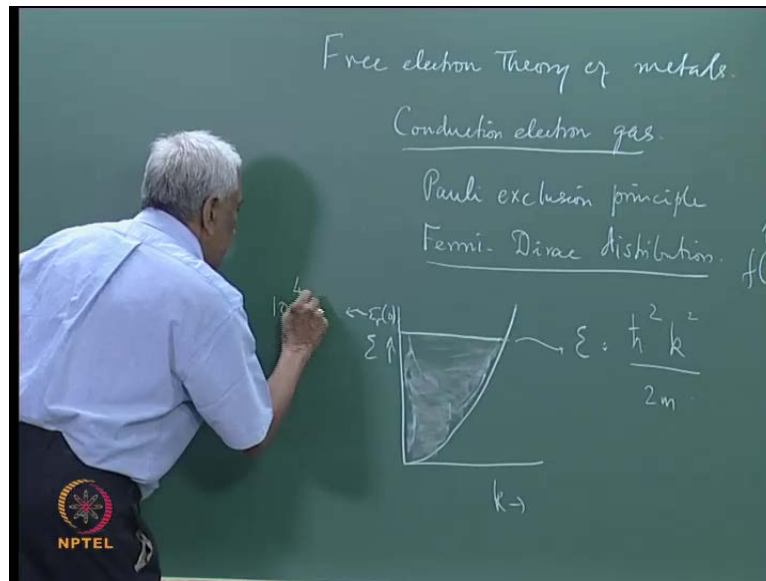


Condensed Matter Physics
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Lecture - 10
The Free Electron Theory of Metals - Electrical Conductivity

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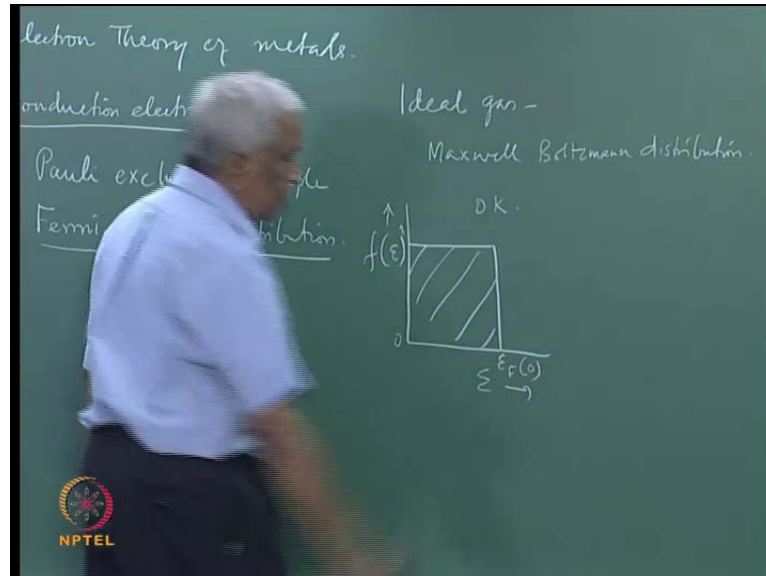


In the last lecture we discussed the free electron theory of metals in this connection we noted that metals constitute a particularly simple kind of solids in which most of the conduction properties and other related thermal behaviour all these are determined by the. So, called conduction electrons which behave very much like an ideal gas atoms or molecules except that the electron gas obeys in subjected to Pauli exclusion principle and therefore, satisfy fermi dirac distribution.

So, even though the metal is a solid crystalline solid it is mainly the electron gas which decides these physical properties like electrical transport heat transport of heat specific heat all these properties are determined by of course, there is a role from the ions the conduction electrons are formed by ionisation of the atoms of the metal. So, that you have positive ions. And then into which there is a free electron gas which is free to wander around as long as it is within the metal it is confined to the metal as a whole the metallic bond is something that binds the electron gas to the metal it is not able to escape it and become completely free.

So, except that they are free to wander around inside the metal under the influence of applied electric or magnetic fields applied heat thermal gradients and so on. So, it is this behaviour of this electron gas which is profoundly different from.

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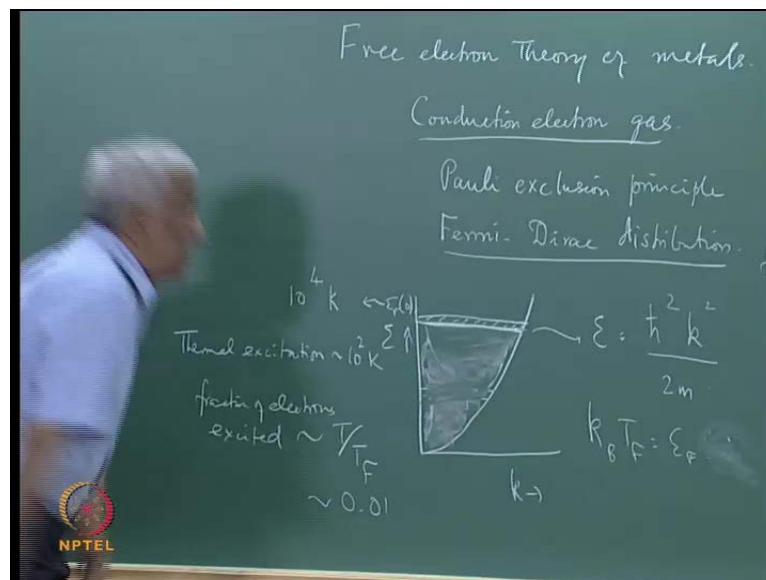
That of an ideal gas atom or molecule because the molecules are atoms of an ideal gas a classical ideal gas or satisfied the or governed by the Maxwell Boltzmann distribution this is familiar already to all of us, but the electron gas is subjected to the fermi dirac distribution. This is because the electrons are quantum mechanical particles and fermi dirac distribution is different from the Maxwell Boltzmann distribution because of the quantum behaviour of the electrons which are determined by the pauli exclusion principle the essence of the pauli exclusion principle is that. If there is an energies level and an electron occupies this energy level then no other electrons can come and occupy the same energy level. So, that is why it is called the exclusion principle and this profoundly affects the way the electrons are distributed in energy and we saw the precise form of the fermi dirac distribution which at absolute zero the distribution function goes like this as a value one here to zero and it is like this and this is known as the fermi energy of this is f zero kelvin.

So, all these states within for energies less than the fermi energy the states are completely occupied each state being occupied by a given single electron and all these states above the fermi level are completely empty. So, the fermi energy at absolute zero

is the highest energy level which is occupied in the case of a metal. And therefore, this will modify the way there are electrons are distributed in energy and this is again given by the dispersion curve of the electron, which is the e versus k curve and this is governed by the kinetic energy of the electrons which is $\frac{h^2 k^2}{2m}$. And therefore, this will be a parabolic curve which will look like this. So, that is a and states up to the fermi energy are filled these are all these states are completely filled.

So, what happens is that we discussed last time the behaviour of the contribution of these electrons to the specific heat, because when there is a thermal excitation the electrons are going to observe this heat. And therefore, there's going to be specific heat contribution due to this electron gas. Now this contribution we saw is like the hound in the hound of baskervilles is the dog that did not bark at night. So, the electronic in specific heat does not appear, it is not a dominant contribution that is the overall result of this, that is because this fermi energy is at the order of 10^4 Kelvin. Whereas normal thermal excitations are of the order of thermal excitation is at the order of 10^2 Kelvin.

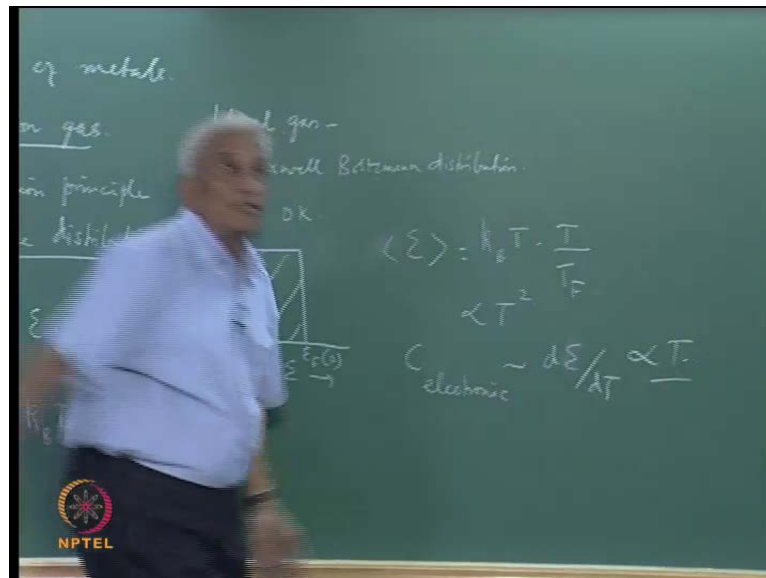
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So, it is a very small quantity in comparison to this. So, if you have a small temperature window here which say this is the energy initial energy, and the thermal excitation suppose it takes the electron to this now this is the initial. And final states are all already occupied and therefore, the electron cannot go into this state. So, even though you excite

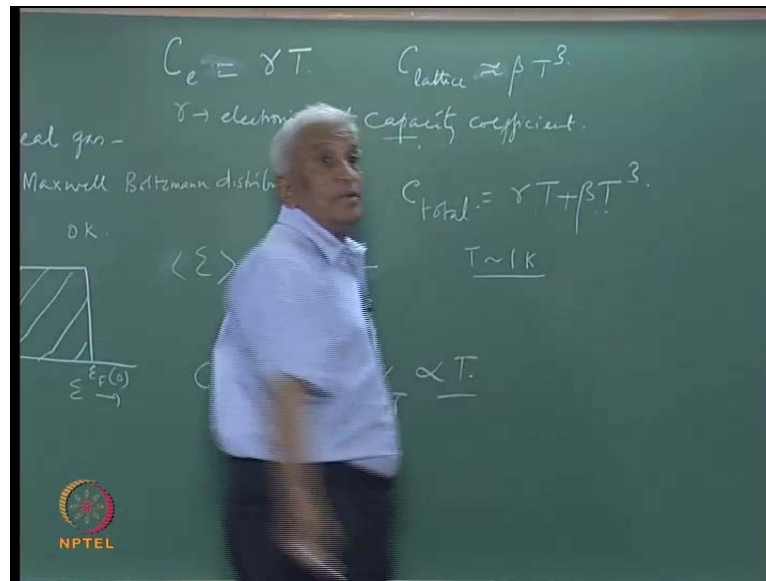
it these electrons which are deep within the energy scheme the occupied energy level they are unable to participate in the thermal excitation it is only the electrons which are the fringe which are here in a small skin layer around the fermi energy these are the fraction of electrons which will be able to contribute to the specific heat by being thermally excited. So, it is this fraction and this fraction as you can see is about a hundredth this ratio of this temperatures is one in hundredth. So, it is only a fraction of point zero one or one in hundred of total of number of electron, which can get excited and therefore, contribute to this specific heat it is for this reason. So, the fraction of electrons excited is of the order of t by t_f , where t_f is given by $k_b t_f$ equals e_f zero or e_f . So, this fraction is only at the order of 0.0.

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One and this fraction of electron each electron will be excited by an amount $k_b t$ by Boltzmann's equipartition theorem therefore, the total contribution is T_f , that is the mean energy of these electrons, which are excited since this goes as t square. So, the specific heat $c_{\text{electronic}}$ the specific heat which is the e by d t is proportional to the absolute temperature.

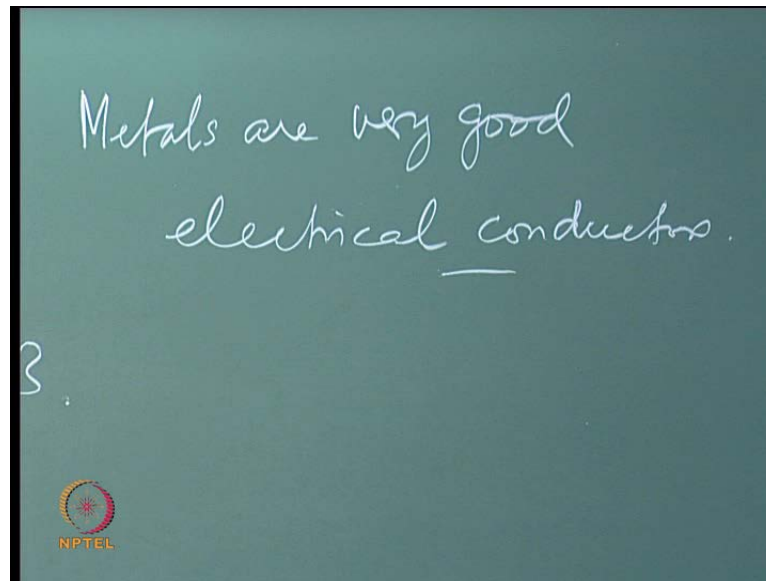
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So, that is what we write as c_e equals it goes as γT where γ is the electronic heat capacity coefficient. So, it is the Pauli exclusion principle and the Fermi-Dirac distribution which profoundly modify the behaviour of the electronic system, and prevent it from absorbing thermal excitation energy to a large extent and confine only a small fraction T/T_f of the total number of electrons to be thermally excited. And therefore, contribute only a term of the order of γT as we will see later the lattice the crystal lattice of ions in a metal will have a contribution which goes as T^3 the cube of the absolute temperature and therefore, the total specific heat will be of the form $\gamma T + \beta T^3$.

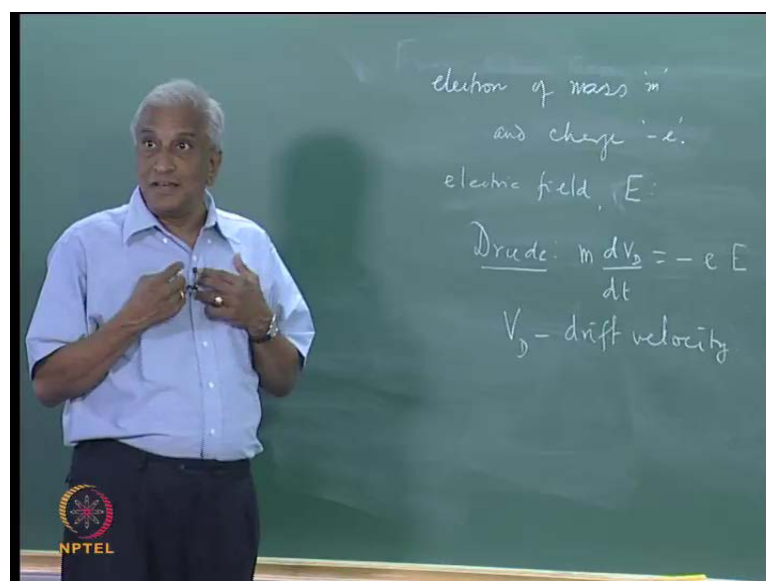
So, at high temperatures it is this term which will dominate therefore, this will be negligible, and you cannot even detect it it is only when you go to temperatures as the order of one Kelvin, which is an extremely low temperature it is only at such low temperature. These two terms will become comparable and then you can detect the electronic contribution. So, this is the important concept that we developed last time.

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Now, we move on to discuss how this picture of conduction electron gas in a metal is going to lead to the very well-known behaviour of metals namely that they are very good electrical conductors. So, we would like to know how and why a metal like silver or gold or copper they are very good conductors of electricity this is a very important characteristic of a metal which we would like to understand in the frame work of the free electron gas picture. So, this is our next aim. So, what do we do we just take this conduction electron gas consider it and then apply an electric field a dc electric field.

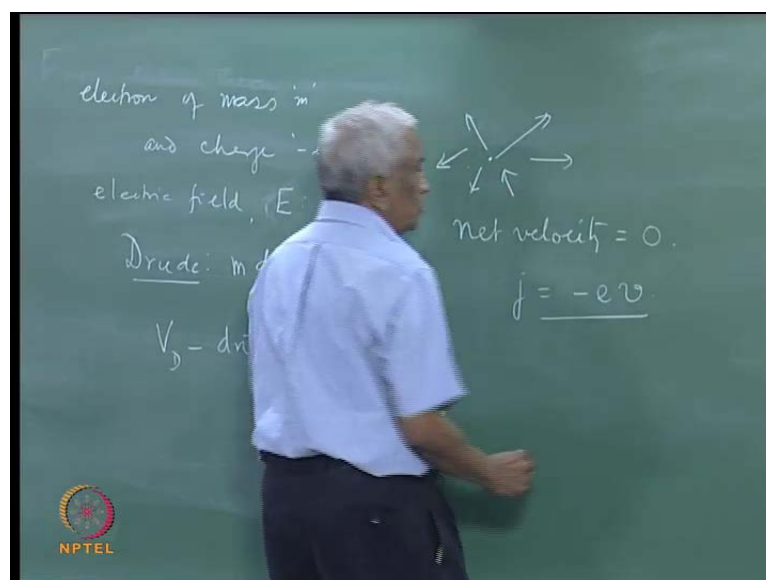
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So, let us first start looking by looking at the behaviour of a single electron of electronic charge electron of mass m and charge minus e . So, let us look at what happens to these electron when we apply a dc electrical field of strength E . So, we know that we can this is a very simple situation. And we will to start with use a classical picture which was due to which was first proposed by a person named Drude. So, this is known as the Drude theory of electrical conductivity this is an extremely simple picture where I have a particle of mass m , but a charged particle carrying the charge minus e and therefore, in an electric field the force on it will be minus eE and that will be equal to this is the force.

So, Newton's law of motion tells us that this should be because this v_d , because v_d is known as the drift velocity of the electron why do we call it drift velocity. This is because normally if you do not have an applied electric field what happens to these electrons, they are still moving around they they are very much like as we said they are very much like the atoms on a ideal gas. So, they are not keeping quite. So, they are free to move around. And therefore, they do move does it mean that they there will be a conductivity there will be electrical conduction whenever an electron moves somewhere there should be a current and therefore, there should be a conduction, but this question is answered because in the classical picture these electrons are free to move around.

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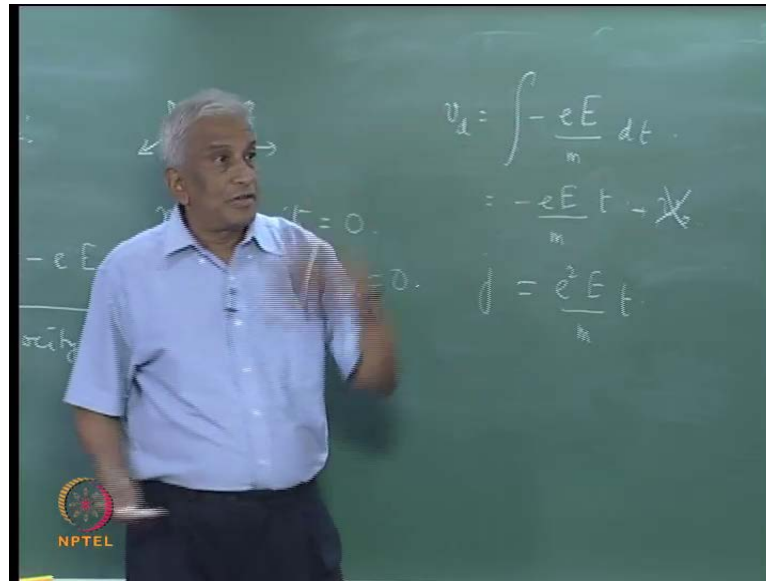


But they move around in perfectly a random fashion very much like what is said in the kinetic theory of gases. So, they are moving around a given electron is moving around in

all possible directions randomly with equal probability. Therefore, this electron is very much like a drunkard what does a drunkard do a drunkard stands here he is under the influence of liquor. So, you watch him he is moving a few steps in this way and then talks to himself and comes, and moves a few steps this way and then this way. So, what happens even after a few hours, if you watch him he if he is standing in a place is moving this moving this way moving this way moving everywhere all the time, but the where is the net displacement he is where is was a few hours ago. So, it is a drunkard who walks all the time, but with no net displacement there is no net displacement. So, in the same way the electrons when they are simply diffusing like the atoms of a gas then the net velocity in any given direction when there is no field vanishes identically it is zero and therefore, when there is these current density is just given by minus $e v$. So, this velocity is zero.

So, it vanishes. So, there is no conduction even though the electrons are moving around they are bumping around in all possible directions, but nothing happens, if you are cannot focusing on a particular direction and trying to measure the conduction conductivity in that direction. So, it vanishes in the absence of an applied electric field, but when you put an applied electric field in then this electric field forces the electron to move in a direction opposite to the applied electric field. Therefore, there is a net drift in a given direction that is why this is called a drift velocity, and this gives you the rate at which this distribute this this drift velocity changes with time and gets accelerated by the applied electric field. So, that is the equation of motion well if this is all there is to head.

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Let us see what happens therefore, integrating this we will see that v_d is integral minus e by m $d t$. Therefore, this is by t plus a constant v_0 the initial speed which is zero to start with there was no velocity when there was no electric field. So, if we start from rest this is the net, and the j the current density will go as e square e by m into t from this equation so; that means, there will be a current build up. And as time passes on the current will go on increasing monotonically, and it will eventually if you wait long enough it can even blow up and become infinitely large, but we all know that this does not happen in any conductor there is a finite current. If you apply a certain voltage producing a certain electric field it produces a certain amount of current which is given by ohm's law, this is the observation that we are all familiar with, but this model does not explain that instead it predicts a current density which goes on increasing monotonically with time.

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The electron-phonon scattering may be described in terms of a relaxation time, τ , which provides a measure of the time in which the drifting electrons relax to a limiting velocity, We thus have:

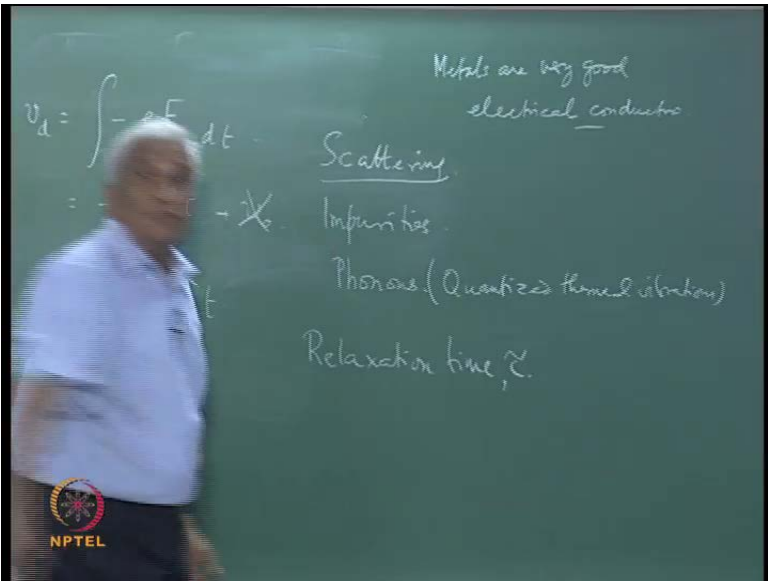
$$\frac{dv_D}{dt} = -\frac{v_0}{\tau} \quad (10.1)$$

We may now combine the effect of the dc electric field (eqn. 9.14) and that of phonon (eqn.10.1) scattering and write:

$$\frac{dv_D}{dt} = -\frac{eE}{m} - \frac{v_0}{\tau} \quad (10.2)$$


If you wait long enough you can get an infinite current from a finite electric field which is up surd, this is because there is something that we ignored you are not taken into account these electrons this is the behaviour of one electron. And even if you have ten thousand or ten to the power 24 electrons the behaviour can be described by a simple addition or super position of these current contributions.

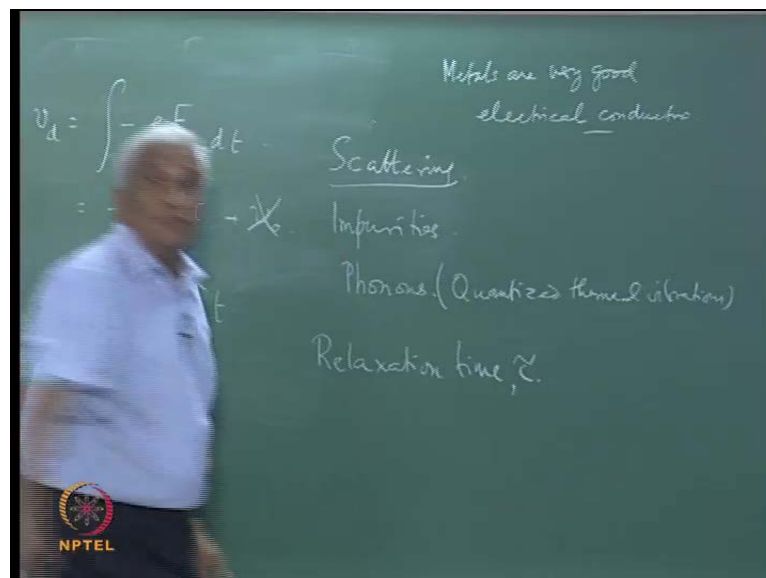
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But this gas is being when it is moving when it is drifting under the influence of an electric field, there are other things that are happening on the path these electrons gets

scattered by various obstacles on their way. For example, in a in a metallic lattice there are many impurities impurity atoms, there are also the positive ions and then there are defects of various kinds like dislocations stacking walls grain boundaries and. So, on all these act as scattering centres. So, this scattering can arise from impurities also these atoms are ions in a crystalline solid are not at rest there are vibrating all the time there are thermal vibrations at any finite temperatures and these thermal vibrations increase as temperature increases.

So, it is a even if you think that these vibrations are simple harmonic there will be an effect due to these vibrations vibrating atoms and therefore, they can act as scattering centres the vibrating ions in the crystal lattice in the metallic crystal lattice. So, these thermal vibrations when they are quantise, they are called phonons we will discuss them a little later for our present discussion, it is enough to know that these are quantised thermal vibrations of the solid.



So, there can be scattering due to phonons, which will increase with temperature unlike the impurities the phonon scattering will depend on the temperature. So, these scattering events have to be considered in order to decide what will be the drift velocity of a given electron the way this scattering is taken into account is by its thinking that suppose there is no scattering of a given electron is scattered at a particular instant of time. Then the entire distribution is affected the distribution of the electrons momentarily, but then this distribution if you leave this like this. And look at only the scattering even immediately after the scattering the entire distribution will relax back to its original value there is an

equilibrium distribution. And then that is momentarily disturbed by the scattering of the electrons and then after a little time this disturbed distribution will relax back to the original equilibrium distribution function. So, this is model which is called the relaxation time model.

So, if this takes as an amount of time τ is known as the relaxation time the characteristic time in which the drifting electron relax back to an equilibrium configuration, when there will be a limiting velocity not a unlimited velocity like that. Then this is described mathematically by any equation of this form these are simple first order differential equation which as you all know will produce a solution which gives you a velocity which decays exponentially with a characteristic time. So, this will a drift velocity which goes as. So, that is why this τ is known as the characteristic time of relaxation through which describes this exponential relaxation process. So, this can now be combined. So, there are two processes one the applied electric field accelerates the electron, and then the electrons which gets scattered by the various scattering centres in the solid they produce a relaxation at the distribution function towards an equilibrium or limiting value.

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which has the steady state solution:

$$(v_D)_{steady\ state} = \frac{-e\bar{E}\tau}{m} \quad (10.3)$$

Using the above equation in equation (10.1) leads to a steady state current density:

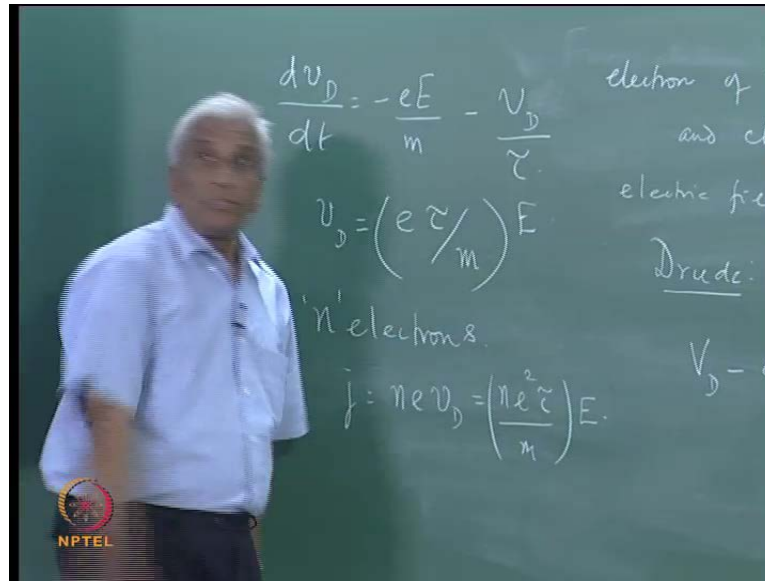
$$(j)_{steady\ state} = \frac{ne^2\tau}{m}\bar{E} \quad (10.4)$$

In other words, the Drude theory predicts an electrical conductivity, $\sigma (=j/E)$ which is given by:

$$\sigma = \frac{ne^2\tau}{m} \quad (10.5)$$


And therefore, we have to consider both of these equations together to describe the rate of change in time of the drift velocity.

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So, when you do this you get an equation a combined equation which is of this form eE by m like this plus an additional term. So, that equation is that is the equation will describe the time rate of change, and when you solve this first order differential equation this will give you a steady state solution which will give you something like. And therefore, if there are if there is a number n electrons if n is the electron concentration then j is $n e v_d$, and this will be $n e$ square τ by m times e and since by ohm's law this is equal to σe where σ is the conductivity.


So, we get the electrical conductivity as $n e$ square τ by m ; that is the drude expression for the electrical conductivity of a metal having a concentration n of conduction electrons each carrying a charge e . And a mass having a mass m , which are drifting under the influence of an electric field getting scattered by the various scattering centres inside the metal. And relax with a characteristic in time τ towards an equilibrium value. So, for such a situation the drude theory, which is a purely classical theory which does not take into account the quantum nature as electrons this is a very old theory, but which gives a remarkably accurate expression for the electrical conductivity. If you we already saw how we can calculate the electron concentrations using fermi dirac distribution, and if you plug in the value one finds a very nice way to describe the electrical resistivity or conductivity behaviour of simple metals well.

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It is convenient to distinguish between the influence of 'fields' and the influence of collisions on the distribution function of the electron gas. By fields we mean either electric and magnetic fields or a temperature gradient etc. Thus we write:

$$df/dt = (df/dt)_{\text{fields}} + (df/dt)_{\text{collisions}}$$

Here $f = f_0 - \frac{\partial f_0}{\partial k_x} \left(\frac{eE_x}{m\hbar} \right) dt$ where $\hbar = \frac{h}{2\pi}$
 and h is the Planck's constant.
 $= f_0 - \left(\frac{\partial f_0}{\partial \epsilon} \right) \hbar v_x \left(\frac{eE_x}{m\hbar} \right) dt$
 and $f_0 = 1 / [\exp\{ (\epsilon - \epsilon_F) / k_B T \} + 1]$




This is all very well, but the question is can we use classical behaviour a classical description the answer is no as we already saw in the connection with the electronic heat capacity. So, we have to require that the electrons obey fermi dirac statistics. So, we have to write the equilibrium distribution function in the presence of scattering, and in the presence of an applied electric field in order to do this we make use of a formalism which was again developed by Boltzmann.

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Boltzmann Transport equation.

$$f_0(\epsilon) \rightarrow \text{Fermi Dirac distribution } f_0 = \frac{1}{\exp\left(\frac{\epsilon - \epsilon_F(\cdot)}{k_B T}\right) + 1}$$

$$\frac{df}{dt} = \left(\frac{df}{dt}\right)_{\text{fields}} + \left(\frac{df}{dt}\right)_{\text{collisions}}$$


This is known as the Boltzmann transport equation the Boltzmann transport equation says tells us what happens to the distribution function in the presence of an applied electric field, and also in the presence of scattering mechanisms. So, we talk about again the distribution function f of e , which is the fermi dirac standard fermi dirac distribution function but we will call it f_0 when it is when there are no applied electric fields, and there are now scattering mechanism. We will call it f_0 , that is the equilibrium distribution function, which has we know has the form one by we saw this last time.

So, this is a standard equilibrium distribution function in the absence of applied electric fields and scattering mechanisms, but now the Boltzmann's transport equation tells us how to write the distribution function in the presence of fields and collisions due to scattering. So, the distribution function changes the f of e changes with time. And now we have to it is convenient to distinguish between the influence of fields fields can be electric fields it can be magnetic fields it can be even temperature gradient. So, depending, if it is an electric field the transfer to the electrons is determined by the electrical conduction mechanism, if it is a thermal gradient then this is determined by the thermal conduction.

So, you can have via this formalism we can at the same time describe electrical as well as thermal conduction and many other processes as you see which come under the general category of transport processes, that is why this equation is known as the transport equation. So, the change in the distribution function with time has two contributions one due to fields and another due to collisions. So, we will evaluate them separately.

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$$f = f_0 - \left(\frac{\partial f_0}{\partial \epsilon} \right) \cdot \left(\frac{e E_x}{\hbar} \right) dt$$

$$= f_0 - \left(\frac{df_0}{d\epsilon} \right) (\hbar v_x) \left(\frac{e E_x}{\hbar} \right) dt$$

$$= \frac{\hbar^2 k_x^2}{2m} \left(\frac{df}{dt} \right)_{\text{field}} = - \left(\frac{df_0}{d\epsilon} \right) e E_x v_x$$

$$\left(\frac{df}{dt} \right)_{\text{collisions}} = \frac{(f_0 - f)}{\tau}$$

$p_x = \hbar k_x$
 $\hbar = \frac{h}{2\pi}$
 $\hbar \rightarrow$ Planck's Constant

So, how do we do this. So, this will be implying this f nought minus I can write this as in terms of the energy using the energy momentum relationship. Therefore, I can write $d\epsilon$ by $\hbar v_x$ here, which will give me $\hbar v_x$, you can check this up times $e E_x$ by \hbar cross $d t$ where v_x is the corresponding speed. So, this is k_x^2 by $2m$. So, this simplifying this we will find now differentiating this $d f$ by $d t$ field.

And now f nought is the equilibrium distribution function in the absence of the fields, and therefore that will not change the fields do not affect the equilibrium configuration the value the way they are distributed under equilibrium in steady state. So, the change is coming only from this and that is given as please note that I am writing the x component of the applied electric field in terms of e in this form, and the energy is written by represented by ϵ in this form. So, please distinguish these two let us keep these two separately not mix them up. So, this gives you this term and the $d f$ by $d t$ due to collisions you have already seen how it goes by the velocity and therefore, this is a similar form very much similar to what happens in the case of the drift velocity.

So, the distribution from this describe this equation describes the exponential relaxation at the distribution function to the equilibrium value f nought with the characteristic time τ . So, these two have to be combined in order to get the total rate of change. So, that will give me f as taking f in this, and combining these two equations the results here, we arrive at the net distribution function in the presence of the applied field into...

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The electrical conductivity is now given by:


$$j_x = (e/4\pi^3) \int v_x dk_x dk_y dk_z$$

where $f = f_0 - (df/d\varepsilon)v_x eE_x \tau$

The part of the above integral involving f_0 vanishes and so

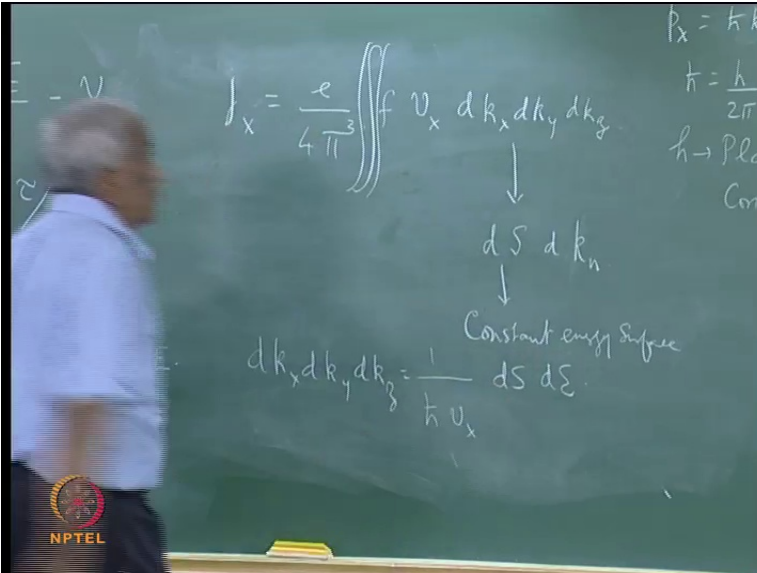
$$j_x = (e/4\pi^3) \int v_x -(df/d\varepsilon)v_x eE_x \tau dk_x dk_y dk_z$$

The volume element in k space can be rewritten as $dS dk_n$ where dS is an element of area of constant energy surface and dk_n is an element of length in k space normal to dS



So, we have to now use this distribution function the new distribution function to describe the average behaviour of various quantities such as the current density.

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$j_x = \frac{e}{4\pi^3} \iiint f v_x dk_x dk_y dk_z$

\downarrow


$dS dk_n$

\downarrow

Constant energy surface

$dk_x dk_y dk_z = \frac{1}{h v_x} dS d\varepsilon$

$p_x = \hbar k$
 $\hbar = \frac{h}{2\pi}$
 $\hbar \rightarrow$ Planck Constant



So, the evaluation of the current density proceeds in the same way as before j_x equals e by four pi cube $f v_x d k_x d k_y d k_z$ integral a triple integral in k's place, where f is what we have on the other side. Now this has two contribution from f naught and $d f$ naught by $d\varepsilon$ now this contribution due to the part involving f naught vanishes, because it is the equilibrium configuration. And it is as we have already seen under steady state

equilibrium in the absence of applied fields this contribution to the current density vanishes because the electron has a random motion. So, it is only the other term which contributes to this in order to evaluate this integral the usual procedure is to consider this volume element in k 's place which can be written rewritten. We rewrite this part as $d s$ times $d k_n$, where $d s$ is an element of area of constant energy surface and $d k_n$ is a length element in the direction normal to this constant energy. So, we evaluate this integral using this relationship.

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The image shows a chalkboard with the following handwritten equations:

$$j_x = \frac{e^2 E_x}{4\pi^3 \hbar} \tau \int \frac{v_x^2}{v} \left(\frac{df}{d\varepsilon} \right) ds d\varepsilon$$

$$j_y \quad E_x = E_y = E_z = E$$

$$j_z \quad \text{Cubic} \quad j_x = j_y = j_z = j$$

In the bottom left corner of the chalkboard, there is a logo for NPTEL (National Programme on Technology Enhanced Learning).

So, that I can write $d k_x d k_y d k_z$ as one by \hbar cross $v_x d s d\varepsilon$, so replacing this and calculating this we arrive at the final result j_x equals evaluating all this $e^2 E_x$ by four pi cube \hbar cross τ integral v_x^2 by $v d s d\varepsilon$ into df by $d\varepsilon$. Now we left E_x we would like to not only calculate j_x , but we will also like to calculate it along with three principle directions xyz . So, we would like to evaluate j_y and j_z .

Under the influence of electric fields directed along the y and z directions setting E_x to be equal to E_y to be equal to E_z , that is we apply the same electric field and we assume that this metal is a cubic metal having cubic symmetry. So, that j_x equal to j_y equal to j_z equal to j in other words we for the moment we ignore the anisotropic of a solid and consider the metal as an isotropic conductor, which has the same behaviour in all the three directions. If we do this and simplify this integral we get the relation connecting j

to e , and using ohm's law j equal to σe we can write the conductivity as e square by 12π cube h cross to τ integral v square by v .

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$$n = \frac{4\pi}{3} k_F^3$$

$$\sigma = \frac{n e^2 \tau}{m}$$

So, which is $v d s$ and evaluating this and using the relation n equal to 4π by 3 k_F^3 divided by 4π cube, that is the electron concentration. We get back we find that simplifying we find again the same relation the old drude formula for the electrical conductivity this means that the application of the fermi dirac distribution does not change the form in the drude's formula. And we get this this expression gives you a very nice way to determine the a calculate the electrical conductivity of a metal. We will continue in the next lecture to see how we can describe other transport process like thermal conduction using the same formulation.