Thermal Physics
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Lecture-23
Topic-Debye Theory of Specific Heat

Hello and welcome back to another lecture of this NPTEL course on thermal physics. Now in last lecture, we were discussing about Debye theory of specific heat. We have already discussed about Einstein's theory of specific heat and we have seen that there are certain drawbacks, especially at low temperature the Einstein's theory does not agree with experimental result. That is where the Debye theory comes in and unlike Einstein actually assumes that there is only 1 vibration mode 1 vibration frequency for the entire system.

Debye assume that there are many possible vibration frequencies but it is like a continuous elastic medium, where all possible vibration frequency can coexist but there is an upper limit which is given by the nu D that is the Debye frequency. And once we write everything in terms of nu D or when we express it and also there is another major assumption has been that the transverse wave and not an assumption actually it is well known that the transverse and longitudinal wave they travel at different speeds.

So, depending on the speed we can compute the density of states for the longitudinal wave and transverse wave separately, we can add them up and we can integrate for all possible nu values frequency values from 0 up to this maximum upper cutoff frequency in order to get the total number of allowed states. And that total number of allowed state has to be equal to the 3 times Avogadro number where Avogadro for the molar specific substance. Now why Avogadro number because in 1 mole of any substance there are N A number of atoms and each atom can be considered as a combination of three independent linear vibrators. So, altogether there are 3 N number of such linear vibrators present in one mole of a solid substance.

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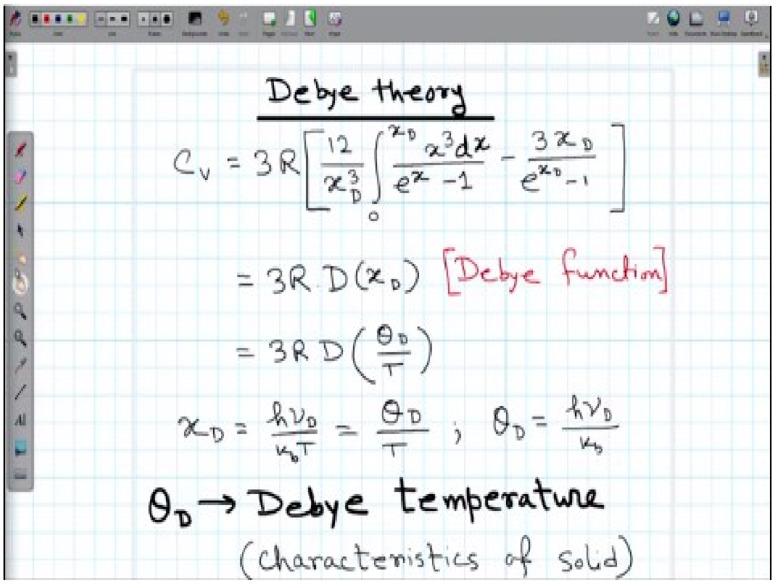

Debye theory

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

$$= 3R\,D(x_D)$$ [Debye function]

$$= 3R\,D\left(\frac{\theta_D}{T}\right)$$

$$x_D = \frac{h\nu_D}{k_b T} = \frac{\theta_D}{T} \;;\quad \theta_D = \frac{h\nu_D}{k_b}$$

$\theta_D \rightarrow$ Debye temperature

(Characteristics of solid)

Now let us quickly review the equations, we finally got to this particular equation where C v is equal to 3R times 12 x D cube 0 to and there is an integration. So, we actually started off with a single integration and after evaluating by part we have one part which is in terms of a definite integral and this is the part where we have already substituted for x is equal x T. Now this function as a whole is called the Debye function which is a function of x D because although there is x here there should be a dx which I just missed out.

So, there should be a dx overall here, but it does not matter once this definite integration is evaluated this whole thing is a function of x D only which is x D is equal Debye temperature by the temperature of the substance. So, these are the definition of x D and theta D, theta D is equal h nu D by k b and this Debye temperature is a characteristic of the state solid. So, like in Einstein theory Einstein frequency or Einstein temperature has been a characteristic of the solid. In a similar manner in Debye theory the Debye frequency nu D or the Debye temperature theta D has been characteristics for a given solid which can be experimentally determined which we will see in a when we will be solving the problems.

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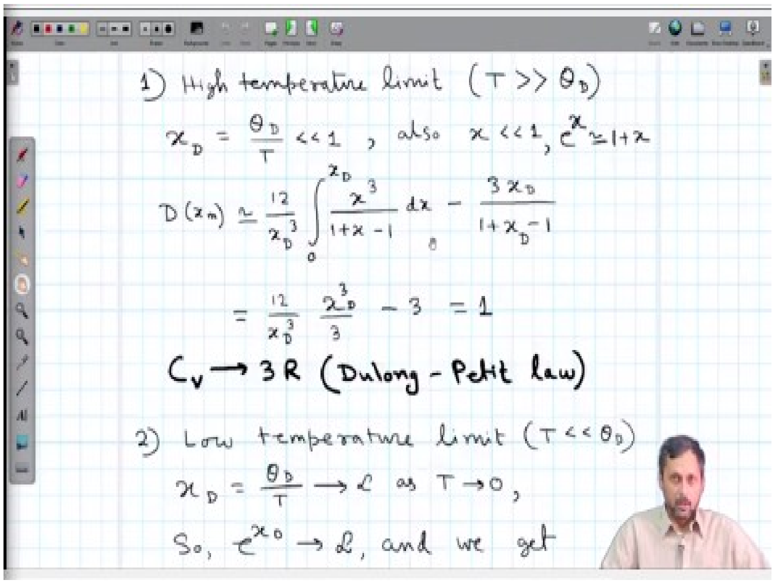

1) High temperature limit $(T >> \theta_D)$

$x_D = \frac{\theta_D}{T} << 1$, also $x << 1$, $e^x \simeq 1+x$

$$D(x_m) \simeq \frac{12}{x_D^3}\int_0^{x_D}\frac{x^3}{1+x-1}\,dx - \frac{3x_D}{1+x_D-1}$$

$$= \frac{12}{x_D^3}\,\frac{x_D^3}{3} - 3 = 1$$

$C_v \rightarrow 3R$ (Dulong - Petit law)

2) Low temperature limit $(T << \theta_D)$

$x_D = \frac{\theta_D}{T} \rightarrow \infty$ as $T \rightarrow 0$,

So, $e^{x_D} \rightarrow \infty$, and we get

Now once we have this we have to explore the two possible limits one is the high temperature limit other is the low temperature limit. So, basically we start with this particular expression up here, this expression here. And we have to explore the limits of this function D and see whether it follows tallies with the experimental results. So, at first we explored the high temperature limits. So, what happens at high temperature?

In high temperature T is much, much greater than theta D, so what is high and what is low that is relative question. Because there has to be some measure or some fixed point with which we have to compare something and we can say that this is high and this is lower, this is short and this is long, so we need to have a reference. In this case, for Einstein case also our reference point was Einstein temperature, in Debye case also our reference point has been the Debye temperature.

Now when T is greater than theta D that means x D which is theta D by T is much, much less than 1. Of course and for any other x values in general for high temperature case that is also less than 1. Because what is x is equal to so, in this relation if I simply replace nu D with nu, so h nu by k b T. So, when we are in the high temperature limit, we have x D less than 1 and x is also very much less compared to 1.

So, e to the power x simply approximates to 1 plus x. Now if I substitute this in this particular function, what do we get? In the first term, see we have 12 x D cubed, which is a fixed number which is already there, then we have this integration 0 to x D and the numerator stays x cube the denominator is 1 plus x minus 1 times dx. And the second term which was already a fixed number is 3 x D 1 plus x D minus 1.

So, have all we have done is instead of e to the power x D we have written 1 plus x D and is in place of e to the power x we have written 1 plus x. Now after this approximation, the integration becomes very straightforward and we have x D cube here x D cube by 3 coming here because this will 1 and 1 cancels we have x, x cube, so that means x square dx which is x cubed by 3 in the limit 0 to x D this is simply x D cube.

So, this term gives you 4, so 3 and 12 cancel x D cube x D cube cancels 3 and 12 gives you 4 and this second term gives you 3 only, so this gives you 1. So, that means the Debye function goes to 1 at high temperature, which essentially means C v goes to 3R in the high temperature regime which is precisely the Dulong-Petit law. So, this is what we get from the classical equipartition theorem the Dulong-Petit law.

And the result in our theory tallies exactly how it should be with experiment. Now interesting is the low temperature element. Now in low temperature we have T much, much less than compared to theta D. So, x D which is equal to theta D by T will be, see T is much higher, so theta D by T, T is a very small quantity. So, in the limit T tends to 0 theta D by T tends to infinity, so e to the power x D tends to infinity.

And look at this term, when e to the power x D, so when x D tends to infinity to the power x D becomes dominant over this minus 1 term. So, it will be approximately the denominator of this expression is approximately e to the power x D and because e to the power x D goes to infinity this term actually vanish, it does not matter. So, basically the second term does not contribute, now what about the first term?

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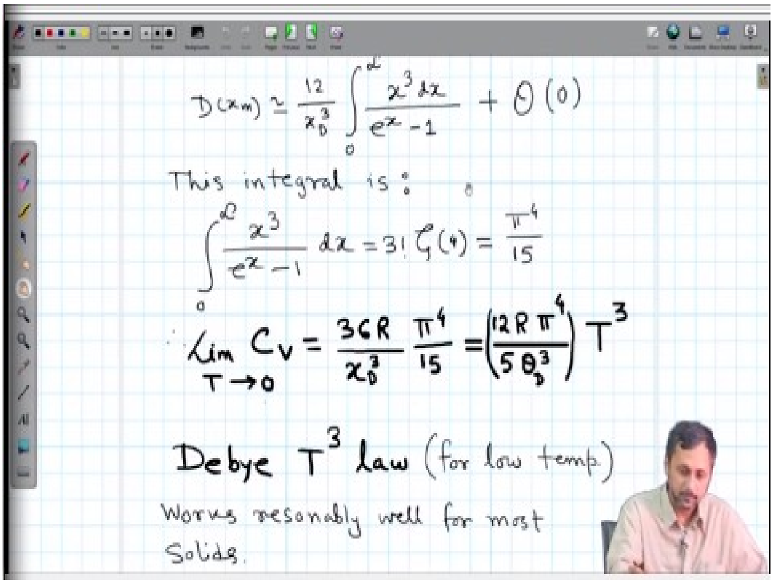

$$D(x_m) \simeq \frac{12}{x_D^3}\int_0^\infty \frac{x^3\,dx}{e^x-1} + \Theta(0)$$

This integral is:

$$\int_0^\infty \frac{x^3}{e^x-1}\,dx = 3!\,\zeta(4) = \frac{\pi^4}{15}$$

$$\lim_{T\to 0} C_V = \frac{36R}{x_D^3}\,\frac{\pi^4}{15} = \left(\frac{12R\pi^4}{5\theta_D^3}\right)T^3$$

Debye T^3 law (for low temp.)

Works resonably well for most Solids.

The first term actually stays of course for low temperature regime see x D, so what happens is, x D tends to infinity. So, for low temperature regime this integration is essentially 12 by x D cubed 0 to infinity x is cubed dx e to the power x minus 1 plus a term which is very closely equal to 0, say it is off the order 0. So, that means 0, it is another way of saying it is 0. So, all we have to do is, we have to evaluate this definite integration in the limit 0 to infinity.

And this turns out to be a standard zeta function integration, this integration I am not going into the details of this because we have not learned zeta function. But I am sure you have heard of it from your mathematical physics courses, if not does not matter. All you understand that it has a fixed value and this fixed value is happened to be pi to the power 4 by 15. So, what do we do? We simply substitute for this pi to the power 4 by 15 and we already have a 12 divided by x D cube term present from our expression.

So, we have C v in the limiting case of T tending to 0 it is 36R by x D cubed pi to the power 4 by 15 upon simplification we get 12R pi to the power 4 divided by 5, so there is a cancellation here. So, we have 12 in the numerator 5 in the denominator and we have 5 theta D cubed multiplied by T cubed. So, this is precisely Debye T cubed law and we have already discussed that the experimental results actually show for most of the solid materials at the low temperature region.

The variation of specific heat with temperature follows a T cubed law and Debye theory very accurately predicts this T cube theory. Now what happens in practice that when T becomes very small, just think of it in this manner. We have oscillators and if you remember, let me take you to the yesterday's lecture notes.

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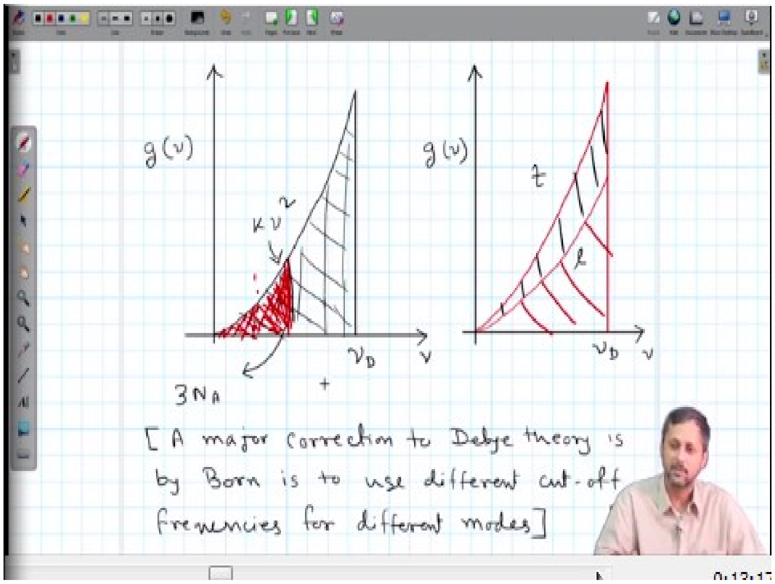

[A major correction to Debye theory is by Born is to use different cut-off frequencies for different modes]

So, forget about the right hand side, let us focus quickly on the left hand side. See we have a cutoff frequency here that is nu D**.** Now at high temperature when the oscillators or the energy of oscillation for each molecule the thermal energy is high. So, that means the oscillators are exploiting all these energy states that means all the energy states this g of nu is actually the number of energy levels that is required that is available there.

So, all this energy states are filled up at high temperature, but at low temperature what happens is only a selected few modes which are low energy mode that are excited and the rest of it is empty. So, in practice what do we have maybe we have filled state up to this portion, only this part is filled at low temperature, this is actually even sometimes it happens that only this tiny part in the first part of this density of state or only a fraction of density of states are filled rest is empty.

So, for a electron or sorry for a phonon of this frequency the upper limit which is nu D which is actually a finite limit, looks like it is already very far from it is own value. So, it feels like it is already upper limit of this integration becomes infinity. So, what happens in reality is only a tiny fraction of these available modes are excited at low temperature, whereas at high temperature the entire available density of states are excited. So, let us come back here once again. So, now we have this Debye T cubed law, it is time that we compared this with the experimental results.

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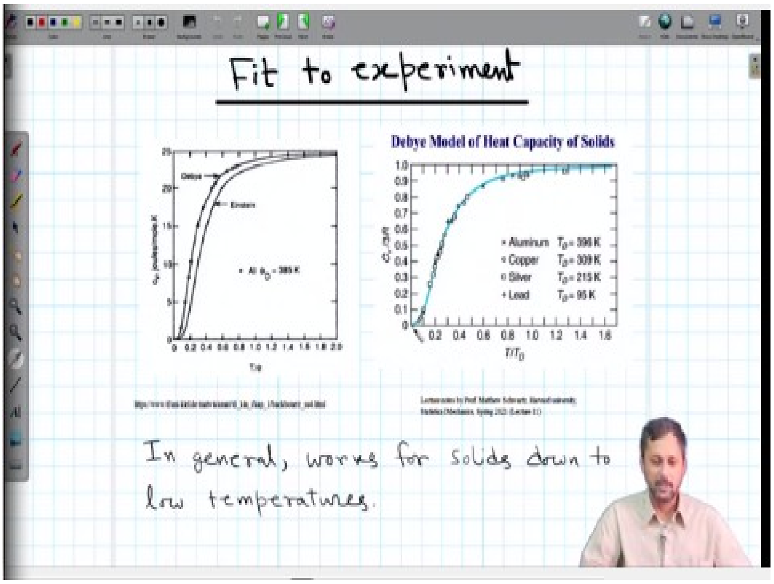

Fit to experiment

In general, works for solids down to low temperatures.

So, I have found out this from these sources; the sources are also mentioned here. So, the right hand side this is actually a lecture note by Professor Matthew Stewart of Harvard University. And the left hand side I found it from this internet source. So, here the specific data as a function of temperature is plotted as for aluminum. So, these dots are the experimental points we can clearly see the dots. Now there are two lines actually, one line that is due to Einstein's theory, see at high temperature side both are matching.

Of course the data is not there up to very high temperature, theta D is 385 Kelvin which is a 85 degrees centigrades above normal room temperatures almost like little over 100 degrees centigrade. So, the data it seems it is up to 0.8, so roughly up to room temperature the data is available but we can see that this entire data range is fitted very well with this Debye expression. So, all we have to do is, we have to choose an appropriate value of theta D for this fitting.

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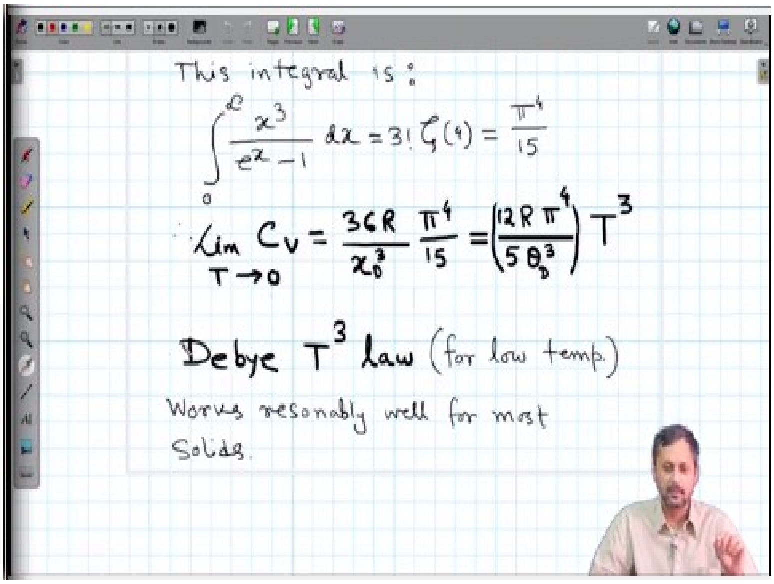

This integral is :

$$\int_0^\infty \frac{x^3}{e^x - 1} dx = 3!\,\zeta(4) = \frac{\pi^4}{15}$$

$$\lim_{T \to 0} C_V = \frac{36R}{x_D^3} \frac{\pi^4}{15} = \left(\frac{12 R \pi^4}{5 \theta_D^3}\right) T^3$$

Debye T^3 law (for low temp.)

Worus resonably well for most Solids.

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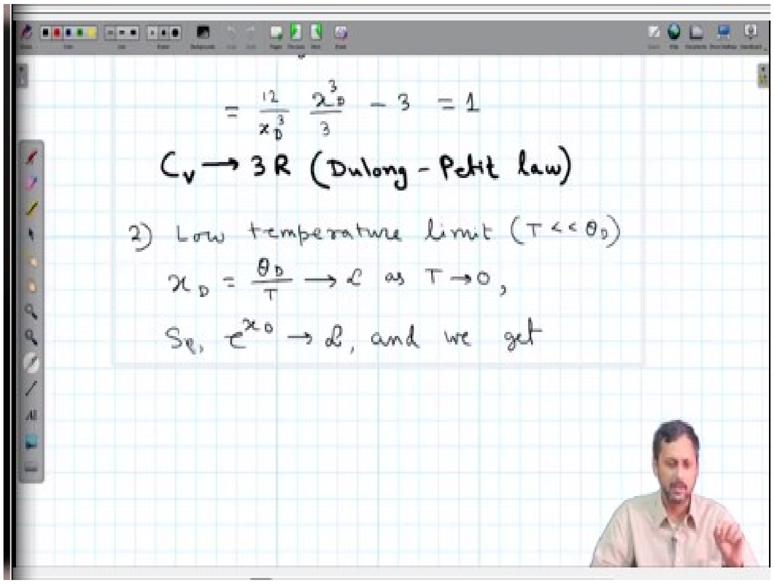

$$= \frac{12}{x_D^3} \frac{x_D^3}{3} - 3 = 1$$

$C_V \longrightarrow 3R$ (Dulong - Petit law)

2) Low temperature limit $(T << \theta_D)$

$x_D = \frac{\theta_D}{T} \longrightarrow \infty$ as $T \to 0$,

So, $e^{x_D} \to \infty$, and we get

And then this function can be numerically calculated in order to. So, once we know the value of x D this part is just a numerical number and this integration has to be evaluated. So, there are of course numerical tools for that. So, we do not need to compute it by hand, it can be done. So, that makes this fitting procedure easier. Now this is the data feed or the Debye function, similarly for Einstein function this is line.

So, what we see here is given that the Einstein temperature and Debye temperature is the same. Einstein fitting or Einstein model does not go to the experimental data. So, maybe if we have data in this high temperature regime some points will be falling on this Einstein line as well because at high temperature both convert to this 3R number which is the Dulong-Petit law essentially.

Now on the right hand side specific heat for aluminum, copper, silver and lead has been plotted and it is please look at the x scale, x scale is not in Kelvin but it is in the reduced form. So, that is E by theta D whatever is the value of theta D if we take the ratio of that this is a reduced scale where there is no unit. So, this is a representation by which we can bring the data points from taken over different temperature ranges together.

So, we see that all 4 of aluminum, copper, silver and lead which has different values of the Debye temperature. And of course you can see that Debye temperature for aluminum here is 396 Kelvin, whereas here it is 385 which is slightly different but it happens. Some people sometimes two different dataset will have slightly different values of the Debye temperature. So, it is within the experimental error I would say, these are correct.

So, all this 4, see it is 396 Kelvin whereas for lead it is 95 Kelvin, so there is a wide distribution of values. But once we go to this reduced scale everything can be plotted into the same curve and for all what we see that in general for solids at least for metallic solids down to a low temperature the fit is appreciative good. Now does it mean that Debye theory is perfect? No, it does not mean that Debye theory is perfect.

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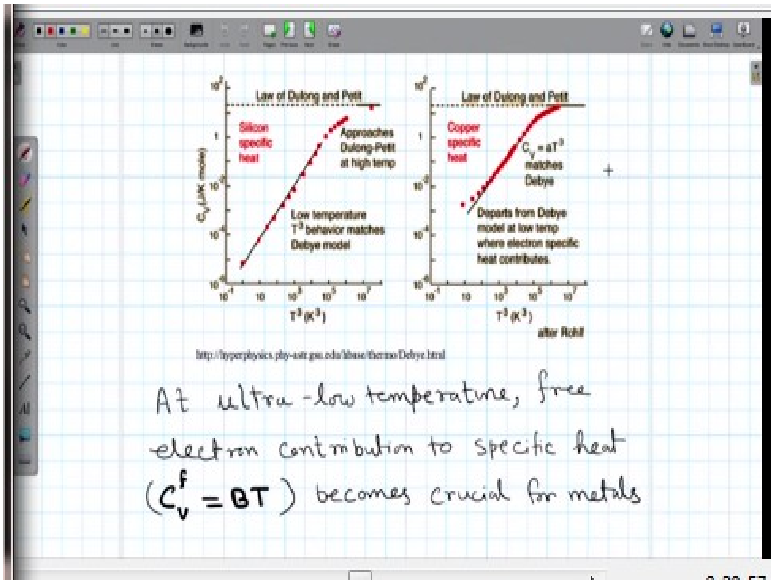

http://hyperphysics.phy-astr.gsu.edu/hbase/thermo/Debye.html

At ultra-low temperature, free electron contribution to specific heat ($C_v^f = BT$) becomes crucial for metals

Especially at very low temperature we see some deviation, this is another example. For example, if we take, so here it is a slightly different plot, please remember this is direct temperature and not a reduced temperature scale. But it is plotted C v versus T cubed because if C v depends on third power, then if we plot C v versus T cubed that should be a straight line, specially at low temperature.

So, that exactly happens, we see that at low temperature side which is this is 10 Kelvin, this is 1 Kelvin, this is 0.1 Kelvin. At very low temperature the T cubed behavior is well established from this fitting the straight line fitting and this is for silica. But when we look into this data for copper which has, so basically around below 100 Kelvin, this is the 100 Kelvin mark, below 100 Kelvin we can see that in this particular representation there is a deviation from this T cubed law.

So, this deviation because what is the difference? Silicon is a semiconductor, indirect band gap, whereas copper is a metal. Now it so happens that in metal at low temperature there is a contribution to specific heat that is coming from the free electron and this is basically a linear temperature dependence. So, B is a constant, so C v do to free electron F the suffix is for free electron is B times T, B being a constant.

And we see that there is a linear portion of this plot here and this is nothing new once again this is also known for many years now. So, this is where the Debye theory I would not say it fails but it fails to predict this particular behaviour. But of course it can predict the T cubed behaviour pretty accurately. And there are corrections I have already talked about one correction by Born and what was it?

If you remember 1 approximation by Debye is that longitudinal and transverse wave both has the same exact same cutoff frequency which is nu D. But Born says no, different waves will have different types of waves will have different types of cutoff frequency, so that is 1 correction. And which was further modified by other scientists but finally the theory of specific heat which is actually what we have discussed here is only the beginning of it.

This continues to be an advanced topic and this further discussion on this is beyond the scope of this lecture. So, we will stop here, I will just give, so whatever I have given you I have, so I will stop to discuss the theory here basically, of course we will do some problems next. So, what I have shown you is that Debye T cubed law is valid for most of the solids down to a moderate temperature and at very low temperatures there is a deviation which is due to the specific heat contribution of free electrons specially in metals.

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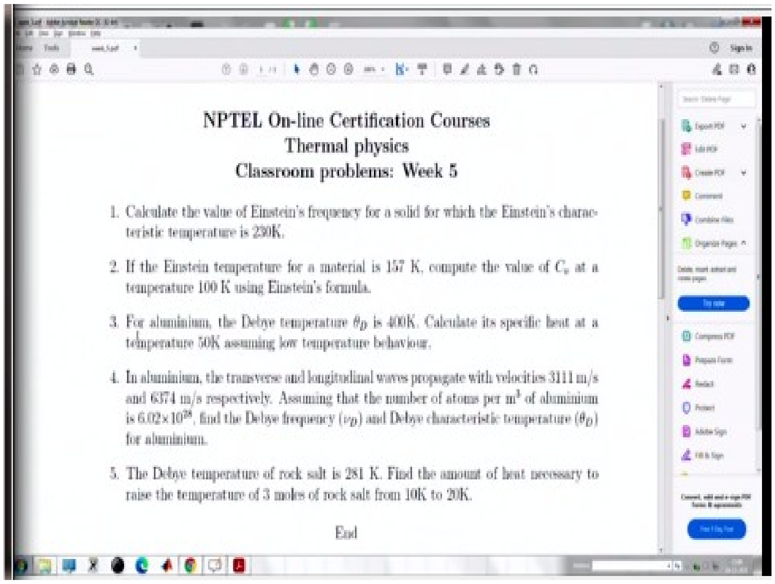

NPTEL On-line Certification Courses
Thermal physics
Classroom problems: Week 5

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 K, compute the value of C_v at a temperature 100 K using Einstein's formula.
3. For aluminium, the Debye temperature θ_D is 400K. Calculate its specific heat at a temperature 50K assuming low temperature behaviour.
4. In aluminium, the transverse and longitudinal waves propagate with velocities 3111 m/s and 6374 m/s respectively. Assuming that the number of atoms per m^3 of aluminium is 6.02×10^{28}, find the Debye frequency (ν_D) and Debye characteristic temperature (θ_D) for aluminium.
5. The Debye temperature of rock salt is 281 K. Find the amount of heat necessary to raise the temperature of 3 moles of rock salt from 10K to 20K.

End

Now let us look at some problems from this problem set. So, first and second problem we have already done let us look at the third problem. So, for aluminum the Debye temperature theta D is 400 Kelvin, once again it is slightly different from what we have shown in the dataset it is 385,

396. So, I have just taken 400 Kelvin for the problem. Calculate it specific heat at a temperature of 50K assuming low temperature behavior.

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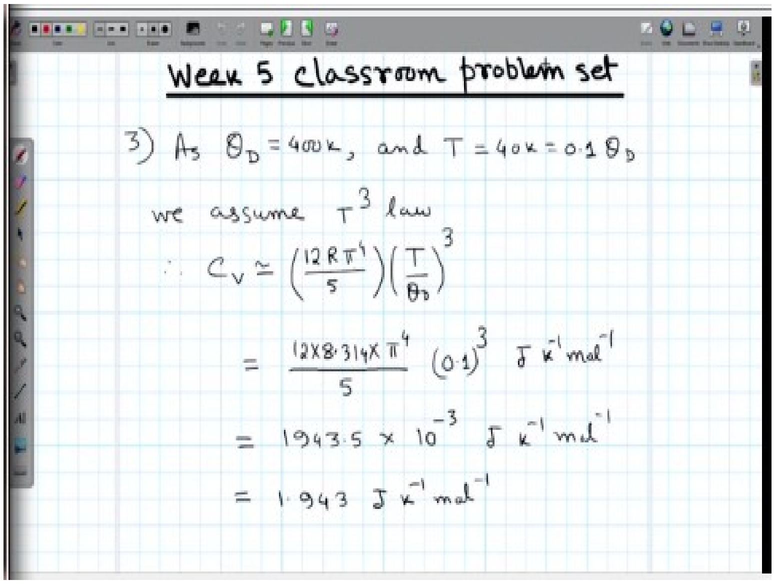

Week 5 classroom problem set

3) As $\theta_D = 400\,K$, and $T = 40\,K = 0.1\,\theta_D$

we assume T^3 law

$$\therefore C_v \simeq \left(\frac{12R\pi^4}{5}\right)\left(\frac{T}{\theta_D}\right)^3$$

$$= \frac{12\times 8.314\times \pi^4}{5}(0.1)^3 \ J\,K^{-1}\,mol^{-1}$$

$$= 1943.5 \times 10^{-3} \ J\,K^{-1}\,mol^{-1}$$

$$= 1.943 \ J\,K^{-1}\,mol^{-1}$$

So, all we have to do is, we have to go back to this relation here which is this one. So, once theta D is specified this whole term inside the parenthesis is a constant. So, all we have to do is, so what I have done here? I have taken theta D outside the parenthesis. So, this is 12R pi to the power 4 by 5 which is a constant anyway, for any system theta D varies. And I did the calculation for 40 Kelvin, my mistake but the problem given for 50 Kelvin I will correct that.

So, let us read this as 40 Kelvin because this makes life easy. So, when T is equal to 40 Kelvin, theta D is equal to 400 Kelvin, then T by theta D is simply 0.1, T by theta D yeah, it is actually 0.1, yes, right, it is 0.1. So, all we have to do is, we have to compute this constant here and once we put the values we have 1943.5. So, this is a constant, please remember keep in mind 1943.5. So, we can simply write the relation as C v is equal to 1943.5 times T by theta D whole cubed.

And then we put 0.1 cubed which is 10 to the power minus 3, so finally, we have 1.943 Joules per Kelvin mole inverse, correct. So, for problem number 4 in aluminum the transverse and longitudinal wave propagates with velocities 311 meters per second and 6374 meters per second, respectively, so that means C l and C t is given. Assuming the number of atoms per meter cube of aluminum is 6.02 into 10 to the power 28, find the Debye frequency nu D and Debye characteristics temperature theta D.

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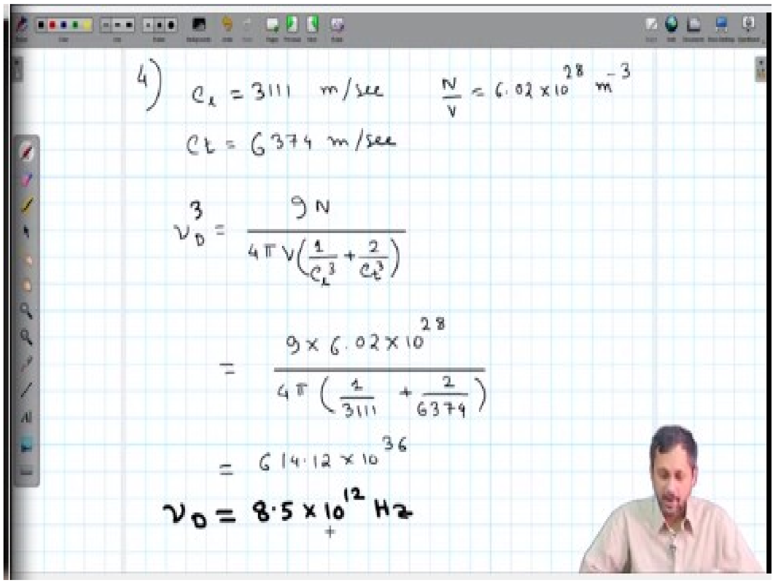

4) $C_l = 3111$ m/sec $\quad \frac{N}{V} = 6.02\times10^{28}\ \text{m}^{-3}$

$C_t = 6374$ m/sec

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

$$= \frac{9\times6.02\times10^{28}}{4\pi\left(\frac{1}{3111}+\frac{2}{6374}\right)}$$

$$= 614.12\times10^{36}$$

$$\nu_D = 8.5\times10^{12}\ \text{Hz}$$

So, in order to solve this problem we have to go back to this relation. So, C l is given, C t is given N by V is given, N by V is the number of molecules per unit volume. So, we have nu D is equal to 9N divided by 4 pi V 1 by C l cubed plus 2 by C t cubed. So, and N by V is already given a 6.02 into 10 to the power 28 and C l and C t values are given over here. So, once we put this numbers we get nu D is equal to 6 nu, this is my mistake, this is nu D cubed I think. Just quickly verify this, yeah nu D cubed, cannot be nu D. So, nu D cubed is equal to this. So, nu D is cube root of this which is 8.5 into 10 to the power 12 Hertz, straightforward.

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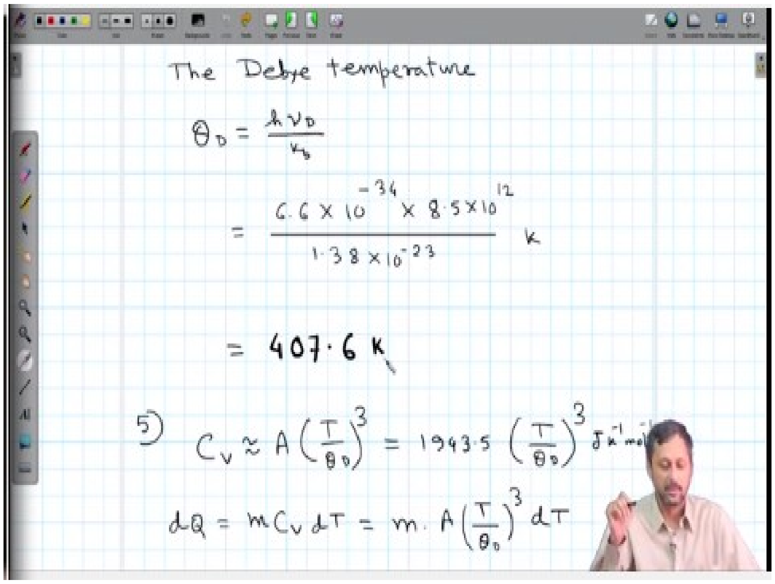

The Debye temperature

$$\theta_D = \frac{h\nu_D}{k_b}$$

$$= \frac{6.6 \times 10^{-34} \times 8.5 \times 10^{12}}{1.38 \times 10^{-23}} \text{ K}$$

$$= 407.6 \text{ K}$$

5) $C_v \approx A\left(\frac{T}{\theta_D}\right)^3 = 1943.5 \left(\frac{T}{\theta_D}\right)^3 \text{ J K}^{-1} \text{mol}^{-1}$

$$dQ = mC_v\,dT = m \cdot A\left(\frac{T}{\theta_D}\right)^3 dT$$

And the other part is also very straightforward because the Debye temperature theta D is equal to h nu D divided by k b. And we simply put h is equal to 6.6 into 10 to the power minus 34 and we have 8.5 into 10 to the power 12, that is from the previous calculation and of course the value of k b is there, once we put it together we get 407.6 Kelvin. So, once again we get another value of nu D for aluminum.

So, it really does not matter because these calculations it only shows you, so what we have got here is not the experimentally measured value. But that this value of theta D is calculated from the elastic coefficients. Please remember in order to measure this speed there has to be a knowledge of elastic coefficients. So, it is a different type of measurement, one way of measuring theta D is from direct experiment.

Direct experimental measurement of C v and then fitting this data with Debye function for this entire temperature range, then we can get one value of theta D. So, why I chose this problem, because this actually gives you an alternative way of measuring theta D from the elastic coefficient. So, I have not discussed what is the connection of elastic coefficient and C l but some of you already know from your general physics textbook that these are elastic coefficients are correlated with this transverse and longitudinal velocity.

So, this is an alternative derivation and we get a value of 407.6 which once again in my opinion is somewhat close to the experimentally measured values of either 385 or 396 Kelvin, correct. So, the last problem is a slightly different problem, the Debye temperature of rock salt is 381 Kelvin. Find the amount of heat necessary to raise the temperature of 3 moles of rock salt from 10 Kelvin to 20 Kelvin. So, that means the functional form of C v is given.

So, once we know Debye temperature what we can do is, we can simply use this relation, this factor 1943.5 times T by theta D in order to calculate the functional form. So, theta D is some constant, so let us do it. So, what is C v? C v is equal to 1943.5 T by theta D whole cubed and dQ the amount of heat that is transferred when the temperature is changing by dT is m C v dT, where m ok I should actually write it is in terms of the M.

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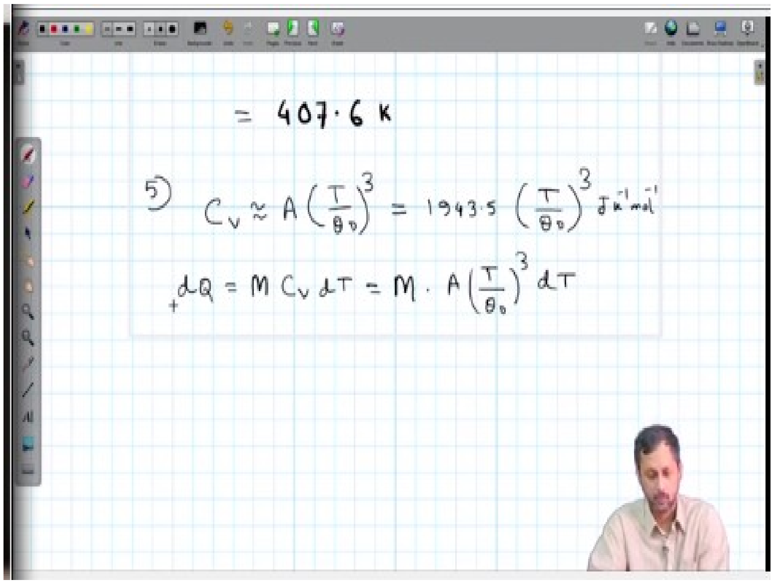

$$= 407 \cdot 6 \text{ K}$$

5)

$$C_v \approx A\left(\frac{T}{\theta_D}\right)^3 = 1943 \cdot 5 \left(\frac{T}{\theta_D}\right)^3 \text{J K}^{-1}\text{mol}^{-1}$$

$$dQ = M C_v dT = M \cdot A\left(\frac{T}{\theta_D}\right)^3 dT$$

Because this is molar mass M, that will be more accurate, technically more correct. So, it is M times A times T by theta D whole cubed dT, dQ is equal to.

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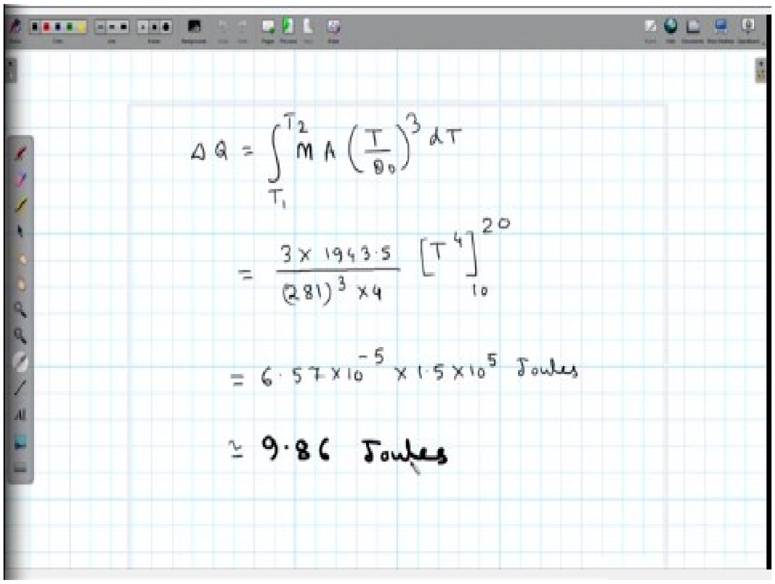

$$\Delta Q = \int_{T_1}^{T_2} M A \left(\frac{T}{\theta_D}\right)^3 dT$$

$$= \frac{3 \times 1943.5}{(281)^3 \times 4} \left[T^4\right]_{10}^{20}$$

$$= 6.57 \times 10^{-5} \times 1.5 \times 10^{5} \text{ Joules}$$

$$\simeq 9.86 \text{ Joules}$$

Now in order to calculate the total heat change to our total heat exchange, we have to perform this integration which is dQ is equal to T 1 to T 2 M, okay once again this should be M but I hope you understand that M times A times T by theta D whole cubed dT. Now this integration will give you, so theta d cubed will come out here. So, we have 3 that is for the molar mass, 1943.5 is the factor which is A, 381 whole cubed times this will be T to the power 4 by 4, 4 comes here.

So And the integration limits are 10 to 20. So, all we have to do is, we have to compute this quantity and compute this quantity and multiply those. This quantity happened to be 6.75 into 10 to the power minus 5. And of course here we are assuming that this entire temperature range between 10 Kelvin and 20 Kelvin the T cubed behavior is valid. Of course we cannot take a very large temperature range.

Because this T cubed law, this particular form for C v is valid only over a limited low temperature range that we have to keep in mind. So, assuming that 10 and 20, I mean 10 Kelvin to 20 Kelvin is within that range, the final expression for the final amount of heat is 9.86 Joules. So, that is where we stop in today's lecture and I hope you have understood and you have realized the basic points which we are trying to convince for last 3 lectures. That is the specific use of solid and the theories behind specific heat of solid and we have solved some problems, so that we have a better idea on how to use these relations.

Now for next 2 lectures of this week, we will be discussing behavior of real gases, where we will see that under certain circumstances gases will deviate from it is ideal gas behavior. Or rather most of the time the behavior of a gas assembly is not ideal. So, we cannot use the ideal gas equation over a wide range of pressure and temperature. So, basically we have to find out an alternative way of representing writing the equation of state of a gas assembly. So, we will discuss that in next two lectures and hopefully this time will be sufficient for you to realize that what are the origins or what are the reasons of non ideal behavior of gases, till then thank you.