

Lecture1- Drude Model

Recap of kinetic theory of gases:

Treats gas molecules as neutral solid spheres; moves in straight line until collision; no forces act on them during the travel time; average time it travels before suffering collision is called Relaxation time/mean free time; collisions completely randomize the velocity – all previous memory erased; particles emerge after collision with a speed appropriate to the temperature of the region where collision happened.

Application of kinetic theory to ‘classical electron gas’:

Ion cores of atoms immobile (core electrons remain tightly bound to nucleus); valence electrons are loosely bound and in metal can wander around the entire metal – form the conduction electrons (referred from now on simply as electrons.)

Note: electrons (unlike gas molecules) are charged and are moving in the background of other charged entities; electron densities also large ($\sim 10^{28}/\text{cm}^3$); still Drude applied kinetic theory (valid for neutral dilute classical gas) to metals.

Basic assumption of Drude model:

1. Between collisions electrons move in straight line (in the absence of a any electromagnetic field) - effect of electron-electron interaction is ignored (independent electron approximation – reasonably valid) – effect of electron-ion in ignored (independent-electron approximation; completely invalid).
2. Mean free time between collisions is τ (probability of collision per unit time is $1/\tau$; probability of having a collision in infinitesimal time interval dt is dt/τ) – τ is independent of electron’s position or velocity (a good assumption).
3. Electrons achieve thermal equilibrium by collisions with lattice – they emerge after collision at a random direction with speed appropriate to the temperature of the region where collision happened – the hotter the region; the higher the speed of the emerging electrons.

What the model tries to tackle

- distinction between metal and insulator
- electrical transport in metals
- thermal conductivity of metals

It is a pre-quantum mechanical semi-classical model – still roughly applicable for simple alkaline metals.

Applications of Drude model:

DC electrical conductivity of metal:

$$V=IR; E= \rho J.$$

Number of electrons with velocity $\mathbf{v}$ crossing area A in time dt is $n\mathbf{v}Adt$; each has charge $-e$; current density is then $\mathbf{j} = -ne\mathbf{v}$.

Electrons are moving randomly; so need to take average velocity for $\mathbf{v}$. In equilibrium average velocity vanishes; no net electrical current.

Apply electric field – an electron will have a velocity $\mathbf{v} = \mathbf{v}_0 - e\mathbf{E}t/m$ (t is time since last collision; $\mathbf{v}_0$ is the velocity it came out with after last collision and hence random).

So,

$$\langle \mathbf{v} \rangle = \langle \mathbf{v}_0 \rangle - \frac{e\mathbf{E}\langle t \rangle}{m} = -\frac{e\mathbf{E}\tau}{m}$$

$$\mathbf{j} = -ne\mathbf{v} = \frac{ne^2\tau}{m}\mathbf{E}$$

$$\sigma = \frac{ne^2\tau}{m} \quad (1)$$

This is the dc conductivity in Drude model. How reasonable is the formula? Estimate mean free path in equilibrium:

τ (from eqn. 1) is of order 10^{-14} to 10^{-15} s; average velocity $v \sim 10^5$ m/s at room temp (using $1/2mv^2 = 3/2 kT$); giving $l = v\tau \sim 1-10$ Angstrom $\sim$ interatomic spacing (Drude happy!!)

In reality l can be very large $\sim$ cm even at low temperatures; also $v \sim 10^6$ m/s.

It is difficult to estimate the exact cause of collision, relaxation time etc. - look for other phenomenon independent of these.

General equations of motion for the electrons under a force $\mathbf{f}(t)$:

Momentum at any time t is $\mathbf{p}(t)$. Two things can happen in the next time interval dt :

- They can undergo collision with probability dt/τ ; lose all momentum and emerge with a random momentum $+ \mathbf{f}(t)dt$. Their contribution to total momentum of system is $dt/\tau \cdot \mathbf{f}(t)dt$
- They do not undergo collision with probability $(1-dt/\tau)$; after time dt their momentum is $\mathbf{p}(t) + \mathbf{f}(t)dt$. Their contribution to total momentum of system is $(1-dt/\tau)(\mathbf{p}(t) + \mathbf{f}(t)dt)$

Thus the net momentum at time $t+dt$ is:

$$\mathbf{p}(t+dt) = (1-dt/\tau)(\mathbf{p}(t) + \mathbf{f}(t)dt) + \text{random component} + \mathbf{f}(t)(dt)^2/\tau$$

Neglecting higher order terms in dt ;

$$\mathbf{p}(t + dt) = \mathbf{p}(t) - \frac{dt}{\tau} \mathbf{p}(t) + \mathbf{f}(t)dt$$

$$\frac{d\mathbf{p}}{dt} = -\frac{\mathbf{p}(t)}{\tau} + \mathbf{f}(t) \quad (2)$$

Collision acts as friction; dampens the motion of the electrons.

Hall Effect and magnetoresistance:

Current j_x , magnetic field B_z Lorentz force $-e\mathbf{v} \times \mathbf{B}$; force same on +ve and -ve charges; hence they move on the same side; Hall voltage has different sign for the two types of carriers. Can measure two quantities:

- magnetoresistance: $\rho(H) = \frac{E_x}{j_x}$
- transverse (Hall) field E_y or Hall coefficient $R_H = \frac{E_y}{j_x B_z}$

Hall co-efficient can determine the sign of the charge carriers – sometimes it was found to be +ve; not explained by Drude theory.

How to calculate Hall coefficient and magnetoresistance?

Equations of motion with B_z :

$$\frac{d\mathbf{p}}{dt} + \frac{\mathbf{p}(t)}{\tau} = -e(\mathbf{E} + \frac{\mathbf{p} \times \mathbf{B}}{m})$$

In steady state current is time-independent and hence:

$$\frac{\mathbf{p}(t)}{\tau} = -e(\mathbf{E} + \frac{\mathbf{p} \times \mathbf{B}}{m})$$

$$\frac{p_x}{\tau} = -eE_x - \frac{ep_y B}{m}$$

$$\frac{p_y}{\tau} = -ey_x + \frac{ep_x B}{m}$$

$$\sigma_o E_x = j_x + \omega_c \tau j_y$$

$$\sigma_o E_y = -\omega_c \tau j_x + j_y$$

$$\mathbf{E} = \frac{1}{\sigma_o} \begin{pmatrix} 1 & \omega_c \tau \\ -\omega_c \tau & 1 \end{pmatrix} \mathbf{j}$$

For Hall samples; $j_y = 0$; so

$$R_H = \frac{E_y}{j_x B_z} = -\frac{1}{ne}$$

In reality, the carrier densities are not always given correctly by the Drude formula; +ve sign was also not understood till Quantum mechanical theories came in.

Magnetoresistance is zero according to Drude since $j_x(H) = \sigma_0 E_x = j_x(H)$; not correct in real systems.

AC electrical conductivity of metal:

Time dependent electrical field $\mathbf{E}(t) = \mathbf{E}_0 e^{-i\omega t}$; eqn of motion is

$$\frac{d\mathbf{p}}{dt} = -\frac{\mathbf{p}(t)}{\tau} - e\mathbf{E}$$

Solution - $\mathbf{p}(t) = \mathbf{p}_0 e^{-i\omega t}$;

$$-i\omega \mathbf{p}_0 = -\frac{\mathbf{p}_0}{\tau} - e\mathbf{E}_0$$

$$\mathbf{j} = -\frac{ne\mathbf{p}}{m} = \frac{\sigma_0}{1 - i\omega\tau} \mathbf{E} = \sigma(\omega) \mathbf{E}$$

The AC conductivity $\sigma(\omega) = \frac{\sigma_0}{1 - i\omega\tau}$

Application to propagation of electromagnetic waves in metal:

Maxwell's equations

$$\begin{aligned} \nabla \cdot \mathbf{E} &= 0; \nabla \cdot \mathbf{B} = 0; \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}; \nabla \times \mathbf{B} = \mu_0 \mathbf{J} + \mu_0 \epsilon_0 \frac{\partial \mathbf{E}}{\partial t} \\ \nabla \times (\nabla \times \mathbf{E}) &= -\frac{\partial}{\partial t} (\nabla \times \mathbf{B}) = -\frac{\partial}{\partial t} \left(\mu_0 \mathbf{J} + \mu_0 \epsilon_0 \frac{\partial \mathbf{E}}{\partial t} \right) = -\frac{\partial}{\partial t} \left(\mu_0 \sigma \mathbf{E} + \mu_0 \epsilon_0 \frac{\partial \mathbf{E}}{\partial t} \right) \end{aligned}$$

Look for solutions of the form $\mathbf{E}(t) = \mathbf{E}(x) e^{-i\omega t}$

$$\nabla^2 \mathbf{E} + \frac{\omega^2}{c^2} \left(1 + \frac{i\sigma}{\omega \epsilon_0} \right) \mathbf{E} = 0$$

Can write it as the wave equation:

$$\nabla^2 \mathbf{E} + \frac{\omega^2}{c^2} \epsilon(\omega) \mathbf{E} = 0$$

where $\epsilon(\omega) = \left(1 + \frac{i\sigma}{\omega \epsilon_0} \right)$ is the complex dielectric constant of the metal.

Now assume working in a regime where $\omega\tau \gg 1$;

Then to a first approximation;

$$\epsilon(\omega) = 1 + \frac{i\sigma}{\omega\epsilon_0} = 1 + \frac{i}{\omega\epsilon_0} \left(\frac{\sigma_0}{1 - i\omega\tau} \right) \approx 1 - \frac{\omega_p^2}{\omega^2}$$

where

$$\omega_p = \sqrt{\frac{ne^2}{m\epsilon_0}}$$

is called the ‘plasma frequency’.

Solve the wave equation for spatial dependence of $E(x) = E_0 \exp(i\kappa x)$

$$\nabla^2 \mathbf{E} + \frac{\omega^2}{c^2} \epsilon(\omega) \mathbf{E} = 0$$

$$\kappa^2 = \frac{\omega^2}{c^2} \epsilon(\omega)$$

Consider two regimes:

1. $\omega < \omega_p$: $\epsilon(\omega)$ is real and negative; κ is imaginary and the wave decays exponentially with distance inside the metal.
2. $\omega > \omega_p$: $\epsilon(\omega)$ is real and positive; κ is real and the wave propagates through the metal without decay – the metal is transparent to the electromagnetic wave!

So for frequencies above plasma frequency metals should become transparent to electromagnetic radiation. Estimate of ω_p for metal is about 10^{15} Hz; alkali metals become transparent above this frequency; others do not because of other contributions to dielectric constant that the Drude theory neglects.

Plasma Oscillations

Plasmons can be described in the classical picture as an oscillation of free electron density with respect to the fixed positive ions in a metal. To visualize a plasma oscillation, imagine a cube of metal placed in an external electric field pointing to the right. Electrons will move to the left side (uncovering positive ions on the right side) until they cancel the field inside the metal. If the electric field is removed, the electrons move to the right, repelled by each other and attracted to the positive ions left bare on the right side. They oscillate back and forth at the plasma frequency until the energy is lost in some kind of resistance or damping. Plasmons are a quantization of this kind of oscillation.

What is the frequency of oscillation?

Charge oscillation means a charge density wave of the type $\rho(t) = \rho_0 e^{-i\omega t}$ should propagate through the solid.

From continuity equation: $\nabla \cdot \mathbf{J} = -\frac{\partial \rho}{\partial t}$ implying $\nabla \cdot \mathbf{J}(\omega) = i\omega \rho(\omega)$

From Gauss’s law: $\nabla \cdot \mathbf{E}(\omega) = \rho(\omega)/\epsilon_0$

Combining these two, $i\omega\rho(\omega) = \sigma\rho(\omega)/\epsilon_0$ or $\left(1 + \frac{i\sigma}{\omega\epsilon_0}\right)\rho(\omega) = 0$

$\rho(\omega)$ can be non-zero (or in other words a charge oscillation can be sustained in a metal) only for a specific value of frequency given by $\omega = \omega_p$ defined by the condition $\left(1 + \frac{i\sigma}{\omega_p\epsilon_0}\right) = 0$. At this frequency the dielectric constant of the metal $\epsilon(\omega) = \left(1 + \frac{i\sigma}{\omega\epsilon_0}\right) = 0$

Physical picture – Assume the entire electron gas moves by amount x to the left. The equation of motion is

$$Nm\ddot{x} = -NeE = -\frac{Ne\sigma}{\epsilon_0} = -\frac{Ne}{\epsilon_0}nex$$

or

$$\ddot{x} = -\frac{ne^2}{m\epsilon_0}x$$

This is simple harmonic motion with frequency $\omega_p = \sqrt{\frac{ne^2}{m\epsilon_0}}$, the plasma frequency.

These oscillations are detected through the enhanced absorption at these frequencies of electromagnetic radiation passing through thin metal foils/particles. There are also surface plasmons. The plasma frequency depends critically on the shape and size of the particles (not captured by this simple theory) – Au nanoparticles display different colours depending on their size.

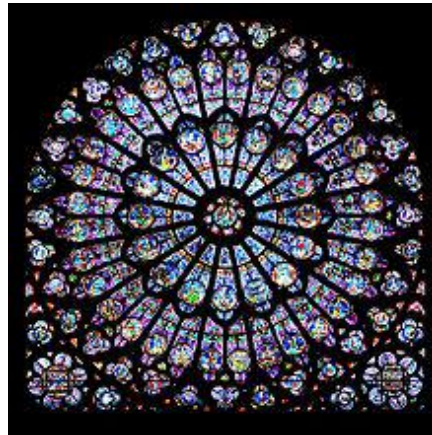


Figure 1: Gothic stained glass rose window of Notre-Dame de Paris. The colors were achieved by colloids of gold nano-particles. (Source –wikipedia)

Thermal conductivity of metals

By Fourier's law, thermal conductivity is given by:

$$\mathbf{j}_q = -\kappa\nabla T$$

We want to estimate κ from the Drude model.

Consider a long rod – temperature at left end is T_1 while that at the right end is T_2 with $T_2 > T_1$ –implying that dT/dx is a positive number.

The energy of an electron depends on the temperature of the place where it had its last collision – the higher the temperature the more the energy it comes with (follows from relaxation time approximation).

The energy per electron at equilibrium at x is $E(T[x])$. These electrons had their last collisions within $x \pm v\tau$. On an average the e^- arriving from the left side will have energy $E(T[x-v\tau])$ while those arriving from the right will have an average energy $E(T[x+v\tau])$. So, the energy arriving at x per unit time per unit area is:

$$\begin{aligned} j_q &= \frac{1}{2}n[vE(T[x-v\tau]) + (-v)E(T[x+v\tau])] \\ &= -nv^2\tau \frac{[E(T[x+v\tau]) - E(T[x-v\tau])]}{(x+v\tau) - (x-v\tau)} \\ &= -nv^2\tau \frac{dE}{dT} \left(\frac{dT}{dx} \right) \end{aligned}$$

Comparing, $\kappa = nv^2\tau \frac{dE}{dT} = v^2\tau C_v$ where C_v is the heat capacity per unit volume. In 3D the result becomes $\kappa = \frac{1}{3}v^2\tau C_v = \frac{1}{3}vlC_v$ where $l = v\tau$ is the mean free path.

Flaws in the argument: v should depend on the temperature of the place where the last collision took place – a fact we have ignored (considerations of this gives second order corrections to the value of thermal conductivity – check for yourself).

Drude used $C_v = 3nk_B$ giving

$$\frac{\kappa}{\sigma} = \frac{3}{2} \left(\frac{k_B}{e} \right)^2 T = 1.11 \times 10^{-8} \text{ watt-ohm}/K^2$$

This is the Lorentz number. The above relation is called *Wiedemann-Franz law* and is obeyed quite well by Alkali metals over a narrow temperature range.

Drude was lucky – he *overestimated* the electronic specific heat by 100 times (electronic C_v at room temperature is nowhere close to $3nk_B$) and *underestimated* the average electronic speed by a factor of 10.

Thermoelectric Effect:

Drude model assumes that the mean electronic velocity at a point vanishes – this cannot be rigorously justified. Electrons coming from the higher temperature side will have higher energy and hence a higher speed – net motion of electrons from higher temperature side to lower temperature side. Thermal properties measured in open circuit conditions – no net current can flow. This implies that electrons will accumulate at the low temperature end of the rod and produce an electric field that would inhibit further accumulation of electrons (similar to Hall Effect) – this is the Seebeck Effect (temperature gradient in a metallic rod is accompanied by a voltage gradient).

$$E = Q\nabla T$$

where Q is the thermopower

Mean electronic velocity at a point x due to the temperature gradient is in a 1-D rod is:

$$v_Q = \frac{1}{2} [v(x - v\tau) - v(x + v\tau)] = -v\tau \frac{dv}{dx} = -\frac{1}{2}\tau \frac{dv^2}{dx}$$

In a 3-D system,

$$v_Q = -\frac{1}{6}\tau \frac{dv^2}{dx} = -\frac{1}{6}\tau \frac{dv^2}{dT} \nabla T$$

Mean velocity due to the induced electric field $\mathbf{E}$ is:

$$v_E = -\frac{e\tau}{m} \mathbf{E}$$

At equilibrium net electronic velocity should vanish (current is zero): $v_Q + v_E = 0$

$$-\frac{1}{6}\tau \frac{dv^2}{dT} \nabla T + -\frac{e\tau}{m} \mathbf{E} = 0$$

$$E = -\frac{1}{3ne} c_v \nabla T$$

or $Q = -\frac{1}{3ne} c_v$.

Using $c_v = \frac{3}{2}nk_B$ Drude estimated $Q = -0.43 \times 10^{-4}V/K$.

Observed values of Q are $\sim \mu V/K$ – about 100 times too small. This is due to over-estimation of c_v by about a factor of 100 (as we shall when we study the Sommerfeld model). Also sometimes the measured value of Q is positive – Drude model has no answer to this.

Need a quantum theory to explain these.