Electronic Theory of Solids
Prof. Arghya Taraphder
Department of Physics
Indian Institute of Technology, Kharagpur

Lecture - 02
Weidemann Franz Law

Hello, let us continue with our discussions on free electron theory and the relaxation time approximation that we have been doing in the previous class. So, let me just recap a bit. The free electron theory constitutes an assumption that in a metal the conduction electrons behave like a gas of classical particles.

And, they are basically free to wander about confined to the solid by the walls of the solid. And these electrons have their properties understood in terms of certain very simplifying assumptions. And one of them is a very major assumption, which is the relaxation time approximation. Using this one calculates the transport properties.

So, what does this approximation tell us, this approximation basically tells us that an electron collides with the ions in the solid and it has no interaction with other electrons nor does it have any Coulomb interaction with the ions. So, the on this basis the relaxation time approximation now says that between two collisions with ions, the electron moves freely. And at each collision, the electron loses its memory of the previous velocity and so it emerges from the collision with the configuration which is consistent with the temperature of that particular position.

So, suppose it collides with a particular ion, then whatever is the temperature around that ion, the electron will emerge with a speed which is consistent with that temperature. Each collision randomizes the electron, and unless there is an electric field it has no drift velocity in any direction. On that basis one starts calculating the transport properties.

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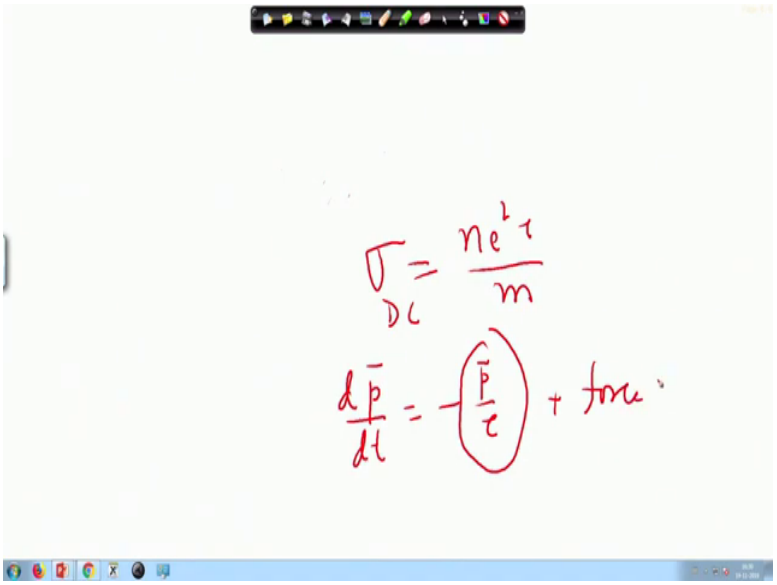

So, which one of them we did which is just the well-known relation that the conductivity is n e square tau by m, so sigma (D C) = ne**2 tau/m.

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i.e., n e square tau by m. So, this relation tells us that there is this relaxation time tau which, along with the density, determines the conductivity and the other two things are universal constant, the electronic charge and the mass of the electron. So, this is a relation that is very easily obtained from the classical Newtonian laws and a relaxation time approximation.

We went further and we also calculated the equation of motion for an electron which is basically Newton's law as such, but there was an additional term which is the term we called the, sometimes it is called the drift term which incorporates the fact that there is a relaxation time tau at which at every relaxation time, the electron basically collides and gets randomized, its velocity gets randomized.

We calculated this equation dp /dt equal to minus p by tau plus the force. Without this dp/dt term this equation is just the force term which is same as Newton's law. So, for an electron in an electric field, one uses this equation to calculate the transport.

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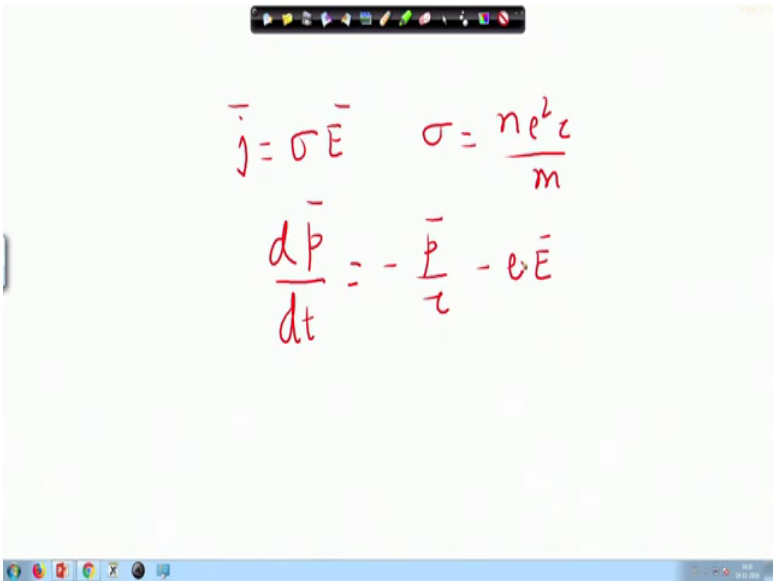

Now, what is the advantage of using this equation? Remember, the sigma equation that we calculated n e square tau by m j equal to sigma E with sigma equal to n e square tau by m versus this for DC fields, that means, there is no time dependence in this equation.

Suppose, your metal is under the influence of a time dependent electric field, now there of course, I cannot use this equation. I have to use the dynamical equation if I want to get the frequency dependence, and that is what that equation does. We will come back to it at a later point, but this is the reason one writes, one actually calculates starting from this equation. So that constitutes the basic equation in the Drude model.

What I do today is that I start with a calculation of the thermal conductivity of a metal. We know that when there is a thermal gradient in a metal, that means, one side of the metal is at higher temperature than the other side, there will be a flow of heat from the higher temperature side to the lower temperature side, so that the heat flow is actually opposite in direction to the temperature gradient. Let us just work that out.

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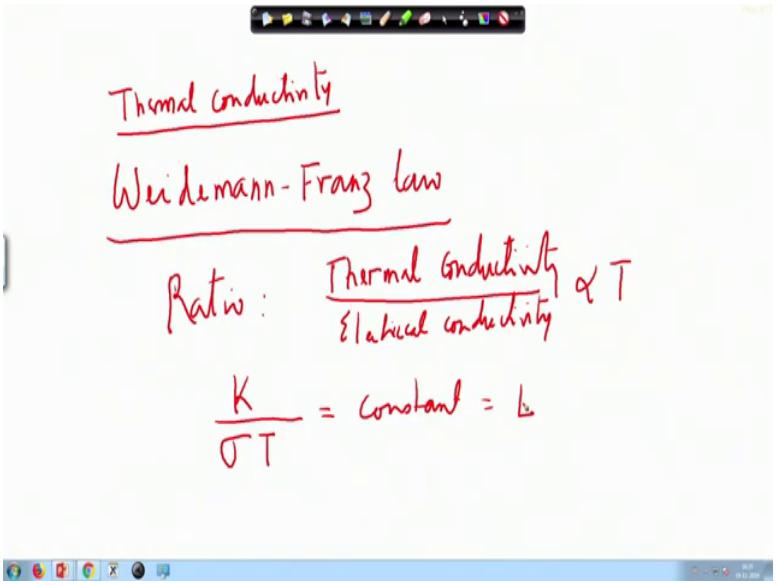

First define the thermal conductivity. Before I define thermal conductivity, let me also introduce you to a very interesting phenomenological relation which was there since 1853, which is called Weidemann-Franz law. This is an empirical law, observed experimentally in several metals, and it was put down as a phenomenological rule. So, it became a law, sort of, but it is basically an observed rule.

What it says is that the ratio of thermal conductivity and electrical conductivity is proportional to temperature. And this proportionately constant is more or less very close in all metals that they studied at that time, in many metals it is certainly the same. And this ratio thermal conductivity divided by the electrical conductivity times temperature is therefore a constant usually called the Lorenz constant, denoted by L. So, this was the empirical law that was existing for about 50 years before the free electron approximation and Drude approximation came in.

One of the greatest successes of Drude's theory is that it could actually explain this simple relation that K by sigma T is a constant for most metals. I will work it out, and then show you how one gets that from Drude's relaxation time approximation.

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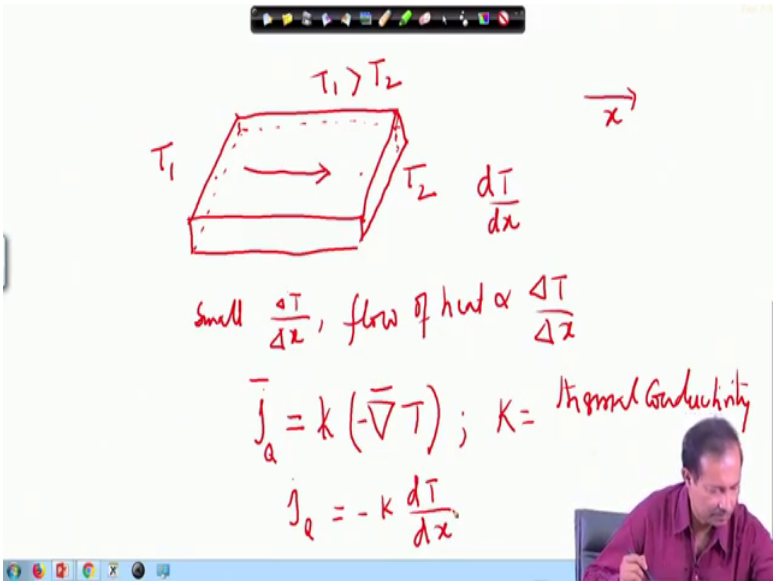

Let us consider a slab. I am trying to work out everything on board simply because it will be easier for you to remember, these calculations are simple calculations, and therefore, easy to remember. So, this is my slab. And I maintain one side at T 1 and the other side at T 2 where T 1 is greater than T 2. These are the two temperatures.

In this condition, we know that heat will flow from the higher temperature side to the lower temperature side. Suppose, I call this the x-direction, I choose a coordinate system in which this is the x-direction. It becomes a one-dimensional heat flow problem in essence because there we are not considering heat flow in any other direction, it is just the direction along this slab from the side which is at higher temperature to the side at lower temperature.

Remember, dT/dx the temperature gradient is negative, because temperature decreases along the positive x-axis. And the heat flow therefore, is just opposite to that because heat flow is in the positive x-direction. That is expected because if the temperature is higher on one side heat will flow from that side to the other side. Temperature drops from higher side to lower side and heat flows in the opposite direction, in the sense that it flows from the higher temperature side to the lower temperature side.

Let us just try to understand what happens to the thermal property of the system. Now, one assumption that goes in here is that the entire heat carried from left to right is being carried by

the electrons, the lattice, the ions are not playing any role here which is certainly is not correct. But this is the way the approximation goes. And it in most cases it works very well for metals particularly, because there is a very large number of electrons and the electrons are free to move, whereas the lattice ions are more or less localized. Of course, if you have an insulator where electrons are not free to move, then this assumption will not work.

Now, in this geometry, the electrons coming from left to right are carrying a higher energy, why, because of the simple principle of Drude approximation that we used. In Drude approximation, the electron emerges from a collision at equilibrium with the surrounding, that means, where it has last its property becomes appropriate to that region.

So, when an electron comes from a higher temperature, it collides in a higher temperature region and moves towards right, the lower temperature side. It actually carries higher energy than the once which are coming from the right side which are at a lower temperature. So, this means that although you do not have a transfer of electrons in equilibrium, the number of electrons remains more or less fixed on both sides in the sense that there is no net transfer of charges as such. But, there is a transfer of heat. In the sense that energy is being transported from left to right, because the electrons that are coming are carrying more energy from the left, so that is the point where the Drude approximation goes in this calculation.

Let us define the thermal conductivity as was originally defined which is that for small dT/dx, it was actually experimentally observed that the flow of heat is proportional to dT/ dx. So, its dT/dx and this proportionality constant is called the thermal conductivity.

That means, that the heat current j of Q, Q stands for heat, is proportional to dT /dx which in three dimension will become the gradient. So, I will write it as the gradient, grad of T. Remember, it flows in the direction opposite to the gradient of temperature and then this proportionality constant kappa is called the thermal conductivity, so far so good.

Now, what is j of Q, it is exactly similarly defined as in the electrical conduction: j of Q is the amount of heat that flows across an unit area in unit time perpendicular to the direction of flow of the heat. So, the definition is very similar to the electrical conductivity, there it was the flow of current, flow of charge; here it is the flow of heat.

For the above example, the heat current is a scalar. In the sense that it has only one component and that is proportional to minus K dT/dx, which is along the x direction. This minus sign is very important, remember that is what dictates things, the direction of flow of heat.

Now, again as I said let us use the concept of Drude, which is that we will again assume that the collision at a particular point gives the electron in equilibrium there. That means, the electrons that are coming from the left in this geometry of this slab, those which are coming from T 1 have a larger energy than the ones that are coming from T 2 side.

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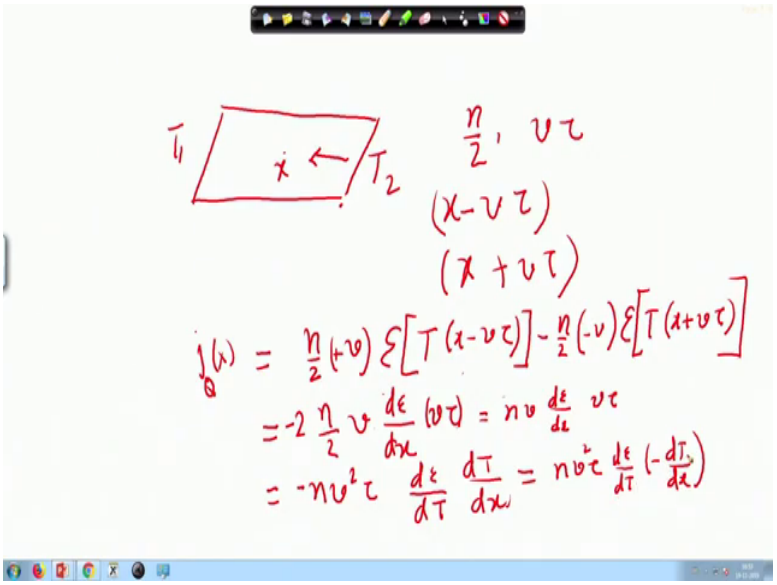

Let us just consider at a particular point x somewhere inside. At this point electrons are coming from the left and also from its right. And since there is no net transfer of charge almost equal number of charges are coming from left and the right.

If the density is say n and we can think that n/2 number coming from either side. But the ones that are coming from the left side had their collision at a higher temperature, and they have travelled a distance of v times tau freely and arrived at this point. So, which are the electrons which had done that? The ones which were within the distance x minus v T. So, they are the ones that came from the left side without any further collision on an average and arrived at x, so they are carrying a higher energy. That is what we are going to now calculate.

Similarly, the ones which are coming from the other side, came from the point within the region x plus v tau, v is the speed of the electrons. And these are the electrons that came uninterrupted, they had no collision in between on an average and they arrived this point. So, they carry the information of the energy, energy information of the point which is x plus v T. So, let us now find out the amount of thermal energy that is coming to the point x. Let me just write down. So, n/2 electrons are coming from the lrft, they have their velocity in the positive x-direction. And the energy they are carrying to x is a function of temperature, not at point x, but at the point x minus v tau.

So, I have to subtract from this the ones that are coming from the right side, they are also carrying energy and that they are carrying energy to the left. So, let us just subtract them. I will come back to the three dimensional case at the end. Now, this again will give me the energy carried by them from here. So, this difference is the thermal current flowing at the point x. So, j of Q at x is basically this (see the calculation).

Let us calculate this now: this is n/2 into v. Now, if I do a Taylor expansion, the first term gets cancelled from these two things, because there is a minus sign here and there is a plus sign here. So, I am left with this term which is n/2 v dE/dx into tau into 2. So, this is basically n v dE/dx into v tau, v tau is the distance so that is why dE dx into v tau.

Now, this energy does not depend on x directly, it depends temperature. So, let us just do one more step. Let me write as dE/dT, dT/dx. So, now, the interesting thing is that, there is a negative sign that has to appear here, and that negative sign is actually reflecting the fact that dT/dx is carrying that sign dE/dT into minus dT/dx. This much is fine. So, let us now finish this in one dimension, the result is n v square tau dE/dT into minus dT/dx. Let us go ahead and then consider a 3D system.

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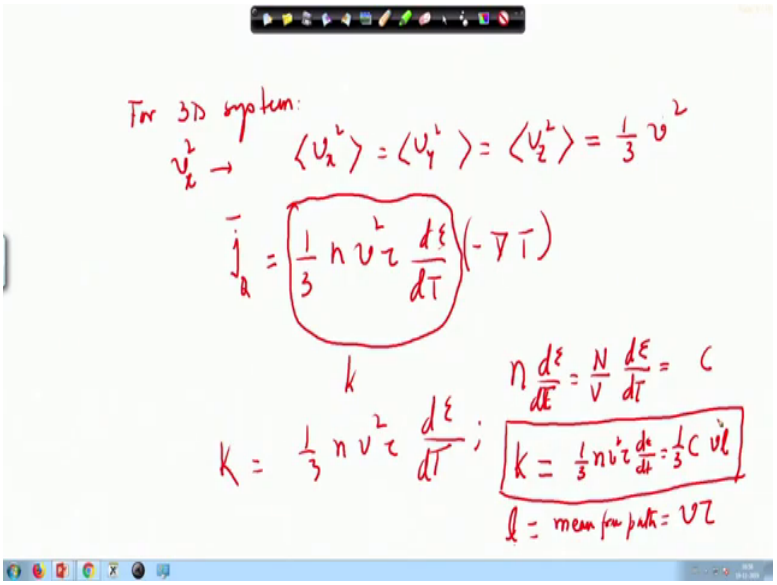

For three-dimension all we have to do is to understand that this v square that we have written is basically v_x square, because there is only one direction we are considering. But in three-dimension, what we have to do is that we have to convert it to average v square. In an isotropic system of course, we know that v_x square is equal to v_y square is equal to v_z square. And this is basically by isotropy, there is nothing to choose between x, y and z directions in an isotropic solid. And therefore, this should be equal to one-third of v square, one-third the average velocity that we have been using in the Drude theory.

That lets me put it in that case, then we have j_Q, now it is a vector equal to one-third n v square tau dE/dT times minus grad T. Now, you can easily identify that this is the part that gives me the from of the definition of thermal conductivity, this is the kappa, equal to one-third n v square tau dE dT.

Now, of course, we know dE/dT can be connected to another property of a system which is the specific heat. So, let us just do that and note that n dE/dT is basically total number of electrons divided the by the volume, dE/dT is nothing but 1 by V C, the specific heat. This is the electronic specific heat of course, we are dealing only with the electron. Then kappa takes the form one-third n v square tau dE/dT equal to one-third C v l. This is a relation that we have worked on for a long time, we know from our high school days probably, and this gives

me thermal conductivity in terms of the specific heat and velocity, and l, where l is the mean free path equal to v into tau,

Here I should not have the v, because I have this is the specific heat, this is the definition of the specific heat. So, this v is not there, that gives me the value of the thermal conductivity in terms of two a simple parameters of the system which are the C v and the mean free path. Of course, mean free path is not easy to determine. So, that is the only thing that is still here which is indeterminate in the sense that we have to determinate from other quantities like conductivity for example. From conductivity one can find out tau, the relaxation time and v times tau will give you the l for example.

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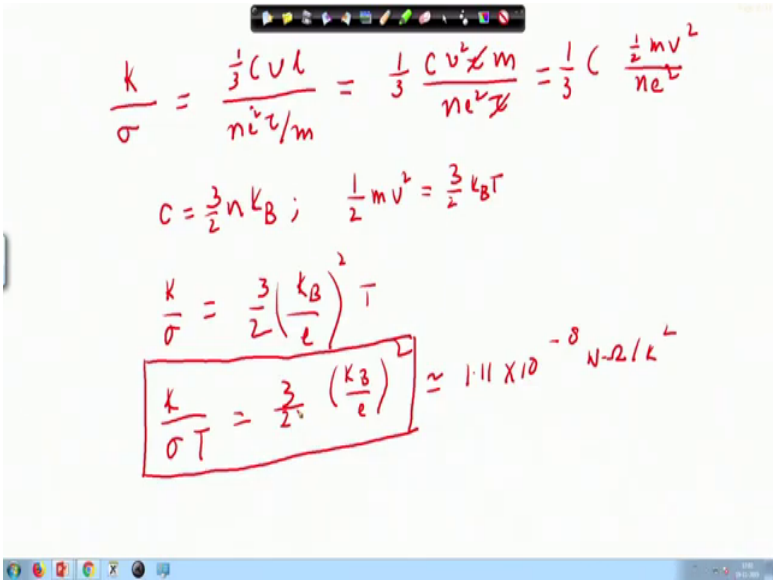

Now, the point we started was Wiedemann-Franz law. So, let us calculate K/ sigma T. K/ sigma for example, can be written from the previous relation of electrical conductivity. Therefore what we got for the thermal conductivity is one-third C v l, and divide by n e square tau by m. Actually it is very simple to write down as one-third C v. Now, l is v square v tau so, it becomes v square tau and times m divided by n e square, and that is n e square tau.

So, this gives me a cancellation of the tau, which is not easy to find. Now it is coming back to the form which is easily connected to experimental quantities; for example, let us see that we write this as one-third C times half m v square by n e square. Now, let us now look at it

classically. We know these values for example, as far as Drude was concerned classically C was 3/2 nK_B and 1/2 m $v^2 = 3/2\ K_BT$.

Therefore this ratio K/sigma is becoming 3/2 and you can put that all in here. As you see the n cancels, and then you are left with only this K_B /e square into temperature. And that means, K/sigmaT is equal to 3/2 K_B/e^2 . And both K_B and E are just universal constants. And if you calculate it, this stands out to be around 1.11 into 10 to the power minus 8 Watt ohm per Kelvin square.

So, this is the explanation of a constant value of this ratio K by sigma that Wiedemann and Franz obtained empirically through experimental results, so observations from the Drude model veifies it. This actually was considered a great success for the Drude theory of relaxation time approximation for free electron model. And it is a puzzle in the sense that these systems are highly quantum systems as we will see later on. And a classical relation completely worked out with relaxation time approximation giving us a value which is, in reality, is good. I can show you that there are systems where this is borne out.

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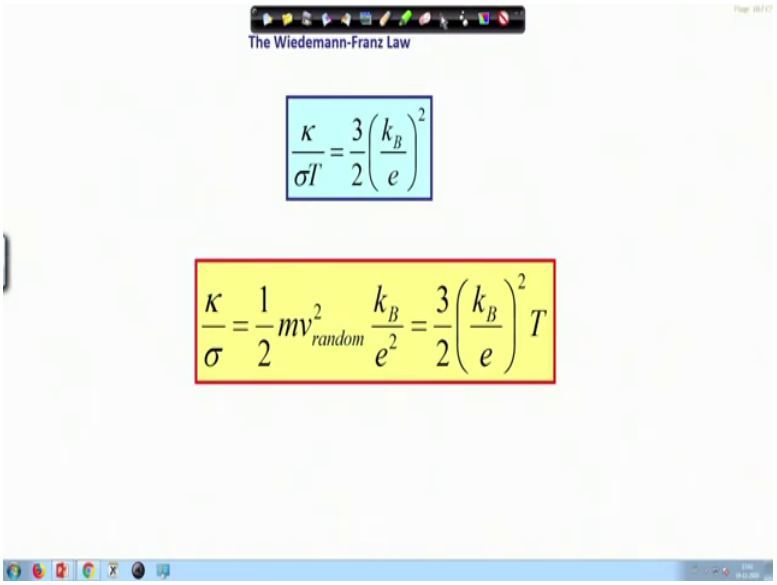

See this is the relation that I mention.

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And you can see that there is a table which shows that most of these metals, for example, silver, aluminum, gold, copper, iron, molybdenum, lead, platinum, tungsten obey this law. In these materials that quantity Lorenz number K by sigma T is 2.31, 2.23, 2.35, 2.30, 2.47, 2.61, 2.45, 2.51, 3.06 and 2.45. It is remarkable that such a classical theory for a large number of electrons which are interacting with themselves through coulomb interaction as well as interacting with the lattice even gives such a good number from a non-interacting classical theory. And it turns out to be a mystery, but one now understands why this thing happens. It looks like a very good approximation for discussing the transport of certain metals.