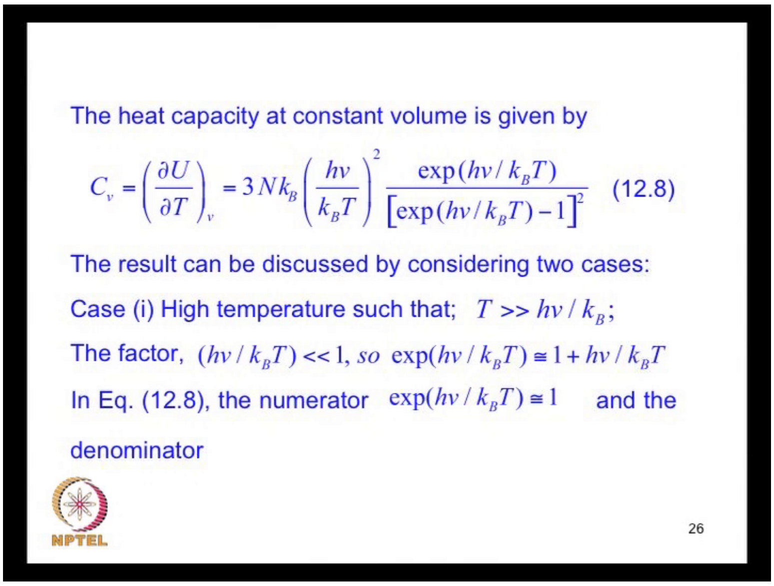

The heat capacity at constant volume is given by

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = 3Nk_B\left(\frac{h\nu}{k_BT}\right)^2 \frac{\exp(h\nu/k_BT)}{\left[\exp(h\nu/k_BT)-1\right]^2} \quad (12.8)$$

The result can be discussed by considering two cases:

Case (i) High temperature such that; $T >> h\nu / k_B$;

The factor, $(h\nu / k_BT) << 1,\ so\ \exp(h\nu/k_BT) \cong 1 + h\nu/k_BT$

In Eq. (12.8), the numerator $\exp(h\nu/k_BT) \cong 1$ and the denominator

So, if we do this.

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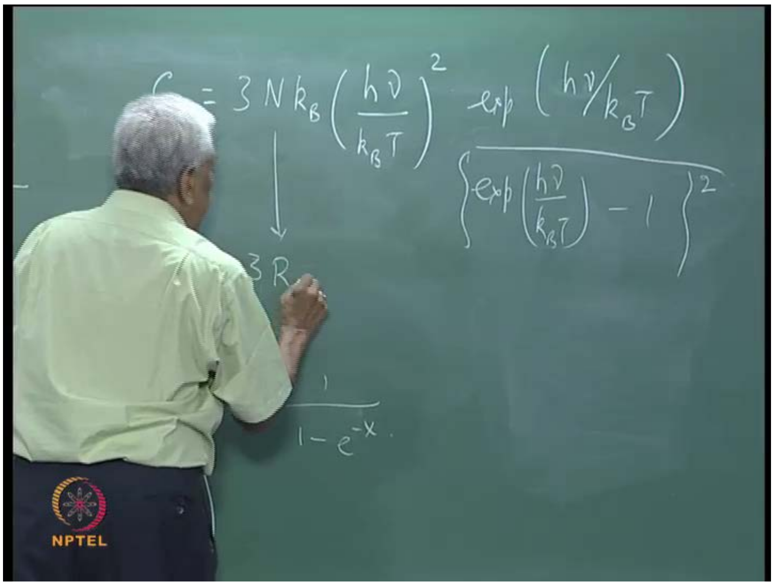

So, the final result for this specific heat will be c v equal to after that the differentiation three n k b times h mu by k B t square in to exponential h mu by k B t by exponential h mu by k B t minus 1 square. So, this is d b, if you look at this form this is the calculation of the Einstein solid this is the specific heat of an Einstein solid. So, you can compare it with the classical due long petit result and see that this corresponds to the same three r, but multiplied by a temperature dependent form which accounts for qualitatively for the absorbed temperature dependence of the specific heat in particular.

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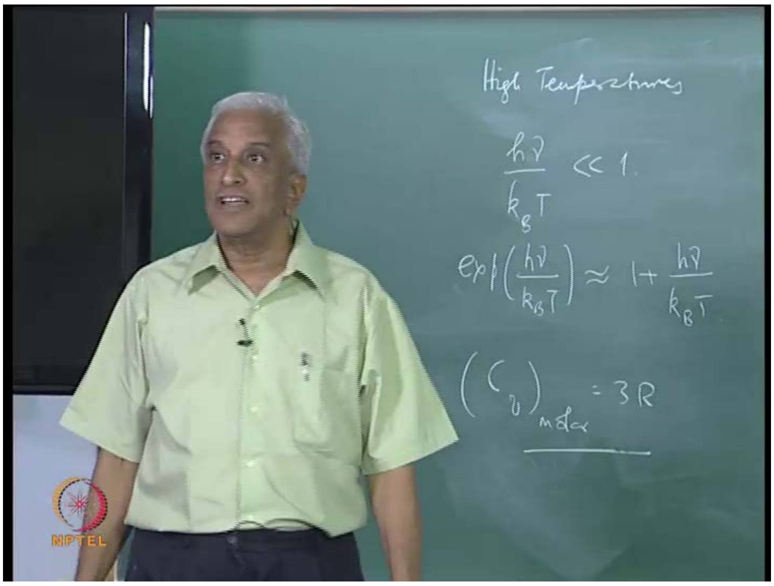

We can distinguish two cases namely that that high temperatures high temperatures is this temperature is. So, high, but h nu by k b t becomes an extremely small quantity compared to one in which case I can write exponential h nu by k b t as just one plus h nu by k b t. So, that this will become this factor this will be small in compare exp nu by k b t. So, this will cancel with this. So, I will get h nu by k b t here I will have one plus h v by k b t here and therefore, this will lead to a i factor which is just one here leading to c v equal to three r c v molar the molar specific heat you will just you have just three r. So, the high temperature limit as the Einstein specific heat goes correctly to the classical value of three r.

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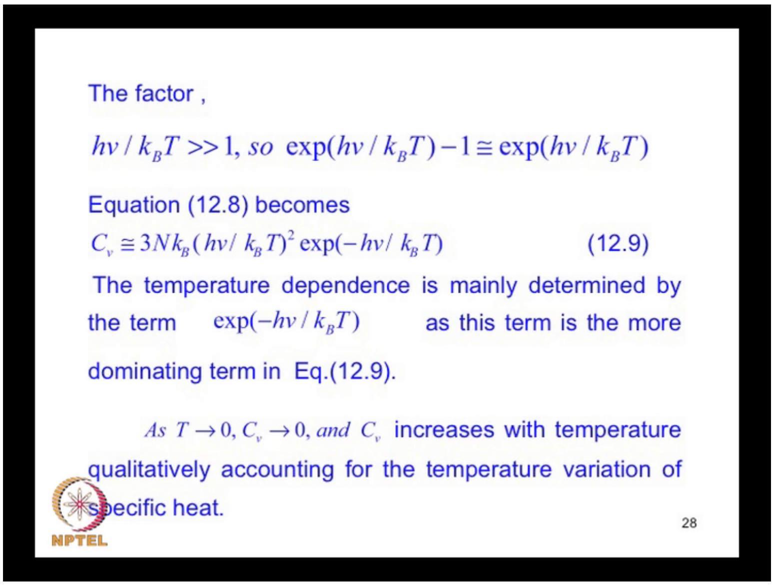

The factor ,

$hv / k_BT >> 1,\ so\ \ \exp(hv / k_BT) - 1 \cong \exp(hv / k_BT)$

Equation (12.8) becomes

$C_v \cong 3Nk_B(hv/ k_BT)^2 \exp(-hv/ k_BT)$ (12.9)

The temperature dependence is mainly determined by the term $\exp(-hv / k_BT)$ as this term is the more dominating term in Eq.(12.9).

$As\ T \to 0, C_v \to 0, and\ C_v$ increases with temperature qualitatively accounting for the temperature variation of specific heat.

Let see what happens then you go to extremely low temperatures we know that at low temperature the specific heat goes to zero. Let us see what happens to the Einstein explanation at low temperature in the low temperature limit h nu by k b t is a large quantity compared to one.

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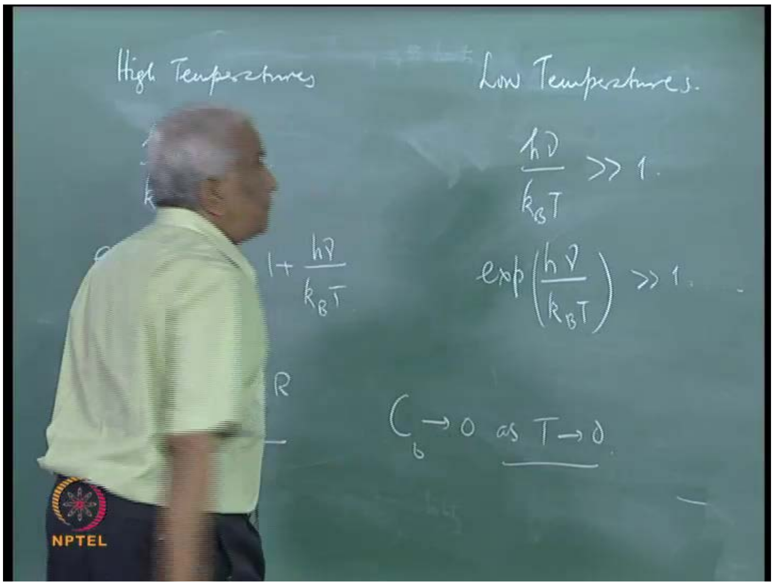

So, exponential h nu by k b t is again very large compare to one. So, in denominator that factor one can be neglected. And therefore, this completely cancelled of. So, we get in the linage c cams to zero as t times to zero. So, it gives the correct limit both at high temperatures and low temperatures, but unfortunately this temperature dependence is not seen experimentally this is not observed experimentally at intermediate temperatures.

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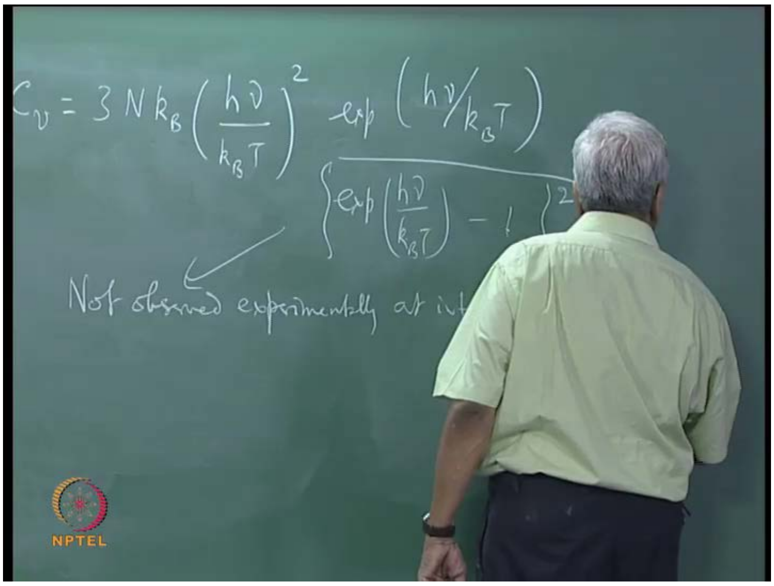

So, while the high-temperature and the low-temperature ends are correctly described by the Einstein theory the intermediate temperature the temperature variation which is observed experimentally is not reproduce theoretically by the Einstein calculation. So, we still know and we already pointed out the shortcomings of the Einstein solid and which assumes that all the three r atoms are vibrate at one given frequency. So, next we have two improve this and get a better description at this specific heat Debye proposed a theory which is an improvement of the Einstein solid take into account this fact that the frequencies of all the atoms are not the same, but we have a distribution of frequencies. So, we will discuss the Debye theory also specifically, so in the next class in the next lecture.