Introduction to Solid State Physics
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Lecture – 52
Average energy of phonons at temperature T

When we started this week what I told you is that, if we wish to calculate the energy of a crystal, because of the vibrations what I need is the average energy per mode times the density of states of these modes and then I integrate over this k or omega how I am looking at the modes.

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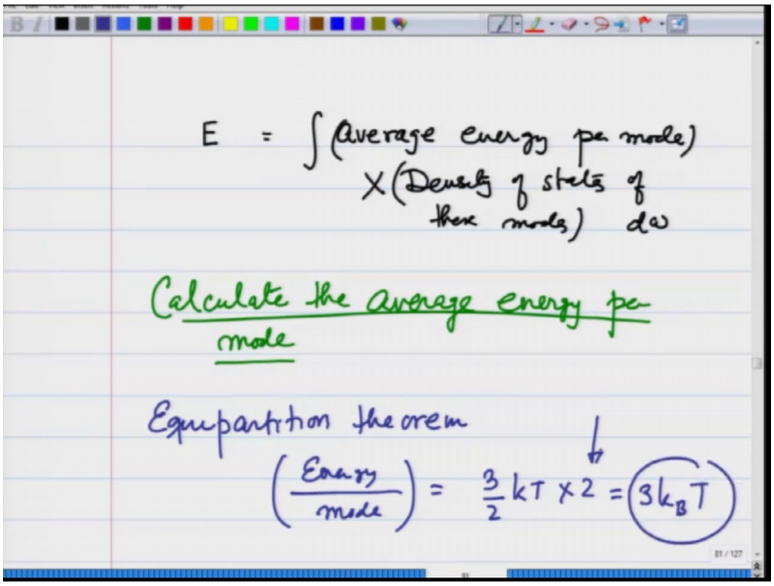

$$E = \int (\text{Average energy per mode}) \times (\text{Density of states of these modes})\, d\omega$$

Calculate the average energy per mode

Equipartition theorem

$$\left(\frac{\text{Energy}}{\text{mode}}\right) = \frac{3}{2} kT \times \overset{\downarrow}{2} = \boxed{3k_B T}$$

What I want to do in this lecture is, calculate the average energy per mode. You may ask what is the big deal about it after all if I do Equipartition theorem. It tells me that per degree of freedom or per mode the energy per degree of freedom or I can say per mode is going to be 3 by 2 kT times 2 this 2 comes because of the potential which is also quadratic.

So, this comes out to be 3 kT and we know what the answer is going to be.

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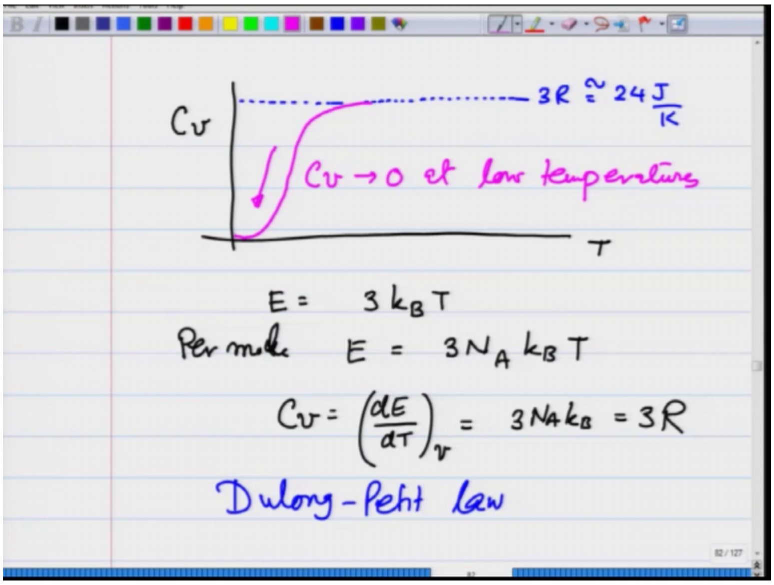

$E = 3 k_B T$

Per mole $E = 3 N_A k_B T$

$C_v = \left(\frac{dE}{dT}\right)_v = 3 N_A k_B = 3R$

Dulong-Peht law

So, initially this was what was thought and if one were to plot the specific heat of a solid with respect to temperature, right the energy is 3 k Boltzmann T. So, for per mole the energy is going to be per mole the energy is going to be 3 and Avogadro kBT, and therefore, Cv is going to be dE dT fixed volume is going to be 3 NA kB or 3 R what is known as the Dulong Peht law.

So, what one expects from this is that the energy is the Cv is constant equal to 3 R which is roughly 24 Joules per Kelvin. This is all fine except when you do the experiments you find that at low temperatures Cv goes to 0 which is in conflict with classical mechanics or the classical equipartition theorem and therefore, one has to bring in quantum mechanical treatment. And that is what explains the C v going to 0 at low temperatures this was initially done by Einstein and this gave a lot of support to the theory of quanta proposed by Planck; so, this has this historical importance also.

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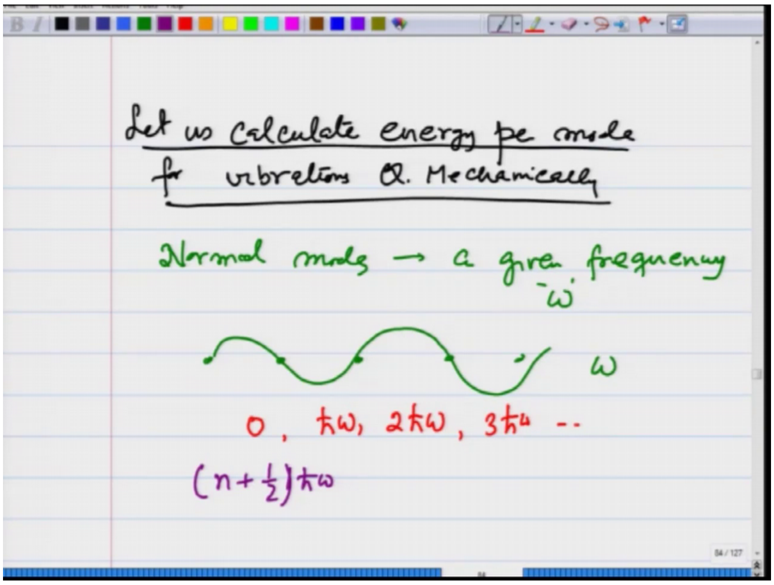

Let us Calculate energy pe mode for vibrations Q. Mechanically

Normal mode → a given frequency ω

ω

$0, \hbar\omega, 2\hbar\omega, 3\hbar\omega$ --

$(n+\frac{1}{2})\hbar\omega$

So, now let us calculate energy per mode for vibrations quantum mechanically ok. So, I hope I have made it clear why experiments necessitated that we treat the energy per mode of vibrations quantum mechanically. There is something which I had said at the beginning of these lectures, when I said that experimentally it is clear that these have to be treated quantum mechanically the vibrations have to be treated quantum mechanically and therefore, the concept of phonon was given. So, how do we treat these modes quantum mechanically? Remember these are normal modes and these are normal modes they have a given frequency omega.

So, these are like all these atoms together are vibrating with a given frequency and this is this normal mode as I have been saying earlier it is like a string on a guitar or a string instrument vibrating with a particular frequency. And then what we are going to say is that quantum mechanically when this is vibrating with frequency omega; it cannot just take any energy it can be at either 0 energy, it can take h cross omega energy, it can take 2 h cross omega energy, 3 h cross omega energy and so on.

The excitation energy is going to be 0 h cross omega or so, on. The energy levels you may wonder why I am not calling it n plus half they come out to be 1 half h cross omega n equals 0 1 2 3. So, energies are half h cross omega 3, half h cross omega, 5 half h cross omega, but I am talking about excitation is h cross omega 2 h cross omega, 3 h cross omega and so on. This I am going to say is as if this normal mode has 1 phonon 2 phonons 3 phonons 4 phonons of that frequency.

So, I can have n phonons and then energy will be an h cross omega and the question is, what is the average number of phonons?

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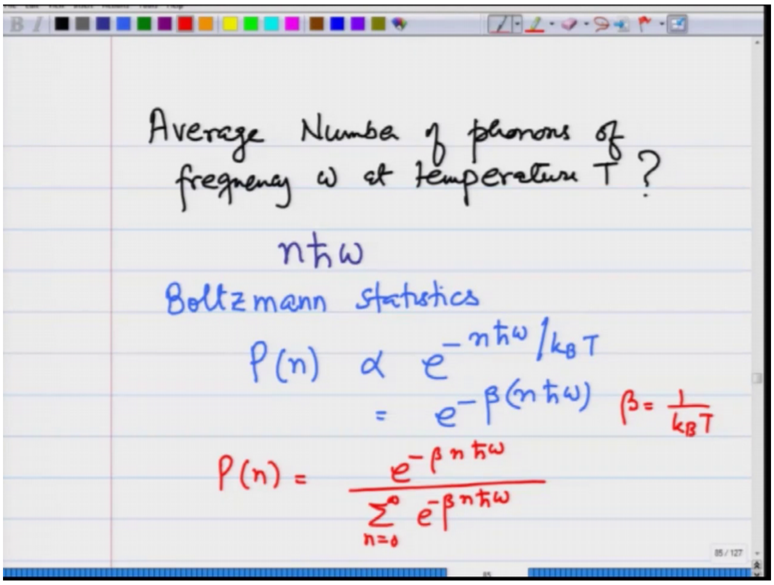

Average Number of phonons of frequency ω at temperature T ?

$n\hbar\omega$

Boltzmann statistics

$$P(n) \propto e^{-n\hbar\omega/k_BT}$$

$$= e^{-\beta(n\hbar\omega)} \qquad \beta = \frac{1}{k_BT}$$

$$P(n) = \frac{e^{-\beta n\hbar\omega}}{\sum_{n=0}^{\infty} e^{-\beta n\hbar\omega}}$$

So, question is average number of phonons of frequency omega at temperature T. This is the question I am asking this also gives you what is the average energy of that mode.

So, now the picture the quantum mechanical picture that is coming is that in this crystal these vibrations can be now thought of the crystal can be thought of as having these phonons moving around with different frequencies. Like very much like the photons move around in a black body which you must have studied in your previous classes. Just exactly like that a crystal I am thinking of as if these phonons are moving around each phonon has a well defined frequency, each phonon represents an energy h cross omega for the frequency omega.

So, average number of phonons we are going to count. Now the energy for n phonons is going to be n h cross omega and by Boltzmann statistics we have that the probability of having these n phonons in the system is going to be proportional to e raised to minus n h cross omega over k BT. For convenience I am just going to write this as e raised to minus beta times n h cross omega, where beta is 1 over k BT I am going to later substitute that.

Now, this is a probability which is proportional to this. Since probability is normalized the probability function will be given as e raised to minus beta n h cross omega divided by sum over n, n equals 0 to infinity because I could have any number n it could be 0 or infinity e raised to minus beta n h cross omega. This is normalized probability because if I again sum it over all n it gives me 1.

So, having a number any number n, the probability is 1 and therefore, this is normalized this is the probability.

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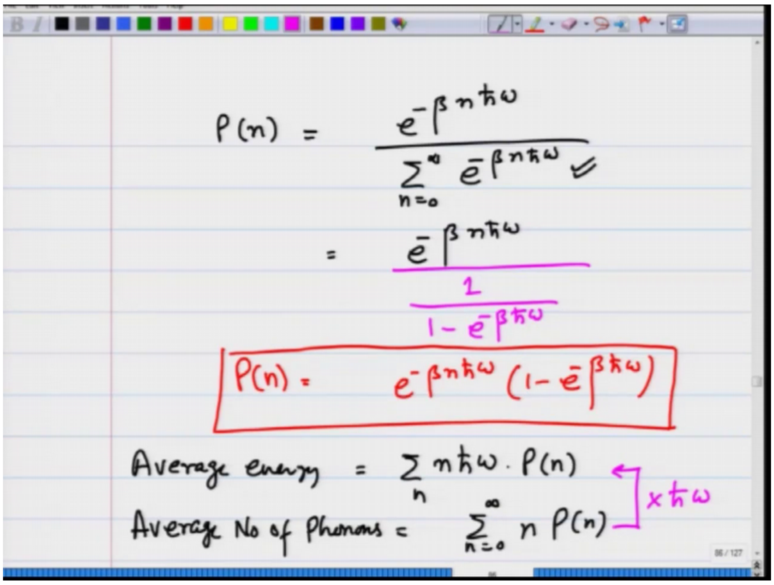

$$P(n) = \frac{e^{-\beta n\hbar\omega}}{\sum_{n=0}^{\infty} e^{-\beta n\hbar\omega}} \checkmark$$

$$= \frac{e^{-\beta n\hbar\omega}}{\frac{1}{1-e^{-\beta\hbar\omega}}}$$

$$\boxed{P(n) = e^{-\beta n\hbar\omega}\left(1-e^{-\beta\hbar\omega}\right)}$$

$$\text{Average energy} = \sum_{n} n\hbar\omega \cdot P(n)$$

$$\text{Average No of Phonons} = \sum_{n=0}^{\infty} n\, P(n) \quad \Big] \times\hbar\omega$$

So, we have written the probability of having n phonons is equal to e raised to minus beta n h cross omega divided by summation over n equals 0 to infinity, e raised to minus beta n h cross omega. And this would be equal to e raised to minus beta and h cross omega, this is a geometric series. So, I can sum it up this is going to be 1 over 1 minus e raised to minus beta h cross omega.

So, probability P n is e raised to minus beta n h cross omega, 1 minus e raised to minus beta h cross omega. This is the probability of having n phonons what about the average energy of the system is therefore, going to be n h cross omega, times the probability of having n phonons sum over n. What is the average number of phonons? This is going to be summation over n equals 0 to infinity n times P n. So, you multiply average number of phonons by h cross omega, you get average energy of that mode. So, in one shot with this probability I am calculating the average number of phonons of frequency omega at temperature T and average energy of that mode.

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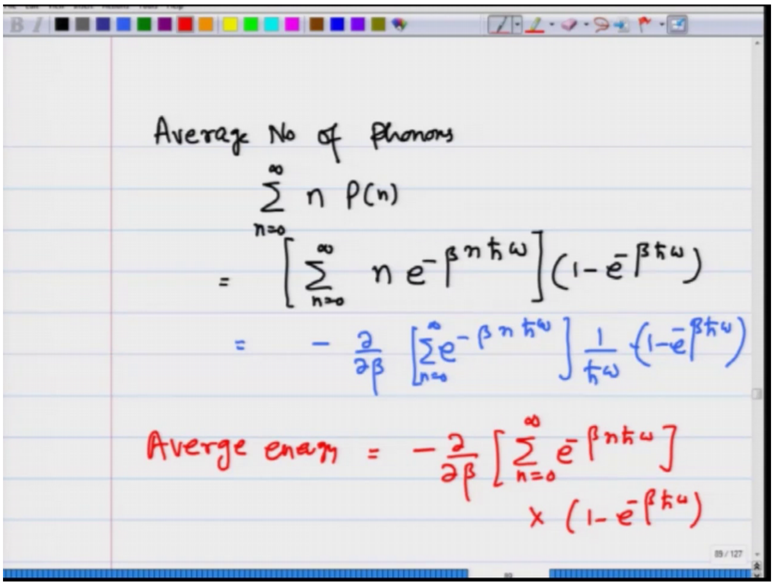

Average No of Phonons

$$\sum_{n=0}^{\infty} n\, P(n)$$

$$= \left[\sum_{n=0}^{\infty} n\, e^{-\beta n \hbar\omega}\right](1-e^{-\beta\hbar\omega})$$

$$= -\frac{\partial}{\partial\beta}\left[\sum_{n=0}^{\infty} e^{-\beta n \hbar\omega}\right]\frac{1}{\hbar\omega}(1-e^{-\beta\hbar\omega})$$

Averge energy $= -\frac{\partial}{\partial\beta}\left[\sum_{n=0}^{\infty} e^{-\beta n\hbar\omega}\right] \times (1-e^{-\beta\hbar\omega})$

So, let us do that now. So, the average number of phonons is going to be equal to summation n Pn n equals 0 to infinity, which comes out to be summation n equals 0 to infinity and e raised to minus beta n h cross omega times 1 minus e raised to minus beta h cross omega. I can put this summation over n here because the other term is independent of n. This I can write as minus d by d beta e raised to minus beta n h cross omega summed over n equals 0 to infinity, 1 over h cross omega times 1 minus e raised to minus beta h cross omega right.

Because when I take the differential it becomes e raised to minus beta n h cross omega times minus n h cross omega, with this minus sign that minus becomes plus and then you divide by h cross omega. You can also write average energy, then I do not have to divide by this as cross omega and it will be minus d by d beta of summation over n equals 0 to infinity, e raised to minus beta n h cross omega times 1 minus e raised to minus beta h cross omega, this is a very easy calculation to do.

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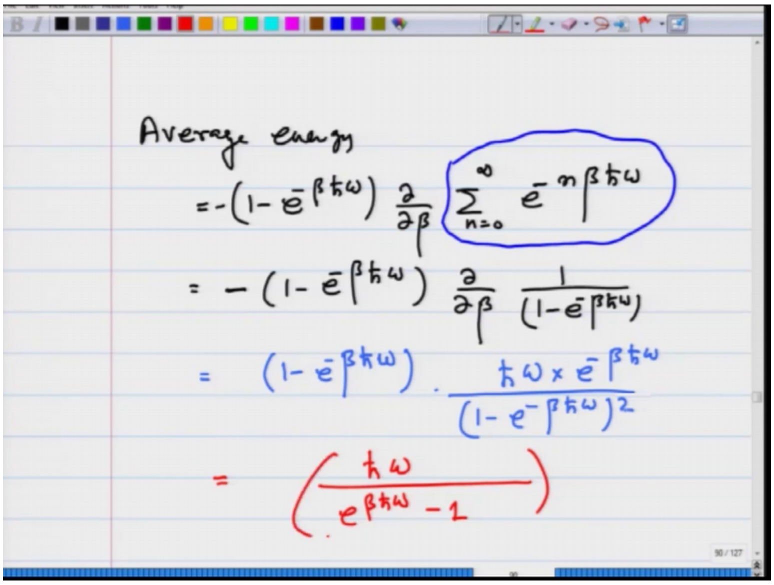

Average energy

$$= -(1-e^{-\beta\hbar\omega}) \frac{\partial}{\partial\beta} \boxed{\sum_{n=0}^{\infty} e^{-n\beta\hbar\omega}}$$

$$= -(1-e^{-\beta\hbar\omega}) \frac{\partial}{\partial\beta} \frac{1}{(1-e^{-\beta\hbar\omega})}$$

$$= (1-e^{-\beta\hbar\omega}) \cdot \frac{\hbar\omega \times e^{-\beta\hbar\omega}}{(1-e^{-\beta\hbar\omega})^2}$$

$$= \left(\frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\right)$$

So, let me just do it for the average energy, this is equal to 1 minus e raised to minus beta h cross omega d by d beta with a minus sign in front, summation n equals 0 to infinity, e raised to minus n beta h cross omega which I can write as minus 1 minus e raised to minus beta h cross omega, d by d beta of 1 over 1 minus e raised to minus beta h cross omega because the sum you recall is that geometric series that we did earlier.

And therefore, this becomes 1 minus e raised to minus beta h cross omega, h cross omega over 1 minus e raised to minus beta h cross omega square and here is one more e raised to minus beta h cross omega. And this when you manipulate comes out to be h cross omega over e raised beta h cross omega minus 1 this is the result we are looking after.

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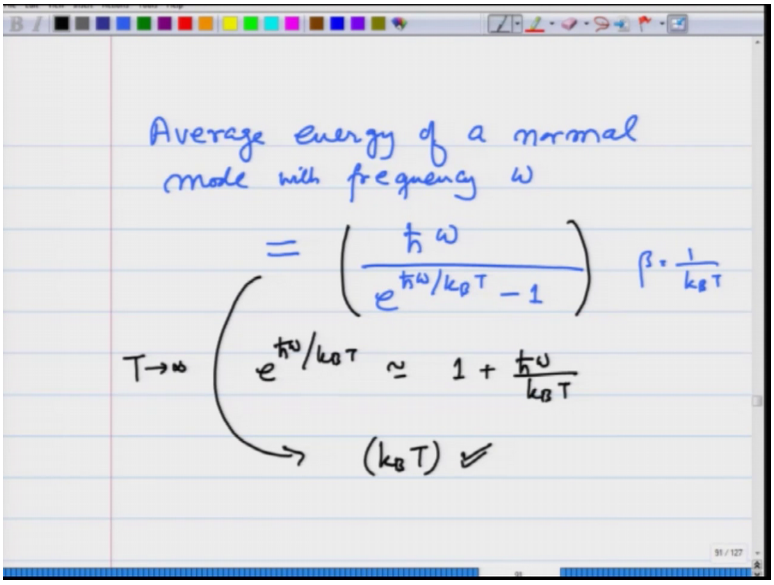

Average energy of a normal mode with frequency ω

$$= \left(\frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} \right) \qquad \beta = \frac{1}{k_B T}$$

$$T \to \infty \qquad e^{\hbar\omega/k_B T} \simeq 1 + \frac{\hbar\omega}{k_B T}$$

$$\to (k_B T) \checkmark$$

So, I can say that the average energy of a normal mode with frequency omega is equal to h cross omega over e raised to h cross omega by k BT minus 1 because beta was nothing, but 1 over k BT and this is using the quantum mechanical treatment. Let us see what happens if T goes to infinity. If T goes to infinity e raised to h cross omega by k BT is roughly equal to 1 plus h cross omega over k BT and therefore, this average energy goes to this term goes to kBT. So, this comes out to be the same as classical result 3 is a factor which will be introduced later for 3 degrees of freedom.

So, this is for high temperature it goes to the classical result; however, at low temperatures it differs from classical results. It is given by this Planck distribution formula and that is what makes all the difference in calculating in obtaining the total energy for e crystal vibrational modes as temperature goes to 0; it correctly explains the Cv the specific heat going to 0 as t goes to 0 which we will explore in the next couple of lectures.

Thank you.