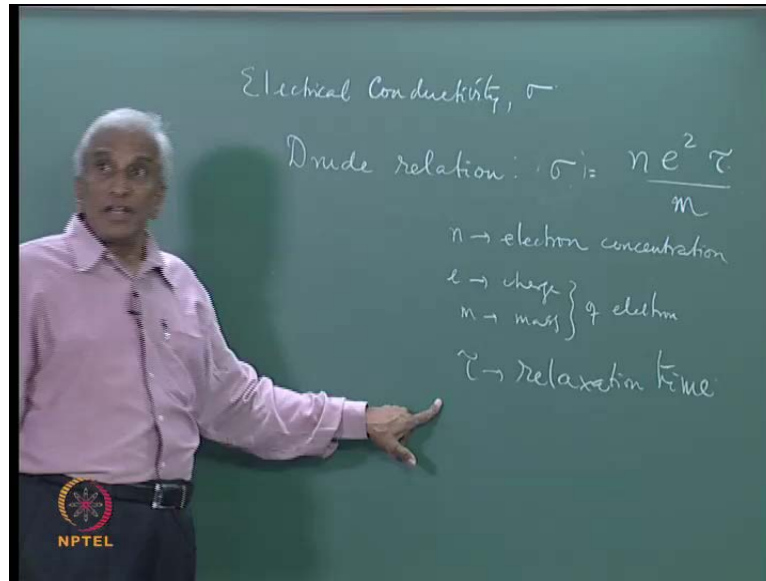**Condensed Matter Physics**
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Lecture - 11
**Thermal Conductivity of Metals**

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So, last time, we talked about one of the most important properties of metals namely the electrical conductivity, and arrived at a very interesting relationship known as the Drude relation which gives the electrical conductivity sigma as n e square tau by m. Where n is the electron concentration, e is the charge and m the mass of electron. And then tau is the so-called relaxation time which determines how the electron gas relaxes after scattering or collision event back to the equilibrium configuration. So, this tau describes the process of relaxation, characteristic exponential relaxation is the time constant of this exponential relaxation process.

Now obviously, e and m are constants, n - the electron concentration in a metal is the constant more or less for a metal, because it depends on the atomic number and the Avogadro number and the not the atomic number, but the atomic weight and the Avogadro number and the density. So, this is the practically a constant, so all these are constants. So, the conductivity is mainly determined by the temperature dependence of the electrical conductivity, mainly depends on the temperature dependence of this relaxation time.

So we all know for example, if you consider a material like platinum, platinum is a very well known as, a resistance thermometer and we know that it is preferred as a resistance thermometer, because it can be available in a very pure form, and also its resistance is strictly proportional to the absolute temperature. So, it is a linear function of the temperature. So, that is the more or less very high degree of accuracy, it is a linear function of the temperature. So, its calibration from the resistance, conversion of the resistance to a temperature is all fairly straight forward and universal. And this is the reason why platinum thermometer; this is preferred by all over the world as a resistance thermometer.

Now this characteristic linear temperature dependence of the electrical conductivity or the electrical resistance, this is got by the temperature dependence of sigma and which is entirely determined by the temperature dependence of the relaxation time. And we already saw that the collision processes or the scattering events for conduction electrons are arise mainly from two principal mechanisms.

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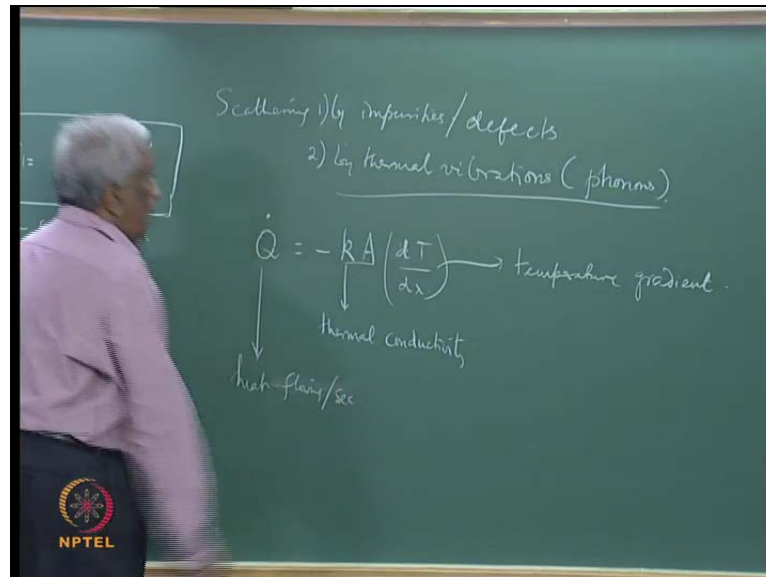
This scattering is from impurities, impurities of various kinds that is impurities interstitial, vacancies, dislocations all sorts of standard defects in crystalline solids, so that is one mechanism. The other mechanism is scattering by thermal vibrations which we wrote as the quantized excitations of thermal vibrations where written as in by the name phonons. We will see it talk about them in a little later. Now these are the two

principal mechanism, and the defect scattering is not very strongly dependent on the temperature in comparison to the temperature-dependents of the thermal vibrations. So, the phonon scattering is very strongly influenced and the linear temperature-dependent of the electrical resistance of a pure metal arises principally from the temperature-dependent of the relaxation time for this scattering by phonons, scattering of electron gas by phonons.

We will see about the details of this after we have discussed the nature of phonons and so on. So, we will postpone the discussion we will be satisfy at this stage with the description of the Drude relation. We will written this a little later to the specific application of electron-phonon scattering process, and how it determines the temperature-dependent of the electrical conductivity of a metal. We will take up this topic a little later. Now we will pass on to another important and interesting characteristic of a metal, namely thermal conductivity. We all know that a good metal is not only a very good conductor of electricity, but also a very good conductor of heat, so that is why we are unable to hold a metallic rod which is being heated at one end, even if the rod is a very long one because the heat is conducted down the metal and it heats of power.

Hence so we know at the same time, we also know this depends to a great extent on the type of metal, for example, stainless steel is does not conduct heat as much as a copper rod for example or a brass rod. So, there is a strong variation of the thermal conductivity. So, we would like to see understand this also in the framework of the free electron theory of metals. So, we all know the standard question for the thermal conduction, it is got by the standard Fourier equation for steady state heat conduction as minus k A dT by dx. Where dT by dx is the temperature gradient, and A is the cross-section, and k is the thermal conductivity, k - this is the thermal conductivity. So this is the temperature gradient.

We all know that the heat flows against a temperature gradient. So, from a hot end to a cold end, whereas the gradient is the directed from the cold end to the hot end, the negative sign is an indication of that, this the heat current or heat quantity of flowing per second, and this is the area of cross-section, A is the area of cross-section. So, this is the standard heat conduction equation, we would now like to know how this thermal

conductivity is determined by the transport of heat by the electron gas. In order to understand this, we go back to the kinetic theory of gasses.

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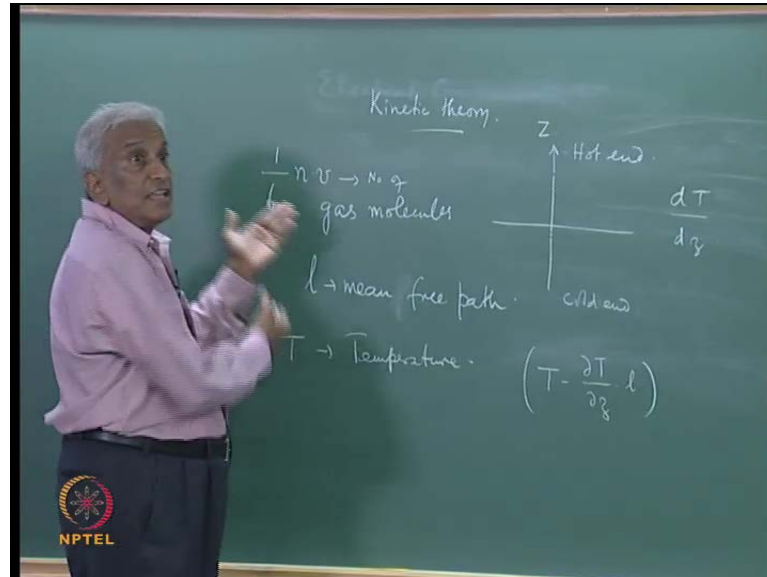
We are talking about an electron gas, but we will still try to keep the classical picture and go to the kinetic theory, which describes how heat is transported in an ideal gas. This is done by if there are if you have a heat gradient, a temperature gradient from say the gradient is like this, so that there is a hot end that is this is z direction. This is the cold end and so there will be a temperature gradient dT by dz. Suppose, we consider a section here, and look at unit area and in this unit area, if there are n gas molecules or atoms per unit volume, then on a average end by three of this will be directed along the z direction. Because x, y and z, the three standard directions in three-dimensional space and if there are n molecule by perfect randomness of the kinetic theory allows us to assume that on an average one-third of these molecules will be flowing along this z direction.

So, all of which half of them will be traveling down, and half of them will be traveling up. So on an average one six n will be the concentration and they will be can find to a if you consider unit area and v is the speed one six n v will be the number of gas molecules which are incident from top to bottom crossing unit area. So, this number and if we considered a temperature thermal transport that transport of heat across this unit area then the transport of heat is determined by the molecule which suffered a coalition before the instant we are talking about. So, from these unit area if l is the mean free path l is the

mean free path. So, just before one coalition before they cross the instance that the molecules cross this unit area at the in the central section of this z axis if we consider that duos molecules would have to travel a distance l in order to reach only those molecule will transport heat from the hot n to this unit area. So, we will have, if I take the temperature in this section as T temperature is the absolute temperature. So this means a Taylor expansion say T minus dT by dz in to l will be the actual temperature of the molecule which starts from the previous coalition and the three which reaches in unit time to this by traveling this. So, so this times this gives you the energy transported.

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Heat energy transported across unit area per sec from below	$= \frac{1}{6} nv \left(T - \frac{\partial T}{\partial z} l \right) C_{el}$	(11.1)
Heat energy transported across unit area per sec from above	$= \frac{1}{6} nv \left(T + \frac{\partial T}{\partial z} l \right) C_{el}$	(11.2)
Net balance, $\dot{q} = \frac{\dot{Q}}{A}$	$= \frac{1}{3} nv \frac{\partial T}{\partial z} l C_{el}$	(11.3)
C_{el}	= electronic specific heat.	
$\therefore K = \frac{1}{3} C_{el} v l$		(11.4)

l, mean free path and v, mean velocity.

So, energy transported across unit area per second off course this is heat energy from above n and which contributes to this heat at the point at a given instant of time that will be given by 1 6 n v times T minus d t by d z times l. So, that would be the this is the this energy will be proportional to this and corresponding there will be also molecules traveling from below and that section which will come will correspond to Q. We start from this expression for the kinetic theory expression for the thermal conductivity the next important question is that since we are talking about finite temperature not at absolute 0. We are talking about heat transport T a finite temperature well about the absolute temperature. So, we would like to have an expression for the electronic heat capacity at a finite temperature where as we talked about it only close to the absolute 0.

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The exact calculation to determine the specific heat capacity of the gas of free electrons is as follows:

Upon heating the Fermi electron gas from 0K to a temperature T, the internal energy per unit volume is increased by an amount U given by
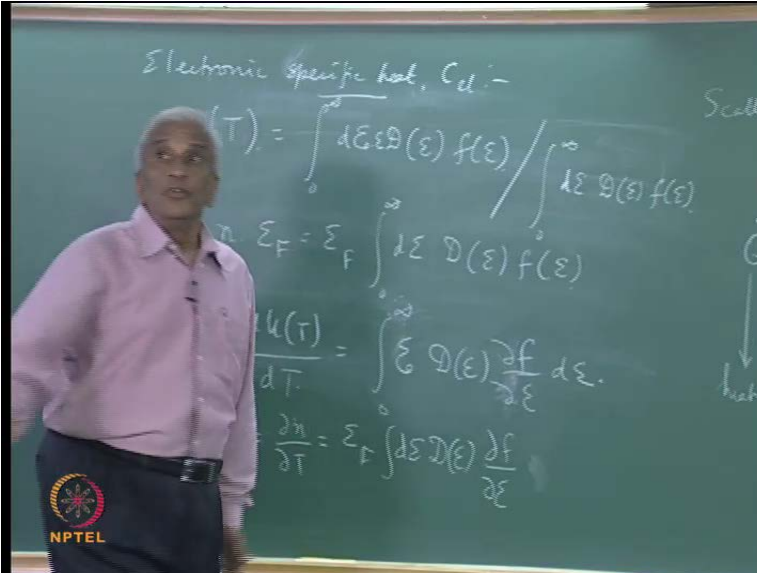
$$U(T) = \int_0^\infty d\varepsilon\, \varepsilon D(\varepsilon) f(\varepsilon) / \int_0^\infty d\varepsilon D(\varepsilon) f(\varepsilon). \qquad (11.5)$$

We also have the relation

$$\varepsilon_F . n = \varepsilon_F \int_0^\infty d\varepsilon D(\varepsilon) f(\varepsilon) \qquad (11.6)$$

So, let us to spend a little time calculating these extra the electronic heat capacity exactly.

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So, the electronic specific heat c electronic how do you calculate it at a finite temperature. In order to do that we start from the internal energy which is a function of temperature and that is by according to the standard that this think this is the standard definition this an integral the average of d f e f of e times e divided by d e d f e f of e from 0 10. So, that would be the statistical average of the internal energy and we also

know that we have the end times e f that would be e f times the electron concentration which is just a d f e f of e d e so this is the concentration of the electrons. So, now we take this to we know that the electronic heat capacitance we are specific heat is just got by differentiating the average internal energy this respect to temperature. So, this by looking at these this is going to be integral and that differentiating this we get since this is a constant number. So, this is going to give me this is e fin to d n by d t and that would be extra e f integral b e you d f by d e.

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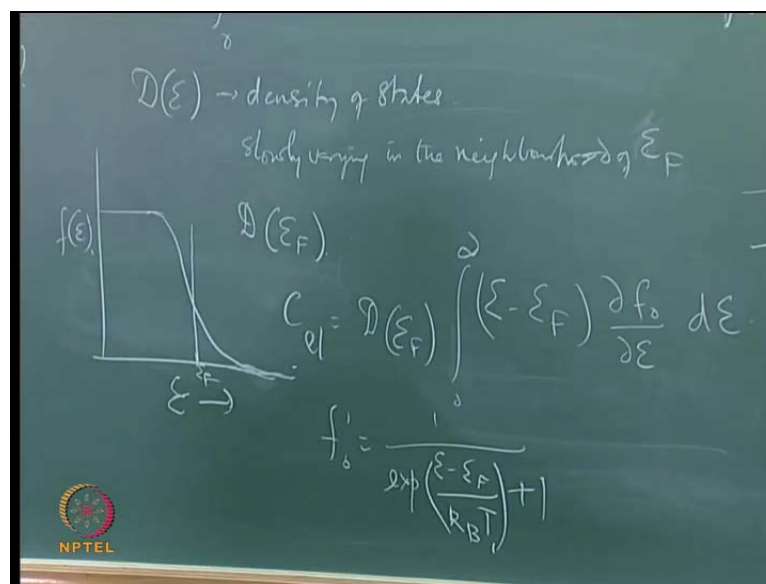
So, taking this two together we can write on an expression for the electronic it capacity c electronics an ass integral d of e E minus E f times d f e d f by d e. Now, since we know that this will be a very only slowly in the neighborhood of the Fermi energy, we can regard the density of state d f e is the density of states which may be regarded as a slowly varying function in the neighborhood slowly varying in the neighborhood of E f.

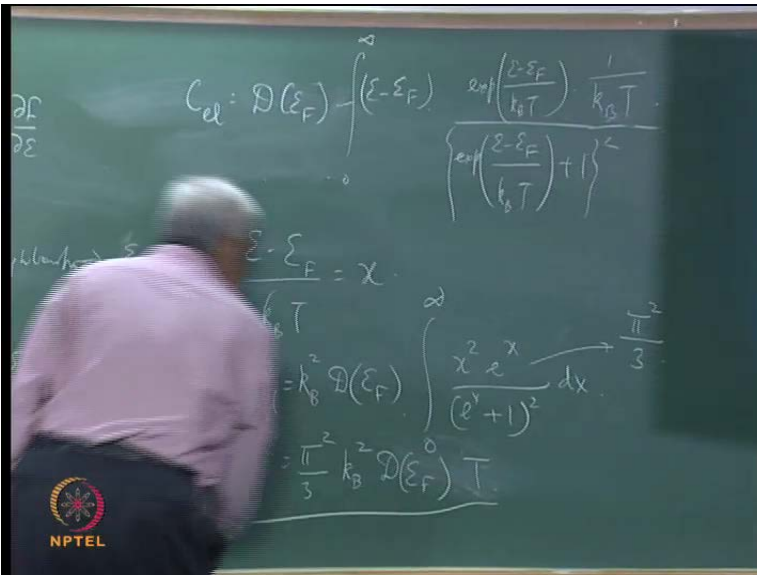Subtracting (11.8) from (11.7) the specific heat capacity of the electrons is obtained as

$$C_v = \frac{\partial U}{\partial T} = \int_0^\infty d\varepsilon (\varepsilon - \varepsilon_F) D(\varepsilon) \frac{\partial f}{\partial T}. \tag{11.9}$$

The derivative $\partial f / \partial T$ has significant values only in the "semeared out" region of $\pm 2 k_B T$ *about* ε_F. The density of states $D(\varepsilon)$ does not vary a great deal in this region and may be approximated by $D(\varepsilon F)$, i.e.,

$$\simeq D(\varepsilon_F) \int_0^\infty d\varepsilon (\varepsilon - \varepsilon_F) \frac{\partial f}{\partial T}, \tag{11.10}$$

Therefore because of that we can take for out of the integral and replace it by its fact by its value at the Fermi energy D of e f. So that we can write C electronics as D of e f and this integral zero to infinity e minus e f d f naught by d e times d e where f naught is equilibrium Fermi Dirac distribution function. And we know it is a form is f naught 1 by exponential E minus E F by k B T plus 1. So, we can differentiate this and get the electronic heat capacity.

So, we arrive at C electronic at D of e f times, if you replace this integral 0 to infinity E minus E F times, I differentiate this I get exponential E minus E F by k B T plus 1 square with a negative sign. And then I have exponential E minus E f by k B T upstairs in the numerator and then minus 1 by k B T square to do the differentiation to 1 by k B T. So, that would give you electronic heat capacity co-efficient and plugging all this and let us make a substitution E minus E F by k B T equal to x. So, that we finally, arrive at the expression C electronic at k square D of E F.

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Since the factor of $exp\, x$ in the integrand is negligible for $x \leq -\varepsilon_F / k_B T$ the lower integration limit can be extended to minus infinity. The resulting integral

$$\int_{-\infty}^{\infty} dx \frac{x^2 e^x}{(e^x + 1)^2} = \frac{\pi^2}{3} \qquad (11.13)$$

is a standard integral whose value can be found in tables. One thus has the following general result for the specific heat capacity if the :free" electrons in metals:

$$C \simeq \frac{\pi^2}{3} D(\varepsilon_F) k_B^2 T. \qquad (11.14)$$

This states that are completely occupied, do not contribute anything to the integral. So, are we may change this to just to zero, and then this is a standard integral which has the value pi square by three. So, this will be a definite integral whose value is known to be pi square by 3. So, we get we arrive at a that the final expression for the electronic heat capacity so that is exact expression for the electronic heat capacity co-efficient at any temperature. And so this is the value of the linear heat capacity co-efficient gamma which we wrote about which we wrote last time. So, this is the expression for the electronic heat capacity which we should import into the expression kinetic theory expression for the thermal conductivity and that is how you finally, arrive at the thermal conductivity of the electron gas.

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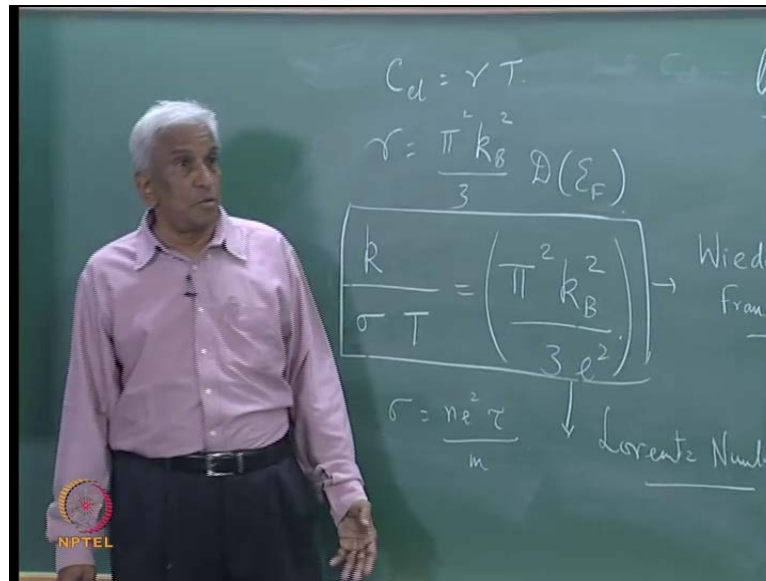
So, doing this so we have see electronic is gamma T; where gamma we have seen now and pi square k B square by 3 in to D of E f.

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where l is the mean free path for electrical conduction which is taken to be the same as for thermal conduction, we get:

$$k / \sigma T = (\pi^2 / 6) k_B^2 \{N / \varepsilon_{F(0)}\} l v / N e^2 (1 / v) m$$
$$= \pi^2 k_B^2 m v_F^2 / 6 e^2 \varepsilon_{F(0)} \qquad (11.18)$$

Here we have taken, $v = v_f$ the Fermi velocity. Hence we finally obtain:

$$k / \sigma T = \pi^2 k_B^2 / 3 e^2, \qquad (11.19)$$

a constant known as Lorenz number.

So, using this expression, we can go back to the thermal conductivity expression and we can see in particular what happens to the ratio of the thermal to the electrical conductivity, and we will write k by sigma t is a very interesting constant, which turns out have this value. This is because we know the Drude expression sigma equal to n e square tau by m and therefore, we have the kinetic theory expression for the conductivity

in which the mean free path can be written as v tau. So that is how simplifying this we arrive at this very interesting expression which is valid for the electron gas free-electron gas in metals in general which is a very interesting relationship which is known as Wiedemann-Franz law. Which gives you a very interesting fact that if you take the ratio of the thermal conductivity to the electrical conductivity for any material and derived by also the absolute temperature you arrive at a universal constant because this involves only the Boltzmann constant the factor pi then the electron a charge. So, this constant is a universal constant known as the Lorentz number. So, this quantity k by sigma T turns out to be a universal constant whose value is the standard Lorentz number.

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So, this has been actually experimentally observed in many metals at low temperatures, of course there are interesting deviation which arrives from the limitation or the relaxation time approximation. We will talk about it later. Now all I want to say is this point by that will one can say that one started from the kinetic theory expression for the thermal conductivity which is a classical description whereas, we have the usual objection that the electron gases is a quantum assembly. And therefore, subject to quantum or Fermi Dirac statistics subject to poorly expression principle if this is. So, one can arrive at the same thing why are the Boltzmann transport equation instead of starting from the kinetic theory. We can go back as we did in the case of the conduction electrons the electrical conductivity problem, we can go onto the Boltzmann transport equation in

which we will now write instead of a electric field which drives the electrons, we now have a temperature gradient.

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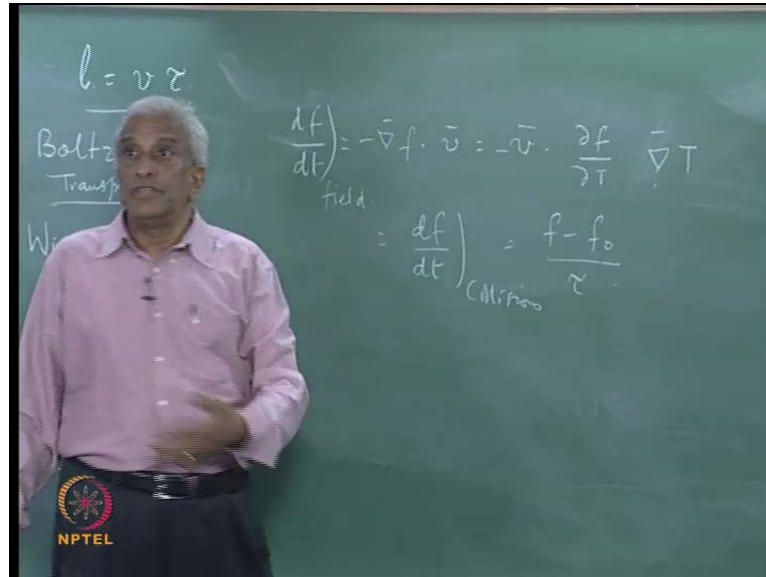
So, we will write d f by d t as field as the left dot v and this del as can be written as. So, this is v dot d f by d t times dt by dx say along a standard direction or del T E. So, we can relate this will be a minus sign to show that the drift of the electrons is against the temperature gradient. And this will give you this is balanced by the d f by d t due to collisions at scattering which is which had the standard form f minus f naught by tau. Now using this, we can express the equal distribution function in terms of the equilibrium distribution function, and the other parameters involving the temperature gradient and they doing the standard behavior of Kenady Fermi Dirac distribution, we can arrive at the same expression for the thermal conductivity.

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Thermoelectric Power :

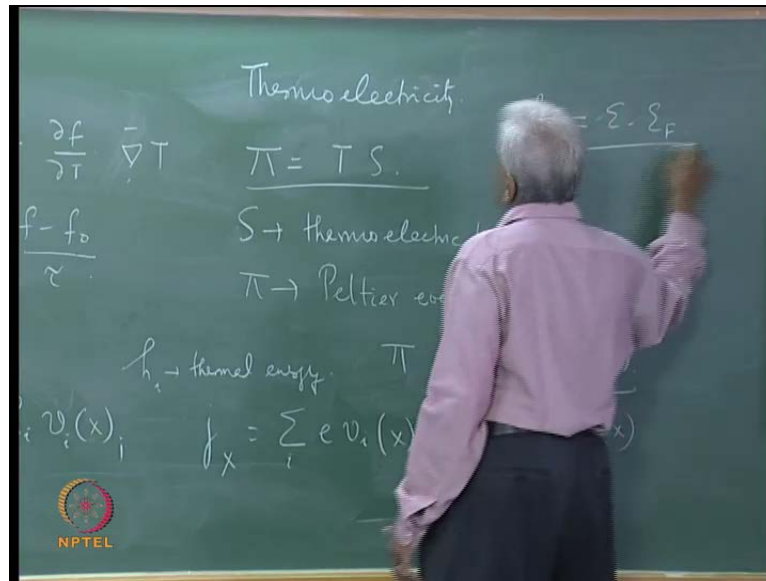A similar approach may be made to determine the thermoelectric power.

The absolute thermoelectric power is defined by:

$\pi = TS$ where π is the Peltier coefficient and T is the temperature.

And in turn to that, we can come back to the Wiedemann - Franz law. Before concluding the this lecture, I would like to spend a little time on another interesting effect which is very well known in metals namely the phenomenon of thermo electricity. Thermo electricity means we all know we have all our heard thermo coupled, which are formed by a junction formed by two dissimilar metals. And then at this junction is kept if a have a pair of identical junction and if they are kept that different temperatures and there is a temperature gradient then there will be an e m f generated. So, this is the phenomenon which includes both thermal transport in the presence of an electrical field or vice versa an electric e m f induce by a temperature gradient.

So, in order to describe a the absolute thermo power is defined by pi equal to t gas and s is the absolute thermo power thermo electric power is also known as the c big co – efficient and pi is the so-called Peltier co-efficient. So, this is and t is the absolute temperature of course, this is the standard expression which links the Peltier effect and the thermo electric power in the Peltier effect we are interested in the heat given out are taken in at a junction between. The conductor of a interest and a reference materials such as a superconductor which makes no contribution to the thermo electric power if you take this if the i tell the electron carry is a thermal energy h i; h i is the thermal energy. Now what does that mean, so if the h i with the thermal energy as the i th electron then h i times v i effects sigma over i is the x component v i x is the velocity of the x component. So, this is the heat current.

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If an electric current j_x flows along the positive x direction then $j_x = \sum_i e \, v_i(x)$.

The Peltier coefficient is then the ratio of the heat current to the electric current at the junction of the conductor and the reference material.

Thus $\pi = \sum_i h_i \, v_i(x) / \sum_i e \, v_i(x) = TS$.
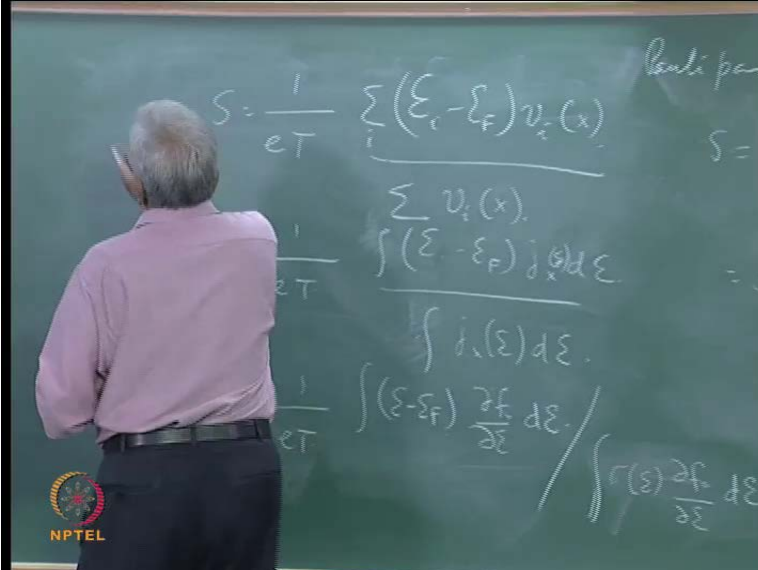
The electrons have different energies ε_i.

The heat energy is then just the difference between the internal energy ε_i and the Fermi energy ε_F.

i.e. $h_i = \varepsilon_i - \varepsilon_F$.

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So, if you take this and if we have also an electric current and jx then the electric current due to electrons flowing is simply given by sigma i e b i a j x. So, that is the Dirac current j x flowing in the same direction. The Peltier co-efficient pi is just the ratio of the heat current to the electric current. And therefore, we can write this as sigma h i v i of x by sigma e where and here h i is the energy which we can write as e minus e f e i minus e f i e i is the energy of the i th electron. So, putting all this together we get the thermo power.

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So, we have the thermo power as one by e t sigma you e i minus e f times v i x this can also be re written using the definition of j - the current density; and in this way, we can replace there summation by an integration over all the energies. Now we already have discuss how to obtain the electrical current due to the transport of electrons. So, we just borrow the expression from that and we can write t s therefore, as one by E t borrowing all these expressions we get integral E minus E F.

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Hence the thermopower S is given by:

$$S = (1/eT) \sum_i (\varepsilon_i - \varepsilon_F) v_i(x) / \sum \gamma_i(x).$$

$$= (1/eT) (\varepsilon - \varepsilon_F) j(x) d\varepsilon / j(x) d\varepsilon$$

Here

$$j(x) = -(e^2 \varepsilon_x /4 \pi^3 h) \iint (\tau v_x^2/v)dS (df_0/d\varepsilon)d\varepsilon$$

$$= - \varepsilon_x \int \sigma_X(\varepsilon) (df_0/d\varepsilon)d\varepsilon$$

and the partial conductivity

$$\sigma_x(\varepsilon) = (e^2 /4 \pi^3 h) \int (\tau v_x^2/v)dS$$

Thus

$$TS = 1/e \int \sigma_x(\varepsilon) (\varepsilon - \varepsilon_F) (df_0/d\varepsilon)d\varepsilon / \int \sigma_x(\varepsilon) (df_0/d\varepsilon)d\varepsilon$$

Now $(df_0/d\varepsilon)$ is appreciable only over a range of energies of the order of $k_B T$ in the neighbourhood of ε_F.

And then the sigma of e in to tau v x square divided by a sigma xt x by dS. Now again we have converted into, and then a integration or the energy if and we know that the this has makes an appreciable contribution only over arrange of energies of the order of k B T in the neighborhood of e f. Therefore, we can again use a tailor expansion in the neighborhood of the Fermi energy and calculate this and the final result turns out to be a very compact expression.

The first term vanishes because of the differential coefficient and the third because we put $\varepsilon = \varepsilon_F$. So finally:

$$\int_0^\infty \sigma(\varepsilon)(\varepsilon - \varepsilon_F)\frac{df_0}{d\varepsilon}d\varepsilon = -\frac{\pi^2}{3}(k_BT)^2\frac{d\sigma(\varepsilon)}{d\varepsilon} \qquad (11.16)$$

In the denominator of the expression we keep only the leading term which is just $-\sigma(\varepsilon_F)$. So for the thermopower we get:
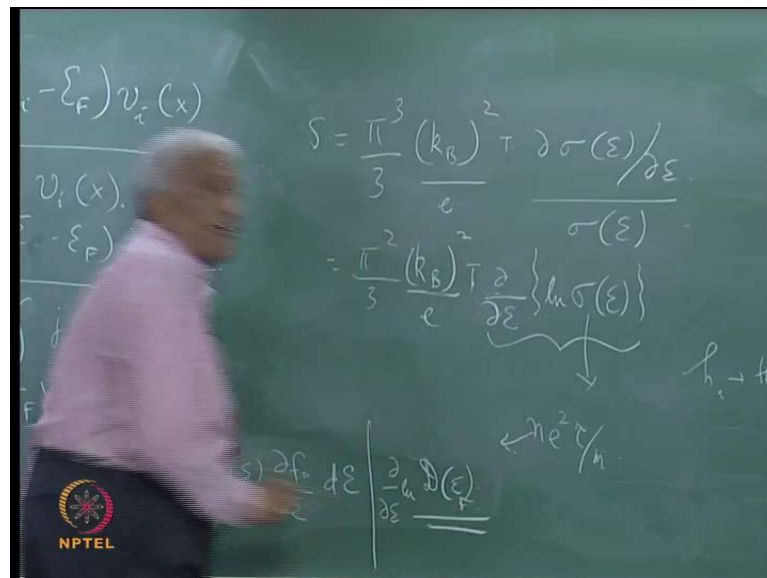
$$S = \frac{\pi^2}{3}\frac{(k_BT)^2}{eT}\frac{1}{\sigma(\varepsilon)}\left(\frac{\partial\sigma(\varepsilon)}{\partial\varepsilon}\right) = \qquad (11.17)$$

or

$$S = \frac{\pi^2}{3}\left(\frac{k}{e}\right)k_BT\left(\frac{\partial\ln\sigma(\varepsilon)}{\partial\varepsilon}\right) \qquad (11.18)$$

So, the Fermi, the final result for the thermo power of a metal going to the algebra we get a very particularly compact expression pi square by 3 k B square by e d sigma of e by d e.

And this can be rewritten as the thermo power of a metal is again proportionate to the linear function of the absolute temperature and then it mainly depends on the logarithmic derivative of the thermal electrical conductivity. Now the electrical conductivity as we know is the given by the Drude expression n e square power by m, and therefore, the

energy-dependence of this factors is not very a strong, the strongest energy dependence comes from this which is the energy-dependent of the d f e. The electronic density of states at the Fermi level saw this he the main factor determining the value of the thermo electric power in a metal.

So, we have now seen how we can combine in all the three transport properties namely the electrical conductivity the thermal conductivity and the thermo electric power can be all explain in the framework of the semi-classical so-called semi-classical theory due to the electron free-electron gas. Later on, we will also discuss effects of an applied magnetic field. So, and this will give rise to interesting effects like the only paramagnetic susceptibility, and the entire theory a free-electrons in metal is we indicated by the organization of phenomenon such as fermion emission, photoelectric emission field emission etcetera.

And so, we can we can talk about the topology of the Fermi surface from experiments such as cyclotron resonant ((Refer Time: 36:59)) like that. So, we will discuss all these at a later stage to go into the details of this interesting physical behavior. For the moment it is in fact, this is also the Fermi surface, the electron, the Fermi energy of an electron moving close to the surface of a metal gives you an image potential which also provides the basis for the so-called field the ion make a scope. So, these are interesting developments in experimental solid state research. We will just I am mentioning it in passing and now move on to the discussion of other classes of solids.

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Reference

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London