

We will start our endeavour in Solid State Physics with a particular type of solid - the metals. Although most of the commonly encountered solids are non-metals, the earliest studied solids from historical perspectives are the metals. Specifically, physicists tried to understand the conduction property of the metals and came up with various models.

The first major step in explaining the electrical conduction of metals was taken by Paul Drude in 1900. Although the model ~~can't~~ did explain few phenomena correctly, there were some inconsistencies and puzzles in this model. These were later tackled with the introduction of quantum mechanics in the theory of metals and solids.

Basic assumptions of Drude model

After the discovery of Sir J.J. Thomson of the electron in 1897, Paul Drude constructed his theory of conduction in metals. He applied the kinetic theory of gases to the metal, considering the

metal having a gas of electrons, although no Dr. exactly as the kinetic theory of gas.

In kinetic theory of gas, the gas molecules are considered as hard sphere which moves in random directions with a uniform velocity until they bump into each other ^(or wall) where they change their directions. The time of collision is taken to be negligible and it is assumed that no force acts between them other than the force of collision. However, the scenario is not the same in metals: For one, there will be two different ^{type of} hard spheres, one is the electron and the other is the ion. Although there were no precise idea of positive ions/charged particles, since the electric or even atoms, Drude used some pre-assumptions. He considered the metal to be composed of some positively charged heavy spheres and a sea of electrons submerged in those spheres to make the total metal neutral from a charge perspective. However, now we know to interpret these electrons as the valence electrons, and the left out positively charged spheres as the positive ions.

Drude applied the kinetic theory of gas to the "gas" of conduction electrons of mass m which is moving on a fixed background of positive ions (while the gas molecules moves without any background). There is another dissimilarity. Kinetic theory is applicable to dilute gases where the density is very low such that one can ~~not~~ consider the ~~size~~ size of a molecule to be negligible as compared to intermolecular distance. However, for electron gas, this is simply not true. According to Drude,

If, ρ_m = mass density of a metallic element

A = atomic mass of the element

Z = ~~atomic number and also no. of electrons~~ that contribute to the electron sea

$$\therefore \frac{\rho_m}{A} = \text{moles per cm}^3$$

$$\left. \begin{aligned} \rho_m &= \text{mass per cm}^3 \\ \therefore \frac{\rho_m}{A} &= \frac{\text{m/cm}^3}{A} \\ &= \text{moles/cm}^3 \end{aligned} \right\}$$

Since there are 6.022×10^{23} molecules/atoms

per mole, the number density will be,

$$n = 6.022 \times 10^{23} \times \frac{\rho_m}{A} \times Z$$

no. of atoms/cm³ contribution
no. of electrons per atom

n basically gives the no. of electrons per cm^3 .

An widely used measure of the number density is r_s , defined as the radius of the volume per conduction electron.

$$\left. \begin{array}{l} n = \text{no. of} \\ \text{conduction elec-} \\ \text{tron per unit} \\ \text{volume} \end{array} \right\} \therefore \frac{V}{N} = \frac{1}{n} = \frac{4}{3}\pi r_s^3$$

$$\therefore r_s = \left(\frac{3}{4\pi n} \right)^{1/3}$$

One can also use the Bohr radius (radius of hydrogen atom in its ground state) $a_0 = \frac{\hbar^2}{me^2} 4\pi \epsilon_0 = 0.53 \text{ \AA}$. The ratio of $\frac{r_s}{a_0}$ is between 2 and 3 in most cases and 6 for alkali materials. Anyways, this density is much higher than those of the classical gas at normal temperature and pressure. Despite this discrepancy in diluteness, and the e-e and e-ion electromagnetic interaction, Drude model boldly uses kinetic theory of gas here with a few slight modifications. Here are the basic assumptions:

1. Between collisions the interactions of a given electron both with themselves and with the positive ions ~~are~~ are neglected. Thus, in the ~~absence~~ absence of externally applied fields, the electron

would follow straight line. If there is an external field present, electrons follow Newton's law ignoring the ^{complex} fields coming from the electrons and ions. The absence of e-e interaction is called ~~independent~~ independent electron approximation and the e-ion interaction is called free electron approximation. Although independent electron approximation is good in many context, ~~is~~ free electron approximation must be abandoned for much detailed metallic behaviour.

2. The collision in Drude model, just like the kinetic theory of gases occurs in negligible time. However, here Drude described that the electrons bounce off impenetrable ion cores. But in kinetic theory, there is molecule to molecule collision. An analogous process would be e-e collision, which is omitted by Drude. The bouncing off of the ion cores is not obviously what's happening here. But, we will just assume there is a scattering mechanism that alters the velocity of electron?

without going into the details of scattering.

3. We assume the time between subsequent collision is τ , meaning that an electron experiences a collision (meaning suffers a change in its velocity) per unit time. with a probability $\frac{1}{\tau}$. We mean by this that the probability of an electron undergoing a collision in any infinitesimal time interval dt is given by $\frac{dt}{\tau}$. τ is called the relaxation time or collision time or mean free time. Also, the collision process is memoryless. It only matters what happened in the collision ~~that~~ that took place just before the collision we are talking about. It doesn't matter how it came ~~to~~ to the previous collision and those paths won't affect the current collision.

The relaxation time τ has an interesting property. An electron picked at random, on average will travel τ time before another collision, and if it would have been travelling for τ time after the last collision.

4. Electrons are assumed to achieve thermal ~~con-~~
 equilibrium conductivity only through collisions. After a collision event,
 the distribution of the velocity and direction of an electron
~~only depends~~ is determined by the local temperature
^(direction is random)
 and is independent of the velocity before collision. The
 electron is considered to be immediately at equilibrium
 with the local temperature after the collision. Thus, if a
 region is hotter where the collision is occurring, the velocity
 of the electron after collision will be faster.

Calculation of conductivity

Let's first talk about the probability distribution of the collisions. We have,

$$P_{\text{coll}} = \begin{cases} \frac{dt}{\tau} & ; \text{ if } dt \leq \tau \\ 1 & ; \text{ if } dt > \tau \end{cases}$$

Then if a particle has a momentum, say $\vec{p}(t)$ and then it undergoes a collision, the momentum gets totally randomized. The average of such random momentum will obviously be, $\langle \vec{p}(t) \rangle = \vec{0}$, if you calculate the average for a reasonably longer time. Now, if there is some external electric or magnetic field, it will

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guide the electrons in accordance with New law.

Given the momentum $\vec{P}(t)$ at time t , we want to calculate the momentum $\vec{P}(t+dt)$ at some immediate time $t+dt$. The probability that the electron undergoes a collision during this time interval dt is $\frac{dt}{\lambda}$. So, the probability that it doesn't undergo a collision or surviv a collision is $(1 - \frac{dt}{\lambda})$. If there is no collision, it will simply move under the influence of external force $\vec{f}(t)$. It will therefore acquire an additional momentum of $\vec{f}(t)dt + O(dt^2)$.

We will calculate the average momentum for all the electrons undergoing a collision or not.

Now, if we want to find the contribution to the momentum per electron $\vec{P}(t+dt)$ of those that didn't undergo a collision, it will simply be found by multiplying the ^{average} momentum per electron by the fraction $(1 - \frac{dt}{\lambda})$.

$$\vec{P}(t+dt) = (1 - \frac{dt}{\lambda}) (\vec{P}(t) + \vec{f}(t)dt + O(dt^2))$$

$$\therefore \vec{P}(t+dt) = \vec{P}(t) - \left(\frac{dt}{\lambda}\right) \vec{P}(t) + \vec{f}(t)dt + O(dt^2) \quad (i)$$

It seems we have not yet calculated the contribution

from the electrons who had undergone the collision process. Such electrons constitute a fraction of $\frac{dt}{\Delta}$ electrons. Since after the collision their momentum gets totally randomized, the only contribution comes from the acquired momentum from the force since its last collision, $\vec{f}(t)dt$. So, the correction to equation (i) is just of the order of,

$$\left(\frac{dt}{\Delta}\right) \vec{f}(t)dt = O(dt^2)$$

So, the colliding particles contribute nothing to the linear term. Hence,

$$\vec{P}(t+dt) = \vec{P}(t) - \left(\frac{dt}{\Delta}\right) \vec{P}(t) + \vec{f}(t)dt + O(dt^2)$$

$$\Rightarrow \vec{P}(t+dt) - \vec{P}(t) = - \left(\frac{dt}{\Delta}\right) \vec{P}(t) + \vec{f}(t)dt + O(dt^2)$$

where we have considered contributions from all the electrons. Now, dividing by dt and taking the limit $dt \rightarrow 0$, we get,

$$\frac{\vec{P}(t+dt) - \vec{P}(t)}{dt} = - \frac{\vec{P}(t)}{\Delta} + \vec{f}(t)$$

$$\boxed{-\frac{d\vec{P}(t)}{dt} = -\frac{\vec{P}(t)}{\Delta} + \vec{f}(t)}$$

So, the effect of collision basically introduces an effect of damping in the equation of motion for momentum

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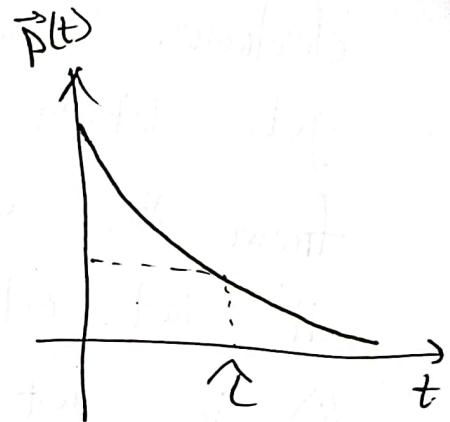
per electron.

If there is no external force, so that, $\vec{f}(t) =$

$$\frac{d\vec{P}}{dt} = -\frac{\vec{P}(t)}{\tau}$$

$$\Rightarrow \int \frac{d\vec{P}}{\vec{P}(t)} = -\frac{1}{\tau} dt$$

$\therefore \vec{P}(t) = \vec{P}_0 e^{-t/\tau}$



So, even if the electrons were given an initial momentum, due to the scattering they will become randomized and eventually become close to zero.

Now, let's consider the equation again.

$$\frac{d\vec{P}}{dt} = -\frac{\vec{P}}{\tau} + \vec{f}(t)$$

$$\tau \approx 10^{-14} \text{ s}$$

Let's now see the effect of an externally applied electric field on the metal. If we apply a constant electric field \vec{E} , then the corresponding force is,

$$\vec{f}(t) = -e\vec{E}$$

$$\therefore \frac{d\vec{P}}{dt} = -\frac{\vec{P}}{\tau} - e\vec{E}$$

We can define the current density \vec{J} , that is parallel to the flow of charge and has a magnitude

of amount of charge passing through an unit area per unit time perpendicular to the direction of the flow. If n electrons move per unit volume with velocity momentum per electron \vec{p} , then within a time dt the electrons will advance by a distance $\vec{v}dt$ in the direction of \vec{v} and so a total of $n(\vec{v}dt)A$ electrons will cross the an area of A perpendicular to the direction of flow. So, total charge moving is $-n\vec{v}dt A e$ and so current density will

be,

$$\vec{J} = \frac{-n\vec{v}dt A e}{dt \times A}$$

$$\therefore \vec{J} = -n\vec{v}e$$

In the absence of external electric field, \vec{v} averages to zero as we discussed. However, for the externally applied electric field, we just solve the equation.

$$\frac{d\vec{p}}{dt} = -\frac{\vec{p}}{\tau} - e\vec{E}$$

You can find the solution to the equation that should give you a solution of \vec{p} that reaches a steady state with time. In that steady state,

$$\frac{d\vec{p}}{dt} = \vec{J}$$

$$-\frac{\vec{P}}{\lambda} = e\vec{E}$$

$$\Rightarrow \vec{P} = -e\vec{E}\lambda$$

$$\therefore \vec{V} = -\frac{e\vec{E}\lambda}{m}$$

$$\vec{J} = -ne \left(-\frac{e\vec{E}\lambda}{m} \right)$$

$$\therefore \vec{J} = \frac{ne^2\lambda}{m} \vec{E}$$

But, then again, the relation to \vec{J} and \vec{E} is given by, $\vec{J} = \sigma \vec{E}$

$$\therefore \sigma = \frac{ne^2\lambda}{m}$$

This equation gives σ in terms of known quantities except λ . We can write λ in terms of the others as,

$$\lambda = \frac{m\sigma}{ne^2}$$

$$\therefore \lambda = \frac{m}{\rho ne^2}$$

where ρ is the resistivity.

One can calculate λ and hence mean free path $l = \lambda v_0$, with v_0 being average electronic speed.

The typical λ being $\sim 10^{-14}$ s, v_0 calculating from $\frac{1}{2}mv_0^2 = \frac{3}{2}k_B T$ (classical equipartition of energy), l comes out in the order of 1 to few μm at room temperature.

This result convinced Drude his calculations and assumptions were correct since an \AA is ~~too~~ typically the interatomic distance. However, the real V_0 is an order of magnitude higher, using the correct statistics, this gives l to be tens of \AA . It means that electrons don't simply bump off the positive ions.