Thermal Physics
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Lecture-21
Topic-Specific Heat of Solids: Dulong-Petit Law and Einstein Theory

Hello and welcome back to this week 5 lecture of NPTEL course on thermal physics. Now for last previous week, we discussed about transport properties and Brownian motion. This week we will be starting from altogether different topic. So, for the first part of this week we will be talking about specific heat of solid. Now we have already discussed about specific heat in gases.

And we have found out that classical equipartition theorem is applicable whenever we have to explain the behavior of specific heat of gases. And we have seen that different types of degrees of freedom. For example, the translational degrees of freedom, the rotational degrees of freedom and the vibrational degrees of freedom unfolds at different temperature regime.

Now when it comes to the specific heat of solids, the situation is slightly different. Now because first of all the specific heat of solid people try to measure specific heat for quite some time, I mean the techniques the first generation colorimetric techniques were already established when the this kinetic theory was came into action I mean came into picture. So, around 1819 two French scientist Dulong and Petit, they have measured a specific heat for a variety of solids and came with a general observation.

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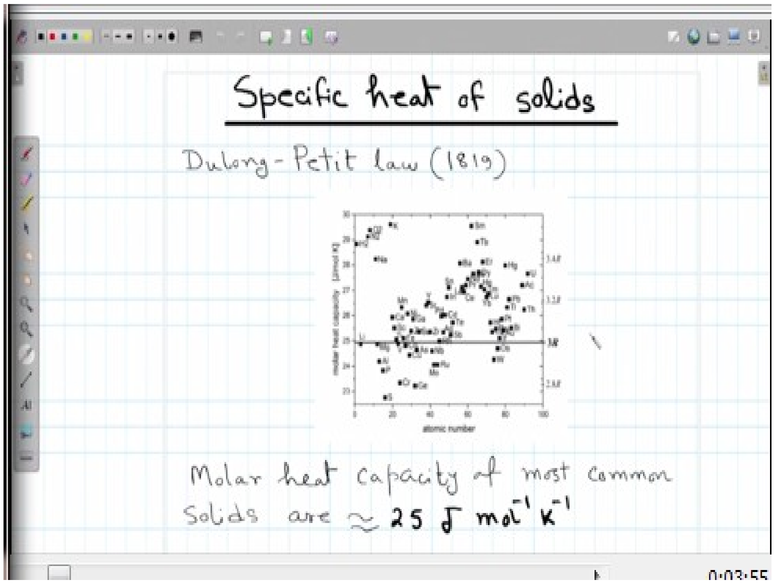

Specific heat of solids

Dulong-Petit law (1819)

Molar heat capacity of most common solids are $\approx 25 \text{ J mol}^{-1} \text{K}^{-1}$

So, let us start from there and then we will go into the more detailed theory. So, what Dulong and Petit originally saw in 1819 is this. So, they measured a variety of solids that specific heat for a variety of solids that also includes the solid oxygen and solid nitrogen, yeah. And so, it mostly what they have found out is the values are mostly concentrated around this 25 Joules per mole inverse per calorie per mole per calorie mark. I mean it is not exactly the mean value but it is somewhere around this number where all the specific heat of all the common solids are found.

Now at that time, the kinetic theory 1819 is where kinetic theory was not established. So, the concept of universal gas constant and all were not properly established at that time. It was already known probably I do not know exactly but it was before kinetic theory. So, later on it was found out that this 25 Joules per mole inverse per calorie inverse is very close to the value 3R, that meet 3 times the universal gas constant which is the numerical number is probably 24.9 Joules per mole inverse per K inverse but which are very close to each other.

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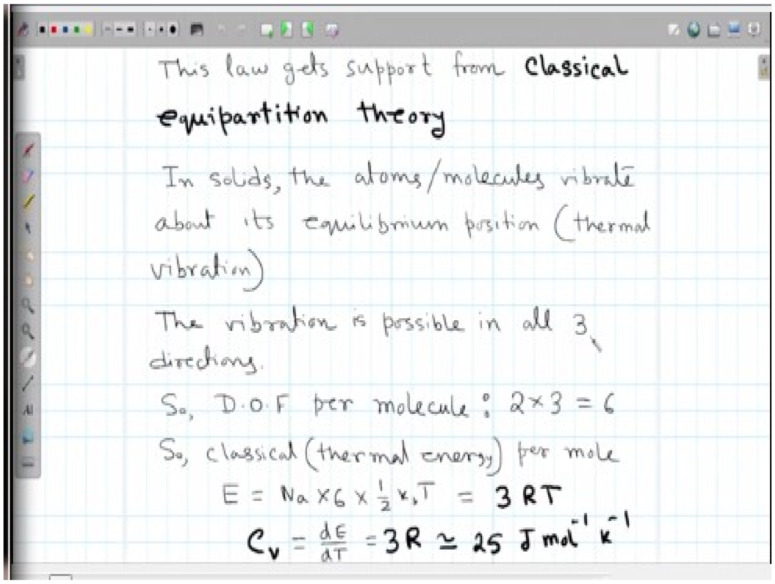

This law gets support from **Classical equipartition theory**

In solids, the atoms/molecules vibrate about its equilibrium position (thermal vibration)

The vibration is possible in all 3 directions.

So, D.O.F per molecule : $2 \times 3 = 6$

So, classical (thermal energy) per mole

$$E = N_a \times 6 \times \frac{1}{2} k_B T = 3RT$$

$$C_v = \frac{dE}{dT} = 3R \simeq 25 \text{ J mol}^{-1} \text{K}^{-1}$$

So, then once this correlation was made; classical equipartition theory was used to put give support for this Dulong-Petit law. Now what happens in a solid? In liquid or in gas in fluids for example, we have already seen that there are different types of movements possible, we can have translation, we can have rotation, we can have vibration, but what about in a solid material? In a solid material, there are the solid the atoms or molecules are fixed in their equilibrium position inside the lattice.

Even if for a disordered solid their position is not changing with respect to each other. Now, but one thing that is present there which is also commonly present in gas and liquid, that vibration, because of the available thermal energy the small, the tiny atoms or molecules they execute thermal vibration around their equilibrium or mean position. Now this is a very well known phenomena because atoms we know that for any finite temperature the atoms or molecules or any particle for that fact is bound to vibrate.

So, this vibration if we go by classical equipartition theorem, these vibration has three different directions, it can vibrate along x, y and z, that means three independent directions. So, all together and we know for one independent vibration, there are two normal modes that we have discussed in details already, so I am not going into the details of that anymore. So, three independent vibrations corresponds to six normal coordinates normal modes for that factor. So, each normal mode according to classical equipartition theory contributes total of half kT.

So, if we look at the thermal energy per mole of any solid from this classical equipartition theorem, we see this will be Na Avogadro's number basically that is the number of atoms or molecules per mole times 6, that is the number of degrees of freedom times half k b T which is again k b times N A is equal to R. So, E is equal to 3 RT, R being the universal gas constant.

So, if we compute the C v that is heat capacity for fixed volume, this is nothing but dE dT which is 3R which is very equal I mean almost equal to 25 Joules per mole inverse but calorie inverse which according to Dulong and Petit is the specific heat for most of the common solids as observed here. I mean look at the y scale, it is 3R, 3.4R, 2.8R, so, more or less in this region.

So, this is the phenomenological law that was proposed by Dulong and Pettit based on the observation. So, and later on the kinetic classical equipartition theorem which is also strongly correlated with the kinetic theory, it has found support from that law but is it universally true. First of all we see that they are not exactly classical equipartition theorem suggests that every specific heat of every solid should be exactly 3R and we already see there is a huge distribution. And classical equipartition theorems says nothing about the temperature variation of specific heat.

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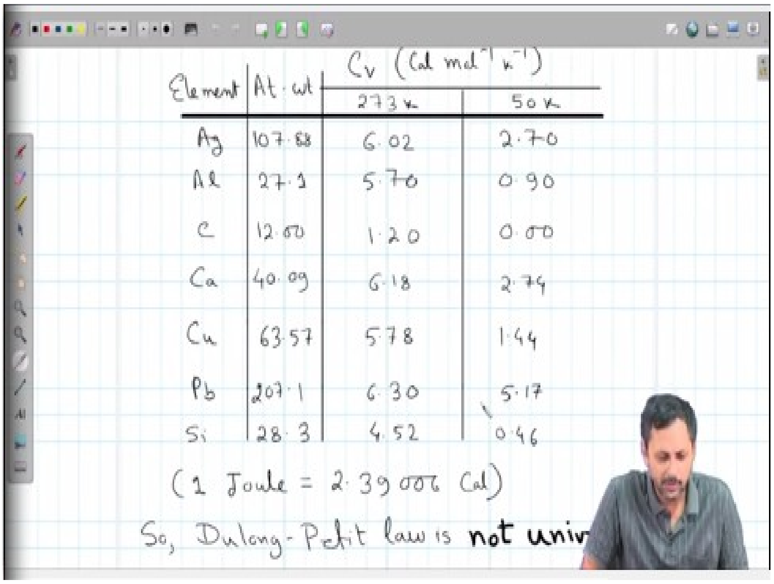

Element	At. wt	C_v (Cal mol^{-1} K^{-1})	
		273 K	50 K
Ag	107.88	6.02	2.70
Al	27.1	5.70	0.90
C	12.00	1.20	0.00
Ca	40.09	6.18	2.74
Cu	63.57	5.78	1.44
Pb	207.1	6.30	5.17
Si	28.3	4.52	0.46

(1 Joule = 2.39006 Cal)

So, Dulong-Petit law is **not univ**

Now when we look at the data and this data I have taken from a book actually one of the textbooks of this course. So, and this is given in calories per mole inverse per k inverse and the conversion between calorie and Joule is 2.39, so it can be easily converted to joules. So, that is well I am not exactly looking at that at this moment. So, now so what is important is? So, what is this 3R? 3R is approximately 6 calories. So, we see that for silver A g it is at 273 Kelvin it is almost 6 and at 50 Kelvin, it goes down to 2.7.

Similarly for aluminum which has a atomic weight of 27.1 in solid state at 273, the specification is close to 6, whereas that 50 Kelvin it goes down to 0.9. Carbon is even worse even at room temperature even at 0 degrees centigrade the specific heat Oh! by the way these measurements were at room temperature. So, approximately 20, 22, 23 degrees centigrade. Now here the temperature is mentioned clearly 273 and 50.

Here, I do not think it was mentioned, I have taken this from Wikipedia. I do not think it was clearly mentioned, it was just mentioned room temperature but we can always cross check that. So, now calcium for example, it is 6.18 which is expected to be around 6 but once again at 50 Kelvin it goes down. So, what we found out from this table that Dulong and Pettit law is not universal, for some atoms or molecules it is valid, close to 0 degrees Centigrade or room temperature.

For example, for silver, for aluminum, maybe for calcium, copper, lead, for this probably we are somewhere close. But even for those at low temperature there is a significant deviation, say except for lead when the measurement was carried out at 50 Kelvin, lead stay somewhere close to 5.17 which is OK I mean not very far from 6. But all other falls drastically from the value that is expected from classical equipartition theory.

So, we make 2 observations here, first of all that Dulong-Petit law is although it is a observational law, it is not universal by any means even at room temperature or higher temperature but at low temperature it fails miserably anyway. Now if I am not very Dulong-Pettit actually mentioned that in the statement of the law that the specific heat should be around this particular number at a high temperature.

But they have not defined what is high temperature you can call room temperature as high temperature, you can call 200 degrees Centigrade are high temperature. So, this is just a phenomenological observation, it has it is own importance because this was the first systematic observation and which was later supported by it was found out that it can be explained by equipartition theorem but in general this law has many loopholes.

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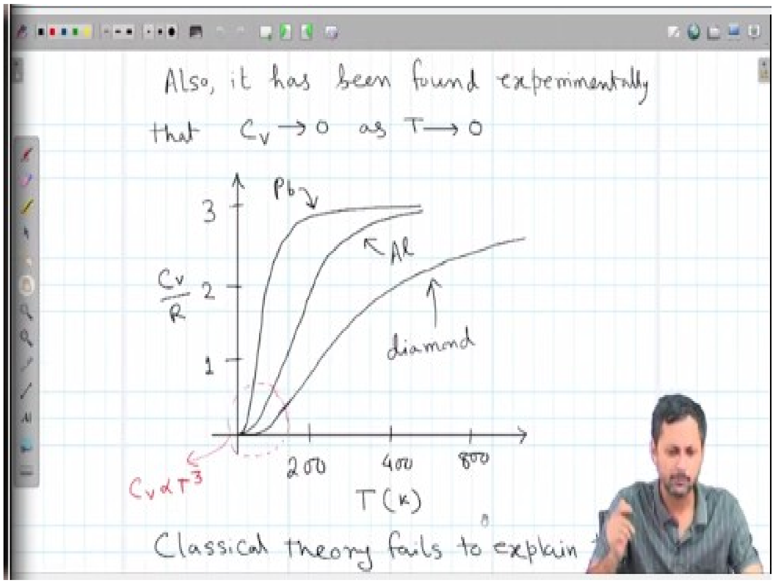

Also, it has been found experimentally that $C_V \to 0$ as $T \to 0$

Classical theory fails to explain

Now when we plot this we see something more interesting, we see that for all the solids, all the known solids, once again this is adapted from a textbook. So, for all the known solids, C v goes to 0 as T goes to 0. Now the slope of this curve or the change in C v with temperature is very different for different solids. So, that is why for diamond which is carbon actually the rate of increment is slow whereas for aluminum it is slightly higher for lead it is super fast as compared to diamond.

So, finally it all levels off, so we can see there is some kind of asymptotic behavior, so initially it starts slowly then it goes up and then it levels off. So, this leveling off is somewhere close to 3R, right, that is universal in nature but the temperature at which it levels off is actually different for different materials. So, what we gather from this is the temperature 273 Kelvin is already high for maybe for silver, may be for lead but it is not high enough for carbon that is what we have gathered.

Because if we look at the temperature variation probably carbon will also level off to this 3R value at a much higher temperature, If it is still stays in a solid form at that temperature, that is a different question altogether but we can see. And also see there is a change C v goes to 0 as T goes to 0. And this change if you remember in order to explain the specific heat of gases, we have also seen this systematic changes.

But that change was slightly different because that we can explain that up to a certain temperature the translational modes are activated. And then as the temperature goes up the rotational modes are activated. So, there is kind of a quantum jump but smooth not exactly quantum jump but it is a smooth transition but it is from one step to the other step. So, we have 1 step for 5 by 2R and then the next step is 7 by 2R, the next step is 9 by 2R like this, we have seen that for hydrogen.

But in here there is no such step, it is a smooth variation. So, the classical existing so those steps can be explained very easily by classical equipartition theorem because we can see that, okay. So, the translational modes and at higher temperatures the rotational modes at even higher temperature vibrational modes they systematically being activated. So, these are all explainable by classical equipartition theory but this type of a smooth variation what we see here is cannot be explained by classical theory.

Also a very interesting observation is at low temperature side at temperature which where it becomes almost close to temperature close to absolute 0, the variation is C v goes as T cubed. So, these are the two things and classical theory as I have already mentioned, classical theory has failed to explain this. So, we need to have a better theory in order to explain the specific heat of solids.

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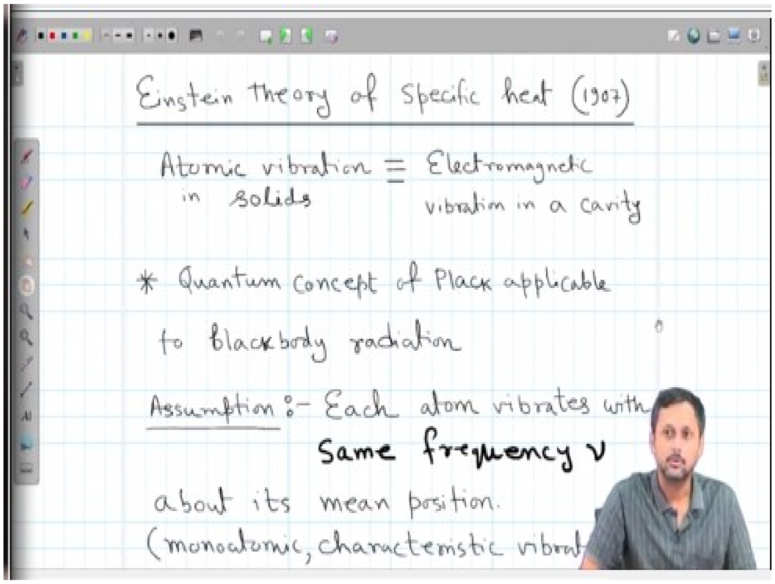

Einstein theory of Specific heat (1907)

Atomic vibration in solids ≡ Electromagnetic vibration in a cavity

* Quantum concept of Plack applicable to blackbody radiation

Assumption :- Each atom vibrates with **Same frequency ν** about its mean position.

(monoatomic, charactemstic vibrat

Then came once again the genius of Einstein. So, more and more we talk about this man more we realize why he is called a genius and probably the greatest physicist of all time. Between 1905 and 1907 how many theories from how many different fields he has worked on in physics is amazing. He has worked on we all know about his work on special relativity, in photoelectric effect. We recently learned about his theory on Brownian motion which is one of it is first fluctuation dissipation theorem.

Now we see that he also tried to explain the specific heat of solids in the lights of electromagnetic vibration in a cavity. So, basically he correlated the vibration in a solid, or the molecular vibe or atomic vibration in a solid with the electromagnetic radiation inside a blackbody radiation inside a cavity which is basically the Planck’s constant Planck’s treatment of blackbody radiation. So, what Einstein did was Einstein directly applied the Planck’s treatment to explain photoelectric Planck’s treatment of quantum of wave packet to explain the photoelectric effect.

In a similar manner, he also used the same concept in order to explain the heat capacity of solids. So, what Einstein assumed that each atom inside a crystal lattice or inside a solid oscillates with someone same characteristics frequency nu above about it is mean position. So, whatever may be the amplitude of vibration, he is not worried about that because according to the Planck's concept the amplitude does not matter, the energy is associated with the frequency of vibration, right.

And actually it was Planck to introduce the concept of quanta of energy h nu is the energy associated with the photon with the with frequency nu.

So, what Einstein suggested that it is a monoatomic characteristic vibrational frequency for associated which is the characteristics vibrational frequency for a given solid. So, 1 given solid every atom vibrates with the same frequency and that frequency is a characteristic of that particular solid. So, in carbon it will be some frequency, in lead it will be some other frequency, in aluminum it will be some other frequency but whatever it is, it is the same for all the atoms. So, that was his primary assumption.

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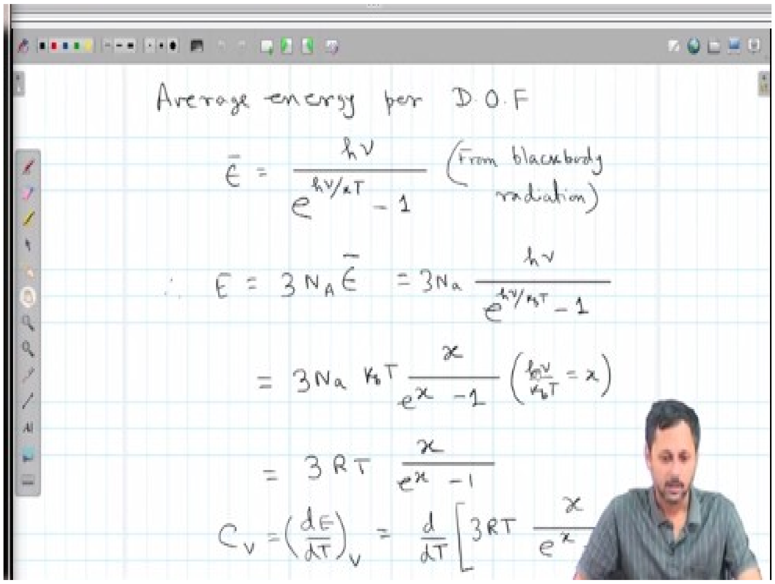

Average energy per D.O.F

$$\bar{E} = \frac{h\nu}{e^{h\nu/kT} - 1} \quad \text{(From blackbody radiation)}$$

$$\therefore E = 3N_A\bar{E} = 3N_a \frac{h\nu}{e^{h\nu/k_BT} - 1}$$

$$= 3N_a k_BT \frac{x}{e^x - 1} \quad \left(\frac{h\nu}{k_BT} = x\right)$$

$$= 3RT \frac{x}{e^x - 1}$$

$$C_v = \left(\frac{dE}{dT}\right)_v = \frac{d}{dT}\left[3RT \frac{x}{e^x\right.$$

Now once again if you are familiar with the concept of blackbody radiation, you know that actually Planck calculated the average energy per quanta and that was E bar which is given by E bar is equal to h nu by e to the power h nu by kT minus 1. So, I am not going into the derivation of this, this will be a different story altogether and towards if we have time to cover blackbody radiation in this course probably I will derive this relation for you but not right now.

So, and as we know that there are total of N a number of particles per mole and there are altogether 3N a modes of vibration because each atom can have 3 modes of vibration. Altogether there are 3N a times epsilon numbers of this is the total energy of the system. This is the total energy of the system. So, we can simply write it in a slightly different manner and this is 3N a k b T.

So, what we can do is, we can just introduce a k b T here and we can divide this h nu by k b T and we can write h nu by k b T is equal to x and then E is equal to 3 N A k b T x into e to the power x minu 1. Once again N a times k b is R, so we can write this as 3RT x divided by e to the power x minus 1. So, that is very straightforward the only assumption we have here is that energy per vibration is h nu by e to the power h nu by kT minus 1.

And finally we have 3. So, here actually what instead of putting degrees of freedom is 6 into half k b T. I think there is a confusion of a factor of half which I check in and discuss once again in the next lecture, maybe there is a factor of half that I have missed on. But anyway the analysis will not change. So, this is 3RT e to the power x into x divided by x minus 1. Now in order to compute C v, what we have to do is we have to take derivative with respect to temperature. So, this is d dT of 3 RT x divided by e to the power x minus 1. Now please remember x is a function of the temperature itself because x is what? x is equal to h nu by k b T.

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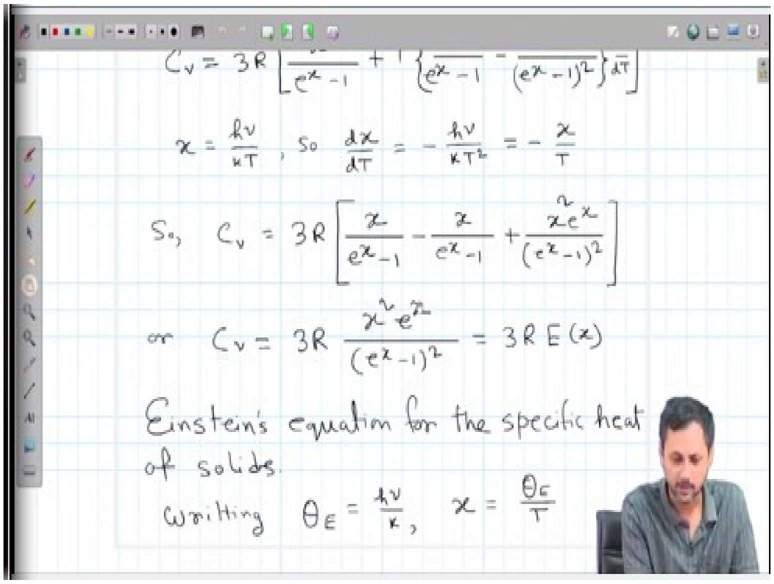

$$C_v = 3R\left[\frac{\quad}{e^x-1} + \left\{\frac{\quad}{e^x-1} - \frac{\quad}{(e^x-1)^2}\right\}\frac{\quad}{dT}\right]$$

$$x = \frac{h\nu}{kT}, \quad \text{So} \quad \frac{dx}{dT} = -\frac{h\nu}{kT^2} = -\frac{x}{T}$$

$$\text{So,} \quad C_v = 3R\left[\frac{x}{e^x-1} - \frac{x}{e^x-1} + \frac{x^2e^x}{(e^x-1)^2}\right]$$

$$\text{or} \quad C_v = 3R\,\frac{x^2e^x}{(e^x-1)^2} = 3R\,E(x)$$

Einstein's equation for the specific heat of solids.

Writing $\theta_E = \frac{h\nu}{k}$, $x = \frac{\theta_E}{T}$

So, this derivative will be 3R times x into e to the power x minus 1 plus T times 1 by e to the power x minus 1 x e to the power x e to the power x minus 1 square dx dT. Now what is dx dT? dx dT is minus h nu by kT square which is minus x by T. So, you substitute here my dx dT is equal to minus x by T and we get C v is equal to 3R x e to the power x minus 1 minus x divided by e to the power x minus 1 plus x square e to the power x divided by e to the power x minus 1 whole square.

So, once again you see the first 2 terms are identical, they cancel out nicely and what we are left with is C v is equal to 3R x square e to the power x e to the power x minus 1 square, which we call E x Einstein function and then C v is equal to 3R times x. So, this is the Einstein's equation for specific heat of solid. Now what we can do is if you look at it x is equal to h nu by k b T and we can define theta E which is equal to h nu by k, then we can write this x is equal to theta E by T.

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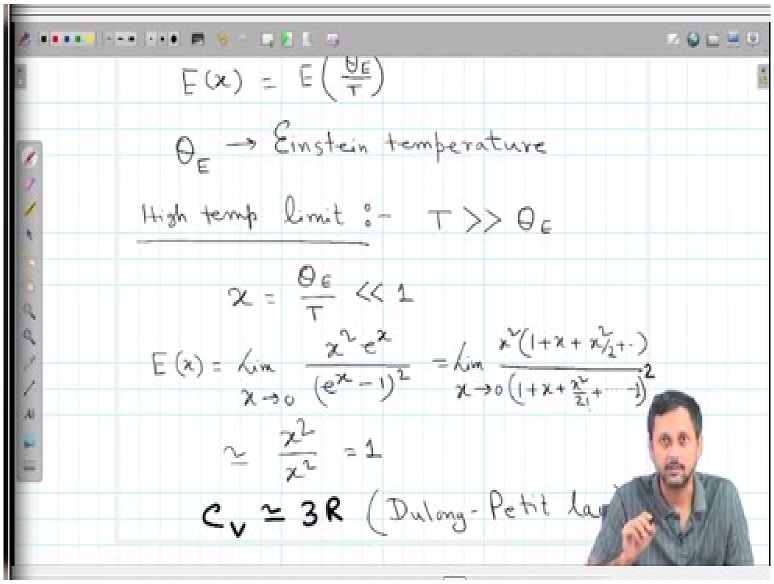

$$E(x) = E\left(\frac{\theta_E}{T}\right)$$

$\theta_E \rightarrow$ Einstein temperature

High temp limit :- $T >> \theta_E$

$$x = \frac{\theta_E}{T} << 1$$

$$E(x) = \lim_{x \to 0} \frac{x^2 e^x}{(e^x - 1)^2} = \lim_{x \to 0} \frac{x^2(1 + x + x^2/2 + \cdots)}{(1 + x + \frac{x^2}{2!} + \cdots - 1)^2}$$

$$\simeq \frac{x^2}{x^2} = 1$$

$C_v \simeq 3R$ (Dulong - Petit la

Then this Einstein function E x can be written as E of theta E by T, so theta is called the Einstein temperature. And it is not only the temperature, but it also discusses talks about a characteristic frequency. Because you see theta E is equal to h nu by k, h by k is a constant, h divided by k whatever the value of this that is a constant. Now nu is the characteristics frequency and this for different solids theta E will be different.

So, we will talk about theta E later, when we will be solving problems, so whatever we have got, so finally what we have got? We have got C v is equal to 3R times E x. So, let us examine the function E x in different limits. So, we take 1 limit when T is much, much greater than theta E then in that case x is equal to theta E by T which is much, much less than 1. So, E x is equal to limit x tends to 0 x square e to the power x divided by e to the power x minus 1 whole square.

Now when x is small what we can do is we can just expand the exponential function in power series of x and we can written terms only up to second order of x maybe not beyond that. That is a typical practice, sometimes we keep first order also but here first order will not help because we have already have an x square here. So, we have decided to keep up 2 terms of the order of x square. So, what do we have here?

We have x square times 1 plus x plus x square by 2 factorial actually it should be 2 factorial but 2 factorial and 2 factorial by 2 is the same thing, so 2 and 2 factorial is the same thing anyway. So, 1 plus x plus x square by 2 like this and in the denominator we have 1 plus x plus x square by 2 plus and then there is a minus 1, sorry the writing is not very clear, I hope you can see this there is a minus 1 here and there is a whole square, okay, let me try to just modify this a bit.

So, I think you can see it better now, so x square. So, for the upper series actually e to the power x does not contribute anything because we already have x square outside here. So, it will multiply with 1 will give you x square it will multiply with x will give you x cube, so only the first term will survive and we will have x square. Similarly there is a minus 1 here and there is a minus 1 here these 2 will cancel out and only the first term will survive.

Because only that itself will give you x square, the next term will give you x to the power 4 which is very, very small, so of course we can ignore that. So, it will be like approximately is equal to x square by x square is equal to 1. So, at very high temperature, what is high? High when the temperature T goes way beyond theta E the characteristics temperature which we call the Einstein temperature and that is the definition of high temperature.

So, now we can define a theta E for each solid and we can say whether the temperature of measurement is high or not with respect to this theta E. So, also it does not only give us a characteristic frequency but also gives us a reference temperature to work with for each solid.

So, we see that when E becomes, in the high temperature limit E becomes 1 and we have C v is equal to 3R which is nothing but the Dulong-Petit law.

So, we see the formulation of Einstein, it could actually explain the observation by Dulong and Petit that although it does not follow classical equipartition theorem. But at higher temperature higher as in high as compared to the characteristics temperature, it becomes equivalent to the result from the classical equipartition theorem which is given by Dulong and Petit. Next step is the low temperature regime. See what happens at low temperature? Look at this function at low temperature.

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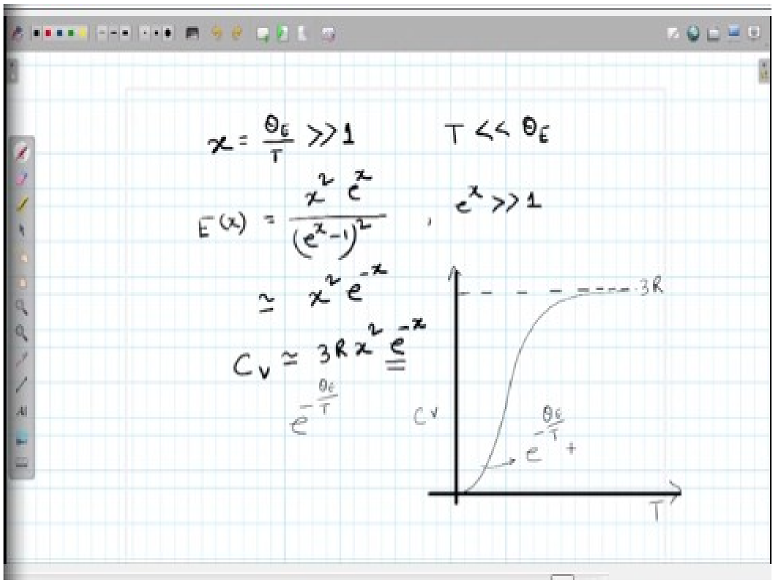

$$x = \frac{\theta_E}{T} >> 1 \qquad T << \theta_E$$

$$E(x) = \frac{x^2 e^x}{(e^x-1)^2} \quad , \quad e^x >> 1$$

$$\simeq x^2 e^{-x}$$

$$C_v \simeq 3R x^2 \underline{\underline{e^{-x}}}$$

$$e^{-\frac{\theta_E}{T}}$$

So, let me try to write this, at low temperature x will be, so T is much, much less than theta E. So, x is equal to theta E by T which is much much greater than 1. So, what happens to E x? E x we have x square e to the power x, so x square e to the power x divided by e to the power x minus 1 whole square. So, when this happens e to the power x becomes much, much greater than 1 and this can approximately written as x square e to the power minus x, why?

Because we have an e to the power x from here and we have, so this 1 can be ignored and we have e to the power 2 x from here, so 2x goes up, so we have x square e to the power x. So, C v goes as 3R x square e to the power minus x. So, this is what we get from the Einstein's theory at low temperature and let me tell you this is very wrong because here the dominant term is exponential. So, if I try to plot this as a function of temperature, so let us say this is 3R this is my 3R, so at high temperature it will follow the Dulong-Petit law it will be something like this, at low temperature it will fall much faster because it is falling exponentially, so this is falling as e to the power minus x.

See between x square and e to the power minus x of course e to the power minus x is the dominating term. So, that is where at low temperature and experimentally we have already explained that at low temperature it follows the T cubed behavior. And here what do we see? It follows an exponential behavior which is e to the power x means e to the power minus theta E by T. So, it follows exponentially decaying function of T.

So, which of course is not the case. So, this is my temperature, this is my C v and e to the power -theta E by T, so which is of course not correct. So, that is where the limitation of Einstein's theory comes into picture. And in the next lecture what we are going to do is, we are going to talk about another theory that explains that takes care of this discrepancy which is given by Debye few years after Einstein.

And tomorrow's lecture we will be talking about Debye’s theory on specific heat, how it circumvents the problem of this low temperature specific heat. And we will try to solve some problems regarding the Einstein theory and Debye theory of specific heat, so till then thank you and goodbye.