ELEMENTS OF MODERN PHYSICS

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Lec 24: Lattice Vibrations, Specific Heat

Having done crystal lattices, different kind of crystal systems, now we know that lattice plus a basis becomes a crystal. We need to know the further properties of these crystals and one of them is the vibration of the ions or the atoms from their beam positions. which are called as phonons. So the quantum of lattice vibrations are called as phonons. And in that context, we'll talk about two simple models, namely monatomic and the diatomic lattices.

And we'll study acoustic and optical modes in them. Both the modes, of course, arise in diatomic lattice. And hence, we'll talk about more properties of the lattice, namely the specific heat of solids basically the lattice contribution. And in that connection, we'll talk about Einstein and Debye's theory of specific heat.

So what's the simplest model of a solid? So a simple model of a solid is just like You see a simple cubic structure with or maybe it's a face centered or rather the body centered cubic structure. There's one atom at the middle. And what you see are they are connected by springs.

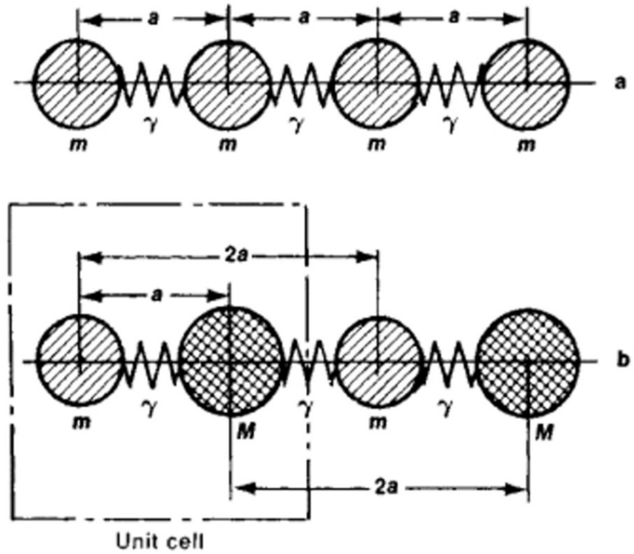
And these atoms kind of execute vibrations about the mean positions. the mean positions are shown as shown in the figure and then they vibrate about the mean positions. This is because of temperature the vibration occurs and we take this solid as if they are connected by these imaginary springs and hence the type of force that they experience or one atom or ion experiences due to the presence of all other ions or atoms in this assembly That is of the Hooke's law type or we have these harmonic interaction between them. So this is just a spring mass model.

If you remember your classical mechanics, there is just a spring mass model of a solid. And given that this is simple enough and there are really no springs attached to the atoms or the ions, But this model works very well at least in, you know, talking about a few properties such as lattice specific heat and so on. Of course, it has deficiencies that it cannot explain certain other things which arise because of the anharmonicity. So, we take a 1D crystal lattice.

1D crystal lattice

Monatomic Lattice →

Diatomic Lattice →



Of course, 1D is just an idealization and just to make sure that we are really in a simple sort of regime so that we can do calculations and so on. So, you see these atoms, each one of mass M. So, it is a monatomic lattice, just one kind of atom which are of mass M and they are connected by springs and the spring constant is written as gamma. I will use this spring constant as K for my calculations. Now, sometimes these K is misleading because you also are going to have a wave vector that is denoted by K. So, the wave vector will be denoted by a small case or small letter K and this is going to be denoted by a large K. So, we will denote it like a large K. So, this gamma would be replaced by large K but other than that everything remains the same.

A diatomic lattice again in one dimension has this structure that the effective unit cell becomes double or you can you know think that there are two atoms small m and capital M such that the distance between the like atoms that is the ones that is you know, like dashed ones and the hatched ones, they are denoted by small m and capital M and small m is not equal to capital M. But then you can also make that approximation that small m equal to capital M in your calculations and get all these modes etc. So, the whole thing is that that these are the atoms that are connected to each other by springs and these springs will allow them to vibrate either they will vibrate in plane or they will vibrate out of plane and we are going to talk about those vibrations and analyze this problem using this, you know, the equation of motion, which is written for a mass spring system.

This is, of course, a coupled pendulum kind of equation that we are going to write. So, the simple application of Hooke's law, the Hooke's law says that the force is proportional to the The displacement and it takes place in the opposite direction is an elastic force. If you have a mass spring system, so this is like a spring here and connected to a mass here and this mass is taken given a small push. In the positive direction or in the rightward direction and then the spring gets stretched and the spring stores a potential energy and this mass will eventually because it's connected to the spring it will come back to its position and it will go a little inside that is the spring will be compressed.

And then this leftward and rightward motion will give rise to a simple harmonic motion. And we have talked about, you know, classical harmonic oscillators and quantum harmonic oscillators. So this classical oscillators, of course, have energy, which is p squared by 2m plus half. m omega square x square and the quantum harmonic oscillators have energy which are n plus half h cross omega. So, let us deal with this problem classically and write down the equation of motion and you know that equation of motion is often the starting point for classical analysis of motion.

So, what we do is say that the force is proportional to x. This is called Hooke's law. Let me write that. And if you have a force like that, and force is given as minus dV/dx in one dimension, or it is a minus gradient of X, that gives a V which is a potential energy, or we can write it as U. Let us just—because V would also be the velocity—so let me change it to U. So, du dx so u is equal to half k x square where k is called as a force constant and for a given problem when the mass of the particle is m and it is undergoing an oscillatory motion with an angular frequency omega then k or rather omega equal to root over k by m that allows you to write this as half m omega square x square. Problem that is well known.

So, what we do is just go back to the picture that we have presented for a 1D solid and write down the equation of motion. Now, there are two coupled masses—or rather, the masses are coupled by these springs—and we have this. Let us call this a harmonic potential energy, which is half of K, and this is u na minus u n plus 1A. So, that is the kind of potential energy that we have, and that is—so u is the displacement; u n a is the displacement of the particle, or which has a mass m at the nth location.

Now, you see, if you look at this 1D solid, either of the pictures that you see on the screen, you see the ones that is the second one and the third one, they have neighbors on both the directions. But the ones that are at the end, we have just drawn four atoms or four ions, but in principle, a very large number of ions or atoms are present. You know, they are connected by springs. Nevertheless, the ones that are inside or the middle, excepting the end ones, they see the same environment. And but the last ones or rather the end ones, they do not see the same environment because the one is not the edge ones only see one neighbor.

But there is a simple way to take care of this is that we do a periodic boundary condition. So, we take this 1D chain and then connect it back to back so that, you know, the n plus 1th atom becomes the same as the first atom that you have, okay. So, we will use a periodic boundary condition, which is also known as the Born-Von Karman boundary condition. All right. So, this is the harmonic potential that we have.

This is exactly what was written above. We have used a displacement to be x. Now we have used a displacement which is given by the small u, and we have specified the nth location or the nth atom or the nth ion. and that between the n plus 1th ion, okay. And, of course, this is a square of that, okay. So, that is the form of the potential energy, okay.

So, we write down the force just by using this del u del x. So, this is equal to k, and then you have a u and n plus 1 a and minus u of n a—that is for the one side that is n is connected to the n plus 1th term—plus there will be another term which is u n minus 1 a and a minus u of n a. So, we are focusing on the nth particle, the particle that is at the nth location; n is arbitrary, it can be anywhere in the lattice. So, it is connected to the n plus 1th side and the n minus 1th side and this is what the force will look like. And if you write the force with this term, we are neglecting a negative sign here, or rather the negative sign is kind of absorbed inside this bracket because you are focusing on the nth particle.

So if you write UNA on the left, then you have a minus sign. So that's why it's reconciled. So now let us write down these equations of motion, which is m u double dot n a. So this is for the nth atom, which is del u harmonic. del u, this is a small u and capital U. So, please make that distinction, and this is equal to n a, and this is equal to a minus k 2 u n a minus u n minus 1 a minus u n plus 1 a.

So, there are these two u n a is the displacement twice the displacement of the nth atom and then minus the displacement of the n minus 1 which is lying on the left and u n plus 1 which is lying on the right. And as we have said that we will use periodic boundary conditions and periodic boundary conditions will allow us to write the u of, you know, n plus 1. So there are capital n atoms in the chain. Okay. So this N is the number of atoms, atoms or ions, of course, in the chain.

Each one is of mass m. That's the total number of atoms. So, u into n plus 1 a is nothing but u into a. That's the first atom. And you also have the displacement of the 0th atom is the same as the displacement of the nth atom. So, these are the signatures of the periodic boundary condition or the periodic boundary condition enters through these, you know, these conditions.

$\vec{F} = -kx$ (Hooke's law).

$f = -\frac{dU}{dx} \Rightarrow U(x) = \frac{1}{2} kx^2. \quad \omega = \sqrt{\frac{K}{m}}.$

$= \frac{1}{2} m\omega^2 x^2.$

N: # of atoms in the chain.

$u(na)$: displacement of mass m at the nth location

$$U^{harmonic} = \frac{1}{2} K \Big[u(na) - u[(n+1)a] \Big]^2$$

$$F = K\Big[u[(n+1)a] - u(na)\Big] + K\Big[u[(n-1)a] - u(na)\Big].$$

$$m\ddot{u}(na) = -\frac{\partial U^{harmonic}}{\partial u(na)} = -K\Big[2u(na) - u[(n-1)a] - u[(n+1)a]\Big].$$

$$\left.\begin{aligned} u[(N+1)a] &= u(a). \\ u(0) &= u(Na). \end{aligned}\right\} \text{Periodic boundary conditions.}$$

Okay, so in order to solve this equation, we can call this as equation 1 and then in order to solve it, we can assume a solution u of n a t that is equal to proportional to exponential i k n a minus omega t, this is for all t. and the periodic boundary condition now requires that exponential ik n a is equal to 1, this is equal to exponential 2 pi ni where n is an integer, small n is an integer and capital N is what we have said earlier that that is the total number of atoms or the lattice size that are involved. So, this is an integer. So, that gives the quantization of K. This is equal to 2 pi over a small n over capital N. So, you can also write it as 2 pi over L. into N where L is equal to that is the total length of the chain is equal to N into A where A is the lattice constant that is the distance between or the difference between the coordinates of these two successive sites or particles or ions, atoms, etc.

So, this tells you that if you change K by 2 pi over a, the displacement u n a, that is the displacement u of the nth atom, it remains unchanged. Also, this tells us that there are n distinct solution, one for each value of K and for convenience, you can put an index that goes with K. That will make sure that there are these n solutions that are there and these n solutions would be restricted between minus a to plus a. So, k, this vector, so now this make sure that you make a small k and a capital K, capital K would go and was sitting at the, you know, the harmonic part. So, this K and then when we come to this wave vector that becomes a small k so that we can write it as small I mean the K n as well that will make it. So, K is or all these K n's are between this minus a to plus a they are contained within that and this is called as the first Brillouin zone.

Alright, so if we substitute this answers in this equation of motion, we get minus, so let us call this as equation 2, it can have an amplitude, so this proportionality can be, you know, cut down and one can write an amplitude and putting 2 in 1, that is the equation of motion that you get, this equation 1, so putting 2 in 1, what one gets is the following. So, it is a minus m omega square exponential i k n a minus omega t and this is equal to minus k and 2 minus exponential minus i k a minus exponential i k a. And this is nothing but equal to minus 2t, 1 minus cosine ka and exponential. So, this Brillouin zone, let me write it here. So, this is the Brillouin zone.

And so, it is 2k 1 minus cos ka. Once again, this is capital K just to remind and sensitize you. If you use, you use another notation, maybe gamma there. So, 2k 1 minus cos k, cos ka and exponential ikna minus omega t. Okay, so here we are not using n as a subscript, but it is n goes with a because we are talking about the nth atom.

So, this is the equation of motion that it becomes and one can really, you know, cancel this exponential ik and a minus omega t from both sides because that is not equal to 0. That is a propagating wave that gives us that omega, which is of course a function of k, the wave vector k, this is equal to a root over 2k omega. capital K and 1 minus small kA divided by m, okay. And this is nothing but 2 capital K by m and then there is a mod of sine kA by 2 and that is the behavior or that is the dependence of this angular frequency of vibration, omega as a function of k. Now, from a simple, you know, mass spring system where omega is a constant and just depends on the mass of the particle and the force constant.

$$u(na,t) = A\, e^{i(kna-\omega t)}. \quad (2)$$

n : integer.

$$e^{ikNa} = 1 = e^{2\pi n i}$$

$$k_n = \frac{2\pi}{a}\frac{n}{N} = \frac{2\pi}{L} n. \qquad \boxed{L = Na} \qquad k_n \in \left[-\frac{\pi}{a} : \frac{\pi}{a}\right]. \text{ BZ}$$

Putting (2) in (1),

$$-m\omega^2 e^{i(kna-\omega t)} = -K\left[2 - e^{-ika} - e^{ika}\right] = -2K(1-\cos ka)\, e^{i(kna-\omega t)}$$

$$\omega(k) = \sqrt{\frac{2K(1-\cos ka)}{m}} = 2\sqrt{\frac{K}{m}}\left|\sin\left(\frac{ka}{2}\right)\right|. \quad (3)$$

$$\omega(k) = \omega(-k)$$

Phase velocity $= \frac{\omega}{K}$; group velocity $= \frac{d\omega}{dK}$.

Here, of course, there is a dependence on the wave vector and these wave vector k, there are any number and these wave vectors are all contained in the first Brillouin zone, which is given by minus pi over a plus pi over a. where a is the lattice constant. One can see that omega is actually an even function of k which means that omega of k is equal to omega of minus k. See, the same problem, if you generalize it to more than one dimension, you would simply acquire a vector sign of K, where K becomes, you know, more than one dimension. It is just a vector quantity, but all these simple calculations will go through.

So now, this is important to note that for each distinct value of K, we get a unique frequency omega k. So, omega k actually yields 2N independent solutions, where 2N means the capital N, and N is the number of atoms in the whole chain. So, these solutions actually propagate through the chain and there are two velocities that one can define is called as a phase velocity which is simply equal to omega by k and we can also define a group velocity of these waves that you know propagate that is wave packet propagates with this velocity which is d omega by dk. Okay.

Now if you want to know that how the long wavelength modes propagate Now these are important because these long wavelength waves means that lambda goes to infinity which means that k goes to 0 or when we say 0 we actually mean the small thing because if you put k equal to 0 then you lose all information about that. So, omega becomes equal to root over capital K by m and a which is the lattice constant and this small k which is a vector. So, this is the definition or rather this is the behaviour of this angular frequency or frequency of oscillation as a function of this wave vector k and these are known as sound modes.

And these sound modes have, of course, this property that your Vp becomes equal to Vg because your omega by k and d omega dk, they become same. And so these have a relation. Why they are called sound modes is that they have a relation which is omega equal to Vs into k. That kind of a relation is called as a sound mode. Of course, similar relation also the photons obey, which are quant of the electromagnetic vibration.

But there the speed is not the speed of sound, but the speed of light, which is given by C. Here, of course, the Vs is the speed of sound. And we know this numerical value in say vacuum or in a metal and so on so forth. So, if we plot this, how would it look? And that is an important thing that we usually want to see. So, this is your omega.

And this is the K and this actually the modes actually rises like this and they nicely sort of saturate at the edges and I have to draw it very symmetrically if I am not that precise, but you know that these are. you know, symmetric things. So, these are pi by a and these are minus pi over a and these are called as a sound mode. So, the close to k equal to 0, this region that you see here, let me highlight it, this region, that you see here and here, these are the sound-like modes because this omega is linearly varying with k, which means the Vs or the sound velocity is a constant, which is given by this omega over k, which is nothing but this root over k by m into a, which all of these are constant for a given setup.

So, this is what we learn from these monatomic lattice and we get these modes which are called as the sound modes. As you go away from k equal to 0, of course, the non-linearities show up and so, you know, there are a few comments are in order, one is that if you go beyond a nearest neighbor interaction, nothing much changes because we have taken these while we wrote down this equation of motion, we have taken a nearest neighbor interaction or the harmonic potential is between the two neighboring atoms or ions. But if you go beyond that and you understand that or rather assume that there is a small contribution coming from the next to next near neighbor or next to next to next neighbor and so on. This problem only changes quantitatively rather the qualitative.

There is no qualitative change that one notices here. And you will have more terms there because then you have n minus 2 and n plus 2 atoms involved and n minus 3 and n plus 3 involved. So you will have a complicated equation but you can still consider a solution to be similar to what we have taken it here as equation 2 and we can do this problem exactly similarly. So there is no qualitative change that occurs. There will be a change in numbers, of course.

Now, there is another important thing: so this is nothing or no qualitative change in the spectrum. Now what happens when you go to k values beyond that and I am just drawing it here where say this is from minus a pi by a. So, this is, say, minus pi over a, and this is pi over a, and this is it—I should draw it a little bit to scale, at least. So, this is 2 pi over a. So, this is the 0 that is there.

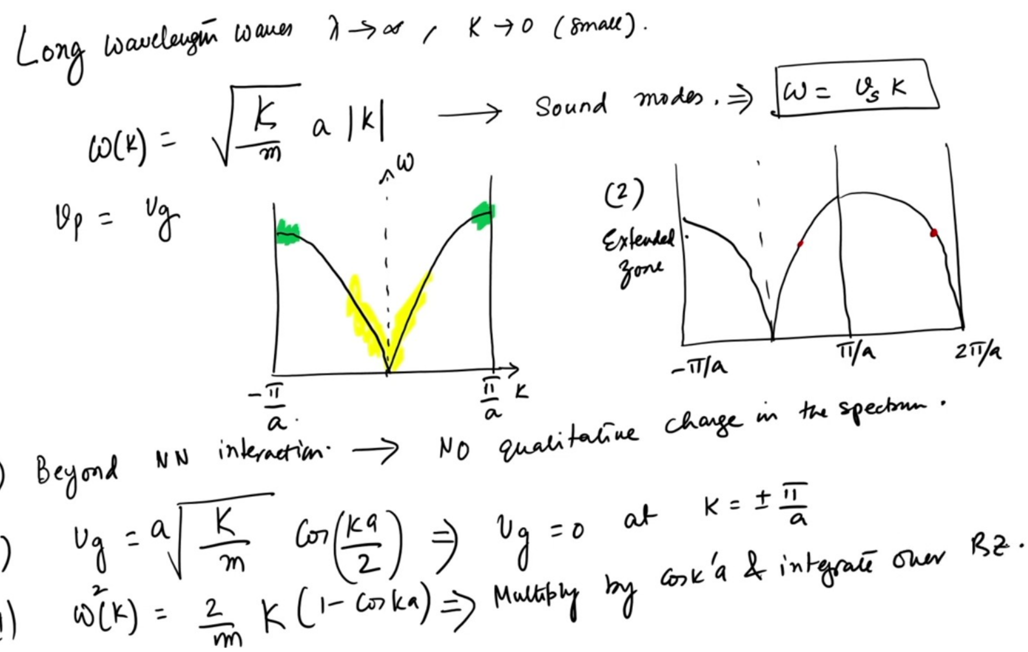
So, we have these modes that will rise like this. And then, as you increase K, it will go like this. Okay. And there is always a reciprocal lattice vector that can be subtracted from the, you know, the extended Brillouin zone, which goes beyond the first Brillouin zone, which is between minus pi by a to plus pi by a. It always comes back to some point. in the first Brillouin zone.

What I mean is that if you take a point here, let me show it by a color. So, and subtract a reciprocal lattice vector, it will come back to the point inside the Brillouin zone. And this tells you that the description that we gather from the first Brillouin zone is good enough. And there is another thing that is there. So, this is about the extended zone scheme.

I just did it here. So, extended zone as you go beyond the first real one zone, the description is always contained within the first real one zone. And if you think that you would try to calculate the group velocity, say, for example, using the full expression, then the full expression has this velocity expression, group velocity expression is equal to a cos k a by 2 and so on. So, this group velocity is important for us because this group velocity tells you that the Vg equal to 0 at k is equal to plus minus pi over a. So, if you put k equal to plus minus pi over a, you get cos pi by 2 which is equal to 0 and that tells you what I was saying here. Let me again put a highlighter here and maybe use a different color.

So, here the velocity, the group velocity, goes to 0, and that is why it just kind of flattens. So, this spectrum flattens there, and there is no group velocity at the edge of the Brillouin zone, which can be seen from here. And the final remark that one can make here is that one can actually calculate these force constants from these equation which we if we just simply square it up. So, omega is a function of K. So, we can write a K here and we can continue writing Ks. We have written omega as a function of K, or we can write omega as a function of K.

with a k in the subscript either way is fine, but let us follow one convention which is omega k. So, we can do a omega k and this is equal to 2 over m capital K over 1 minus cos k a and what you can do is that you can calculate or rather extract. This capital K, which is a force constant, by multiplying it by some cos k prime a and then integrate it over the Brillouin zone, and that would sort of extract out this K there because this cos k a and cos k prime a will have an orthogonal relation between them, and then one can do that. So, I just write down this step and say that multiply by K. Cos K prime A and integrate over the Brillouin zone, the first Brillouin zone. So, we write Brillouin zone by BZ, and so that should be fine.



So, let us now go to the diatomic lattice and that diatomic lattice is a little more complicated because of the presence of two ions and let me show you the equation of motion and the solution exactly proceeds in the same manner as we have seen. For the monatomic lattice. So, this diatomic lattice going back once again. So, there are two atoms, each one has mass m and the other has mass capital M. So, small m and capital M, each of them is a small m has a neighbor as a capital M and capital M has a neighbor or rather two neighbors as small m and same goes for the small m, it has two neighbors as a capital M. And the distance between the m and capital M is called as a lattice constant, which is A, and because they are alternatingly placed.

So, the distance between two small m's or two capital M's is equal to 2a. So, the unit cell actually becomes twice as big as that in a monatomic lattice because the unit cell will have to contain. The entire structure, which is exactly what we have said in the last class, the structure that can be replicated to get the entire lattice. So, let me use a color here. So, the unit cell is actually now this.

which is basically the boxed one, it is already boxed there, so that is the unit cell and then you have it at 2a. Okay, so we have these alternating atoms which are of small mass, small m and capital M and we can write down the equation of motion for, okay, let me use this black color that we have been using. So, we have for small m, We have these m, d2u, 2s. Now, we will just use this notation because we have these, you know, the unit cell has doubled and this is equal to k.

and u2s plus 1 plus u2s minus 1 and minus u2s. That is a similar equation that we have written down. So, let us call this as equation 1 and for capital M, we write down a similar equation. So, M d2 u2s plus 1. So, this is in the S unit cell.

So, this dt2, this is equal to k and we have this u2s plus 2 plus u2s and minus 2u2s plus 1 and that is the equation of motion and then one can assume solutions of the form which is exponential i or say a exponential i. k into 2sa minus omega t. Ultimately, we want these omega as a function of k and u2s plus 1. So, this is for mass small m and this is for capital M and this is a B exponential i k 2s plus 1, well, let me write it with a square bracket then. So, this 2s plus 1a minus omega t. So, we have not done anything else excepting that these are two different atoms and their amplitudes of vibrations would be different and we have assumed similar solutions, but with different amplitudes and so on.

So, in general, you know, one has a k to be also different. But we are assuming the K to be same in this particular case. So what we do is that if we take these as equation 3 and equation 4. So, in principle, we have these, as I said, K1 and K2 to be different, that is two different Ks and two different omegas. However, we take them to be same here and will not cause any trouble in the analysis that we want to make.

So, what we do is that so we get a 2s minus 1. So, this is from 4. So, or yeah, so this from 4, we get u 2s minus 1 or let me write it for 2s plus 2. So, this is from 3. So, 2S plus 2 is equal to exponential 2I Ka U2S.

Remember, 2S plus 2 and 2S, they correspond to the same atom, that is, each one with small m. And similarly, from 4, we get U 2S minus 1. This is equal to exponential minus

2I Ka U 2S plus 1. So, this is say equation 5 and 6. So, 5 and 6. So these are the same equations.

And then, if you put these solutions 3 and 4 and use, you know, 5 and 6 and so on, we get these equations which are minus m omega square U2 S. This is equal to capital K. This is 2s plus 1. Plus exponential minus 2i ka u2s plus 1 minus 2u2 u2s, and that is one equation. We can call it as, you know, or both the equations can be called as. Let me just rearrange this equation. So, this is equal to minus m omega square plus twice of k U 2S. This is equal to k and 1 plus exponential minus 2ika and u2s plus 1.

For m

$$m\frac{d^2u_{2s}}{dt^2} = K\left(u_{2s+1} + u_{2s-1} - 2u_{2s}\right) \quad (1)$$

For M

$$M\frac{d^2u_{2s+1}}{dt^2} = K\left(u_{2s+2} + u_{2s} - 2u_{2s+1}\right) \quad (2)$$

$$\underbrace{u_{2s}}_{m} = Ae^{i(k\cdot 2sa - \omega t)} \quad (3) \qquad ; \qquad \underbrace{u_{2s+1}}_{M} = Be^{i[k(2s+1)a - \omega t]} \quad (4).$$

from (3)

$$u_{2s+2} = e^{2ika}u_{2s} \quad (5)$$

from (4)

$$u_{2s-1} = e^{-2ika}u_{2s+1} \quad (6)$$

$$-m\omega^2 u_{2s} = K\left[u_{2s+1} + e^{-2ika}u_{2s+1} - 2u_{2s}\right]$$

So this is the coupled equation let us call it as equation 7 or we can what we can do is that we can combine these two combined can be called as 5 these two equations that is this equation and this equation can be combined called as 5 and this let us then call this equation as equation 6. So, that is connecting the displacement of mass small m to that of capital M. And so, if we put them into equation number 2, then what we get is that minus capital M omega square plus 2k, this is equal to, so this is and so u2s plus 1 and k1 plus exponential 2i ka. Please do these steps yourself so that you are comfortable with this. So, we have written down an equation of motion in 1 and 2 for the mass small m and capital M and have taken these solutions very similar to the ones that we have taken earlier.

And put them into these equations. So, these are propagating wave solutions because these are wave equations, and then the solutions will be some waves. So, these propagating waves are put there, and omega has to be calculated from that. So, this is, say, equation 7, and from 6, one gets u of 2s plus 1 divided by u of 2s, this is the ratio of these, the displacements of the two masses and that is equal to small m omega square plus 2k.

And this is divided by k into 1 plus exponential minus 2 i k a. So, once again, make this distinction that small k is the force constant and large k is the force constant, and small k is the wave vector. So, this is from 6, and from 7 we get a similar equation, which is u 2 s plus 1 divided by u 2 s. This is equal to u. k and 1 plus exponential 2 i k a. Divided by minus m omega square plus 2k. So, these are equations. This is equation 8, that is equation 7, and so let us call these two as maybe equation 8 and so maybe 8 and 9, which would be more appropriate.

$$\left(-M\omega^2 + 2K\right)u_{2s+1} = K\left[1 + e^{2ika}\right]u_{2s} \quad (7).$$

from (6), $$\frac{u_{2s+1}}{u_{2s}} = \frac{-m\omega^2 + 2K}{K\left(1 + e^{-2ika}\right)} \quad (8)$$

from (7), $$\frac{u_{2s+1}}{u_{2s}} = \frac{K\left(1 + e^{2ika}\right)}{-M\omega^2 + 2K.} \quad (9).$$

Equating (8) & (9).

$$\frac{-m\omega^2 + 2K}{K\left(1 + e^{-2ika}\right)} = \frac{K\left(1 + e^{2ika}\right)}{-M\omega^2 + 2K.}$$

Solve ω. in terms of K, m, M, k.

So, these are the same ratios, and if we equate these 8 and 9, which is the most natural thing to do here. So, if you do that, then what you get is that a minus small m omega square plus 2k, this is equal to k into 1 plus exponential minus 2 i k a. This is equal to k 1 plus exponential 2 i k a divided by minus m 2, I mean this capital M omega square plus 2k. And that gives you this solution for this omega. You can now solve omega in terms of, so solve omega in terms of capital K, small m, capital M, and of course, the wave vector K, so that you get omega as a function of K. And once you do that, what happens is the following.

So, we have these omega square, which is equal to capital K 1 over m plus 1 over small m and capital M, and then there are these plus minus signs, which are coming from here. These are like 1 over m plus 1 over m whole square minus 4. m1 mm, small m capital M and sin square ka by 2. So, this is actually one can get an omega here, and these, if you put a square root of that, you get an omega here. And there are two of these masses, and if you define alpha to be the ratio of the two masses, that is small m by capital M, and then what one gets is this nice. Modes that are there, and we have to again restrict ourselves between minus pi over A to plus pi over A, and we have these acoustic modes that you see here. They are very symmetric.

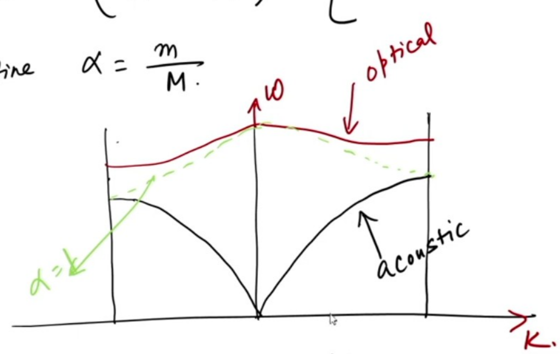
If it does not look right, please draw it; it is a little hard to draw on the left side. Okay, that looks more or less straightforward. And so, this is, you know, something one can actually do for a number of things. So, these are called the acoustic modes that we have seen. And now, because of the plus-minus sign, we will get the optical modes and other modes as well.

And these other modes will, you know, kind of give that. So, there are modes like this. Okay. And you can tune alpha and get different modes such that, you know, these gaps kind of merge as a function of alpha. So, we have drawn it for one.

So, this is omega as a function of K, and we have just drawn it. So, these are called optical modes. And these are called the acoustic modes, which is what we have. The word acoustic means sound, I mean related to sound. So, acoustic modes and optical modes.

$$\omega = K\left(\frac{1}{m} + \frac{1}{M}\right) \pm \left[\left(\frac{1}{m} + \frac{1}{M}\right)^2 - \frac{4}{mM}\sin^2\left(\frac{ka}{2}\right)\right]^{1/2}.$$

Define $\alpha = \frac{m}{M}.$



$$v_s = \frac{\omega}{K} = \frac{a}{2}\sqrt{\frac{K}{2(m+M)}}.$$

So, these optical modes are higher and you can tune them, you can plot them and and show that for alpha equal to 1, which means the two masses are the same, you have a margin that I will just draw using a color and then probably remove it. So, this is the or we can keep it as also. So, this is like a sort of plot for—so, this is for alpha equal to 1. There is no gap between the optical and acoustic modes at the Brillouin zone.

So, the sound velocity would be given by here. So, the sound velocity which is Vs which is equal to omega over K which would be given as a over 2. And root over capital K divided by twice of small m plus capital M. And that's the velocity of sound for this particular case. Okay. So, let us just you know sort of see that what we have learned so far and we have actually talked about phonons and so these are a set of moving quasi particles with momentum p which is the momentum is h cross k and the energy is h cross omega.

Phonons:

A set of moving quasiparticles with momentum $p = \hbar k$ and energy $E = \hbar\omega$, ($\hbar$: Planck's constant), may be considered in correspondence with each traveling plane wave with vector k and frequency ω.

These quasiparticles are the field quanta of crystal lattice vibrations and are called phono ns by analogy with photons, the quanta of the electromagnetic field.

And we have this h cross as a Planck's constant and this is maybe considered in correspondence with each of the traveling plane waves with you know wave vector k and frequency omega and this quasi particles or these are quasi particle that is a technical term it just means dressed particles. these are quanta of the lattice vibration we have used this word before because these in you know analogy with photons which are quanta of the electromagnetic fields and these are the lattice vibrations have important implications on the crystal properties so higher the temperature of the crystal this more intensely or these Atoms will oscillate about their equilibrium position with larger amplitudes and when the amplitude of the vibration exceeds certain critical value, melting begins and the crystal structure would be entirely destroyed. But, however, the harmonic theory that we have learned so far will be unable to take into account this this melting or this you know the melting of the because in this situation in the harmonic approximation the expectation value of this U or the mean displacement always goes to 0. So, that will never diverge, even as a function of temperature.

So, this is unable to—this harmonic theory is unable to take care of the melting of solids. And we will see in just a while that the lattice heat capacity is a quantitative characteristic of a crystal's ability to store heat in the form of potential energy. And the heat capacity per atom is found to be approximately equal to 3K. This is not KB, but this is KB. The KB is the Boltzmann constant.

Or high temperature rate. So, this at high temperature, it is 3K or 3R, as we say—if you multiply K by N, N is the number of atoms—or is proportional to T cube as T approaches 0. So, we point out again the deficiency of the theory of crystal vibrations and harmonicity that is not included there, and in reality, the linear forces are not strictly proportional to the displacement, but they are anharmonic effects that need to be taken into account, and this non-linearity of the interatomic forces is often small. Because the amplitudes of oscillations are small. However, by virtue of this non-linearity, individual normal vibrations are not independent, but they are interconnected, and resonance is possible, as it happens in a system of coupled oscillators or coupled pendulums.

The anharmonicity explains the thermal expansion of the crystals and hence melting, and this would register severe deviations from these Dulong and Petit's law for specific heat in the high-temperature regime. And diamond is one such example where you see a lot of deviation from the Dulong and Petit law even at large temperatures. So, how do we experimentally determine lattice vibrations? There are various experimental methods for determining lattice vibrations. Excitations by means of infrared radiation is one method of studying lattice vibrations.

It is possible not only detection of this vibration, but also determination of this frequency by the infrared radiation. And then there are studies on the inelastic scattering of neutrons in crystals. It makes it possible to determine the dispersion law. And the polarization of normal vibrations. The dispersion law can also be constructed using the diffuse scattering of X-rays.

These are some technical experimental facts. We are just stating the facts, and also the Mössbauer effect, which makes it possible to directly determine the mean square displacement and moment of the atoms in the lattice vibration. So we come to the specific heat of solids, which is one of the last things one describes for the lattice contribution, and the electronic contribution comes separately. And in this connection, there are two theories. One is called as the Einstein's theory and the other is called as a device theory.

And the Einstein theory was that or Einstein's law or Einstein's specific heat theory. It says that all the atoms, they vibrate with one single frequency. That's like too much of an approximation, but that's what he thought it to be correct. It's like a delta function with just one frequency involved, and all the atoms or the ions, they vibrate with that frequency of oscillation. And we know that the energy is given for such oscillators in the quantum limit

as n plus half h cross omega. Omega is nothing but root over k by m and n can take values which are 0, 1, 2 and so on. So, there is a zero-point energy involved here. Now, one can take a statistical root in order to calculate this specific heat. So, what one can do is that one can write down the partition function which is exponential minus beta E n.

Sum over n, and from there, you calculate the average energy. So, the average energy is nothing but equal to minus 1 over z del z del beta. We have written z; taking del z del beta is not difficult, and in fact, this has a simpler expression, which is del del beta of log z. So, you can actually calculate z in a closed form by doing this sum, and n goes from 0 to infinity. It becomes a GP series, or rather, we can write it as exponential half beta h cross omega, and then there is a sum over n from 0 to infinity of exponential minus n beta h cross omega. And this GP series can be summed up, one gets minus half beta h cross omega and this is 1 minus exponential minus beta h cross omega and so on.

So, one can take the log of z and then calculate this average energy. So, this is the average energy. And why do we need the average energy? Because the specific heat is just del E bar del T. So, we can calculate this, and with just a little bit of algebra, we will get it. So, there is a half h cross omega minus h cross omega exponential minus beta h cross omega divided by 1 minus exponential beta h cross omega.

And what you do is take a derivative with respect to T. And if you do not do that, you can also do a del E del beta, del beta del T. So, that is also going to give us, so del E del T is this and this is nothing but minus 1 over KT square because beta is 1 over KT. So, what one gets is that for T to be high, for T large, that is 0. you know, when beta h cross omega, which is nothing but equal to h cross omega over kT, that is much smaller than 1 because kT is much larger than h cross omega. You can do an exponential x to be equal to 1 plus x and so on.

You can cut down all other terms. So, these exponentials that you see on the step above can be expanded and one gets a So, average energy equal to h cross omega divided by half plus 1 by beta h cross omega. that is your expression and this is nothing but equal to h cross omega and you know divided by beta h cross omega you can neglect this half because the temperature is large so beta is 1 over T so the T goes in the numerator of the second term so T is large so you neglect half so it is h cross omega a beta h cross omega so this is equal to you know, it is equal to kT.

Einstein's law

$$\mathcal{E}_n = \left(n+\tfrac{1}{2}\right)\hbar\omega \qquad n = 0, 1, 2 \ldots$$

Average energy

$$Z = \sum_{n=0}^{\infty} e^{-\beta\mathcal{E}_n} \Rightarrow \bar{\mathcal{E}} = -\frac{1}{Z}\frac{\partial Z}{\partial\beta} = -\frac{\partial}{\partial\beta}\ln Z$$

$$Z = e^{-\frac{1}{2}\beta\hbar\omega}\sum_{n=0}^{\infty} e^{-n\beta\hbar\omega} = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}$$

$$\frac{\partial\bar{\mathcal{E}}}{\partial T} = \frac{\partial\bar{\mathcal{E}}}{\partial\beta}\cdot\frac{\partial\beta}{\partial T}, \qquad \frac{\partial\beta}{\partial T} = -\frac{1}{k_B T^2}$$

$$\bar{\mathcal{E}} = \left[\frac{1}{2}\hbar\omega - \frac{\hbar\omega e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\right]$$

$$e^{x} = 1 + x + \cdots$$

For T large: $\beta\hbar\omega = \frac{\hbar\omega}{k_B T} \ll 1$.

$$\bar{\mathcal{E}} = \hbar\omega\left[\frac{1}{2} + \frac{1}{\beta\hbar\omega}\right] = \frac{\hbar\omega}{\beta\hbar\omega} = k_B T$$

$$\frac{\partial\mathcal{E}}{\partial T} = k_B \Rightarrow 3N \text{ oscillator } \frac{\partial\bar{\mathcal{E}}}{\partial T} = C_V = 3Nk_B = 3R \text{ (Dulong Petit law)}$$

So, del E del k that becomes equal to k, which is the result that you get. For 3N oscillators, 3 is the dimension, and N is the number of oscillators in each dimension. For 3N oscillators, we get a real, so this del E del T, which is nothing but equal to CV, specific heat, this is equal to 3NK, which is equal to 3R, and this is called as a Dulong and Petit law. So we recover the Dulong and Pettit's law correctly even with a crude approximation that is all the atoms are vibrating with the same angular frequency about the mean position.

However, the low temperature behavior which is another important thing that one needs to you know worry about. So, at low temperature, So, in the other limit, when h cross omega is greater than T, one gets a Cv equal to del u or del t, or rather del e del t, and this is equal to del e del beta del beta del t. As we have said, and this, with a little bit of calculation, one actually gets it as 3R. And this theta E is called the Einstein temperature; we will define it in a while.

So, exponential theta E divided by T. Exponential theta E divided by T minus 1 whole squared, where theta E by T is equal to this ratio, which is h cross omega by kT. So, this theta is called a characteristic temperature or the Einstein temperature. Now, of course, in the other limit, that is T much. So, this is a general expression from what we have found out.

You know, we are still not at low temperature. So, let me remove this. We will be there at low temperature, at any temperature rather. So, T greater than theta E, which is h cross omega by K, you have Cv coming out as equal to 3R. But in the other limit, so this is fine. This is the Dulong and Petit law, that is—I am sorry—Dulong and Petit DP. That is obeyed.

At any temp,

$$C_v = \frac{\partial \bar{E}}{\partial T} = \frac{\partial \bar{E}}{\partial \beta}\frac{\partial \beta}{\partial T}$$

$$= 3R\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{\left(e^{\theta_E/T}-1\right)^2}. \qquad \frac{\theta_E}{T} = \frac{\hbar\omega}{k_B T}$$

(i) $T \gg \theta_E$

$C_v = 3R \rightarrow$ DP law.

(ii) $T \ll \theta_E$.

$$C_v = 3R\left(\frac{\theta_E}{T}\right)^2 e^{-\theta_E/T}.$$

$$\sim \frac{1}{T} e^{-1/T}. \rightarrow \text{Much smaller than experimental values !!}$$

In the other limit which is T to be much much smaller than this Einstein temperature, your Cv comes out to be 3R theta E by T. whole square and exponential minus theta E by T. Now, this is a slightly complicated dependence and it goes as 1 over T square and exponential minus 1 over T and this is much smaller than what is observed experimentally. So, this is much smaller than experimental values, which means that this is incorrect even though the or experimental values. So this tells you that this oversimplified picture of all the atoms vibrating with the same frequency may not be correct.

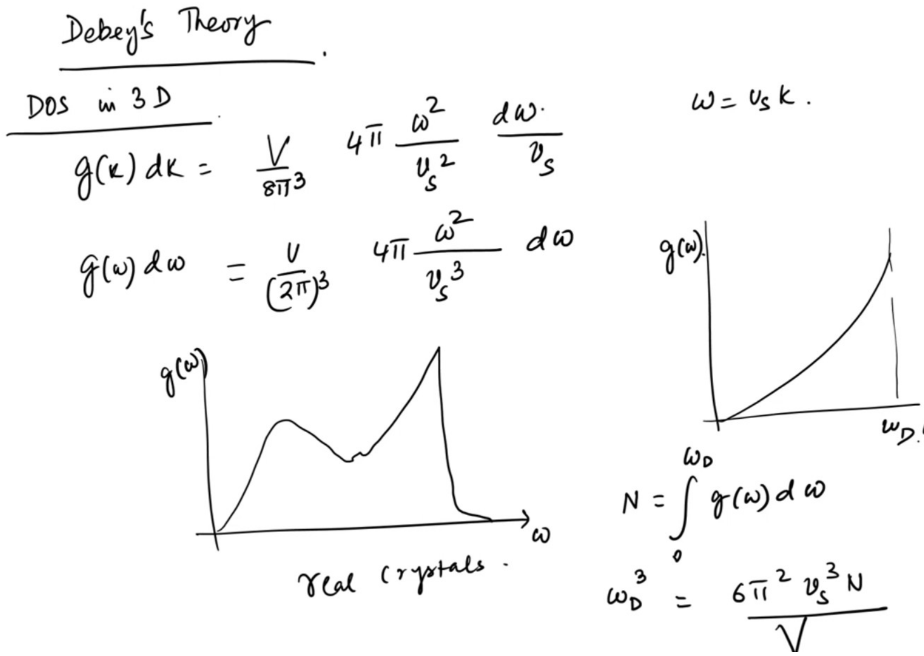
And what Debye did was to, you know, come and correct it. And he said that not all the atoms vibrate with the same frequency, but there's a distribution of frequencies. And with a cutoff, which one calls a Debye cutoff, because he, Debye actually said, proposed it. So device theory or device law says that there is a cut off and this cut off actually has I mean according to his theory it has a smooth cut off but in real materials when people have actually calculated the density of states it shows kind of rugged structure but nevertheless these picture is correct that not all the atoms vibrate with the same frequency but they have a distribution of frequencies.

and this distribution gets cut off that is if distribution ceases to exist beyond omega equal to omega D called as a Debye frequency. And in that one can actually find out that how to calculate these Debye or rather the density of states. So, the density of states in 3D which has been shown in different parts of the course. So, we have a gk dk, this is equal to V which is a volume by 8 pi cube and then we have a 4 pi omega square and Vs square and you know a d omega by Vs and we are assuming a dispersion which is omega equal to Vsk.

So, I will sort of leave it to you to figure out and it has been done at other places. So, it is omega square is the dependence and then Vs cube. d omega. So, this is like a g omega d omega. So, how many modes are there between omega and omega plus d omega that is phonon modes or the lattice vibration modes that is given by this variation which is omega square variation and this is exactly what we have said that these variation really looks like this.

So, for a Debye solid this is like the variation with a cutoff. So, this is your G omega versus omega with a cutoff at omega D, whereas in real systems you have, you see there is some kind of, you know, sort of these real crystals. which is very rugged. I am just saying it is a schematic plot and it is not drawn to scale, but it is like this, whereas there is an omega squared dependence that you see there.

So in this oversimplified, or rather this is relaxed, not as simplified as the Einstein case, but with this distribution of frequencies, what one gets is that we get a correct result and let us see how that comes. So, what can be done is that one can find out that this omega D by equating the number of modes which is 0 to omega D, G omega D omega. So, that is the number of phonon modes you integrate over all frequencies from 0 to omega D. And that gives you omega d cube, this is equal to 6 pi square V s cube n by the volume V. So, that is the cube root of this will give you the Debye frequency.



So, that is the cutoff frequency for our case, okay. And now we can write this down as the Debye wave vector. Now, this has to be written as a small k. So, Kd is equal to omega d by Vs, that is the dispersion that we use, this is equal to 6 pi square N over V and then we have a one-third here. So, you can calculate the average energy now.

By, you know, integrating this d omega, g omega, and of course, the average energy and now the Bose distribution function. So, because these phonons are, they obey Bose-Einstein statistics. So, this is the general scheme that the average energy is equal to the quantum of energy G omega, then you have F, either Bose or Fermi here, of course, it is Bose. And this integral from over, you know, all possible frequencies. In this particular case, it should in principle go from 0 to infinity.

In this particular case, it goes from 0 to omega d, and that will give you the average energy. Once you get the average energy, you can take a derivative with respect to temperature, which should give you the specific heat, okay. So, if you write all of that down, so it becomes equal to 3 V h cross omega. 2 pi square Vs cube 0 to omega d and omega cube d omega, this is what you saw, the omega square was the density of states and then there is another omega, all the constant terms have been taken out, it is h cross omega by kT minus 1 and if you take this quantity x to be equal to h cross omega by kT, And take this xd to be equal to h cross omega d by kt.

$$k_D = \frac{\omega_D}{v_s} = \left(\frac{6\pi^2 N}{V}\right)^{1/3}.$$

$$\bar{\mathcal{E}} = \int_0^\infty \varepsilon\, g(\omega) f_B(\omega).$$

$$\bar{\mathcal{E}} = \int_0^{\omega_D} d\omega\, g(\omega) \frac{\hbar\omega}{e^{\hbar\omega/k_BT} - 1}$$

$$= \frac{3V\hbar}{2\pi^2 v_s^3} \int_0^{\omega_D} \frac{\omega^3\, d\omega}{e^{\hbar\omega/k_BT} - 1}$$

$$x = \frac{\hbar\omega}{k_BT} \;;\; x_D = \frac{\hbar\omega_D}{k_BT} = \frac{\theta_D}{T}$$

$$\theta_D = \frac{\hbar v_s}{k_B}\left(\frac{6\pi^2 N}{V}\right)^{1/3}$$

Then, of course, so this is—let us call it the Debye temperature, in analogy with the Einstein temperature. So, this Debye temperature actually comes out to be h-bar Vs divided by k and a 6 pi squared n over V, all to the power of one-third. And these—the average energy comes out to be equal to 9 kT T over theta D whole cube 0 to X D, we have defined X D, so it is X cube divided by exponential X minus 1. And this particular thing, which, you know, has a value which is pi to the power of 4 by

So, your CV becomes equal to a del E del T and we lose this T in the process of differentiation. So, it becomes 9 NK (T over theta_D), and then this integral is going to give us pi^4 over 15. So, this again at large temperature, T to be much, much greater than h cross omega or KT is much greater than h cross omega, we recover Cv equal to 3R. At low temperature—that is, low temperature means your KT is smaller than h-bar omega—and your C_V becomes equal to 3NK. T over theta D whole cube and we have pi, you know, so there is a 9 there and then there is a pi 4 over 15.

You can do some simplification by, you know, this 3 and 5 and so on. And nevertheless, what is important here is that Cv is proportional to T cube and at low temperature, all the solids actually show this T cube behavior and that is why this is so very important and it sort of removes the inconsistency with the experimental data and one gets this at low temperature, Cv goes as T cube. In fact, there is a simple way of seeing this because, you know, only the lattice modes—so, a simple picture, okay, without doing all these extensive calculations. So, the lattice modes with energy which are h-bar omega, you know, less than or equal to kT—or of that order of kT—will be excited, okay.

$$\bar{\mathcal{E}} = 9Nk_BT\left(\frac{T}{T_\theta}\right)^3 \underbrace{\int_0^{x_D} \frac{dx\; x^3}{e^x - 1}}_{\frac{\pi^4}{15}}.$$

$$C_v = \frac{\partial \bar{\mathcal{E}}}{\partial T} = 9Nk_B\left(\frac{T}{\theta_D}\right)\cdot\frac{\pi^4}{15}.$$

Again $k_BT \gg \hbar\omega \Rightarrow C_v = 3R$

At low temp $k_BT \ll \hbar\omega$.

$$C_v = \overset{3}{\not 9} N k_B \left(\frac{T}{\theta_D}\right)^3 \frac{\pi^4}{\not{15}\,5} \qquad \boxed{C_v \sim T^3}$$

And how many such modes are there? That is obtained by this number of modes or the number of modes. They are proportional to the density of states, which are like omega by omega d whole cube. So, this is really like the thermal wavelength divided by the Debye wavelength. So, this is the kT by whole cube and KT, so the thermal wavelength. So, this KT is the thermal wavelength, and KD is the Debye wavelength or rather wave vector, thermal wave vector.

And the thermal wave vector can be, you know, defined as like h cross Vs into kT is same as kT, I mean T. So, the number of modes that you get they go as a function of temperature; they go as T cube. And so, there are, you know, so if you really think that more careful ones will give you a T over theta D whole cube. So, and each one will have energy 3 KT. So, each mode

Simple Picture.

Lattice modes with energy $\hbar\omega \lesssim k_B T$ will be excited.

K_T : Thermal wavevector

# of modes $\left(\frac{\omega}{\omega_D}\right)^3 \simeq \left(\frac{K_T}{K_D}\right)^3$.

$\hbar v_s K_T = k_B T$

# of modes T^3. $\Rightarrow$ $3N\left(\frac{T}{\theta_D}\right)^3$.

Each mode has energy $3k_BT$

$\bar{\mathcal{E}} \propto T^4$

$C_v \propto T^3$.

3 kT and so 3, you multiply this, so there will be the temperature dependence for the average energy is T to the power 4. I am just neglecting all other factors, so C actually goes as T cube, which is what we have said. So, it is just a simple picture and doing back-of-the-envelope calculations that you calculate the number of modes that are excited at a temperature T. And then each one of them has an energy which is kT or 3n kT for the full 3n modes; multiply them, that will give you the average energy. Take a derivative with respect to temperature that will give you the specific heat. So, we get this T cube law, which fits very well with experimental observations.

So, we shall stop here, and we have covered this crystal part and the lattice vibration completely here. Thank you. Thank you.