Statistical Mechanics
Prof. Ashwin Joy
Department of Physics
Indian Institute of Technology, Madras

Lecture - 31
Vibrations of Solids (Continuation)

Good afternoon students. Today we will proceed with the discussion of heat capacity at low temperature solid and model that I am going to discuss today is that of a Debye solid.

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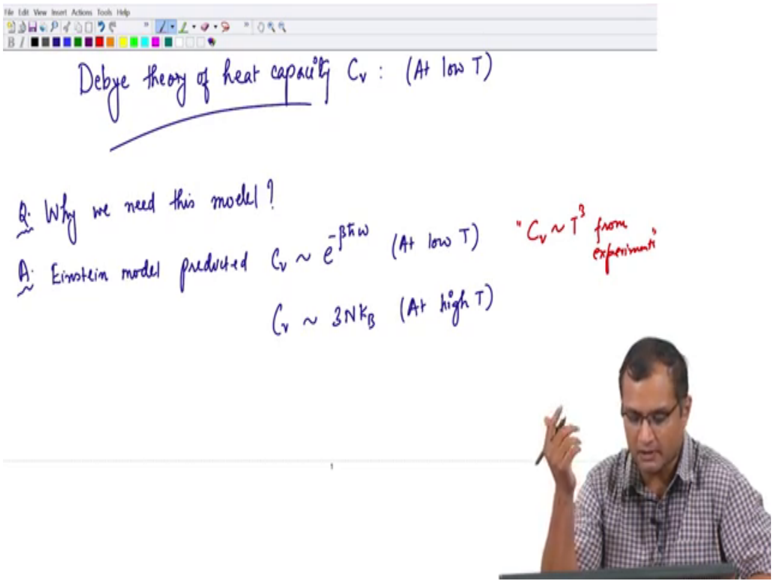

So, we will be discussing Debye theory or Debye model of a heat capacity and of course, the discussion would be limited to low temperatures. So, some of the questions: that I would like to ask here why we need this model? Well, the answer is basically the fact that the low temperature behavior predicted by the Einstein's model was not observed experimentally for most materials.

So, Einstein's model predicted if you recall the last lecture; predicted that the heat capacity has a exponential behavior at low temperature. As T goes to 0 in the heat capacity model predicted by Einstein; we saw an exponential decay to 0. The high temperature behavior was fine ok. So, where we saw that the heat capacity goes as 3 by 2 Nk B as T goes to infinity we saw that the heat capacity becomes a constant.

So, the low temperature behavior is something that is problematic because experimentally, I would say that the low temperature behavior is expected to behave as T cube from experiments.

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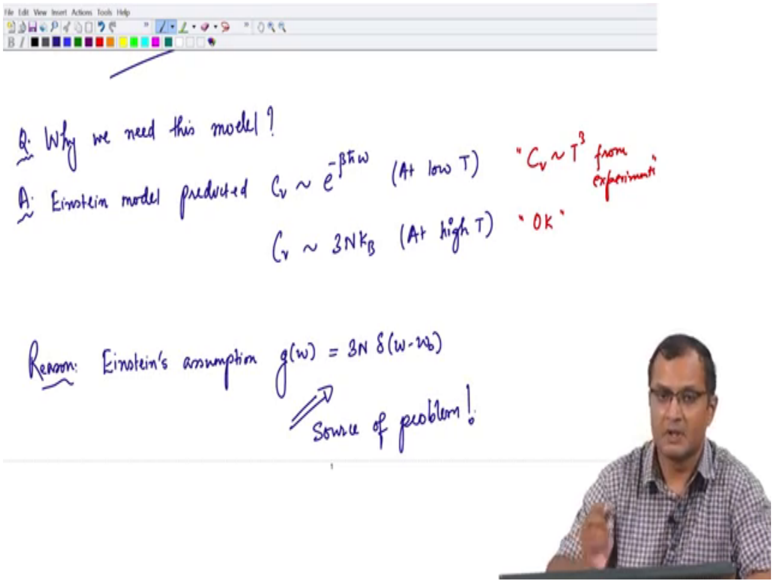

So, this is a; this is a problematic scenario that is that needs to be corrected and the reason why the low temperature behavior. So, the high temperature behavior is fine, but the low temperature behavior is not commensurate with experimental findings. And, the reason why we do not see and this e raised to minus beta h cut omega is because Einstein assumed a very simplistic assumption that the density of states is a direct delta distribution ok.

So, Einstein's assumption that all oscillators have the same frequency was the source of the problem. So, we need to correct that assumption that the density of states is basically a direct delta distribution meaning that all oscillators have the frequency omega naught is basically the source of the problem. So, this is the; I would say the source of the problem.

So, you cannot take all oscillators to have the same frequency. Especially at low temperatures when that is the regime of low energy excitations; you expect the oscillators or most of the oscillators to vibrate with low frequencies because h cut omega summed over all oscillators is the total energy and if energy is low you expect all those oscillators to be vibrating with low frequency or long wavelength oscillations.

Now, when that happens you need to allow for a density of states which preferentially becomes higher for low frequencies something like a 1 upon omega to the power 2. So, as the frequencies turn lower and lower you would find more oscillators with that frequency. So, Debye proposed a correction.

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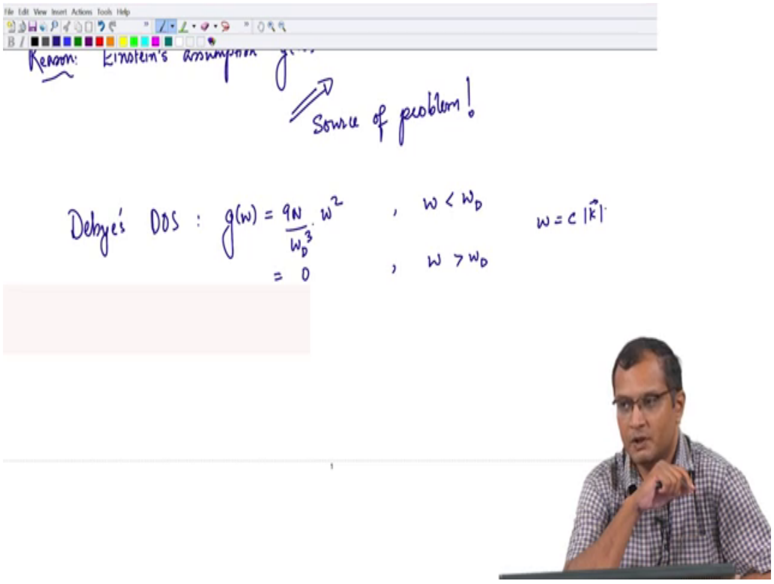

So, Debye's the density of states is basically more realistic and I want to have the density of states to have a dimensions of 1 upon omega. So, the most natural combination of the prefactors appears to be you know 9 N by omega D to the power 3 into omega square.

So, Debye's proposal is basically to take a density of states which goes like omega square over omega D cube. So, that the dimensions remain 1 upon omega and with this density of states you see that the calculation becomes slightly different and of course, Debye said that this density of states is only valid if the frequency is below the Debye frequency and it is equal to 0 if the frequencies exceed the Debye frequency.

So, the Debye is a frequency here in some sense corresponds to the wave vector of the Brillouin zone where you suddenly have no you know the entire frequency spectrum is cut off. So, which means you cannot have frequencies below omega D or you cannot have wave vectors above you know you cannot have frequencies above omega D or you cannot have their vectors above KD.

So, because omega here is nothing but you know C times K. So, since you are restricted to have a wave vectors below KD; you are also restricted to have frequencies below omega D. To show that the; to show why this is the form of density of states chosen by Debye, it is very simple.

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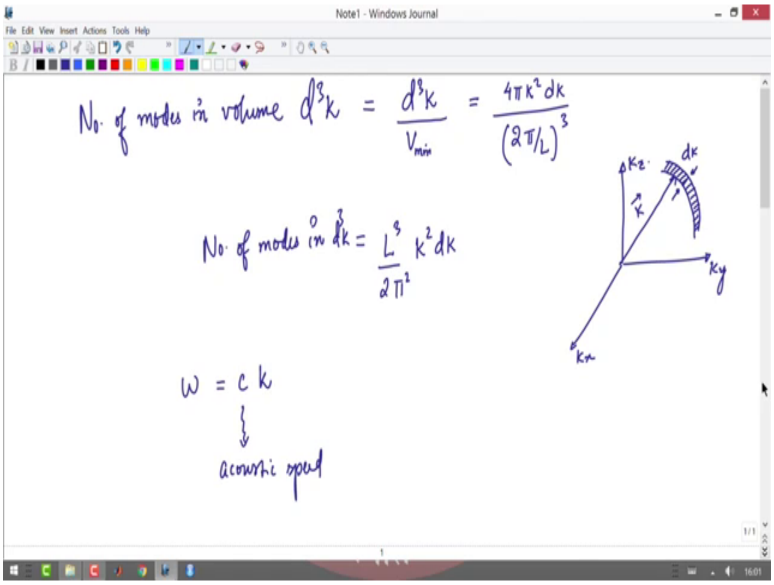

So, you look at the number of modes in the k space volume d cube k. So, number of modes in the volume d cube k is nothing but the volume divided by the minimum volume occupied in the k space. So, I will say it is minimum volume in the k space and the minimum volume that I can occupy is nothing but 2 pi by L to the power 3 and the k space volume element can be written as 4 pi k square which is the surface area times the thickness of the shell that gives me the volume element d cube k.

So, we can think of your k space as; some volume element, here is basically at some radius k and see if I take this as a vector k this 3D vector; its magnitude is mod k and this is my small shell of width dk ok. So, if I integrate over entire values of k going from 0 to infinity; k being the magnitude of the wave vector, magnitude will always be positive. I will get the entire same momentum space integrated.

So, then I can write this as simply L cube over 2 pi square into k square dk and I know that. So, this is the number of modes in d cube k and I know that the relationship between angular frequency and the wave vector is C times K where this C is nothing but the acoustic speed do not confuse it with the velocity of light.

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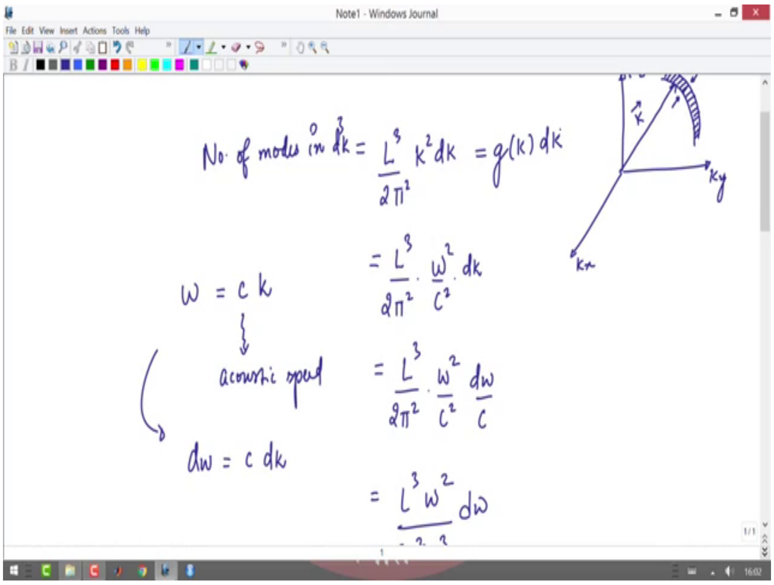

And I can then write down the number of modes as nothing but L cube by 2 pi square into k square can be written as omega square by C square and dk from here can be written as d omega by C ok. So, I can write this in turn as L cube over 2 pi square into omega square by C square and this is nothing but d omega by C.

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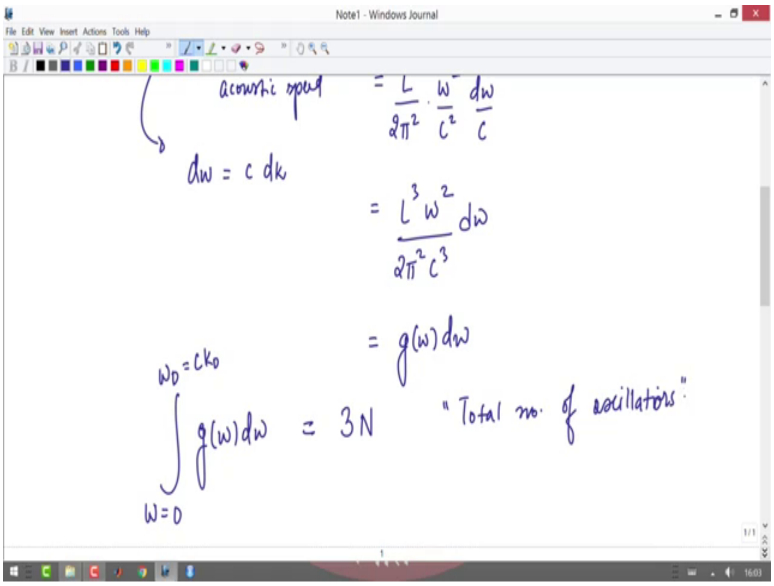

So, this is nothing but L cube omega square by 2 pi square C cube d omega and I know for sure that this is my density of states multiplied by d omega because the number of states are conserved. So, this is also equal to I can write this as g of k dk number of modes in the interval k and k plus dk or you can write it as a number of modes in the interval omega and omega plus d omega; number of modes is conserved and the conservation here is the simple understanding that if I take all the modes that has modes with frequency 0 upto the maximum mode that corresponds to the wave vector KD.

KD here is nothing but the wave vector corresponding the first Brillouin zone and if I integrate this g omega; well, it should give me nothing but the total number of modes which is 3 N. There are total 3 N oscillators in my system. N oscillators; each oscillator has 3 independent degrees of motion then eventually if I integrate g omega it should give me the total number of oscillators. So, that is 3 N total number of oscillators. What I am integrating is number of oscillators per unit frequency. So, when I integrate over all frequency it should give me the number of oscillators.

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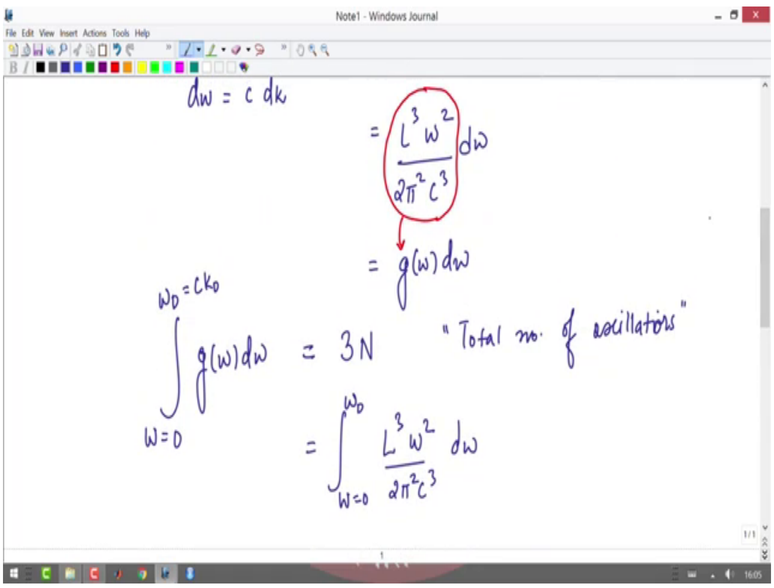

So, I can use the definition of g of omega from here. So, if I compare my you know g of omega with; if I substitute my g of omega with L cube omega square by 2 pi square C cube. So, I can write it as integral omega going from 0 to omega D L cube omega square by 2 pi square C cube; this is my g of omega into d omega.

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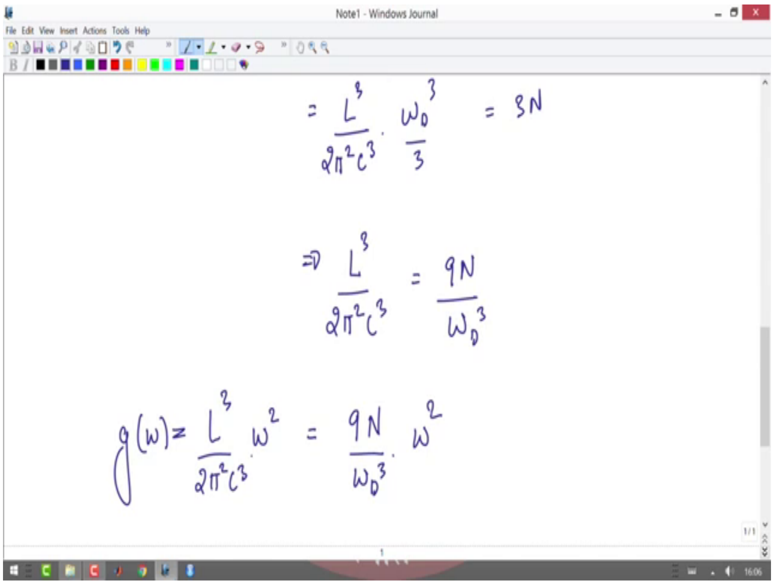

And that would be nothing but if I take all the constants outside this would give me L cube by 2 pi square C cube omega D cube by 3. Now this has to be 3 N as already established; number of modes is 3 N. So, then you can say that L cube over 2 pi square C square; C cube is nothing but 9 N by omega D to the power 3 and look at this; our g of omega is already L cube by 2 pi square C square into omega square. So, if I recall my g of omega from here; the thing that is underlined with which is encircled by the red color.

So, I can write it as L cube by 2 pi square C cube into omega square. So, just putting the value of L cube by 2 pi square C cube; I get g of omega is 9 N over omega D the whole cube into omega square.

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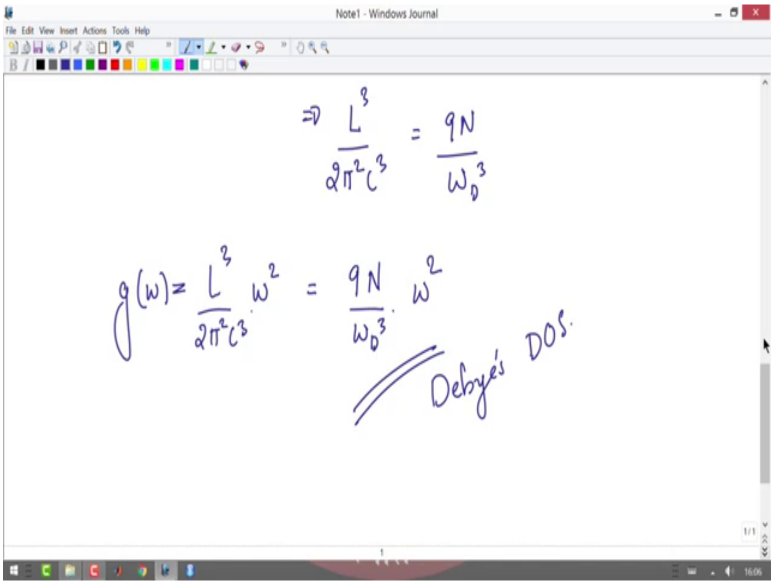

So, this is the expression of the density of states taken by Debye. Debye's density of states that is the origin; so, as I said the exact derivation is just given here to explain the point, but it is sufficient to see that the density of states goes as 1 upon omega and Debye's construction of this density of states has this derivation.

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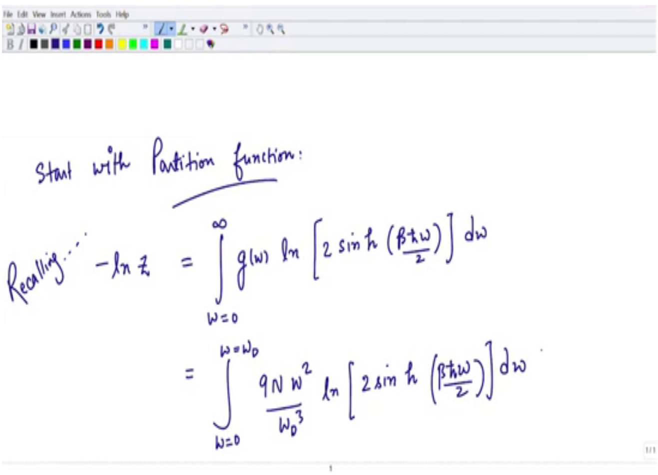

And you will start with the partition function ok. So, when you start with your partition function.

So, we can write down the partition function as negative ln z. Just look at your previous lecture for the partition function where we have taken the integral omega going from 0 to infinity; the density of states into ln of twice sine hyperbolic beta h cut omega by 2 d omega. But now if I am going to substitute g omega ok; so, this is the partition functions expression.

So, if I substitute the density of states provided by Debye you will see that this expression modifies in the sense that the upper limit will now not be infinity because you cannot have the frequencies above omega D. Because it is restricted to below frequencies; omega D so, your integral will now transform to integral 9 N omega square by omega D the whole cube and you have ln of twice sine hyperbolic beta h cut omega d omega.

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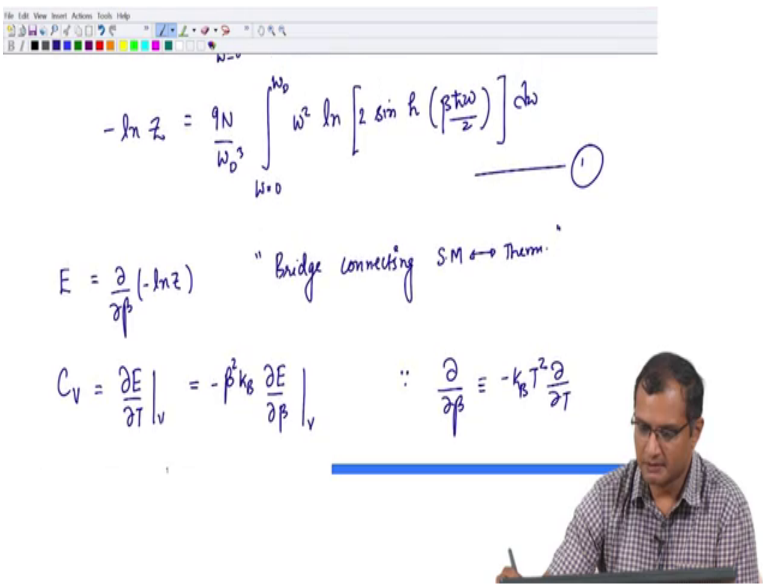

We can take out all these pre-factors and write down this as omega D cube integral omega going from 0 to omega D omega square ln twice sine hyperbolic beta h cut omega by 2 d omega.

Now, this is my negative ln z. So, instead of solving this integral which is not simple or straightforward because you cannot do integration by parts straight away; why not take the derivatives because this is an integral on frequency; I know for sure that my internal energy can be computed from the partition function by simply invoking this derivative. and from the internal energy.

And from the internal energy; so I know this is from the bridge that connects or the bridge connecting statistical mechanics to thermodynamics. So, I also know that my heat capacity at constant volume is dE by dT at constant volume; which means I can write down this as you know in terms of derivative with respect to beta this is like minus beta square kB dE by d beta at constant volume.

And this is because d over d beta can be visualized as minus kB T square d over dT. So, if I want to transform temperature derivative with respect to beta; you have to take the reciprocal of kT square that is beta square kB. Now let us put everything into one place. So, combining these three expressions I can write for heat capacity as minus beta square kB E is already d by d beta of this thing.

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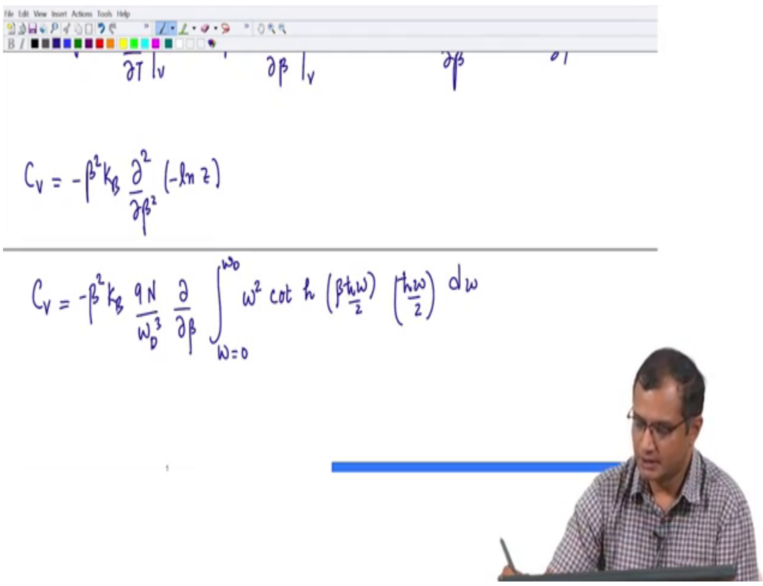

So, I am going to write it as d square by d beta square of minus ln z and simply plugging the expression for ln z from equation 1; I can get CV as minus beta square kB and I am going to bring out all those pre-factors which is 9 N by omega D cube. So, 9 N by omega D cube and I am going to write down d by d beta and take one derivative inside.

So, the first derivative would be so, I am going to take (Refer Time: 20:19) derivative that will give me simply omega square into different derivative of ln twice sine hyperbolic is nothing but cot hyperbolic beta h cut omega and I will have a pre-factor h cut omega by 2. Let us look at it; correct and then we can do one more derivative here.

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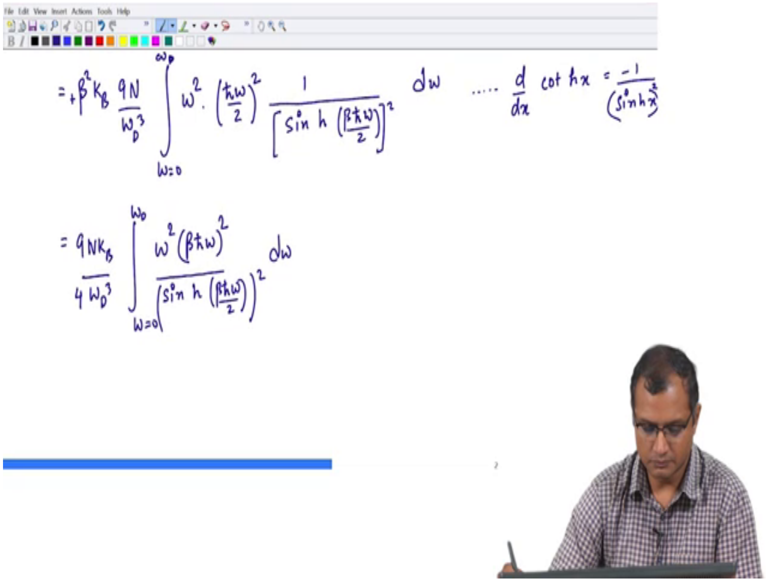

So, I can write it as minus beta square kB into 9 N by omega D whole cube. So, I can write it as omega going from 0 to omega naught omega D; this is omega D and this would be omega square into h cut omega by 2; derivative of cot hyperbolic is minus 1 by sine hyperbolic the whole square. So, that minus becomes plus here and I am going to write it as 1 upon sine hyperbolic beta h cut omega by 2 the whole square and again one h cut omega by 2 will come out.

So, it will become h cut omega by 2 the whole square where I have used the fact that d by dx of cot hyperbolic x is minus 1 by sine hyperbolic x the whole square. This is the result I have used. If you; if this confuses you; you can simply write it as ok; now if you proceed further.

I can write down 9 Nk B and what I am going to do here is the following; just going to rewrite a few things here and there. So, what I will do here is the following. I will take one beta square inside and I will take the factor 4 outside. So, this becomes 9 by 4 and I am going to write beta h cut omega the whole square divided by sine hyperbolic beta h cut omega by 2 the whole square d omega; is it ok?.

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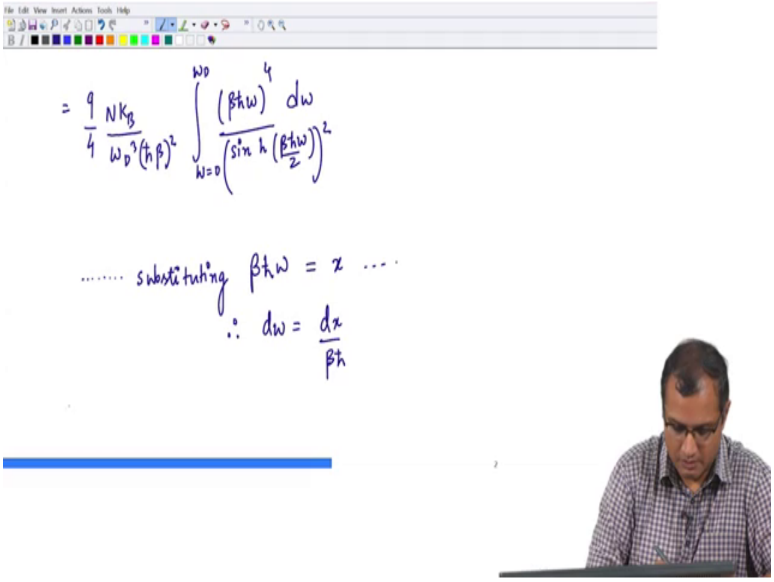

So, then I can also do one more thing here; I can since I have omega D cube here in the denominator. So, I am going to do something about it. So, that it becomes a nice prefactor a dimensionless pre factor; I can nondimensionalize it. So, what I am going to do here is the following. I can divide by h cut beta omega D the whole cube; which means I need a h cut cube beta cube. So, what I will do here is the following. I will take; no, what I will do here is the following. So, I will write down this; in fact, this is even simpler.

So, what I will do is; I will divide by h cut beta the whole square and then take one more combination of this dimensionless factor and call this as beta h cut omega the whole 4 and this will be an integral on sine hyperbolic beta h cut omega by 2 the whole square and I can write this as 9 by 4 Nk B over omega D whole cube into h cut beta the whole square and let me transform this integral in such a way that.

So, I am going to write down; so, just make a variable transformation. So, substitute beta h cut omega as some x. So, therefore, you can write down d omega as dx over beta h cut.

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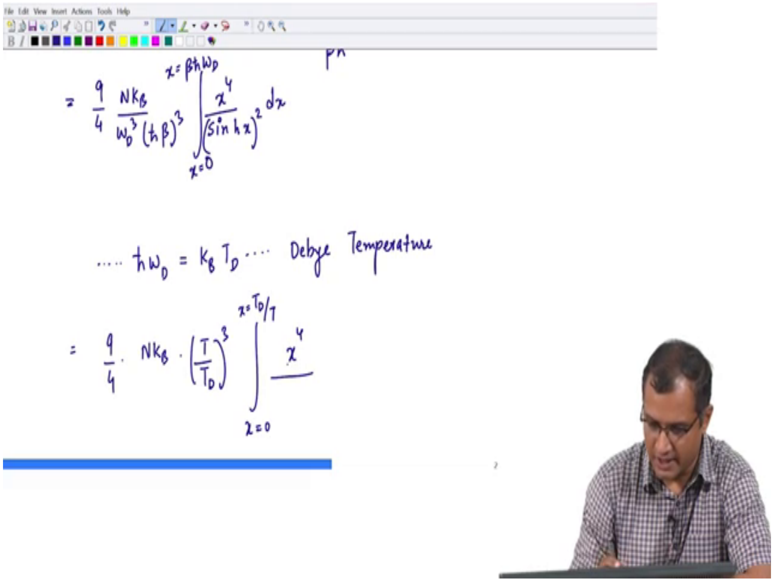

So, then this integral becomes you can write this as 9 by 4 Nk B over omega D the whole cube into h cut beta the whole cube and this integral becomes 0 to beta h cut omega D. So, when omega goes to omega D; x becomes beta h cut omega D and you will have x to the power 4 upon sine hyperbolic beta h cut omega by 2 the whole square dx and this can be written as 9 by 4 Nk B and I am going to introduce of another energy scale here. So, before I do that let me realize the fact that yeah.

So, this would be I just have to change it to sine hyperbolic x the whole square; absolutely. So, this is the limits are x going from 0 to x going to beta h cut omega D and then I am going to just realize that this energy scale h cut omega D; if I write it as some kB times Debye temperature; some; you know just realizing this energy scale the Debye temperature. Then we can write down this integral as simply 9 by 4 Nk B into T by TD the whole cube into x going from 0 to beta h cut omega D is nothing but TD by T; because h cut omega D is already kB TD. So, beta into kB TD is nothing but TD by T and the integral is over x 4 over sine hyperbolic x square.

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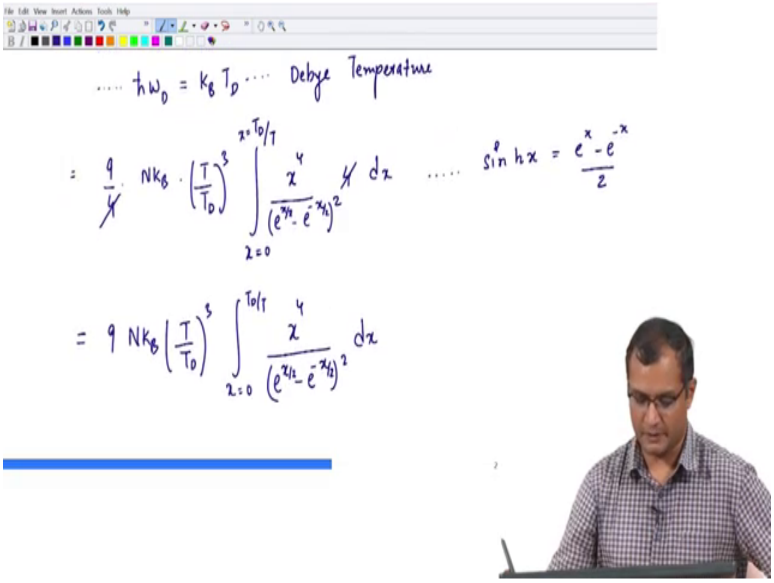

I am going to write it as e raise to x minus e raise to minus x the whole square by 4. So, I am knocking off this 4 with this 4. So, I have written sine as e raised to x minus e raised to minus x by 2. So, the square of sine hyperbolic will give me a factor of 4 in the numerator and that I can knock off.

So, now I have this integral which is 9 kB into T by TD to the power 3 and the integral on x goes from x equal to 0 to this ratio of Debye temperature over the temperature under consideration and that becomes this integral. So, I can actually write this integral slightly differently. So, I can; so, this there is a factor of; so, this is actually x by 2 because I substituted beta h cut omega as x. So, then I have to write everywhere. So, only the exponents here; nothing else changes; only the sine hyperbolic argument was x by 2.

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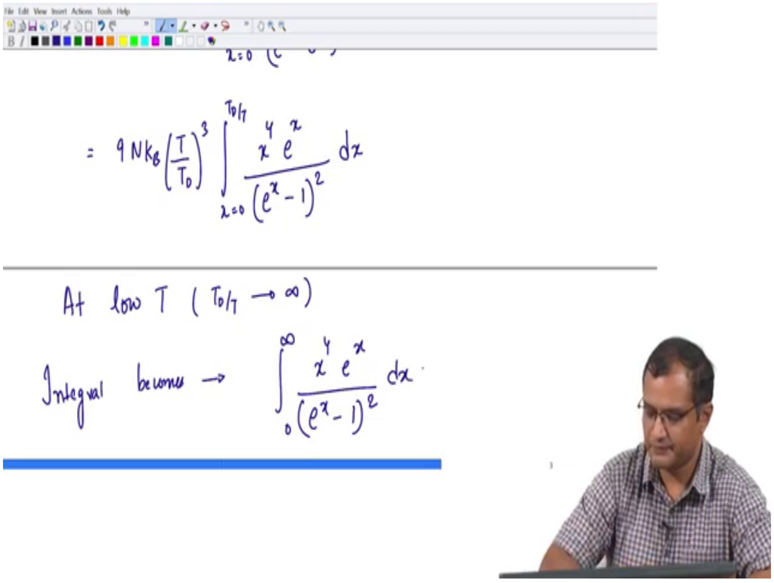

So, I can now write it as if I take e raise to x by 2 common; e raised to minus x by 2 if I take it outside from the denominator; this will simply go to the numerator as e raised to x and what you will have inside is e raised to x minus 1 the whole square dx and final step is basically to see that at low temperatures which is the regime of beta going to infinity.

So, what low temperature here would mean; I would take I have a reference scale here in the sense that I will take the ratio of TD over T going to 0; going to infinity which means if my the ratio of the Debye temperature over thermal temperature goes to infinity. Or, if the temperature under consideration is much smaller than Debye temperature; then I can approximate this integral 0 to infinity x to the power 4 e raise to x upon e raised to x minus 1 the whole square dx and this integral can be computed using a gamma function and a Riemann zeta function. I am going to discuss this only in the mathematical preliminaries as a separate lecture.

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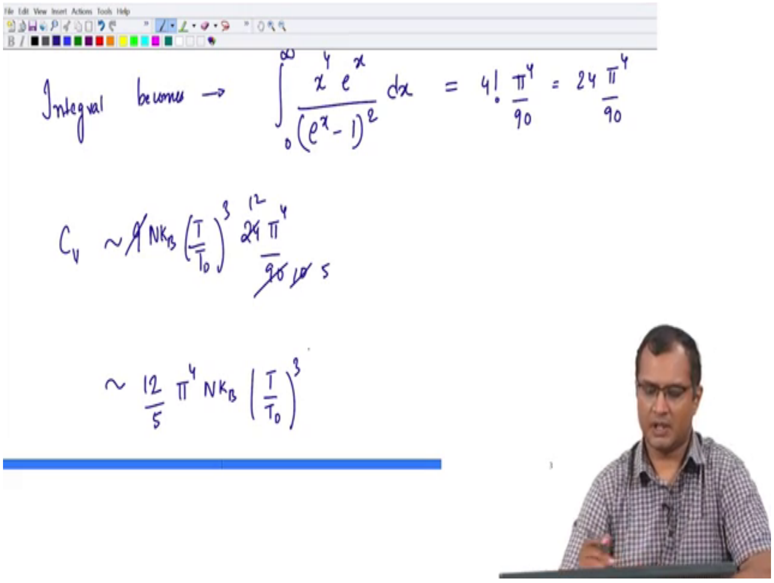

So, here I am just going to write down the answer to this integral which is the value of this integral is 4 factorial into pi by pi raise to 4 by 90. So, that is the value that I am going to substitute. So, this is nothing, but 24 by 90 and that is nothing but so, if you take this pre-factor and substitute in your heat capacity. So, this becomes at low temperature we already had a pre-factor of 9 kB T by TD to the power 3 and this integral was 24 pi to the 4 by 90.

And if you knock off the factors that cancel; this simply becomes we can knock it off and so, this is roughly 12 by 5 into pi raised to 4 Nk B to the power T by TD to the power 3. So, as you can see this behavior if you do not care about these pre-factors this behavior is nothing but to T cube behavior.

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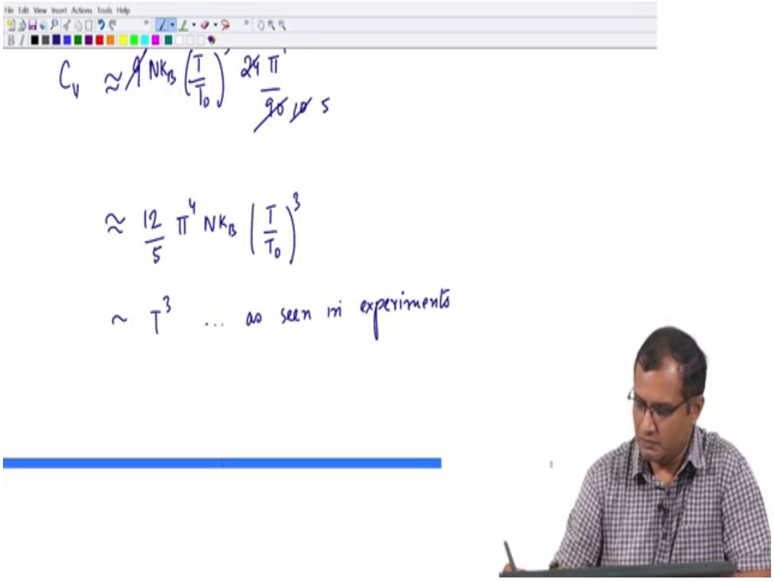

You know as expected or as seen in experiments. So, Einstein's model which failed to capture this T cube behavior of heat capacity is resolved in Debye's model where you see at low temperatures the T cube behavior. Now at high temperatures Debye model also predicts heat capacity that becomes constant and becomes 3 Nk B which can be seen.

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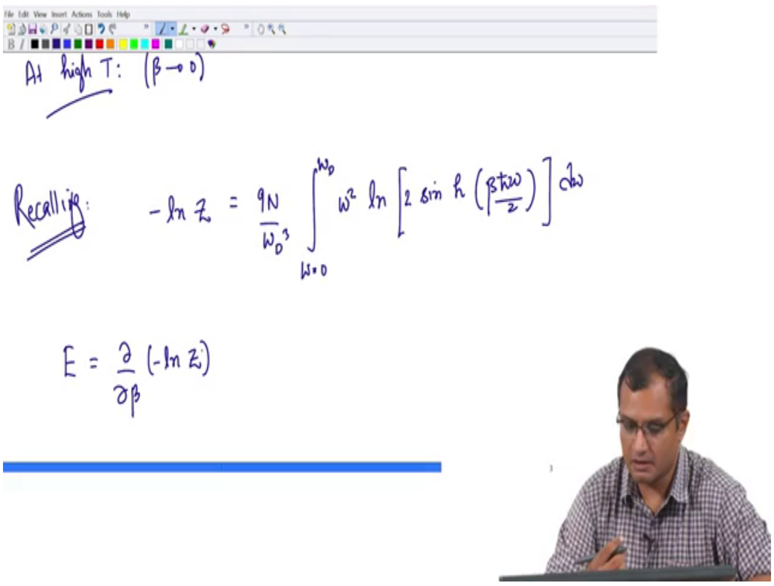

So, we have to; you know it is necessary to invoke both the low temperature and high temperature behavior. So, the high temperature behavior is basically the limit beta going 0 or infinite. So, when I say high temperature; I do not need a reference scale here in the sense I can take the temperature tending to infinity much much larger than your Debye temperature. So, that can be seen by looking at your; by looking at your partition function here.

So, here if you take this expression of your partition function; so, recall that this is your partition function and from here I can recover the high temperature behavior. So, what I am going to do here is; first take the derivative with respect to beta. So, the energy is given as d over d beta of the negative logarithm of partition function this is from the statistical mechanics. So, let us take the derivative here with respect to beta.

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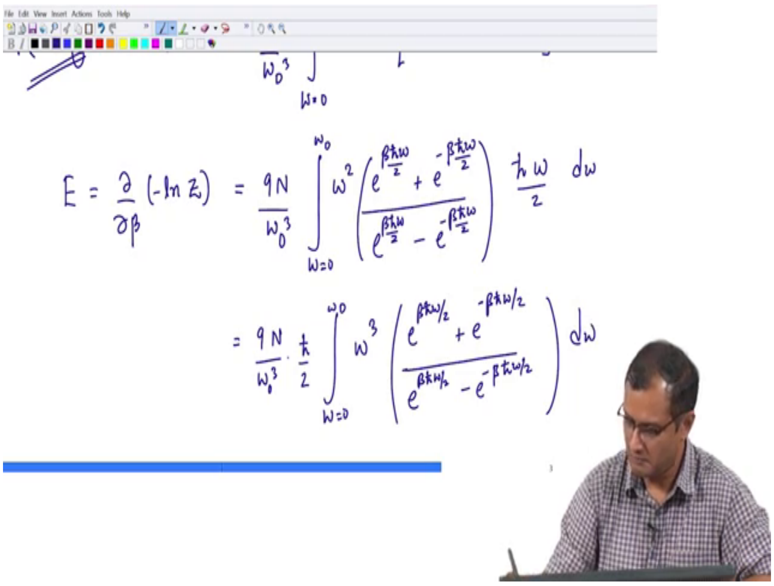

So, what you will get here is nothing but I am going to take 9 N by omega D cube outside and when you take the derivative with respect to beta; you will get omega square into cot. I am going to write down cot hyperbolic as cos hyperbolic over sine hyperbolic and which is nothing but e to the power beta h cut omega by 2 plus e raised to minus beta h cut omega by 2 over e raised to beta h cut omega by 2 minus; this is just the derivative and we need to take the derivative of the argument also.

So, that would be just h cut omega by 2 correct; that is the derivative of the argument and let us write it as 9 N omega 0 the whole cube into I am pulling the h cut by 2 outside and the integral inside can be written as omega cube and if you see I am going to write down this as you know and then take its high temperature limit.

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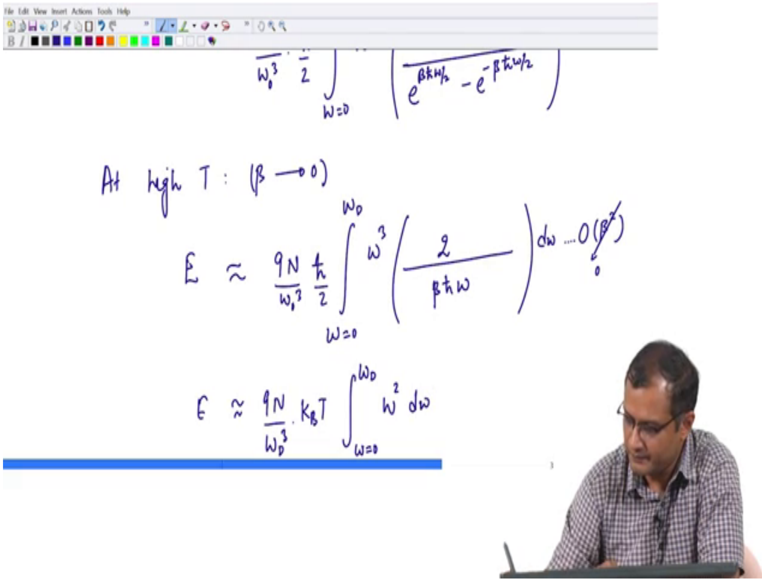

So, then take high temperature limit which is you know the limit beta tending to 0; you can see that the when you take the high temperature limit; the denominator is simply. I can write it as 9 N by omega 0 cube into h cut by 2 and integral here is on omega going from 0 to omega D. So, if you look at the denominator; I can expand both these exponentials and you can see the two linear order because, I have to take terms only in linear order for the expansion because beta square will be much much smaller than beta and beta cube will be even smaller.

So, both the exponentials in the denominator I will expand to only linear order; the unity will cancel and what you will have is just beta h cut omega that is it and in the numerator I will do a similar expansion and here I will again retain only 2 because the linear terms in beta will cancel, higher order terms I am going to drop.

So, I am going to retain in my expansion terms of only order beta and all other terms higher order are dropped. So, then you can see that I can knock off. So, my this is total energy. So, I can knock off the h cut by 2 inside outside and get 9 N over omega D cube kB T from the beta that is inside; integral omega going from 0 to omega D omega square d omega. So, when you perform this definite integral this would be nothing but omega D cube by 3.

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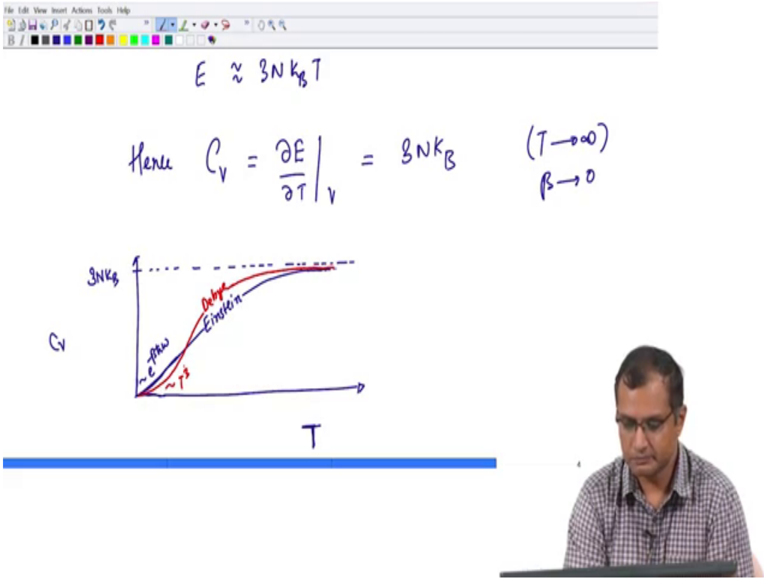

And so, my internal energy would be just thrice Nk B T and hence if you look at the heat capacity at constant volume; this would be simply thrice Nk B T as expected at high temperatures. So, this would be the heat capacity as T tends to infinity or beta tends to 0. So, if you sketch the Debye's heat capacity; it is better than Einstein definitely at low temperature and it also has an asymptote that becomes thrice Nk B. So, both of them will start from 0 and become constant; approach this constant value at infinity.

So, this is the T cube behavior. Einstein's heat capacity basically is a sharper fall at low temperatures and eventually it becomes slower at high temperatures and, but it also becomes I am going to plot the Einstein's heat capacity as a sort of with a different color. So, this would be the Debye heat capacity and or I can just say that this is and the Debye is; the Einstein's heat capacity is a much sharper fall, but eventually so, I am going to; so just want to show; let me show the Einstein's and then the Debye's because one is small; slower than the other at lower temperatures.

So, let me just show the Einstein first; and this is the e to the power minus beta h cut omega behavior and I am going to show the Debye behavior as slower. So, this is the Debye behavior. So, they both tend to asymptote to 3 by 2 Nk B at high temperature. So, at high temperature practically there is no difference between the two models. The difference arises only at very low temperature where one predicts T cube behavior and the other predicts exponential behavior.

So, this is the end of our discussion on heat capacity in solids; when we meet in the next lecture we will talk about Fermi-Dirac statistics and discuss some important examples.