SCPY 371: Solid State Physics **1^{st} Semester 2021**

Lecture 6: Theory of Metals

Kit Matan

Mahidol University

In this chapter, we will consider the properties of metals. The majority of elements in the periodic table or roughly two thirds forms metals. Therefore, metals are considered one of the most important groups of materials. Some of the basic physical properties of metals are:

1. Ability to conduct heat
2. Excellent electrical conductor
3. Ductile and malleable
4. Shiny surface

In this class, we will only study some of the key properties of metal such as thermal and electrical conductivity. We will start with the electrical conductivity

6.1 The Drude Theory of Metals

The most basic model used to described the electrical conductivity in metal was proposed by Paul Drude in 1900 and hence named "the Drude model". The model is based on the same assumption as the kinetic theory of gasses, which is successfully used to described properties of gases. In this case, we will think of electrons as non-interacting molecules of gas. Similar to the ideal gas, we will assume that electrons travels in a straight line until it collides with impurity in the lattice or nuclei. Furthermore, the collision time is much shorter than the time between the successive collisions and there is no other interaction acted on the electrons besides the collision. We can see right away that these assumptions is the same as in the case of the diluted ideal gas. One different is that we ignore the electron-electron collision whereas in the ideal gas the collision occurs among the molecules of the gas. The question is why we can ignore the electron-electron interaction.

From experiments, we found that electrons mostly collide with impurities or defects but rarely with nuclei or other electrons due to the following reasons:

1. Electrons rarely collide with nuclei because of the periodic arrangement of atoms in the lattice. Quantum mechanically, electrons can be described by a wave function. We can think of this wave as a standing wave inside the lattice. The electrons are mostly likely found around the nucleus. However, they will not collide with the nuclei.
2. Electron will not collide with other electrons because of the Pauli exclusion principle, which states that since electrons are fermion, any two electrons cannot be in the same quantum state. Being in different states reduces the chance of the collision between electrons.

Therefore, the most important effect that influences the electrically transport in metals is the collision of electrons and impurities. We can then expect that for a perfect crystal without defects the mean free path of electrons, which indicates the average distance electrons travel without a collision, can be very large. In some case, it can be as large as 10^8 of the interatomic distance or about 1 cm.

When Drude came up with the model in 1900, electrons were discovered by J. J. Thomson a few years earlier in 1897. However, the structure of atoms was then unknown. The Drude model is based on the assumption that atoms are consisted of positive and negative charge and the electrical conductivity is due to the motion of electrons while positive charge of protons are fixed in the middle of the nucleus. Furthermore, there are two types of electrons. The first type is the **core electrons** that bind to the positively-charged nucleus and the second type is the **valence electrons** that locate at the most outer part of atoms. When forming a matter, each atom shares the valence electrons that can move around the lattice and are responsible for the electrically conductivity. We call the shared valence electron the **conduction electrons**. They also form metallic bonding between atoms in metals.

After having the picture of atoms in the crystal, Drude applied the kinetic theory of gas to explain the conductivity of the metal. As mentioned before, the kinetic theory of gas is applicable in the case where the gas is dilute. In metals the electron density is normally more than 1,000 time bigger than the gas density. Therefore, one would expect that the kinetic theory of gas should not be applicable for electrons in the metals. However, due to the Pauli exclusion principle and the wave property of electrons, the mean free path of electron is large enough that the kinetic theory of gas can be applied.

Assumptions of the Drude Model

1. Similar to the ideal gas, we assume that in the absence of the external electric field electrons travel in a straight line until they collide with impurities or defects and nuclei and there is no other force acting on the electrons.

   On the other hand, in the presence of the external electric field electrons will move according to the Newton's laws and we can ignore the forces between electron-electron and electron-nucleus. The assumption that there is no electron-electron interaction is called **independent electron approximation** whereas the assumption that there is no electron-nucleus interaction is called **free-electron approximation**.

   We found that the independent electron approximation works very well in most cases, but the free electron approximation fails to capture many fundamental properties of the metal such as band structure, which is due to the periodic arrangement of the nuclei. Therefore, we sometimes call the Drude model the **free electron model**.

2. Electrons will not collide with other electrons but will collide with impurities or nuclei. Furthermore, the electric conductivity will not depend on the detailed process of the collision.

3. We will suppose that the average time between two successive collisions is equal to τ, which we call the **mean free time**. That is, on average each electron moves in a straight line for the duration equal to τ. We will further assume that τ does not depend on the position and velocity of electrons.

4. Electrons are in thermal equilibrium with the surrounding or the lattice since electrons exchange energy with the lattice through the collisions with the nuclei. Therefore, the velocity of electrons after collisions only depend on the local temperature at the region where the collisions occur and is independent of the velocity before the collisions.

We will use these assumptions to describe some key properties of metals. The first properties we will consider is the DC electrical conductivity.

DC electrical conductivity of metals We will derive Ohm's law $V = IR$ where R is the resistance using the Drude model. We will start with the definition of resistivity ρ.

$$\vec{E} = \rho \vec{j}$$

where $\vec{E}$ is an electric field and $\vec{j}$ is a current density or an amount of charge per unit area per unit time. For a uniform current, we have

$$\begin{aligned} j &= \frac{I}{A} \\ V &= El, \end{aligned} \tag{6.1}$$

where A and l is the cross-section area and the length through which the current travel. Combining the above two equations, we obtain the Ohm's law:

$$V = \frac{\rho l}{A} I.$$

$$\Rightarrow \quad R = \frac{\rho l}{A}$$

We will now calculate ρ assuming that the motion of electrons can be described according to the Drude model. Suppose that the density of moving electrons n and all move with the velocity $\vec{v}$. We can then calculate $\vec{j}$:

$$\vec{j} = \frac{-en \cdot A \cdot dt \cdot v}{A \cdot dt} = -nev,$$

where we can think of v as the average velocity of electrons. If the external electric field is absent ($E = 0$), v is equal to zero, that is, the collision gives a random distribution of the velocity. However if $E \neq 0$, v of electrons will be non-zero with the direction opposite to the direction of E.

Suppose that v_0 is the velocity of an electron right after the collision. v_0 is then randomly distribution and its average value is zero. Now if there is an external electric field, the electric field will increase the velocity of the electron according to the Newton's law. The increase of the average velocity is equal to

$$v_{avg} = -\frac{eE\tau}{m},$$

where τ is the mean free time as mentioned before. This implies that

$$j = \left(\frac{ne^2\tau}{m}\right) E \equiv \sigma E.$$

Therefore, the conductivity and the resistivity are equal to

$$\Rightarrow \quad \sigma = \frac{1}{\rho} = \frac{ne^2\tau}{m}.$$

Normally, we can measure the resistivity or conductivity from an experiment, from which we can extract the value of the mean free time and the mean free path. For example, if $\rho \approx 10^{-6}$ Ω·m at the room temperature, $\tau \approx 10^{-14} - 10^{-15}$ sec. And the mean free path can be calculated from $l = v\tau$, where v is the average velocity. We can estimate v from the temperature of the electron "gas" using the equipartition of energy.

$$\frac{1}{2}mv^2 = \frac{3}{2}k_B T.$$

At the room temperature $T = 300$ K, $v \approx 10^7$ cm/sec, which mean $l \approx 1 - 10$ Å. We can see that the value of l is roughly a typical distance between atoms in the lattice. Therefore, we can expect that at room temperature electrons will collide with almost all nuclei in their path, which is not totally wrong. However, an experiment also indicates that the mean free path at low temperature can become very long, in an order of 1 cm. How can we explain this temperature dependence of l? It turns out that the current model is not sufficient since τ is temperature independent and v decreases as temperature decreases, which is opposite to what we expect. This failure of the current model is one indication that at very low temperature electrons rarely collide with nuclei and the resistivity is dominated by the electron collision with the impurities or defects.

In order to improve on the model, we will now let the force equation be time dependent, that is,

$$\frac{d\vec{p}}{dt} = \vec{f}(t),$$

and

$$\vec{j} = \frac{-ne\vec{p}(t)}{m}.$$

We need to calculate the momentum at time $t+dt$ or $\vec{p}(t+dt)$ given that there is no collision between time t and $t+dt$. However, we know that some electrons will collide with nuclei during that time and the probability of collision to occur is $\frac{dt}{\tau}$, where τ is the mean free time, that is, on average there is one collision during time τ. Therefore, the probability of having no collision is $1-\frac{dt}{\tau}$ and we can write $\vec{p}(t+dt)$ as

$$\begin{aligned} \vec{p}(t+dt) &= \left(1-\frac{dt}{\tau}\right)\left[\vec{p}(t)+\vec{f}(t)dt\right] \\ &= \vec{p}(t)-\frac{\vec{p}(t)dt}{\tau}+\vec{f}(t)dt, \\ \Rightarrow \quad \frac{\vec{p}(t+dt)-\vec{p}(t)}{dt} &= \vec{f}(t)-\frac{\vec{p}(t)}{\tau}. \qquad (6.2) \end{aligned}$$

where the dt^2 term is ignored. Now if we take the limit where $dt \to 0$, we obtain

$$\frac{d\vec{p}(t)}{dt} = \vec{f}(t)-\frac{\vec{p}(t)}{\tau},$$

or

$$\left(\frac{d}{dt}+\frac{1}{\tau}\right)\vec{p}(dt) = \vec{f}(t),$$

In the section, we will apply this formula to study the Hall effect and the transport properties in magnetic field.

6.2 Hall effect and magnetoresistance

In the presence of magnetic field, the moving change will be deflected by the field. The Hall effect is the phenomenon which charge particles gather on one side of a planar conductor creating the electric potential difference and electric field across two sides of the conductor. The direction of this electric field is perpendicular to the direction of the current or of the moving electrons.

In the Hall effect, there are two quantities which we can measure. The first quantity is the ratio between the applied electric field E_x and the density current j_x along the same direction. This ratio is called **magnetoresistance**:

$$\rho(H) = \frac{E_x}{j_x},$$

which is field-dependent. The second quantity is the ratio between the electric field across the conductor E_y in the perpendicular direction with the current and the product of the current density j_x and the magnetic field H. This quantity is called **Hall coefficient**.

$$R_H = \frac{E_y}{j_x H}.$$

Note that if E_y can be either positive or negative depending on the direction of the electric field. Therefore, R_H can also be either positive or negative and the sign of R_H points to the type of the charge carrier. If $R_H > 0$, then the charge carrier is positively charged. On the other hand, if $R_H < 0$, then the charge carrier is negatively charged.

We will now calculated the magnetoresistance and the Hall coefficient. Consider a slap of conductor with the perpendicular magnetic field. Since there are both magnetic and electric fields, the Lorentz force can be written as

$$f = -e\left(\vec{E} + \vec{v} \times \vec{H}\right)$$

Using the equation from the Drude model, we obtain

$$\Rightarrow \quad \frac{d\vec{p}}{dt} = -e\left(\vec{E} + \frac{\vec{p}}{m} \times \vec{H}\right) - \frac{\vec{p}}{\tau}$$

We will only consider the steady state where $\vec{p}$ does not change with time, that is, $\frac{d\vec{p}}{dt} = 0$. We can write two equations for p_x and p_y:

$$\begin{aligned} p_x: \quad 0 &= -eE_x - \frac{eH}{m} p_y - \frac{p_x}{\tau} \\ p_y: \quad 0 &= -eE_y + \frac{eH}{m} p_x - \frac{p_y}{\tau} \end{aligned}$$

Let $\omega_c = \frac{eH}{m}$, which is the cyclotron frequency. We can rewrite the above equations as

$$\begin{aligned} p_x: \qquad eE_x &= -\omega_c p_y - \frac{p_x}{\tau} \\ \frac{ne^2\tau}{m} E_x &= -\frac{ne\tau}{m} \omega_c p_y - \frac{ne\tau}{m} \cdot \frac{p_x}{\tau} \\ \sigma_0 E_x &= \omega_c \tau j_y + j_x. \end{aligned}$$

In the second step, we multiple both sides of the equation by $\dfrac{ne\tau}{m}$, and in the third step, we use the expressions for the conductivity $\sigma_0 = \dfrac{ne^2\tau}{m}$ and for the current $j_i = -\dfrac{nep_i}{m}$ where $i = x, y$.

Similarly for p_y, we have

$$\sigma_0 E_y = -\omega_c \tau j_x + j_y.$$

In the steady state, j_y is zero. The Hal coefficient can be calculated by letting $j_y = 0$, that is, there is no current along $\hat{y}$.

$$\begin{aligned} \Rightarrow \quad E_y &= -\left(\frac{\omega_c \tau}{\sigma_0}\right) j_x = -\left(\frac{H}{ne}\right) j_x \\ \Rightarrow \quad R_H &= -\frac{1}{ne}, \end{aligned}$$

where n is the density of charge carrier. The negative sign indicates that the charge carrier is a negatively-charged electron. Along the $x-$axis, we can calculate the magnetoresistance

$$\rho_0 = \frac{E_x}{j_x},$$

or the magnetoconductivity

$$\sigma_0 = \frac{j_x}{E_x}.$$

AC electrical conductivity of a metal In this case, the applied electric field is oscillating with time and can be described by the following equation

$$\vec{E}(t) = \mathrm{Re}\left[\vec{E}(\omega)e^{-i\omega t}\right].$$

In the steady state, the momentum of electrons can be described by

$$\vec{p}(t) = \mathrm{Re}\left[\vec{p}(\omega)e^{-i\omega t}\right].$$

From the equation of motion of the Drude model, we have

$$\begin{aligned} \frac{d\vec{p}}{dt} &= -\frac{\vec{p}}{\tau} - e\vec{E} \\ -i\omega\vec{p}(\omega) &= -\frac{\vec{p}(\omega)}{\tau} - e\vec{E}(\omega) \\ \Rightarrow \quad \vec{p}(\omega) &= \frac{-e\vec{E}(\omega)}{\frac{1}{\tau} - i\omega} \end{aligned} \tag{6.3}$$

Knowing $\vec{p}$, we can now calculate $\vec{j}$. Assume that $\vec{j}$ is oscillating with the same frequency as the electric field and momentum.

$$\begin{aligned} \vec{j}(t) &= \mathrm{Re}\left[\vec{j}(\omega)e^{-i\omega t}\right] \\ \Rightarrow \quad \vec{j}(\omega) &= -\frac{ne\vec{p}(\omega)}{m} = \frac{(ne^2/m)\vec{E}(\omega)}{\frac{1}{\tau} - i\omega} \\ \Rightarrow \quad \sigma(\omega) &= \frac{\sigma_0}{1 - i\omega\tau}, \end{aligned}$$

where $\sigma_0 = \frac{ne^2\tau}{m}$. In addition, there is also the oscillating magnetic field but its affect on the motion of electron is much smaller due to the v/c factor. Therefore, we will ignore the effect of the AC magnetic field.

6.3 Heat capacity of the free electron model

We will proceed to calculate the electronic heat capacity the same way as we have done to calculate the phonon heat capacity, that is, we will first calculate the total energy and then take the derivative with respect to temperature. However, unlike the phonon, an electron is a fermion and we need to use the **Fermi-Dirac distribution function** in stead of the Planck distribution function as in the case of phonons.

$$f(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/k_B T} + 1},$$

where μ is the chemical potential and is a function of temperature. At the absolute-zero temperature, $\mu = \varepsilon_F$ or the Fermi energy.

Density of states We can calculate the density of states for free electrons using the similar approach for the phonon case. If N is the total number of electrons, then

$$N = 2 \cdot \frac{4\pi k_F^3/3}{(2\pi/L)^3} = \frac{V}{3\pi^2}k_F^3,$$

where the factor 2 indicates two degenerate states of electrons with spin-up and spin-down. From this equation, we can calculate the Fermi wavevector k_F, the Fermi energy ε_F, and the Fermi velocity v_F.

$$\begin{aligned} k_F &= \left(\frac{3\pi^2 N}{V}\right)^{1/3} \\ e_F &= \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3} \\ v_F &= \frac{\hbar k_F}{m} = \frac{\hbar}{m}\left(\frac{3\pi^2 N}{V}\right)^{1/3}. \end{aligned}$$

We can rewrite N in terms of energy as

$$N = \frac{V}{3\pi^2}\left(\frac{2m\varepsilon}{\hbar^2}\right)^{3/2}.$$

Therefore, the density of states is equal to

$$D(\varepsilon) \equiv \frac{dN}{d\varepsilon} = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \cdot \varepsilon^{1/2},$$

or

$$D(\varepsilon) = \frac{3N}{2\varepsilon}.$$

We will proceed to calculated the energy of electrons at a finite temperature, which is equal to

$$U = \int_0^\infty d\varepsilon\ \varepsilon D(\varepsilon)\ f(\varepsilon) - \int_0^{\varepsilon_F} d\varepsilon\ \varepsilon D(\varepsilon).$$

We can rewrite this equation using the following identity

$$\begin{aligned} N = \int_0^\infty d\varepsilon\ D(\varepsilon)\ f(\varepsilon) &= \int_0^{\varepsilon_F} d\varepsilon\ D(\varepsilon) \\ \Rightarrow \quad \left(\int_0^{\varepsilon_F} + \int_{\varepsilon_F}^\infty\right) \varepsilon_F D(\varepsilon)(\varepsilon) &= \int_0^{\varepsilon_F} d\varepsilon\ \varepsilon_F D(\varepsilon) \end{aligned}$$

where from the first to second equation we multiply ε_F on both sides. We can now rewrite the equation for U as

$$U = \int_{\varepsilon_F}^\infty d\varepsilon\ (\varepsilon - \varepsilon_F) D(\varepsilon)\ f(\varepsilon) + \int_0^{\varepsilon_F} d\varepsilon\ (\varepsilon_F - \varepsilon)[1 - f(\varepsilon)] D(\varepsilon).$$

As we can see that $f(\varepsilon)$ is the only term that is temperature dependent. Therefore, we can take derivative of U with respect to T and obtain

$$C_e = \frac{dU}{dT} = \int_0^\infty d\varepsilon (\varepsilon - \varepsilon_F) \frac{df}{dT} D(\varepsilon).$$

Since $\frac{df}{dT}$ peaks sharply at ε_F, we can approximate $D(\varepsilon)$ with $D(\varepsilon_F)$ and pull it out from the integral, that is,

$$C_e \approx D(\varepsilon_F) \int_0^\infty d\varepsilon (\varepsilon - \varepsilon_F) \frac{df}{dT}.$$

If we will let $\tau = k_B T$ (τ **IS NOT** the mean free time), then $\frac{df}{dT}$ is

$$\frac{df}{dT} = \frac{\varepsilon - \varepsilon_F}{\tau^2} \cdot \frac{e^{(\varepsilon - \varepsilon_F)/\tau}}{\left[e^{(\varepsilon - \varepsilon_F)/\tau} + 1\right]^2}$$

If we let $x \equiv \frac{\varepsilon-\varepsilon_F}{\tau}$, we obtain

$$C_e = k_B^2 T D(\varepsilon_F) \int_{-\varepsilon_F/\tau}^{\infty} dx\, x^2 \frac{e^x}{(e^x+1)^2}.$$

Since ε_F is much larger than τ, the lower limit of the integral is approximately equal to $-\infty$. The integral then becomes

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

and the heat capacity becomes

$$C_e = \frac{1}{3}\pi^2 D(\varepsilon_F) k_B^2 T = \frac{1}{2}\pi^2 N k_B \cdot \frac{T}{T_F},$$

where $D(\varepsilon_F) = \frac{3N}{2\varepsilon_F} = \frac{3N}{2k_B T_F}$ and T_F is the Fermi temperature. Therefore, the electronic heat capacity is linearly proportional to T and becomes dominated at low temperature where the phonon contribution, which is proportional to T^3, is negligible.

References

[1] Kittel, C.: Introduction to Solid State Physics 7th Edition (Chapter 3), John Wiley & Sons, Inc. (1996).

[2] Ashcroft, N. W. and Mermin, N. D.: Solid State Physics (Chapter 20), Thomson Learning, Inc. (1976).