Condensed Matter Physics
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Lecture - 15
Anharmonicity and Thermal Expansion

We have discussed how the thermal conductivity of an insulator arises from phonon scattering and we have considered in the last lecture the temperature dependence of the thermal conductivity of such an insulator and compared it with that of a metal. I would just like to mention at this point an important point regarding a nature of phonon scattering in contributing to the thermal conductivity of an insulator. If you have a perfectly harmonic crystal, the phonon states are stationary states. If a phonon distribution carries a thermal current then that distribution will remain unaltered in the course of time and the thermal current will remain un degraded forever. In other words, a perfect click harmonic crystal will have infinite thermal conductivity.

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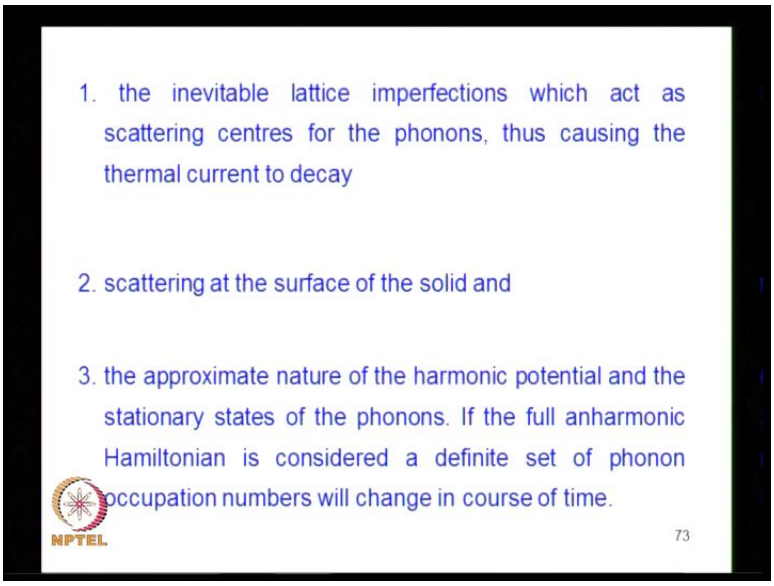

1. the inevitable lattice imperfections which act as scattering centres for the phonons, thus causing the thermal current to decay
2. scattering at the surface of the solid and
3. the approximate nature of the harmonic potential and the stationary states of the phonons. If the full anharmonic Hamiltonian is considered a definite set of phonon occupation numbers will change in course of time.

However the thermal conductivity of a real insulator will be a finite for the following reasons. One - the inevitable lattice imperfection which act as a scattering centers for the phonon’s thus causing the thermal current to decay in time two this scattering at the surface of the solid and three the approximate nature of the harmonic potential and this stationary states of phonons. If the full anharmonic hamiltonian is considered a definite set of phonon occupation numbers will change in course of time this again will mean that the thermal conductivity becomes finite. So, anharmonicity is the key to understanding the behavior of thermal conductivity of solids.

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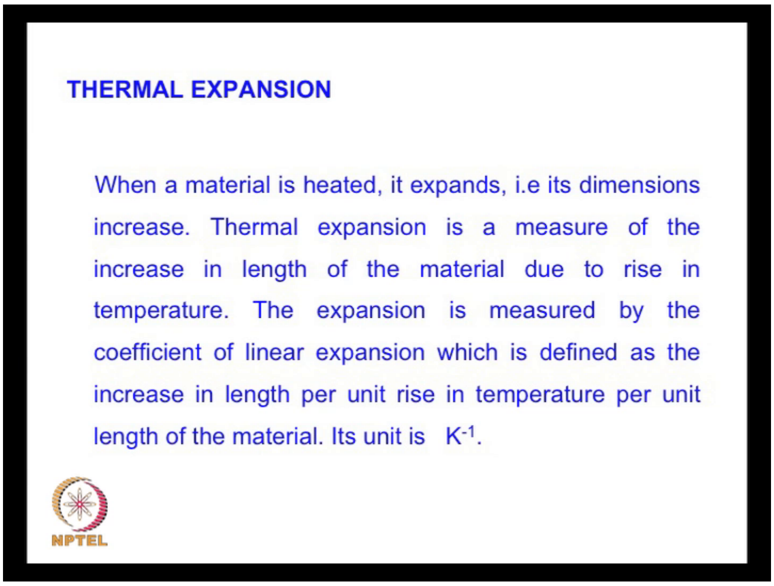

THERMAL EXPANSION

When a material is heated, it expands, i.e its dimensions increase. Thermal expansion is a measure of the increase in length of the material due to rise in temperature. The expansion is measured by the coefficient of linear expansion which is defined as the increase in length per unit rise in temperature per unit length of the material. Its unit is K^{-1}.

This is an important point, because we now pass on to consider a another interesting property of solids and liquids this is thermal expansion we all know that when a material is heated it expands usually. In other words, it is dimensions increase thermal expansion is a measure of the increase in the length of the material due to rise in the temperature. This expansion is measured by the coefficient of linear thermal expansion which is defined as the increase in length per-unit rise in temperature with respect to the unit length of the material per unit length of the material. Well again the expansion of the solids on heating is a direct consequence of anharmonicity in the vibration of lattice atoms. For example, let us consider a one-dimensional solid for simplicity if the vibrations of the atoms a perfectly harmonic the potential energy will be will have the form.

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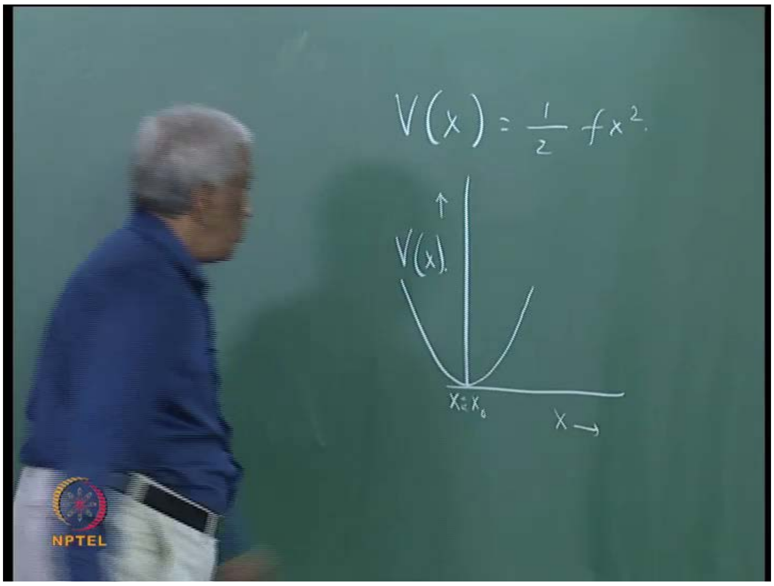

V of x equals half f x square where f is the force constant since this potential energy is proportional to square of x the curve v of x if it is plotted it’ll be a parabola.

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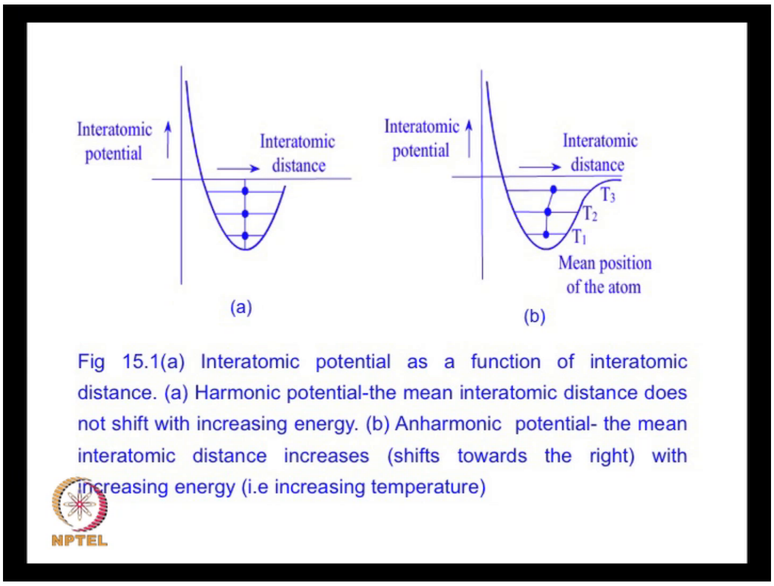

Fig 15.1(a) Interatomic potential as a function of interatomic distance. (a) Harmonic potential-the mean interatomic distance does not shift with increasing energy. (b) Anharmonic potential- the mean interatomic distance increases (shifts towards the right) with increasing energy (i.e increasing temperature)

So, x naught is the equilibrium position the harmonic vibrations around this will create a perfectly parabolic shaped potential function in such a harmonic potential.

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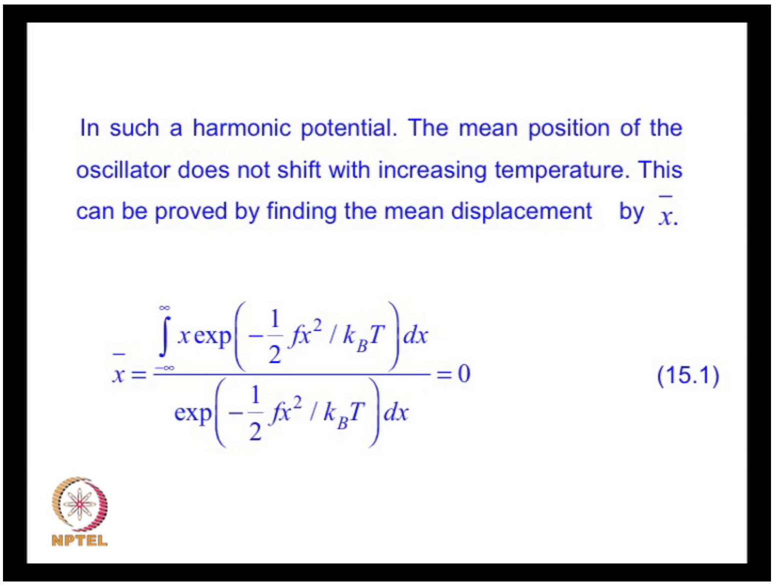

In such a harmonic potential. The mean position of the oscillator does not shift with increasing temperature. This can be proved by finding the mean displacement by $\bar{x}$.

$$\bar{x} = \frac{\int_{-\infty}^{\infty} x \exp\left(-\frac{1}{2} f x^2 / k_B T\right) dx}{\exp\left(-\frac{1}{2} f x^2 / k_B T\right) dx} = 0 \qquad (15.1)$$

The mean position of the oscillator does not shift with increasing temperature this can be proved readily by calculating the mean displacement x bar.

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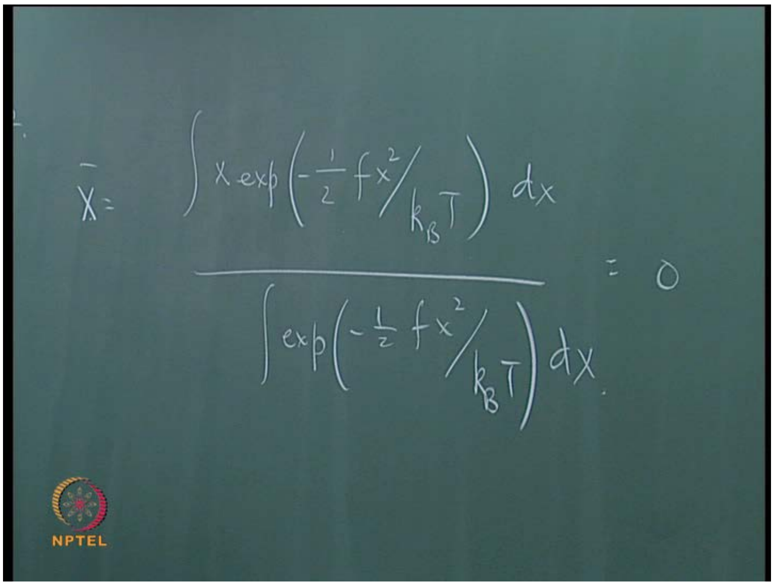

$$\bar{X} = \frac{\int x \exp\left(-\frac{1}{2} f x^2 / k_B T\right) dx}{\int \exp\left(-\frac{1}{2} f x^2 / k_B T\right) dx} = 0$$

Which is given by x bar equals integral x exponential half f x square by k b t d x by and this will turn out to be if it is evaluated shown to be vanishing, so there is no change.

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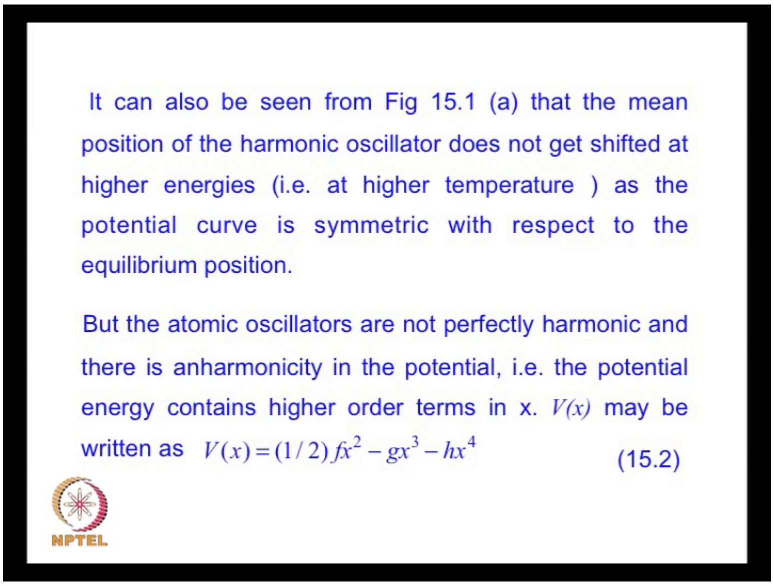

It can also be seen from Fig 15.1 (a) that the mean position of the harmonic oscillator does not get shifted at higher energies (i.e. at higher temperature) as the potential curve is symmetric with respect to the equilibrium position.

But the atomic oscillators are not perfectly harmonic and there is anharmonicity in the potential, i.e. the potential energy contains higher order terms in x. *V(x)* may be written as $V(x) = (1/2)fx^2 - gx^3 - hx^4$ (15.2)

Now you can also see this by looking at the graph here which portrays figures, which portray the interatomic potential as a function of interatomic distance and you see that you have this various states here. And this when there is an increase in temperature vibration amplitude changes, but as long as this remains harmonic the centre of this will be the same the equilibrium position does not change in other words, there is no shift and there is there cannot be a thermal expansion its only when there is…

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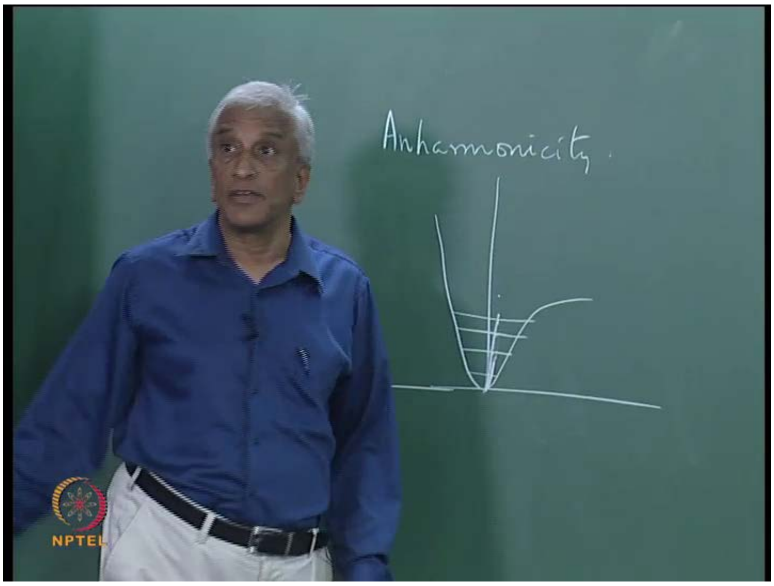

There is a an harmonicity or a departure from harmonic behavior it is than that this curve will start looking like somewhat like this a deviation from parabolic behavior and then the mean position will start shifting like this. So, there is a net shift of the mean position x bar and with an increase in temperature. So, this corresponds to the states of different temperatures and the mean position shifts like this. So, this gives rise to a thermal expansion.

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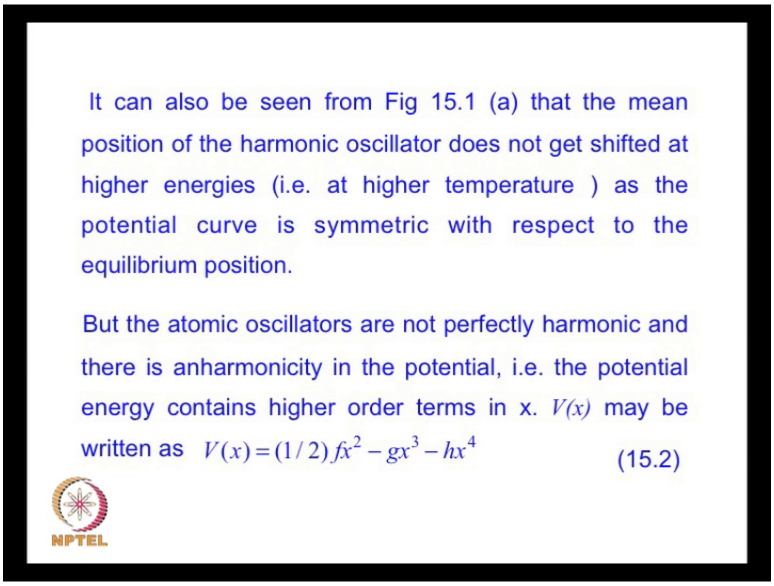

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So, these are the pictorial explanation the atomic oscillators then there are not perfectly harmonic can be written by a potential function which is not a just half f x square. So, these are the anharmonic terms. So, when you include them and calculate this integral we can perform this calculation. So, let us take this.

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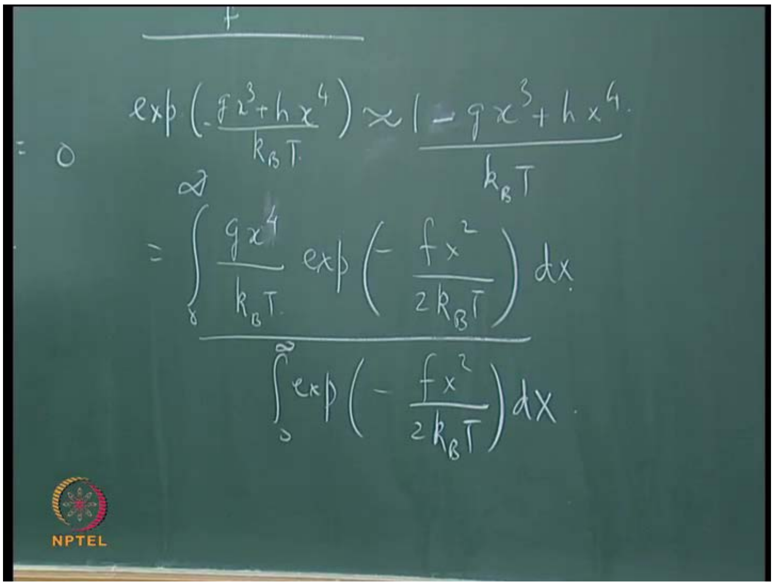

f

$$\exp\left(-\frac{gx^3+hx^4}{k_BT}\right) \approx 1 - \frac{gx^3+hx^4}{k_BT}$$

$= 0$

$$= \frac{\int_0^\infty \frac{gx^4}{k_BT}\exp\left(-\frac{fx^2}{2k_BT}\right)dx}{\int_0^\infty \exp\left(-\frac{fx^2}{2k_BT}\right)dx}$$

So, we can show that x bar is three g by f square k b t we can I show the calculation in the transparency.

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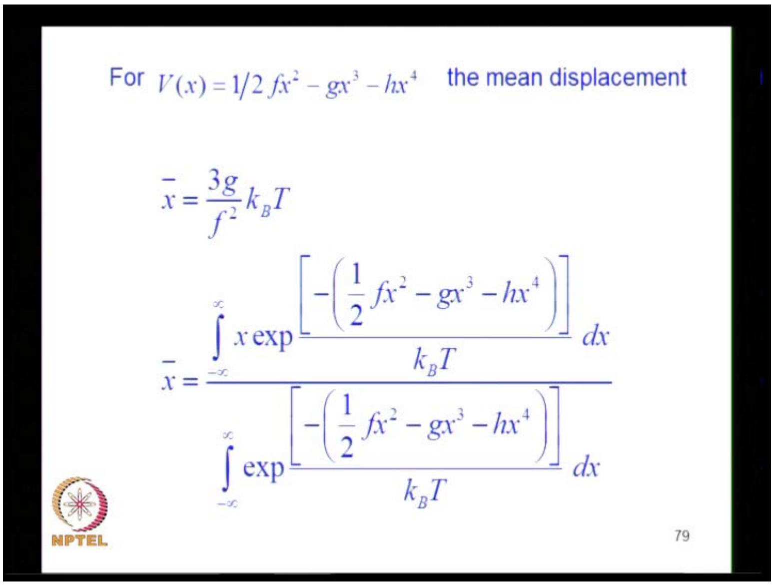

For $V(x) = 1/2\, fx^2 - gx^3 - hx^4$ the mean displacement

$$\bar{x} = \frac{3g}{f^2}k_BT$$

$$\bar{x} = \frac{\int_{-\infty}^{\infty} x \exp\frac{\left[-\left(\frac{1}{2}fx^2 - gx^3 - hx^4\right)\right]}{k_BT}dx}{\int_{-\infty}^{\infty} \exp\frac{\left[-\left(\frac{1}{2}fx^2 - gx^3 - hx^4\right)\right]}{k_BT}dx}$$

So, you can see that x bar is written like this x exponential here anharmonic potential divided by k B T negative of that d x and denominator you have the same integral exponential again the anharmonic potential fine negative of that by k b t d x.

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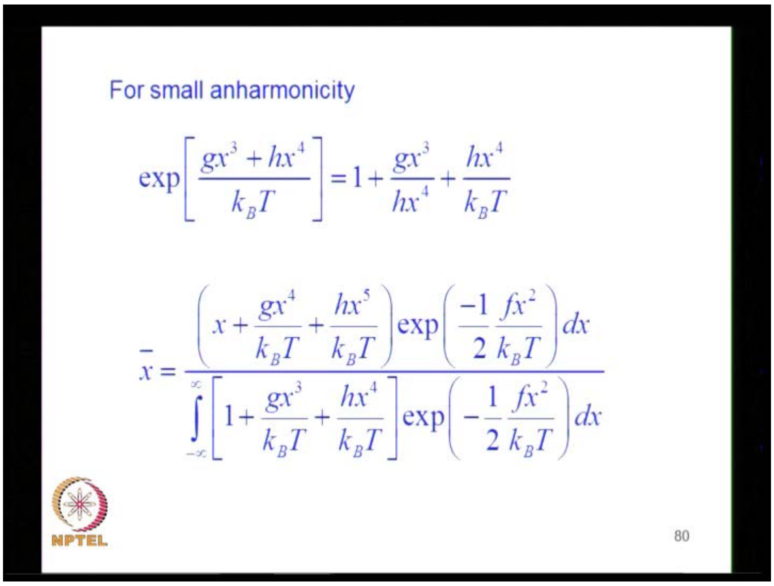

For small anharmonicity

$$\exp\left[\frac{gx^3+hx^4}{k_BT}\right]=1+\frac{gx^3}{hx^4}+\frac{hx^4}{k_BT}$$

$$\bar{x}=\frac{\left(x+\frac{gx^4}{k_BT}+\frac{hx^5}{k_BT}\right)\exp\left(\frac{-1}{2}\frac{fx^2}{k_BT}\right)dx}{\int_{-\infty}^{\infty}\left[1+\frac{gx^3}{k_BT}+\frac{hx^4}{k_BT}\right]\exp\left(-\frac{1}{2}\frac{fx^2}{k_BT}\right)dx}$$

If you calculate that first of all we notice that for small anharmonicity. The terms exponential g x cube plus h x t to the power four can be approximated by one plus g x cube plus h x to the power four. So, by have k b t this will be, so that we can use this and calculate the rest of the integral.

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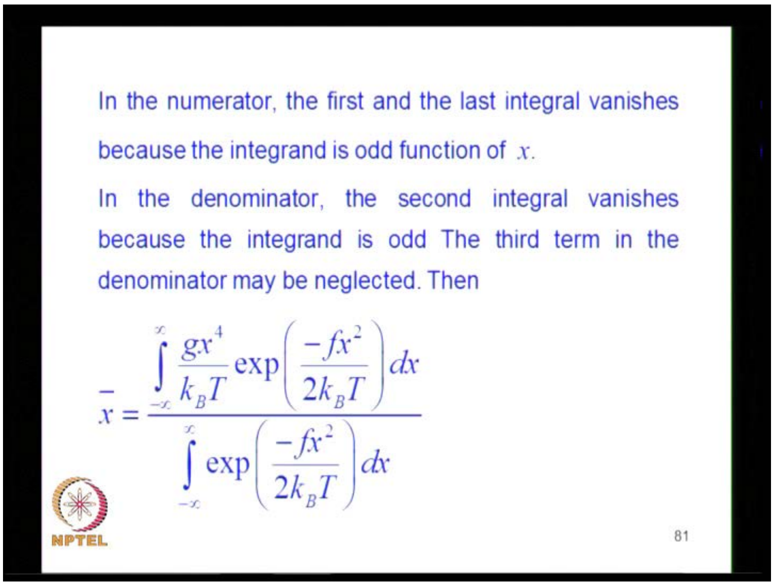

In the numerator, the first and the last integral vanishes because the integrand is odd function of x.

In the denominator, the second integral vanishes because the integrand is odd The third term in the denominator may be neglected. Then

$$\bar{x}=\frac{\int_{-\infty}^{\infty}\frac{gx^4}{k_BT}\exp\left(\frac{-fx^2}{2k_BT}\right)dx}{\int_{-\infty}^{\infty}\exp\left(\frac{-fx^2}{2k_BT}\right)dx}$$

And this leads to a expression of the form integral g x cube g x to the power four like k b t exponential minus f x square by two k b t d x divided by this will by suitable substitution. This can be shown to be equal to four k b t by f square times gamma five by two psi gamma half these are the gamma functions that would give you the result three k b t. So, you can see that there is a net exchange and non-zero mean displacement in the presence of the an harmonicity and that is what contributes to thermal expansion. So, you can see that the energy there is a shift and mean displacement is directly proportional to the temperature and it is also directly proportional to the coefficient G an harmonicity coefficient, but its inversely proportional to the square of the force constant, if you have a solid which is strongly bonded. For example, covalently bonded solid or very strongly bounded diamond is an example the force constant will then be very high. So, the mean displacement and hence the expansion coefficient will be very small whereas, in weekly bonded solid the force constant will be small, but the coefficient g will be higher therefore, the mean displacement is large and hence the thermal expansion coefficient will be higher.

So, covalently bounded solids like diamond and silicon have very low thermal expansion variables polymers such as rubber and prospects have much higher coefficient of thermal expansion in the k m metals the thermal expansion coefficient lies between the values of solids like diamond and silicon on the even side and rubber and prospects and the other. So, the thermal expansion coefficient are some of the typical material which are commonly used are all shown in table you can see values given for materials like aluminum copper silver.

Alumina concrete Glass perspex wood you can see the thermal expansion coefficient this also along with this the specific heat and thermal conductivity values are given. So, together this give you the entire spectrum of thermal properties of so, we have considered all the thermal properties such as specific heat thermal conductivity and thermal expansion coefficient based on our understanding of phonons states phonons and as well as the electron.

What is now left is one layer discussion of the temperature dependence of the electrical. Conductivity of metals this is a very important property. So, we would like to discuss this at this stage we will consult this in the detail in the next lecture, but at the moment I will give a brief introduction about what is happening. Now we are equipped with all concept about phonons and electron gases in the metal has we know it is the electron gas as well as the phonon gas which you rise to scattering processes which take away the electron carriers the charge carriers from the from their normal trajectories under the influence of a play directory field. So, the current density decays. So, it is this scattering processes scattering of electrons by phonons this is what that the bottom of the temperature dependence of electrical conductivity of metals.

So, the Drude theory the simple Drude theory which we have already considered the is the expression for the electrical conductivity Drude expression in this n is the concentration of electrons. Of course, the Drude expression is a very general one not only valid for metals, but in general for any, but we are now applying it to the case of a metal. Now we know that the concentration of free electrons which are responsible for conductivity in a metal are constant. There are not dependent on the temperature m and e are also constant.

So, the entire temperature dependence is due to the temperature dependence of the relaxation time tau. So, the key to understanding the temperature dependence and the electrical conductivity of a metal is contained in an understanding of the temperature dependence of the relaxation time for this is the relaxation time for electron phonon scattering there is also scattering by impurities any kind of impurities. So, both processes are scattering give rise to the relaxation behavior and hence contribute to the conductivity; however, if we have for example, a perfectly periodic pure solid than there would not be any scattering even at a finite temperature and therefore, there would not be a temperature dependence here.

So, it is the scattering processes due to deviation such this perfect periodicity due to the presence of different kind of impurities like point effect vacancies interstitials grain boundaries stacking falls all this will contribute to impurities scattering, but this impurities scattering is not temperature dependent it is something which is constant. So, it gives rise to a temperature independent in terms of we will speak in term of the reciprocal of sigma namely the electrical resistivity. So, this gives rise to a temperature independent resistivity whereas, the electron phonon scattering gives you the temperature dependent resistivity. So, that rho is rho naught plus rho one t.

So, this is due to impurities and this is due to phonon scattering. Total resistivity and its temperature dependence is determined by this. We will now discuss the temperature dependence of electrical resistivity of metal as we already pointed out this temperature dependence arises from the scattering of the electrons. These are free conduction electrons by phonons to discuss this. Let us write the periodic potential of a rigid ion lattice. Now this is given by let us write this as u periodic which is the function of position coordinate r of the atom in the lattice which is a summation over all the lattice site of the potential at any given lattice site over all the trivial lattices r this is well-known. But this is only approximate because actually we ions are not rigid in the lattice.

And we actually have the actual potential is really a sum of this individual atomic potential which are function of not only this, but also where u write this as capital u distinguish this from the displacement from equilibrium position. So, strictly this can be written as the u periodic this one minus sigma over r u of r dot the gradient of the potential del v of r by omega plus higher-order terms that is the expression. So, the difference between the actual potential and the periodic potential is a kind of perturbation this is the perturbation which acts on the stationary states of the periodic Hamiltonian now which will give Bloch levels. So, we have this perturbation causes transition among the Bloch levels which are the stationary states of the periodic Hamiltonian this is what causes degradation of the electric Currents which otherwise would be infinite.

So, this is the mechanism for how we get a temperature dependent electrical resistivity due to the degradation the electrical current which arises from this perturbation which is due to the electron phonon interaction. So, for the phonon scattering as we already discussed we have a which is an elastic scattering. So, which it should satisfy the relation. So, this is a energy conservation q is a phonon vector. So, the real situation this this is the constraint an equation which constraints a two-dimensional surface. So, this needs to this defines a two-dimensional surface of allowed wave vectors allowed by the conservation condition wave vectors q in the three-dimensional phonon wave vector space.

So, that is the mechanism and figure shows the electron phonon scattering event which can be described in the Fermi surface this become Fermi c and they have a state with k wave vector k being scattered onto a state of wave vector k prime such that keep which is k plus q . So, that describes the conservation situation energy conservation. So, that is the event and space angle theta if this scattering angle. So, that is the overall picture of how a temperature dependent electrical arise a resistivity arises from electron phonon scattering let us look at this situation at different temperatures because we want to discuss temperature dependence first let us consider high-temperatures. So, temperature which are high in comparison d by temperatures that is the first limiting situation in this for any normal mode the number of phonons n of q is given by one by e to the power h cross omega q by k b t minus one.

Since the phonons or boson and then the temperature is high compared to the t d by temperature this can be written as. So, the number of phonons increases linearly with t for any normal mode q. So, if the number of phonons increases linearly with temperature. So, does the electrical resistivity at such temperature this scattering. So, the electrical resistivity also increases linearly with temperature at temperatures large at high temperatures compared to the theta d lecture now what happens at the low-temperature when the temperature is small in comparison to the theta d, this is high temperatures.

So, at low temperatures we do not have enough phonons to scatter the electrons only phonons with energy h cross omega q comparable to or less than k b t they will be emitted are observed by the electrons. So, when this is the condition then in this domain we know that the dispersion relationship is of this form of omega equal to v q where v is the speed of sound in the medium. So, that q is of order of k b t by h cross v, so that the condition for the phonon wave vector. So, only within the surface of phonon with energy conservation law permits only a subsurface of a linear dimension is proportional to T.

And therefore, surface area T square linear dimensional is proportional to t therefore, surface area is proportional to the t square can actually participate this is shown in the next figure. There you have wave vectors of those phonons allowed by the conservation law to participate in one phonon scattering event with electron whose wave vector is k, and this is shown in this figure and therefore, the number of phonons decreases as t square because of this. Now the electron scattering rate actually declines faster than this this is because we have the electron phonon coupling constant whose square is given by l and stating this without proof. These are the standard result into half h cross omega q k k prime well that is why I gave k minus k prime here k naught is the so-called Thomas Fermi wave vector which is defined by k naught equals four phi e square d n naught by d mu.

Because of this the consequence is that this matrix element coupling constant g k k prime is such that when k minus k prime is small at low time low temperatures then the coupling constant the square of the coupling constant is proportional to k minus k prime.

And therefore, this is at the order of k b t by h cross omega. And therefore, this decreases with the temperature linearly. Therefore, for till very small compared to theta d the electron phonon scattering scattering rate decreases as the cube of the temperature.

However, we also have to consider an extra factor in this situation that this one phonon process which is due to an elastic scattering only favor the forward scattering in the forward direction elastic scattering with a only a very small change in the wave vector favors scattering in the forward direction. So, this can be shown to be taken into account the preferential concentration of the scattered of the phonons in the forward direction can be taken into account by considering and effective scattering rate which is an angular average over all scattering angles theta weighted with a factor p of theta equals one minus cos theta. And now this factor p of theta is one minus is really two signs by r theta by two and it can see the situation here.

So, this is really half of q by k f square where k f is Fermi wave vector. So, this again gives you a t square. So, this gives you an other t-square dependence. So, the combined with this t cube dependence the net t to the power five dependence there is a t to the power five dependence of the scattering rate and therefore, the resistivity at low temperatures the situation can be rigorously discussed it has been done by Bloch and Gruneisen, they discuss this situation theoretically for all temperature.

Now this leads to a vigorous expression which gives a electrical resistivity has integral zero to x e to the power z minus one z to the power five d z one minus e to the power z. Now this leads to a lattice resistivity role l which goes as four point two two five evaluating this integral t by theta d cube five into j five of theta d by t times the resistivity at the b by temperature were j five of x is this a . So, this gives you the actual Bloch Gruneisen law for the phonon resistivity rho l which is depicted in figure as the relation between the reduced resistivity a rho of t by rho of theta t as a function of t by theta d. So, this goes is a linear relationship for large values of t by theta d and then it becomes non-linear goes like this.

So, this is a behavior which have been experimentally observed for wide variety of metals like gold sodium copper aluminum and nickel and by fitting the actual measured temperature with theoretical expression like this. You can actually obtain a value for the d by temperature and comparative with values reduced from the specific heat measurements. However, this discussion as not taken into account unclip processes consider only a normal process, but his we know from the thermal conductivity discussion unclip processes are quite important and also a possible non spherical Fermi surface may have considered only a isotropic spherical Fermi surface. So, these are the two factors which have not been taken into account, but these effects are not dominant in the alkali metals for which the Bloch Gruneisen law has been verified by the experimental results. Now this I given some references for this discussion by ashcroft and mermen and the book by j s dug dale which I already discussed electrical resistivity metals and dallies and also feng contents matter physics is the world scientific book. So, these are discussing some other salient feathers of this Bloch Gruneisen theory.