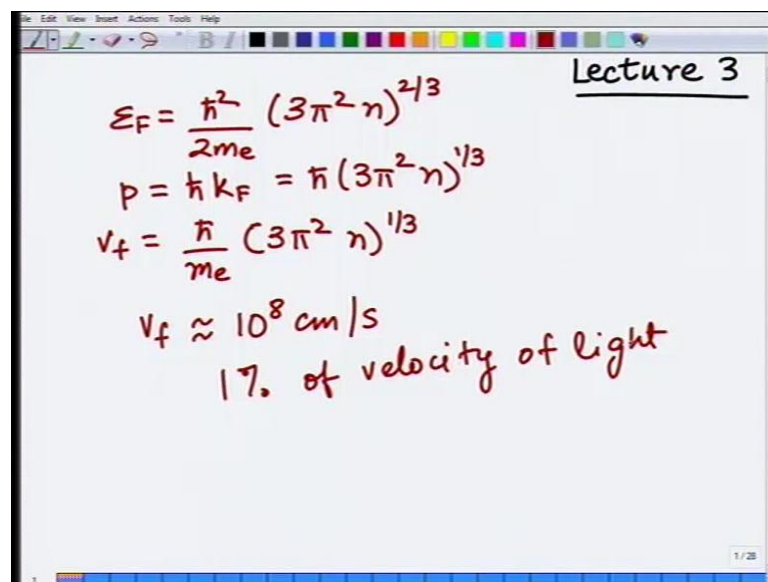


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**Lecture - 3**  
**Free electron theory**

Welcome to lecture number 3. So, what are we going to do is, we will start with where we finished off in lecture number 2. So, let us recall what we did in at the end of lecture number 2 was we had said that if you know that you have  $n$  electrons per unit volume which is this  $n$  write here.

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The image shows a whiteboard with handwritten equations in red ink. The equations are:

$$\epsilon_F = \frac{\hbar^2}{2m_e} (3\pi^2 n)^{2/3}$$
$$p = \hbar k_F = \hbar (3\pi^2 n)^{1/3}$$
$$v_f = \frac{\hbar}{m_e} (3\pi^2 n)^{1/3}$$

Below the equations, it is noted that  $v_f \approx 10^8 \text{ cm/s}$  and is  $17\%$  of the velocity of light. The whiteboard also has a toolbar at the top and the text "Lecture 3" in the top right corner.

Is the  $n$  electron per unit volume, then as you start filling, now you have a different case state, we derived quantized case state available and now we said that if you want to take this  $n$  electrons and start putting them from lowest energy up slowly, slowly start putting them up. We will start looking at this graphically also in little bit as you start putting them up, then you will fill up the last electron up to the energy level  $E_f$ , which is this energy.

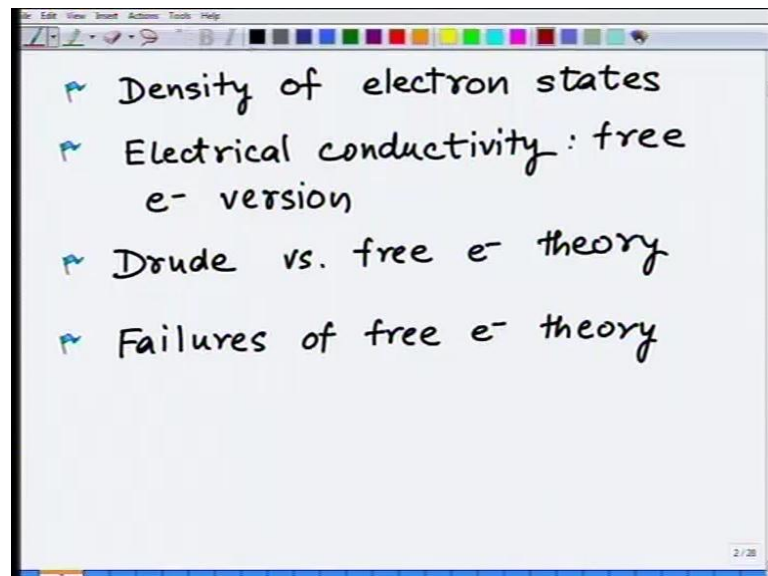
This relationship between them this  $n$  and this  $E_f$  was derived has to be this  $\pi$  there as shown here. Similarly, we had said if you want momentum, then if you want to do momentum then this momentum was equal to  $\hbar k_f$  and even this we can now in terms of this quantity  $n$  in terms of  $n$  we can also determine momentum. Once we determine

momentum, then in terms of this  $n$ , we can also determine what is the fermi velocity? And as a momentum, we mean momentum of the electrons which are at the fermi energy.

That means, the highest energy which electrons are having from lowest energy onwards is up to that energy where electrons are filling up. The velocity of those electrons then is also given by this quantity which is where we finished in the previous lecture. Now, let us look at this little bit further that we also said that, now that you know since you know how to calculate this quantity  $n$ . So, substitute  $n$  in to this equation of  $v_f$  and say  $v_f$  we will find is about  $10^8$  centimeters per second.

That is the kind of velocity which you have which means that you are in about one percent of velocity of light. Remember in Drude's theory, this velocity turned out the velocity of the electrons that were conducting turned out to be  $10^7$  centimeters per seconds, that is the difference we have. Gain in free electron is what the free electronics theory is saying so far. Now, we want to move forward in this lecture three what we will do is that we will look at four topics today will look at the density of electron stage.

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This is a side topic, this topics is going to be useful when we start doing semiconductors, then I am going to use the result from this. Also after that we will start looking at electrical conductivity which we derived in context of Drude theory. Now, we will start

looking at the looking at that point of free electron version, once we have done that I will show you the difference between Drude theory and free electron theory.

Finally, today I will show you that even free electron theory has series limitation and we have to see what next. So, that is what this lecture number 3 would be today. So, let us get going let us start with this density of electrons state let us start with this topic. So, what we derive was the less turn around this equation for fermi energy we have derive if we take this equation right here if you take this equation and turn this around then I would write this equation.

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The image shows a whiteboard with handwritten mathematical derivations. At the top, the Fermi energy equation is written: 
$$n = \frac{1}{3\pi^2} \left( \frac{2me}{\hbar^2} \right)^{3/2} E_F^{3/2}$$
 Below this, a note explains the meaning of the density of states: "Meaning of density of states  $g(E)$   $g(E)dE$  is the number of  $e^-$  states in  $[E, E+dE]$ ". Then, the Fermi energy equation is rearranged to solve for  $E$ : 
$$n' = \frac{1}{3\pi^2} \left( \frac{2me}{\hbar^2} \right)^{3/2} E^{3/2}$$
 Finally, the density of states  $g(E)$  is defined as the derivative of  $n'$  with respect to  $E$ : 
$$g(E) = \frac{dn'}{dE} \quad (dn' = g(E)dE)$$

Then, I would write it as  $n$  as equal to I will write  $n$  as equal to  $\frac{1}{3\pi^2} \left( \frac{2me}{\hbar^2} \right)^{3/2} E_F^{3/2}$ . So, what we mean by density of states that was defined meaning of density of states. This is the symbol I am going to use. So, we will say that  $g(E)dE$  is the number of electron states in energy interval of  $E$  and  $E+dE$ . This is the number of electrons that is number of electrons states which are in energy level energy  $E$  and  $E+dE$ .

So, that is what the meaning of this density of states says, now I like to pause for a minute and clear up whole idea which may become confusing later. So, let us clear it up right now. First thing is, we could also define something called as density of  $k$  states remember what we have is the way you should think is like this that there are allowed  $k$  energies, the allowed  $k$  states, not  $k$  energy the allowed  $k$  states.

So, if you have different  $k$  states which allowed then you can ask the question what is the density of these  $k$  states. So, therefore I could have defined another quantity called density of  $k$  states then since each of this  $k$  states can take two electrons. So, if I multiply by 2 these densities of  $k$  states, then I would get what I what we call as density of electron states. So, either you work with density of electrons states or you can rather density of  $k$  states as long as you remember whether you multiply with this factor of 2 then you would be ok.

In this course what we will do is, we will never deal with density of  $k$  states, we will always deal with density of electron states which means that there is a difference of factor 2 only. That means, I have certain days to  $k$  states, since each  $k$  state could have taken 2 electrons it has been up, it has been down electrons. Therefore, I will always call that density multiplied by 2 as the density of electron states; remember these are density of electron state. It does not mean that electron indeed is necessarily present on those states is that the states are there. Then that means, electron can occupy that it is not necessary that electron does occupy those states.

In fact, if you want to know whether electron is there or not we will have to do something else which I will do later, but notice I have been silent so far about this aspect. I have derived this relationship right there saying that if I have  $n$  electrons up to what energy they will fill. In that sense it is a hypothetical question that if I have  $n$  electron then how far they will fill that is the question. That is the question I have answered I have not said whether I have indeed put those electrons in or not.

So, you can think it think of it like that or you can think it think differently that indeed all these states are indeed filled with the electrons you remember that all this calculation are revealed for 0 k. It is possible we will see later that if we go for higher temperature above 0 k, then some of these electrons could go to even higher energies leaving some of state vacant. In that case, these formulas directly will not be valid. So, that is why I am saying that you think as if I have all this  $k$  states and therefore, electron states multiplied by 2. If I had  $n$  electrons, then how far they will fill is the questions we have answered so far, and indeed if they do occupy if that the probability of occupying those states is 1; that means, indeed all those states are occupied.

Then precisely, these would be the energy, these would be the momentum, these would be the velocity, fermi velocity etcetera of those electrons. So, with this background, now is very simple to derive what the, remember now I can instead of writing this Fermi energy, let me write another quantity called  $n'$  and I will write this same expression as like this  $n'$ . I am using only for explanation in future; I will drop this and keep calling back again and itself. So, there is no confusion sorry let me remove this  $f$  here I just want  $E$ , what I am trying to show is by exactly same logic instead of saying earlier I said I have  $n$  electrons, if I have  $n$  electrons how far they fill and defined that is a fermi energy.

But, you could think slightly differently the way which will also think is that up to energy  $E$ . I can fill total of  $n'$  electrons and if I go slightly  $dE$  energy higher then I would have filled this  $n'$  plus the  $n'$  electrons extra and we are seeking what is that number of electrons. So, if you can calculate that number of electron, then you can immediately define our  $g(E)$  clearly, then this quantity  $g(E)$  would be equal to simply  $d n'$  by  $dE$  why because  $d n'$  would be equal to  $g(E) dE$ .

This is the quantity we are trying to what is that mean this is the number of electron in energy, this is the number of electron we read the definition, here is the number of electron states in energy of this intervals. So, I will explain  $n'$  electrons are filling up to energy  $E$  and if I go slightly higher energy, the  $dE$  then the number increase the electrons is  $d n'$ . So, we are basically trying to calculate  $d n'$  by  $dE$  for the density of states. So, now once we have this definition it is straight forward enough to write this.

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$$g(E) = \frac{dn'}{dE} = \frac{1}{2\pi^2} \left( \frac{2me}{\hbar^2} \right)^{3/2} E^{1/2}$$

**Electrical Conductivity:**  
 free e- version  
 $\vec{v} = \frac{\hbar \vec{k}}{me}$  for every  $\vec{k}$   
 in fermi sphere there is a  $-\vec{k}$  vector also.  
 net velocity = 0

Density of states has been equal to just taking the derivative of this quantity  $n$   $d n d E$  call it prime or do not drop this prime does not matter really  $1$  over  $2 \pi$  square  $2 m e$ . At presume you can carry out this derivation I have just written it out here and to save time,  $3$  by  $2$  energy to power now half, which is what density of state is. So, what density of state goes as square root of energy? If this is it this energy then  $g$  of  $E$  goes as square root, it goes something like this.

Given this, now you stop at this topic, these density electrons, density of electron states just remember this expression I am going to use as about 4, 5, 6 lecture down the line. I will start using this when I start doing semiconductors, but in context of free electron theory, we derived this we given this definition and from gives given this certain definition which will use subsequently. So, now let us move on to the next topic which is electrical conductivity free electron version is now what you want to do.

So, what do we have we know that  $\hbar k$  is momentum. So, if I divide this by mass of electron I get velocity of any electron, I get velocity of any electron in this in this way now let look at this the way I am saying is that if you have all this  $k$  states. If you have all this  $k$  states that is a  $k_x k_y k_z$  and in this in there is a sphere up to which electrons are all filling up. All these electrons are filling up to these this  $k_f$  and this is what  $k_f$  is up to here all these electrons are filling up. Now, if we notice that for every  $k$  in for fermi

sphere, there is a minus, there is a minus k vector also. What is that mean for every velocity of electron, there is exactly opposite velocity of electrons also.

So, net velocity net velocity is equal to 0, so that means, clearly if nothing then this electron cannot cut material is this as this no conductivity, we expected there should be no net velocity if there was net velocity then we would have correct. But, clearly without application of electric field, we can't be having current. And therefore, as we expected the net velocity must be 0, but what happens if I apply high electric field.

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If we now apply  $\vec{E}$  field

$$\frac{d\vec{p}}{dt} = -q\vec{E} \Rightarrow \hbar \frac{d\vec{k}}{dt} = -q\vec{E}$$

in time  $t$

$$\vec{k}(t) - \vec{k}(0) = -\frac{q}{\hbar} \vec{E} t$$

$$\vec{k}(z) = \vec{k}(0) + \left( -\frac{q}{\hbar} \vec{E} z \right)$$

The diagram shows two  $k_x$ - $k_y$  plots. The left plot at  $t=0$  shows a Fermi sphere (red circle) centered at the origin with  $\vec{E}_x = 0$ . The right plot at  $t=z$  shows the Fermi sphere (blue circle) shifted to the left along the  $k_x$  axis, with  $\vec{E} = -|E|\hat{x}$ . A dashed red circle indicates the original position at  $t=0$ .

If we now apply electric field then what happens, we know that  $dP$  its rate of change of momentum, now should be equal to minus  $q$  times their electric field which is a minus sign because a electron  $q$  is a absolute charge 1, but positive number  $1.6$  into  $10$  to the power minus  $19$ . So, erase that number any way. So, this is the rate of change of momentum which implies, I can write this us  $\hbar d\vec{k} / dt$  as equal to minus  $q$  times this electric field  $e$ , what are that this mean.

So, in time  $t$  this fermi sphere starts moving, this start moving how does it move? If I integrate this expression right here, equation what do I get, I get that  $k$  vector at any time  $t$  then will be equal to  $k$  vector at time equal to  $0$ . That at time equal to  $0$  is when we apply the electric field say  $t$  equal to  $0$  electric field is applied in time, this  $k$  vector began to move and this becomes equals to  $q$  minus  $q E$  by  $\hbar$  bar  $t$ .

This amount by which this  $k$  vector moves in time  $t$ , now that in time as time increases this  $k$  vector can keep increasing is like shifting of origin of the Fermi sphere. We can think of this as follows, we can imagine we have drawn in a minute, but before that you can think this is just a center the Fermi sphere changing from a different  $k$  position moving from one  $k$  position other  $k$  position, but the problem is now that  $t$  is changing, this Fermi's surface keeps shifting.

So, this causes of problem same problem which we had when we started that if I applied electric field if there is nothing to damp the motion then the current will continuously increase for a given electric field which is contrary to all observation. Same thing will happen here if  $k$  continuously increases then therefore, the same token this will continuously increase. And therefore, current will continuously increase the current will also continuously increase.

So, we face with exactly same problem as we started in the lecture number one where we started Drude's theory and we invoked collision which was really giving as damping. Hence, the velocity we found to be average velocity was a fixed velocity when we could it collisions. Now, in this free electron theory we will make more such statement as to what the mechanism of mechanism of this damping is, but we know that from experience they must be some damping.

So, let us assume, let us invoke the same time  $\tau$  let say that by some mechanism there is a relaxation time called  $\tau$  the same relaxation  $\tau$ , we started using in Drude's theory may be because of collision with ions. But, same idea that in time  $\tau$  that this  $k$  state changes to that value to  $k$  state changes up to this time  $\tau$ , and then it is held at that Fermi, then no more changes happened. You think of  $\tau$  of relaxation time, means if you want to think same way as Drude, then mean time between collisions. And therefore, after time  $\tau$  on average is it a value of  $k$  average value of  $k$  would have.

Then, in that case become as you write then the same expression by saying  $k$ , then they will become after applying electric field  $k$ , then will become equal to  $k$ . Whatever it was a 0 minus or plus, I should say minus  $q$  times plus  $E$ , what is the expression was minus  $q$   $E$  by  $\hbar$  minus  $q$   $E$  by  $\hbar$  down here. So, if  $\tau$  is the relaxation time, then  $k$  average value  $k$  states where is a state applying when apply electric field is then  $k$  of  $\tau$ , this quantity.



So, effectively therefore I can show in two dimensions is easy to show you can imagine this to be  $c$ . You can imagine this as a 3 dimensional figure, also what I will do is let us say this is  $k_x$ . Let us say this is  $k_y$  and let us say that I am going to draw it at a circle or everything not as sphere for a circle in two dimensions. You can keep imagine, this is a 3 dimensional figure as a sphere. So, what I do is I will draw a circle here. Let us chose a different color, we will chose a circle here like this. So, here is a circle I have drawn here and this is at  $t$  this is a  $t$  equal to 0 and what you have done is what you have done is we applied a electric field  $E$ .

Let us say, we applied a electric field in  $x$  direction initially  $t$  equal to 0. We have electric field equal to 0 and then at  $t$  equal to 0, turn on electric field and what happens then when we applied an electric field what happens is a the picture will draw here right here. This is  $k_x$ , this is  $k_y$  and let me draw the same sphere first, the same sphere which I had for I will draw, show it is a dotted line. So, this is the sphere at  $t$  equal to 0 which originally I draw in the previous figure.

Now, I will show with another color pen, let us say blue, let us say now I have a situation where this is  $t$  is equal to  $\tau$  and  $E$  field which I have lied is let us say minus  $E$  magnitude  $n_x$ . I have direction we applied this field, let us say if we applied this field then this now see where the  $k$  will be every  $k$  point, whatever the  $k$  point was a time equal to 0 in time  $\tau$ . Its value would be that number plus this number plus this number at I have taken  $E$  to be minus field with every where plus number here.

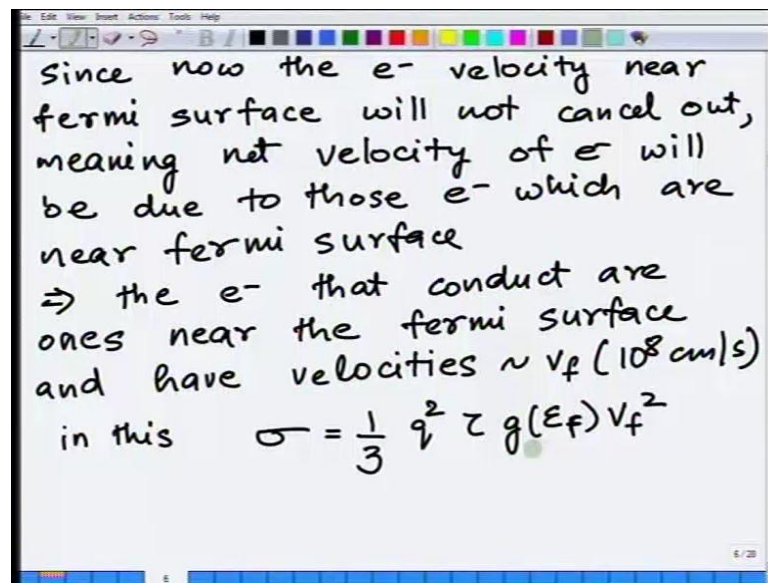
So, it is going to shift in the  $x$  direction. So, let us draw that is speed also the circle now in this case and you can imagine sphere, then this after shifting will become something like this right this whole thing as shifted this center is shifted to here. Now, this whole thing moves something like this now something like this. So, this was at  $t$  equal to 0 and this is at and this is at  $t$  equal to  $\tau$ . So, what you notice. So, what do you see here. So, what has happened you my figures are not nice you can imagine all of these to be circles, but anyway. So, now what you see now notice that there as in this particular case.

For every vector  $k$  for every vector  $k$  I had exactly equal minus  $k$  vector also and therefore, what happened was for every vector  $k$  any vector  $k$  I had a equal and opposite minus vector. Therefore, net velocity was 0 where I when if we go for 0 at that time the

net velocity will it trans for zero and therefore, no current. But, now its notice in this blue circle which is what it will be at t equal to tau when I have applied electric field.

When I applied electric field now the net velocity will not cancel, now notice again a velocity, like this will have exactly component like this. And all this velocity will cancel out, but the electrons which have velocity corresponding to k states which are near the surface of this blue circle rose velocity. Now, will not cancel out what is that mean this very important fact this very important.

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Therefore, since now the electrons the electron velocity near fermi surface will not cancel out meaning net velocity of electrons will be due to those electrons, which are near fermi surface. What is that mean? Let me repeat what I said again I said that most of these velocity like this k component will cancel out this minus k component, but the k now there will be those case, which will not cancel out. And on those case will be the once which lie on the surface which are not going to cancel out any more.

So, what do we see that the electrons that conduct implies the electrons that conduct are once near the Fermi surface and have velocities. Approximately as  $v_f$  Fermi velocity which we recall was  $10^8$  centimeters per seconds not  $10^7$  centimeter per second at root s we assume in Drude's theory. Therefore, you can see the first error which was in Drude's theory. Now, we can we have we have a better estimates of what the velocity of electrons that conduct should be now I will not derive the expression, but

only thing is that if you go through a process of calculating this average that velocity through this process exactly, what the way it has been.

Describe if you carry out summation over  $v$  if you average over all the velocity then calculate what the net velocity is and you also calculate, what will be the number of electrons that will be what the number of electrons, which will be  $n$ . Therefore, conducting then you will find if you go through this whole process, what I will do is write the final expression that. In this case we find that the conductivity will become equal to  $\frac{1}{3} n q^2 \tau$  the same, which is going to have to appear and this becomes equal to then  $\tau$  I am going to choose the punting test  $g$  itself.

This is the density of electrons near the fermi energy for this expression for conductivity becomes this which should make sense, it should have a dependence on the number of electrons that are near the fermi energy. It should depend on the velocity of the electrons which is of the velocity of those electrons, which conduct, which is the fermi velocity this gives to say estimates of what the conductivity of a material will be any way this was only side topic I just since, we derive the same expression for Drude's theory. So, therefore, I am done that for free electron theory, now let us there is a time to take stop of what is happened lets analyze what we have gain.

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Drude's theory vs. free e- theory

What have we gained?

- Thermal conductivity in metals

Wiedemann Franz law

Classical approach  $K = \frac{1}{3} v^2 n C_v = \frac{1}{3} v l C_v$  } specific heat

Specific heat of metal  $= \frac{3}{2} n k_B$  ✓

estimate of velocity is by:  $\frac{1}{2} m_e v^2 = \frac{3}{2} k_B T$  ✓

$\frac{K}{\sigma T} = \text{constant}$

[  $v l = \tau$  ]

So, far and where the problem continues to be. So, let us first start looking at what have been gain Drude's velocity verses while talk about Drude's per velocity Drude's theory

verses free electron theory. Let us do this first what is happened what are we gain by doing this free electrons theory clearly find this case our estimates of things will become better where ever velocity is going involve where velocity is going involve. Since, we know that the velocity is order without between Drude's theory and free electron theory we found the disciplines of order of magnitude in velocity.

Velocity being higher in case of free electron theory, then we know that root theory wherever velocity of electrons works will be involve independently for that. It does not cancel with something else then that case free electron theory will make it better prediction. Then Drude's theory in order to really show you advantage of brief free electron theory I will take you through some other topic couple of topics.

This means sound out of context in context is electronic properties of material, what I want to talk about this thermal conductivity and thermal electric power we just show you how free electron gives free electron theory gives you better estimates then Drude's theory. So, let us let us look at two topics in this case one is thermal conductivity in metals in particular I am going to talk about this what is called as Wiedemann-Franz law. I will try to show you what have we gained, now if we without any remember the conduction thermal conduction in metals occurs by same process by which electrical conduction occurs. That means, the mechanism by which the heat transport remember we said electrons are arrive local thermal equilibrium.

So, now if electrons are moving now due to electric field for example, if you wish that gives you correct, but then this motion of motion of electrons also carries heat. So, the thermal conduction in metals also happen through this m not same exact same motion of electrons in that sense we are not talking out of context some. When you talk of thermal conductivity in metals we are at microscopic level at atomic level, we are talking about the same process which we talk for electrical conductions.

So, if is you therefore, you are free to apply the same theory to develop the idea of thermal conduction also in which case by classic in roots approach or classical approach without proof. I will write this thermal conductivity or capital  $k$  to be equal to  $\frac{1}{3} n v^2 \tau C_v$  in quantity of Drude's theory. If we just derive then this quantity is half derived as half  $n v^2 \tau C_v$  this is the specific heat  $C_v$  this is the specific heats of a material. This also can be written as  $\frac{1}{3} n v^2 \tau C_v$  being the  $1$  being  $v^2 \tau C_v$  of

what being that  $\frac{1}{3} v^2 \tau c v$  should here  $\frac{1}{3} v^2 \tau c v$  see the weight room number  $v$  times  $\tau$  as been equal to  $l$  therefore, we using here.

This quantity is derived like this second thing also, I say there by classical approach by same approach its specific heats specific heat is derived as  $\frac{3}{2} n$  times Boltzmann constant  $k_b$ . There is a Boltzmann constant and estimate of velocity is estimate of velocity is by half  $m m e v^2$  is equal to  $\frac{3}{2} k_b T$  which you have seen before which is same thing. This we have use before also in when we are doing Drude's theory I am giving it two expressions right here.

This I am giving without proof that in root context of root theory you can derive specific heat of metals to be  $\frac{3}{2} n k_b T$ . You can derive thermal conductivity by same transport mechanism to be equal to  $\frac{1}{3} v^2 \tau c v$  or  $\frac{1}{3} v^2 \tau c v$ . For this you can derive by classical theory Drude's theory now there is a law which is called Wiedemann-Franz law, which says for metal  $\frac{k}{\sigma T}$  will be a constant and this is this law.

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$$\frac{k}{\sigma T} = \frac{\frac{1}{3} v^2 \tau c v}{\frac{n q^2 \tau}{m e} T} = \frac{\frac{1}{3} \frac{3 k_b T}{m e} \tau \frac{3}{2} n k_b}{\frac{n q^2 \tau}{m e} T}$$

$$= \frac{3}{2} \left( \frac{k_b}{q} \right)^2$$

$$= 1.11 \times 10^{-8} \text{ W } \Omega / \text{K}^2$$

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

$$v^2 = \frac{3 k_b T}{m e}$$

$$c_v = \frac{3}{2} n k_b$$

So, this is what this Wiedemann-Franz law is, let's derive this expression got it now. So, what is this quantity  $\frac{k}{\sigma T}$  equal to? So, this we going to derive, so let us write down this quantity  $\frac{k}{\sigma T}$  will be equal to the substitute  $\frac{k}{\sigma T} = \frac{\frac{1}{3} v^2 \tau c v}{\frac{n q^2 \tau}{m e} T}$  divided by conductivity. Remember what is conductivity, conductivity we had derived as equal to  $\frac{n q^2 \tau}{m e}$ . That is what we derive, this as therefore, you can write substitute

that in head. So,  $n q^2 \tau$  by  $m e$  times  $t$ . Therefore, then substitute here also for, now we gone substitute, make two substitution which is what we are going to substitute. First we substitute for velocity this square of velocity we should estimate from right from here.

So, will say these square as being equal to  $3 k b T$  by  $m e$ , that is what will substitute in here and we will also substitute  $C v$  what equal to of course, we have written there  $C v$  is already there given there. So, let us substitute this in here also, so 1 by 3, we going to write and then for  $v$  square we going to write  $3 k b T$  by  $m e$ .

And then there is a  $\tau$  here, then  $C v$  we substitute in here as  $3$  by  $2 n k b$  and this whole thing divided by  $n q^2 \tau m e$  by  $T$ . Now, notice this  $\tau$  and  $\tau$  cancels this  $t$  and this  $t$  cancels this  $m e$  and  $m e$  cancels and this  $n$  and this  $n$  cancels. So, what have we left with and lets allow the  $3$  to cancel this three. So, we have left with essentially  $3$  by  $2 k b$  by  $q$  whole square, indeed is a constant Boltzmann constant divided by this happens for charge electronic charge  $1.6$  into  $10$  power minus  $19$ , indeed this is constant which is what is observe.

In this Wiedemann-Franz law, which is  $\chi$  remittal observation even in roots theory. This value came out this constant which and this value went plugged in. You can plugged in this value what you get is the number which is like  $1.11$  into  $10$  to power minus  $8$  watts ohms or kelvin square. Now, if you look at this number, this number is about only half of what actually is observed. So, it is pretty remarkable that even Drude's theory basically predicted right result anybody thought. At this, Drude's theory is predicting this Wiedemann-Franz law will because only half of what is experimentally observed. So, the thing of it is this that what happen was that electronic contribution.

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Electronic contribution to specific heat is at least 100 times more than observed ( $\frac{3}{2} n k_B$ ) & velocity is underestimated 10 times

free e-theory

$$C_v = \frac{\pi^2}{2} \left( \frac{k_B T}{E_F} \right) n k_B \quad \left[ C_v = \frac{3}{2} n k_B \right]$$

$$v = \sqrt{\frac{2E_F}{m_e}} \quad \left( \frac{1}{2} m_e v^2 = E_F \right) \quad \left[ \frac{1}{2} m_e v^2 = \frac{3}{2} k_B T \right]$$

The electronic contribution to specific heat is at least hundred times more than observed and what is the electronic contribution remember 3 by 2 n k b. This is the classical theory and this is the electronic contribution, the specific heat and this number is at least hundred times more than ever done any electrons. Then what the electronic contribution to specific heat is, so what happens, how it still work does.

Now, let us go back if you go back notice then also v square term in here there is the v square term also in here and this v square is what is helped this. And remember Drude's theory v also under estimates we under estimates velocity by 10 times. We have v square and over estimates of C v 100 times, therefore 2 error canceled out, and you got something very close to what reality is in Drude's theory 10 times. Let me just repeat this part, so this is in the Drude's theory this is in the Drude's theory.

Now, let us see what happens in free electrons, free electron theory in free electron theory, the estimate of C v becomes equal to pi square without proof. Again I just simply give you by free electron theory what happens k b Boltzmann constant, this fermi energy now 10 times k b another post two in Drude's theory. Where it was C v equal to 3 by 2 n k b this factor right here, then k b remember is same in both of them classical theory, the free electron theory. This factor if you look at even at room temperature, this t at room temperature if you look at this factor this pi square by 2 k b t by E f, this factor at least hundred times smaller than this 3 by 2.

Compare it 3 by 2 this factor is about hundred times smaller which is why you are saying that the electronic contribution to the specific heat is at least 100 times more than observed. This is what electronic contribution really is which is being predicted well by this free electron theory. Now, if you put this simultaneously estimates this velocity if you estimates by the velocity by 2 times E f by m e not where is according to half m v square m e v square mass of electron as equal to the fermi energy.

If we going that to fermi energy then you estimate the velocity to be like this if you estimate the velocity to be like this. Then remember in classical theory we have estimate this by as equal to 3 by 2 k b t and we have under estimated this velocity 10 times. So, now this velocity estimate is 10 for 8 centimeter per second, as we have derived in free electron theory earlier if you now plug in this number.

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$$\frac{K}{\sigma T} = \frac{\pi^2}{3} \left( \frac{k_B}{q} \right)^2 = 2.44 \times 10^{-8} \text{ W } \Omega / \text{K}^2$$

Thermoelectric power  
 $T_1$   $T_2$   $T_1 > T_2$   
 $\vec{E} = Q \nabla T$  → Thermo-electric power  
 $Q = - \frac{C_v}{3nq}$

Classical estimate  
 $Q = -4.3 \times 10^{-4} \text{ V/K}$   
 which is 100 times more than observed value

Then in this case, k by sigma t becomes equal to pi square by 3 k b by q whole squared again constant number even by free electron theory we were getting k by sigma T with the Wiedemann-Franz law. I have we say that this constant indeed, we find derive by free electron theory also that k divided by sigma T is constant. Now, this substitute in the numbers this number comes out as 2.44 into 10 to power minus 8 watts ohms per Kelvin square which is a even better estimates of which is now correct estimates. Of what we have what observed value, because remember I said this was 1.11 in case of root theory and it is more half of what it is actually observe.



Now, this is beginning to predict even better of course, it is a minor gain if you look at another example which is thermo electric power. Now, you will see what we are going to do is, what we going to do is in case of thermal conductivity thermal conductivity. The two errors velocity and specific heat canceled out each other, now we were going to take a example where there is no velocity term, but only  $C v$  term.

This means, now Drude's theory will completely go here where I will show to you the free electron theory continues to predict. Now, predict much better and that incase of thermo electric power let us look at this, which means if I take a hot bar, first on material, then the number what will happen, if we keep one end at  $T_1$  temperature other one at  $T_2$  temperature where  $T_1$  is greater than  $T_2$ . Then what will happen, remember electrons come to thermal equilibrium we had assume that local thermal equilibrium. So, the once which are near  $T_1$  will have high energy higher kinetic energy then the once which have other end at  $T_2$  end, which have lower kinetic energy.

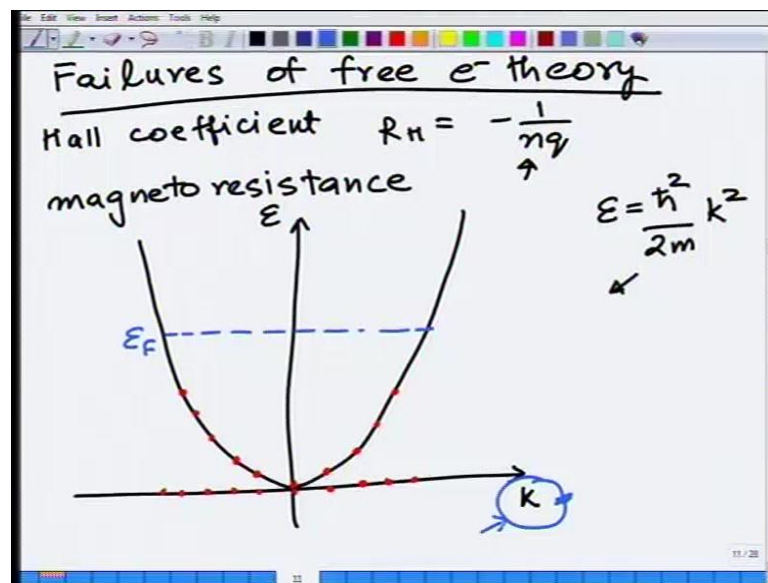
So, there will be net flux of electrons going from  $T_1$  side to  $T_2$  side, but that cannot continue in differently because it can't be a current flow in this system. So, what will happen as more and more electrons move from  $T_1$  sides to  $T_2$  temperature sides. Then a electric field will set up, this electric field will oppose the motion of motion of electrons from  $T_1$  side to  $T_2$ , that mean due to electric field you will have electron going from  $T_2$  to  $T_1$ . Due to thermal energy, the net flow will be from  $T_1$  to  $T_2$  and in equilibrium these two will balance out. So, that there no current and this is well known effect called See-back effect. Remember that fewer the electric field that will develop if you apply temperature gradient across the bar.

Then, the field that will develop inside for that the system comes in a steady state is  $E$  equal to few times gradient in gradient in temperature. That is the electric field that is develops and this is called the thermo electric power and this is well known See back effect which you have seen in a various situations thought in schools also. So, this the thermo electric power, now if you go through this again to have net 0 velocities, no current flow, when there is temperature gradient electric field also developing and both balancing. So, there is no net velocity under those conditions the expression which derives for  $q$  is the  $q$  should be equal to minus  $C v$  divided by  $3 n q$  that what this  $q$  should be thermo power.

Now, notice in thermo power we have only have  $C_v$  if we incorrectly estimated, we going to get wrong thermo power and if you put it right number then only we get thermo power which is today, if you use classical estimates of specific heats. So, roots theory classical estimates if you use estimate we get  $q$  which is equal to minus 4.3 into 10 to power minus 4 volts per Kelvin, which is hundred times more than observed value clearly.

Then, since estimates of free electron theory of  $C_v$  is hundred times less we will start getting right numbers. So, that is really the success free electron theory. This is where the free electron theory has there is an improvement from roots theory for classical theory going to quantum mechanical free electron theory, this is where we start seeing improvement.

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Now, let us look at also failures of free electronic and there are many, now notice what about hall coefficient they call  $R_H$  was equal to  $1/nq$ . Now, notice that Drude's theory we found that does not work for metal such as aluminum. Now, when you are done, free electron theory what we have gained nothing, we cannot say anything about hall coefficient I mean no improvement, there is nothing is only  $n$  appearing here that estimates have not change. Therefore, we can't and we found aluminum the Halls sign of Hall coefficient was positive the hall efficient was sorry the hall coefficient, it appeared hall for conducting.

So, therefore, in free electron theory also we make no improvement in this regard same following magneto resistance in this regard also. The field depended of magneto resistance is again not predicted give nothing done nothing. In this theory which says that let me ask many questions to you, now as we start discussing this there too many thing which are which are problem. How would you explain that carbon comes in many form diamond, it comes in graphite. Why is it carbon which is insulator why its graphite which is conductor why that happen Wiedemann-Franz law which is obeyed well at in room temperature.

But, we go to low temperature that even Wiedemann-Franz law its cooperated well by this what is observed this discrepancy between free electron theory and free electron theory and what is berated by what is observed. Similarly, this directed constant of a material could be very, very complex which is not by pirated by free electron theory. Now, already talked you talked about, I give you already hint that when you talk about thermal when you talk about conductivity in graphite or in diamond.

Now, both are carbon, this nothing we said about differences between graphite and diamond and therefore, the difference in conductivity we just can't bring it. Bring it in why is a aluminum good conductor, but bismuth and antimony which are also metal which are not why boron is insulator. Why boron is insulator, now these are the things which these are the things, which are not coming, which are the other observation. However, this free electron theory we are not gaining anything out of it why is it. So, you should already have it to that our materials have special structure.

Then that materials are, they have a structure also they underline atom that periodicity in what is that mean, remember the true form graphite is conductor diamond is not what is the difference between them both are carbon-carbon based materials. Now, all we have done is in copper we have taken copper atom and consider valence electron and went ahead and did both this case.

But, you see there are underline latex, underline periodicity, in these materials these periodicity the electron wave which is coming. Now, you notice this electron wave is traveling. Now, there is interference of this electron wave if the latex is perfect, then there could be constructive interference, and this electron wave could just simply go through, where as if we break the periodicity of the latex somewhere.

Then you can have destructive interference and therefore, you could have the electron wave dying out and; that means, conductivity being low. Now, all these there, therefore in all the explain conductivity, we must take into home what is the underline structure of the material. So, what in the next lecture I will do is I will cover two topic, one just to build up the case, I will cover two topics one is that will start with crystal structure of material then after that I will take you to something take you through, what is called reciprocal lattice. Some of you would all ready be familiar with it in context of X-ray diffractions or electron diffraction.

So, you see will go through these two topic first and then you will see the relevance where we are heading what ultimately, I want to do is now I am going to write down here that what have we done. So, far we have said that energy is equal to  $\hbar^2 k^2 / 2m$  square, but ultimately I want to show you is that there is something called E k diagram. So, thought this E k diagram E k verses energy, then clearly it look something like this it clear looks it look something like this, this is this, this expression being ported here.

What I am doing of course, k appears only a distinct levels allowed values of k r. Only these are the allowed values of k and corresponding energy is ported here, but now these k also totally pack that we draw then continues line that it the line that the lack line I have drawn is sufficient enough because this k also. So, in this picture I show you by red dot which a far apart, but in practice there, so close there is no need to show those dot they look like the black line which is continuous line.

Now, what happens when what we have done so far is that when we start filling of electron, when we start filling of these electron we start putting them two electrons in each of these k states. In each of these k states we start putting 2 electrons and when you start putting them in we fill up to let us say these energy and this energy we call use  $E_f$ . This energy we call  $E_f$  that is the something which we have done, I shown you the question is what this quantity.

You also remember I have pointed out that this is E k diagram, meaning this energy was a momentum diagram k precociously represent momentum as well.  $\hbar$  multiplied by k represents momentum. So, if I get a proper E k diagram for each material, I should energy and momentum there is 2 quantity of sufficient to do all the dynamics we want to do whatever we want to do.

With the dynamics of a electron you can do if you have a E k diagram essentially for a real material, I want to do this E k diagram. In order to understand this E k diagram I was understand k this k remembered in out of plot like this, I have drawn at as a k. But, the k really is a vector k is a big vector, which is a in which direction should I draw it how to draw with e k diagram this issue we will start looking at almost 2, 3 lectures on the line slowly will build the case in order to use. So, we have to understand reciprocal lattice because k belongs to reciprocal space and in order to understand reciprocal lattice, we must do real lattice, which we will start next lecture.

Thank you.