Thermal Physics

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Lecture-22
Topic-Limitation of Einstein Theory of Specific Heat

Hello and welcome back to another lecture of this NPTEL course on thermal physics. Now this week we have started our discussion on specific heat of solids. Now the last lecture we have discussed about Dulong-Pettit law which is an extension of classical equipartition theorems for solid. And they are only the thermal vibration of the atoms has been considered for the prime reason for specific heat.

And also it has been assumed in that law that specific heat does not change as a function of temperature. So, whatever we have for a solid system whatever specific heat we measure, for example at room temperature according to Dulong-Petit law that should be valid over the entire measurable temperature range. But definitely that is not the case, experimentalists have already found out that high temperature and low temperature.

Specially at low temperature side there are deviations from Dulong-Petit law, the specific heat decreases from the value at and it is high temperature value. And most importantly it tends to 0 as the temperature goes to 0. So, definitely there was some issue. Then Einstein came up with his theory of specific heat instead of considering only for the thermal vibration in place of the classical equipartition theory, he applied Planck's theory of quantum of energy.

And he has assumed that all the molecules inside a solid they are vibrating with one unique frequency called the Einstein frequency. Now his results as we have seen already, he is adequate in a sense that it can describe the general behavior of the measured specific heat versus temperature very well. So, at high as in when the temperature is high above the Einstein temperature as the characteristics temperature, then it will level off to this 3R value per mole of specific heat which is the Dulong-Petit law from the classical equipartition theorem.

And at low temperature it falls off gradually and goes to 0, but then it was found out that the falling off is far too fast as compared to the experimentally measured value. The experimental derivation, so the experimental results shows a kind of T cubed behavior at low temperature regime, whereas Einstein predicted a e to the power minus x when exponentially falling function at low temperature. So, of course there are some issues, now in today's lecture we will be discussing the Debye theory of specific heat.

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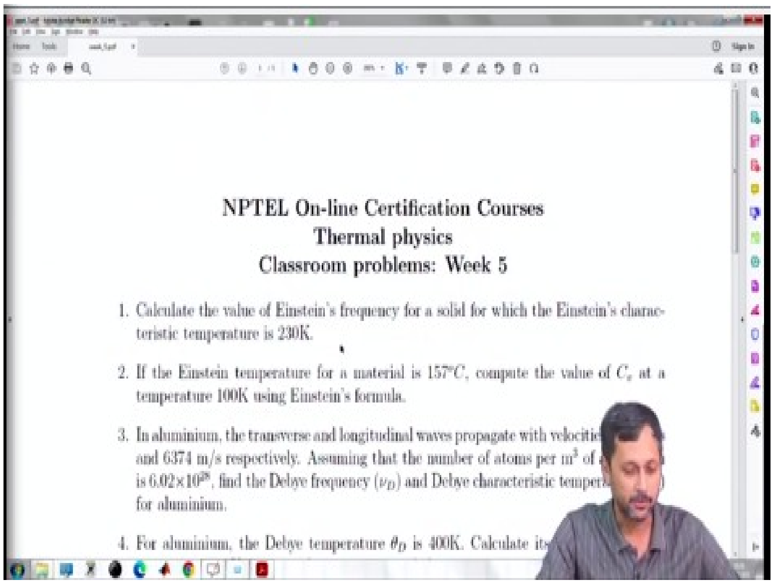

NPTEL On-line Certification Courses
Thermal physics
Classroom problems: Week 5

1. Calculate the value of Einstein's frequency for a solid for which the Einstein's characteristic temperature is 230K.
2. If the Einstein temperature for a material is 157°C, compute the value of C_v at a temperature 100K using Einstein's formula.
3. In aluminium, the transverse and longitudinal waves propagate with velocitie and 6374 m/s respectively. Assuming that the number of atoms per m^3 of is 6.02×10^{28}, find the Debye frequency (ν_D) and Debye characteristic temper for aluminium.
4. For aluminium, the Debye temperature θ_D is 400K. Calculate it

But before going there we will start with two very simple problems or basically the first two problems of the week 5 problem set. So, the first problem is, calculate the Einstein's frequency for the solid for which the Einstein temperature is 230 Kelvin.

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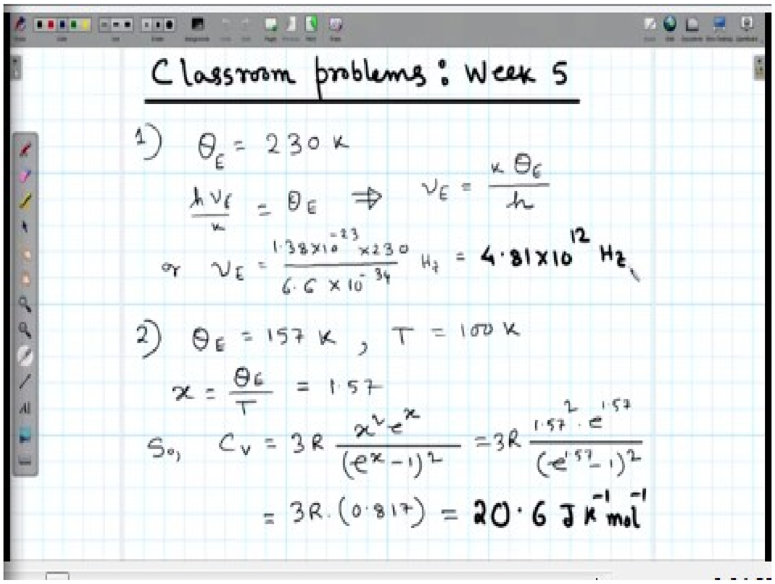

Classroom problems : Week 5

1) $\theta_E = 230\ K$

$\frac{h\nu_E}{k} = \theta_E \Rightarrow \nu_E = \frac{k\theta_E}{h}$

or $\nu_E = \frac{1.38\times10^{-23}\times230}{6.6\times10^{-34}}\ Hz = 4.81\times10^{12}\ Hz$

2) $\theta_E = 157\ K\ ,\ T = 100\ K$

$x = \frac{\theta_E}{T} = 1.57$

So, $C_V = 3R\frac{x^2e^x}{(e^x-1)^2} = 3R\frac{1.57^2\cdot e^{1.57}}{(e^{1.57}-1)^2}$

$= 3R.(0.817) = 20.6\ J\ K^{-1}\ mol^{-1}$

Now this is a very straightforward problem there is nothing tricky about it. We have theta E is equal to 230 Kelvin, now h nu E by k which is equal to theta E this is a relation for theta E that is Einstein temperature. And we can slightly rearrange that and write nu E is equal to k theta E by h. Now all we have to do is we have to put these values simply and we have found out the frequency of 4.81 into 10 to the power 12 Hertz.

Now this is a very high frequency, I mean this is already in the terahertz range. Now this terahertz has frequency although it is very high, it is lower as compared to the optical frequencies typically when we talk about photons and all we talk about this optical electromagnetic wave we talk about the optical frequencies. But anyway, this is a frequency range and these are typical phonon frequencies of vibration in an atomic solid.

Now, the second problem is the first problem was to give you an idea of what is the typical frequency of vibration we have inside a solid. And the second problem is application of by Einstein's formula, where the Einstein's temperature has been given which is it should be 157 centigrade Kelvin my mistake, it is 157 Kelvin, compute the value of C v at a temperature of 100 Kelvin using Einstein's formula.

So, the problem is the following with the value of C v is or value of Einstein temperature is given which is 157 Kelvin and we need to compute the value of C v at a given temperature. So, remember the Einstein's formula which is C v is equal to 3R times x square e to the power x e to the power x minus 1 whole square divided by e to the power x minus 1 whole square. So, all we have to do is we have to compute the value of x. So, x is equal to theta E by T which is 157 divided by 100 which is 1.57. So, next we; just need to put this value here, so it will be 1.57 square times e to the power 1.57 divided by e to the power 1.57 minus 1 whole square. So, this factors the entire numerical value of this factor is 0.0817 and times 3R.

So, if I put the value of R the final answer is 20.6 Joules per calorie inverse per mole inverse. So, that is all we can do from Einstein's theory, so basically we have 1 simple formula, 1 simple relation and if we know the value of x we can compute C v at any temperature. And we can also use this relation to compute the value of nu E or theta E whichever is not given to us and vice versa. The next modification to this specific heat of solid was provided by Debye few years 5, 6, 7 years after Einstein I think 1912.

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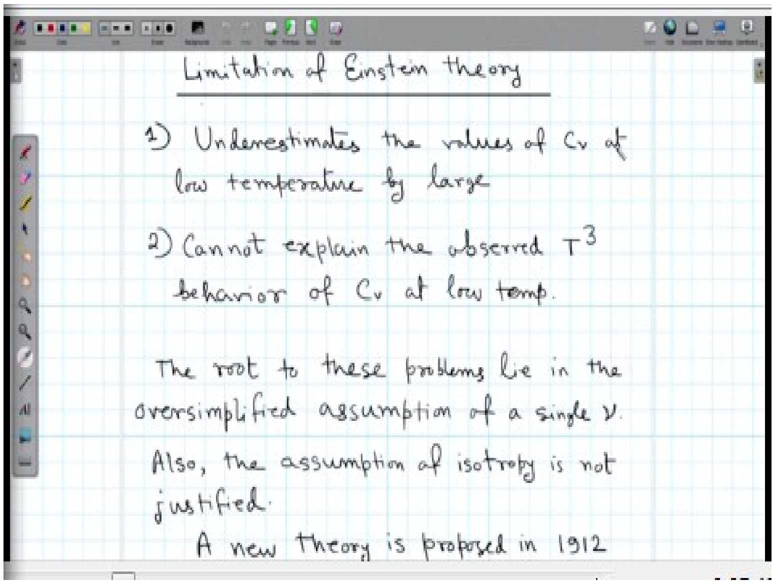

Limitation of Einstein theory

1) Underestimates the values of C_v at low temperature by large

2) Cannot explain the observed T^3 behavior of C_v at low temp.

The root to these problems lie in the oversimplified assumption of a single ν.

Also, the assumption of isotropy is not justified.

A new theory is proposed in 1912

That is where the Debye theory came in. So, let us quickly once again revisit the limitations of Einstein theory. So, basically it underestimates the value of C v at low temperature by large. So, whatever value is recorded experimentally according to Einstein's theory the value will be much lesser, so that is the underestimation. And of course it cannot explain the T cubed behavior at low temperature.

So, the primary cause of these two the failure of Einstein theory lies into the oversimplified assumption.

Oversimplified assumption that all the; molecules in the atom vibrate with a simultaneous unique frequency which is definitely not the case. I mean it is a solid and there is a possibility that some part of it the molecules in one part of solid will vibrate with one frequency another part will vibrate with another frequency that possibility cannot be ruled out. Depending on the local environment and depending on the geometry of the there are many other factors actually. So, overall the assumption that all the solid molecules are vibrating simultaneously with same frequency is the vast oversimplification.

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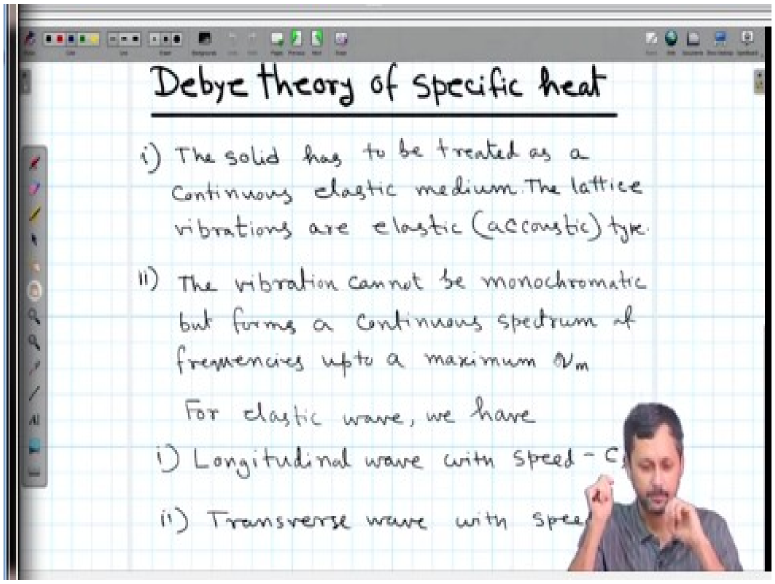

Debye theory of specific heat

i) The solid has to be treated as a continuous elastic medium. The lattice vibrations are elastic (accoustic) type.

ii) The vibration cannot be monochromatic but forms a continuous spectrum of frequencies upto a maximum ν_m

For elastic wave, we have

i) Longitudinal wave with speed - C

ii) Transverse wave with spee

So, in 1912 Debye came up with his theory of specific heat which actually addresses some of these problems. So, what Debye proposed is instead of considering discrete point masses, he will treat the solid as an elastic medium. Of course, this also has a downside none of his theories completely perfect. But at least when we are talking about bulk solids, the elastic medium is probably a better approximation.

Now, the vibration that is propagating is acoustic type of vibration that means for example the sound wave is propagating through the solid medium. And he has assumed that this vibration is not monochromatic, that means it does not have one frequency but it has a maximum cutoff frequency. So, his assumption was all the molecules are vibrating with different, different frequencies.

So, basically it is different groups of molecule that constitutes different parts of the solid. So, one group vibrates with one frequency another group vibrates with another frequency. So, different parts have different frequencies and these frequencies are like sound wave that is propagating through a solid medium. And what he has assumed that there is an upper cutoff for this frequency. So, it cannot be above this particular cutoff, which is given by nu m.

Or actually sometimes it is better to write it as nu D just to correlate this strongly with Debye. So, I will just call it nu D for the rest of the discussion. Now for elastic wave, we know that another property of an elastic medium is there are two types of waves one is longitudinal wave, one is the transverse wave and it is not necessary that both these waves will have the same speed. Actually it is most of the time in a solid we have longitudinal vibration and a transverse vibration moving with different speeds. So, Debye assume that there is a longitudinal wave with speed C l and transverse wave with speed C t at l and t stands for longitudinal and transverse respectively.

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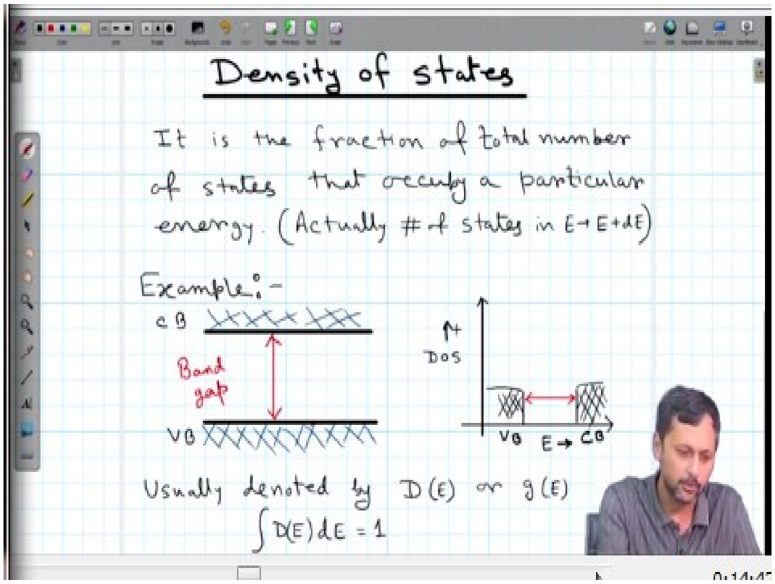

Density of states

It is the fraction of total number of states that occupy a particular energy. (Actually # of states in $E \to E+dE$)

Example:-

Usually denoted by $D(E)$ or $g(E)$

$\int D(E)\,dE = 1$

Now, one important assumption has been the vibration is not monochromatic, so different parts will have different vibration frequency. So, whenever that concept comes into the picture, I think it is important that we understand what is the meaning of density of state. In very soon I will just correlate this density of state with this vibration frequency. So, one possible definition of density of state, which is a term which probably we are already familiar from your solid state physics lecture.

It is actually the fraction of total number of states that occupy a particular energy. So, actually it is not 1 number of states at a given energy but typically it is defined as the number of state for example, between E to E plus dE, right. So, the example of one example that I always prefer for density of state is say if this is the band gap. We have the valence band, we have the conduction band and this part is band gap.

So, forget about defect states, let us assume that it is a pure semiconductor system I am just deviating slightly, to solid state physics now. So, for this we have electrons occupying these valance band energy levels and electrons occupying this conduction band energy levels and nothing in between. Now if I try to represent this as energy versus density of state plot, we have something like this.

So, we have one set of density of state that is for the valence band, one set of density of state that is for the conduction band and this is the band gap in between, here. So, this is a representative diagram. Once again I am just drawing two steps here for the valence band and the conduction band and there are numerous theories available for which predicts the shape of this valence band and conduction band density of states the shape of this curve.

I am not going into this; I am just trying to give you a concept. So, whenever there is no state, the density of state is actually zero, whenever there is an above this particular energy the number of state increases and all of a sudden the density of state becomes nonzero. Similarly below this particular energy here, the density of state becomes nonzero once again. So, this axis is energy axis, this axis is density of state that is basically the number of states for a given energy range.

Now usually density of state is denoted by D E or g E and the usual definition is when it is integrated over all possible energy values D E times dE is gives you the integration of dE gives you 1. So, that is because we have assumed that D E and g E they are fraction of total energy states. Now why it is important in Debye theory, because see in Einstein theory it was all monochromatic. In Einstein's theory it was and please remembers that there is a strong connection in between energy and frequency.

So, when Einstein said that all vibrations are monochromatic that basically means that all atoms are vibrating with equal energy. When Debye says atoms are vibrating with different energies but there is a different frequencies but there is an upper cutoff frequency. So, that means the density of state above this cutoff frequency will be 0 and below this cutoff frequency all frequencies in between will have some given number of states. So, that is why the concept of density of state is important.

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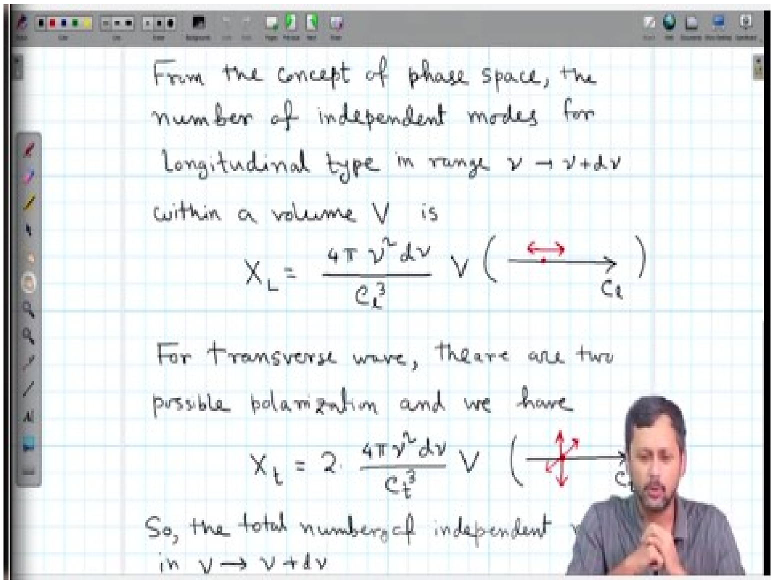

From the concept of phase space, the number of independent modes for longitudinal type in range $\nu \to \nu + d\nu$ within a volume V is

$$X_L = \frac{4\pi \nu^2 d\nu}{C_L^3} V \left(\xrightarrow[C_L]{\leftrightarrow} \right)$$

For transverse wave, theare are two possible polarization and we have

$$X_t = 2 \cdot \frac{4\pi \nu^2 d\nu}{C_t^3} V$$

So, the total number of independent

in $\nu \to \nu + d\nu$

Now I am not going into the details of statistical mechanical treatment of the system here, but there is something called phase space which can be defined. Once again I just do not want to complicate it as of now. So, according to the theory of phase space, the number of independent modes for a given wave that elastic wave that travels with the speed C is given by, so what we are concerned about?

We are concerned about number of modes that is present in the energy frequency range of nu to nu plus d nu. And that is equivalent of saying that it is the number of states that is present in the energy E to E plus D E. Of course there should be some factor conversion factor mostly the h, h being the Planck's constant. So, these are semi classical semi quantum type of treatment although we are taking the classical picture of acoustic wave propagating.

We are calculating or basically we are using the concept of quantum phase space here. And for longitudinal modes, the number of states between energy level nu and nu plus d nu is given by 4 pi nu square d nu C l cubed multiplied by V, that is the please remember X L is not exactly the density of state, this quantity here is the density of state and we multiply this with V, V being the volume of the whole space. So, whatever solid we are considering it has a volume V.

So, X L is here and this is for the longitudinal wave, now what is longitudinal wave? Longitudinal wave is let us say this black arrow is the direction of wave propagation and this red dot here represents a molecule or 1 atom in this path of propagation and the vibration of this is along the path, red mark arrow here indicates the vibration, so this is longitudinal. And longitudinal wave can have one mode only that is along the direction of propagation, the vibration along the direction of propagation.

Now for transverse waves exact same expression, but we have to have a factor of 2, why because for simple reason the transverse wave can have 2 independent modes of vibration. One is let us say just for sake of simplicity if I call this z this direction of propagation is z, then I have 1 x-axis and 1 y-axis arbitrarily chosen, the only criteria is they have to be perpendicular to each other. So, that is how you choose x and y, no other criteria, but now there has to be 2 independent modes of a transverse wave, so that is why a factor of 2 is coming here. Now the total number of independent modes in range nu to nu plus d nu in a volume V.

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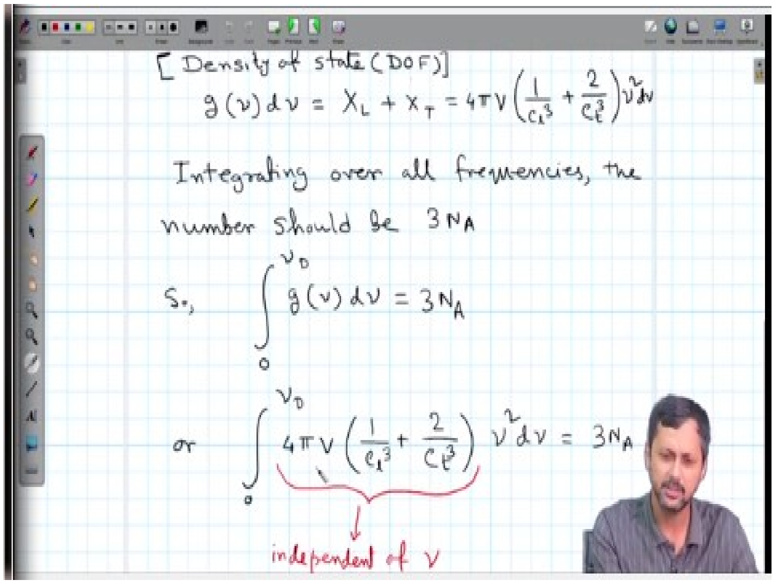

[Density of state (DOF)]

$$g(\nu)\,d\nu = X_L + X_T = 4\pi V\left(\frac{1}{C_l^3}+\frac{2}{C_t^3}\right)\nu^2 d\nu$$

Integrating over all frequencies, the number should be $3N_A$

So, $$\int_0^{\nu_D} g(\nu)\,d\nu = 3N_A$$

or $$\int_0^{\nu_D} \underbrace{4\pi V\left(\frac{1}{C_l^3}+\frac{2}{C_t^3}\right)}_{\downarrow\ \text{independent of } \nu} \nu^2 d\nu = 3N_A$$

Which is once again the density of state multiplied by V actually, it is not exactly density of state, which is X L plus X T is equal to 4 pi V 1 by C l cubed plus 2 by C t cubed times nu square d nu, so, basically just adding this one and this one, nothing else. So, only thing that we have not discussed what is the origin of this particular expression? And let me tell you once again this comes from the mind Maxwell's Boltzmann statistics.

So, this is the elemental volume in phase space and all, so we are not going into the details here. Now integrating this g nu d nu over all possible frequencies starting from 0 to nu d, what is the Debye cutoff frequency should actually give you 3N A, why? For a molar solid N A is the number of molecules and each molecule can be considered as 3 independent linear harmonic oscillators. There is actually a small correction, in the last class I talked about energy per density in while deriving Einstein's theory.

I said something like energy part degrees of freedom, no; it is actually not true it is energy per independent vibrator. So, the number of independent vibrator is 3N A. So, there is a correction, I have corrected it in the notes, please have a look. So, it is 0 to nu D, if I integrate it from 0 to nu D, g nu d nu will give you 3N A and when I substitute for g nu simply by putting this expression over here, so I get this 0 to nu D 4 pi V 1 plus C l cubed plus 2 by C t cubed nu square d nu. Now this quantity over here is independent of frequency.

So, it is the characteristics of the solid, V is the volume C l and C t their characteristics of the solid and can be measured irrespective of course we assume that if there is a transverse wave this transverse wave will be of whatever frequency the transverse wave will have the same velocity. Similarly for a longitudinal wave whatever may be the frequency of this vibration the wave velocity will be the same which is once again some oversimplification to some extent. But these are material properties nonetheless. And at present we considered them to be independent of nu. So, what we can do is, we can simply take this out and compute this nu square d nu from 0 to nu D.

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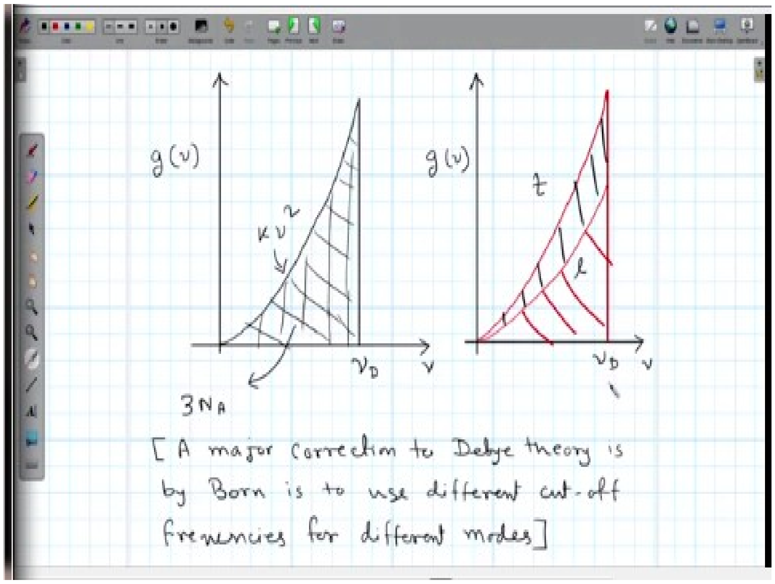

[A major correction to Debye theory is by Born is to use different cut-off frequencies for different modes]

So, we will just give me a second. So, before we do that, let me quickly focus on this expression here. So, you see here nu square g nu the density of state, it is actually density of state multiplied by the total volume, but that is okay, it is just a constant multiplication is actually a function of nu square. So, g of nu is proportional to nu square.

So, just to give you a representative idea of how Debye theory looks like, you see, if I plot g nu as a function of nu, it is something like this, there is a constant times nu square. And the total area under this curve is actually 3N A. Now this curve has 2 contributions one for this area is the contribution for the longitudinal wave and this is the contribution for the transverse wave.

So, this one is a combination of a longitudinal and transverse component, which I am just trying to show you graphically. Now later on we will see that or we will discuss that Debye theory is also not complete of course no theory is complete. And so the major correction has been to Debye theory is the Born approximation, which says the same cutoff frequency for longitudinal and transverse vibration is probably not right. So, we will come back to that later.

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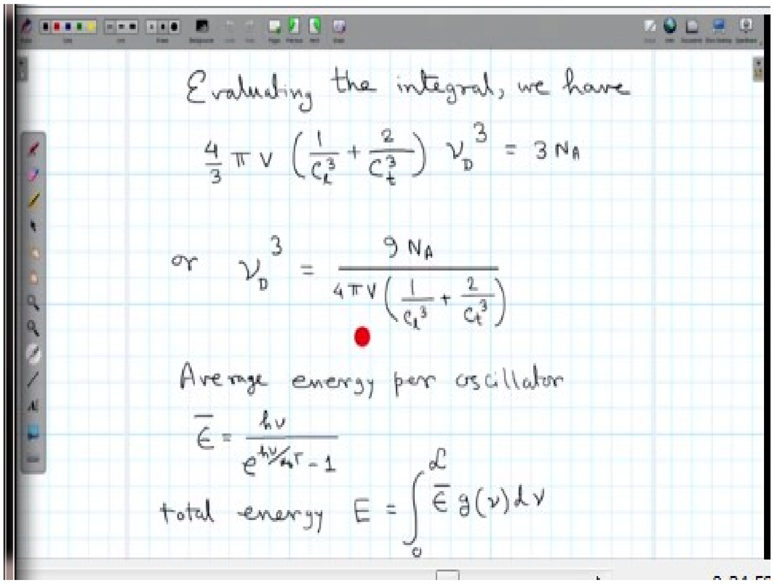

Evaluating the integral, we have

$$\frac{4}{3}\pi V\left(\frac{1}{C_l^3}+\frac{2}{C_t^3}\right)\nu_D^3 = 3N_A$$

or $$\nu_D^3 = \frac{9N_A}{4\pi V\left(\frac{1}{C_l^3}+\frac{2}{C_t^3}\right)}$$

Average energy per oscillator

$$\bar{\epsilon} = \frac{h\nu}{e^{h\nu/kT}-1}$$

total energy $$E = \int_0^{\mathcal{L}} \bar{\epsilon}\, g(\nu)\, d\nu$$

So, now from here, what do we do? We just compute the integration and we get nu D so four third pi V, this expression times nu D cubed is equal to 3N A. And just writing this will give me an expression for nu D cubed, what is nu D, nu D cubed is equal to 9 N a divided by 4 pi V 1 by C l cubed plus 2 by C t cubed. So, this actually gives you a way of measuring the Debye cutoff frequency experimentally, all we have to do is we have to measure C l and C t for a given solid.

Once we know that, we can always put this in this formula and compute the cutoff frequency for any given solid. So, once again the average energy per oscillator, please remember in the last lecture by mistake I have mentioned that average energy per degree of freedom which is not the case, average energy per oscillator is E bar is equal to h nu divided by e to the power h nu by k b T minus 1. So, once again the total energy E is equal to 0 to infinity in this case it will not be infinity.

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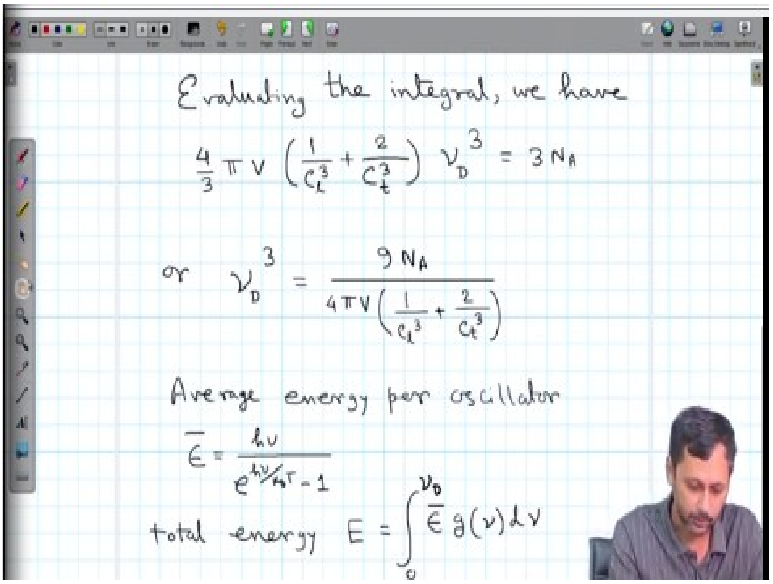

Evaluating the integral, we have

$$\frac{4}{3}\pi V\left(\frac{1}{c_l^3}+\frac{2}{c_t^3}\right)\nu_D^3 = 3N_A$$

or $$\nu_D^3 = \frac{9N_A}{4\pi V\left(\frac{1}{c_l^3}+\frac{2}{c_t^3}\right)}$$

Average energy per oscillator

$$\bar{E} = \frac{h\nu}{e^{h\nu/k_BT}-1}$$

total energy $$E = \int_0^{\nu_D}\bar{E}\,g(\nu)\,d\nu$$

Because there is a cutoff frequency which I think I did I have already done that. So, this is just by mistake, it should be nu D. So, this is nu D total energy is given by E is equal to 0 to nu D E bar g nu d nu.

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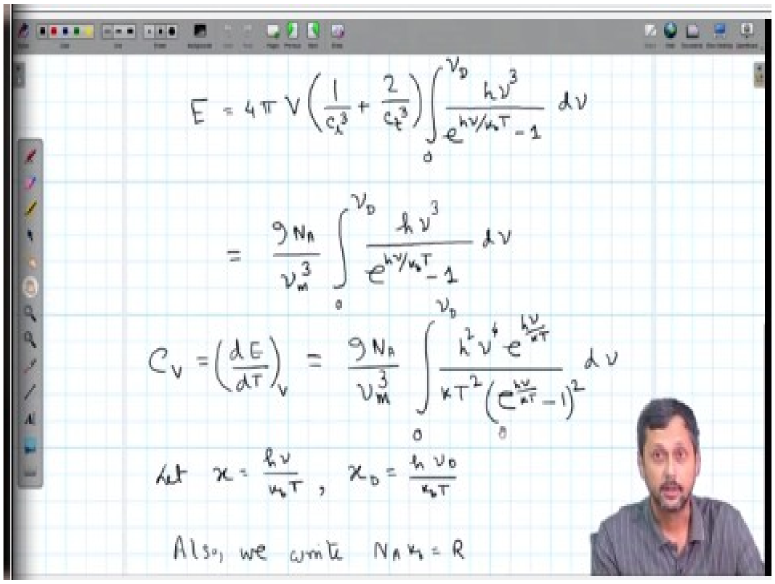

$$E = 4\pi V\left(\frac{1}{c_l^3}+\frac{2}{c_t^3}\right)\int_0^{\nu_D}\frac{h\nu^3}{e^{h\nu/k_BT}-1}\,d\nu$$

$$= \frac{9N_A}{\nu_m^3}\int_0^{\nu_D}\frac{h\nu^3}{e^{h\nu/k_BT}-1}\,d\nu$$

$$C_V = \left(\frac{dE}{dT}\right)_V = \frac{9N_A}{\nu_m^3}\int_0^{\nu_D}\frac{h^2\nu^4 e^{\frac{h\nu}{kT}}}{kT^2\left(e^{\frac{h\nu}{kT}}-1\right)^2}\,d\nu$$

Let $x = \frac{h\nu}{k_BT}$, $x_D = \frac{h\nu_D}{k_BT}$

Also, we write $N_A k_B = R$

Now this integration has to be computed. So, there is a constant factor over here in G nu and then we are left with this integration. Now this actually we do not have to keep it in this kind of long format, what we can do is we can simply use this relation over here. And we can reduce it to once again small mistake it should be D.

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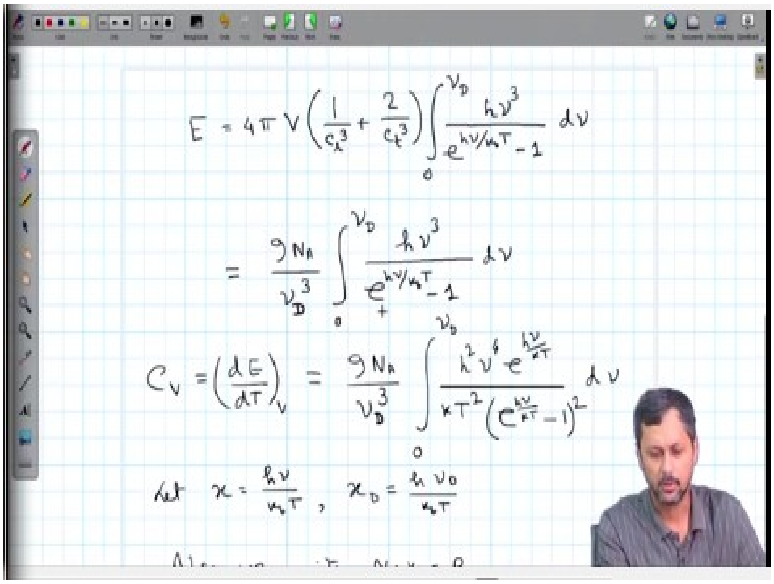

$$E = 4\pi V\left(\frac{1}{c_l^3} + \frac{2}{c_t^3}\right)\int_0^{\nu_D} \frac{h\nu^3}{e^{h\nu/k_BT} - 1}\, d\nu$$

$$= \frac{9N_A}{\nu_D^3}\int_0^{\nu_D} \frac{h\nu^3}{e^{h\nu/k_BT} - 1}\, d\nu$$

$$C_V = \left(\frac{dE}{dT}\right)_V = \frac{9N_A}{\nu_D^3}\int_0^{\nu_D} \frac{h^2\nu^4 e^{\frac{h\nu}{kT}}}{kT^2\left(e^{\frac{h\nu}{kT}} - 1\right)^2}\, d\nu$$

Let $x = \frac{h\nu}{k_BT}$, $x_D = \frac{h\nu_0}{k_BT}$

We can reduce it to 9 N A by nu D cube D sorry it should be D once again, so times this integration. Now this is for the total energy E here, for C v it will be dE dT at constant volume and the volume term is already included here. So, we can take this as constant, please remember that the volume is included in nu D here, so this is constant. So, the integration or the differentiation will be whatever inside this integration symbol that is the integrand which are functions of temperature.

This k b T is a function of temperature e to the power h nu way k b T minus 1 is a function of temperature. So, finally once we compute the differentiation, so it should be 0 to nu D h square nu to the power 4 e to the power h nu by k b T divided by this k T square and this quantity. Once again we write just like in Einstein case, we write x is equal to h nu by k b T and we also define x D which is h nu D by k b T. Also there is a trick here what we can do is we can write there is a N A k b, so we also have to write N A k b is equal to R and right.

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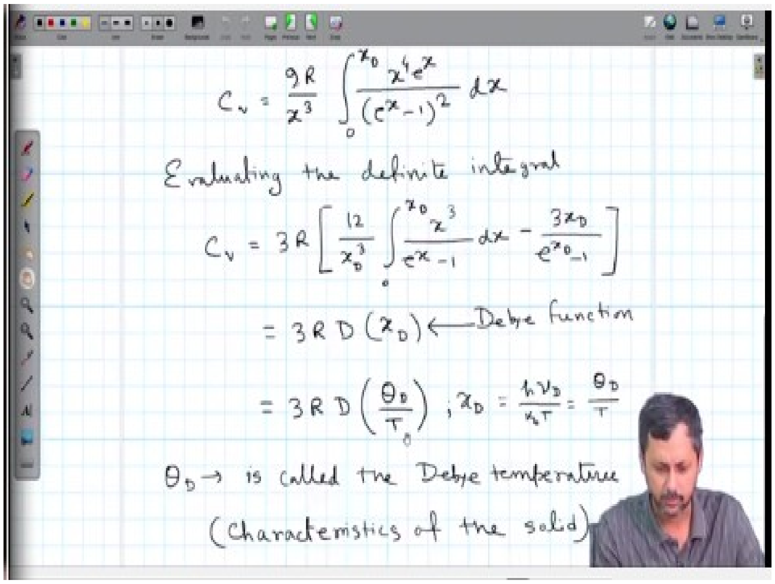

$$C_v = \frac{9R}{x^3}\int_0^{x_D} \frac{x^4 e^x}{(e^x-1)^2}\,dx$$

Evaluating the definite integral

$$C_v = 3R\left[\frac{12}{x_D^3}\int_0^{x_D}\frac{x^3}{e^x-1}\,dx - \frac{3x_D}{e^{x_D}-1}\right]$$

$$= 3R\,D(x_D) \longleftarrow \text{Debye function}$$

$$= 3R\,D\left(\frac{\theta_D}{T}\right) \;;\; x_D = \frac{h\nu_D}{k_B T} = \frac{\theta_D}{T}$$

$\theta_D \rightarrow$ is called the Debye temperature

(Characteristics of the solid)

So, what we can do is I think there is a mistake I will just correct this, I think this k should go here something like this because otherwise this relation will not make sense, anyway I can check that. So, it will be 3 by R this is a correction here it will be x D 3 by R x D cubed from 0 to x D x to the power 4 e to the power x divided by e to the power x minus 1 whole square dx. Now, so we have a definite integral in hand.

Now this a definite integral can be evaluated by parts. So, what do we have here? We can do this integration by parts taking 3R out, what we have finally is this one 12 by x D cubed integration 0 to x T, x cubed e to the power x minus 1 dx minus 3x D divided by e to the power x D minus 1. Now this function over here, so, we have just taken 3R out, so that we can compare it with the Dulong-Petit law or Einstein's law for example.

And we can write this as 3R D of x D, where D is a Debye function, also there is a way of writing this x D as theta D by T where theta x D is equal to theta D by T, this is the relation here. So, D is called the Debye function and theta D is called the Debye temperature which once again is a characteristics of a solid, but unlike Einstein temperature which actually well, or Einstein frequency which is one unique frequency for all the oscillators.

Debye temperature or Debye frequency marks the upper cutoff of phonon vibration. So, we will talk about the low temperature and high temperature limit from here in the next lecture. So, at present we have found out that there is a expression for C v in terms of this Debye function. And next what we need to do is, we need to explore the low temperature and high temperature behavior which we will do in the next lecture and compare it with the experimentally determined values, thank you.