MTLE-6120: Advanced Electronic Properties of Materials

Classical Drude theory of conduction

Reading:

- Kasap: 2.1 - 2.3, 2.5

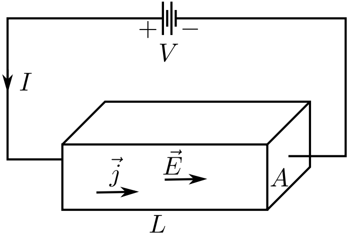
Ohm's law

- Local Ohm's law: current density driven by electric field

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

- Current in a sample of cross section A is $I = jA$
- Voltage drop across a sample of length L is $V = EL$
- Ohm's law defines resistance

$$R \equiv \frac{V}{I} = \frac{EL}{jA} = \sigma^{-1} \frac{L}{A}$$



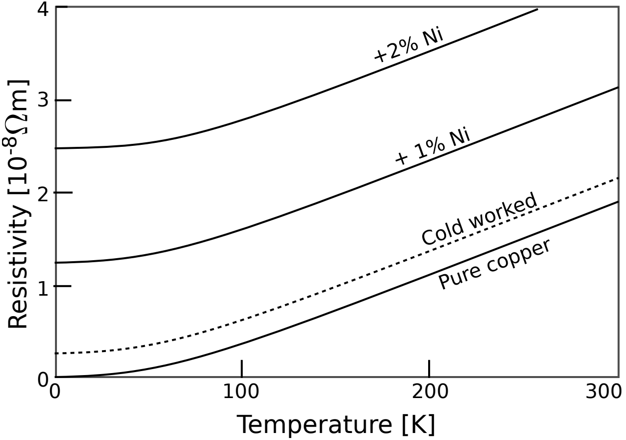
- Units: Resistance in Ω, resistivity $\rho = \sigma^{-1}$ in $\Omega\mathrm{m}$, conductivity σ in $(\Omega\mathrm{m})^{-1}$

Typical values at 293 K

Substance	ρ [Ωm]	σ [$(\Omega\text{m})^{-1}$]	$\frac{d\rho}{\rho dT}$ [K^{-1}]
Silver	1.59×10^{-8}	6.30×10^{7}	0.0038
Copper	1.68×10^{-8}	5.96×10^{7}	0.0039
Tungsten	5.6×10^{-8}	1.79×10^{7}	0.0045
Lead	2.2×10^{-7}	4.55×10^{6}	0.0039
Titanium	4.2×10^{-7}	2.38×10^{6}	0.0038
Stainless steel	6.9×10^{-7}	1.45×10^{6}	0.0009
Mercury	9.8×10^{-7}	1.02×10^{6}	0.0009
Carbon (amorph)	$5 - 8 \times 10^{-4}$	$1 - 2 \times 10^{3}$	-0.0005
Germanium	4.6×10^{-1}	2.17	-0.048
Silicon	6.4×10^{2}	1.56×10^{-3}	-0.075
Diamond	1.0×10^{12}	1.0×10^{-12}	
Quartz	7.5×10^{17}	1.3×10^{-18}	
Teflon	$10^{23} - 10^{25}$	$10^{-25} - 10^{-23}$	

Note $1/T = 0.0034$ K^{-1} at 293 K $\Rightarrow$ approximately $\rho \propto T$ for the best conducting metals.

Temperature dependence



- Linear at higher temperatures
- Residual resistivity (constant at low T) due to defects and impurities

Drude model setup

- Fixed nuclei (positive ion cores) + gas of moving electrons
- Electrons move freely with random velocities
- Electrons periodically scatter which randomizes velocity again
- Average time between collisions: mean free time τ
- Average distance travelled between collisions: mean free path λ
- In zero field, drift velocity (averaged over all electrons)

$$\vec{v}_d \equiv \langle \vec{v} \rangle = 0$$

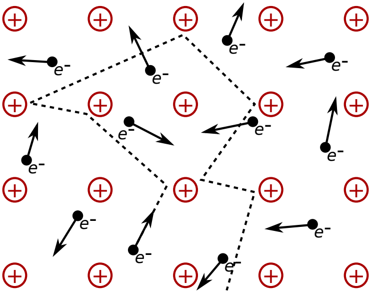
but electrons are not stationary:

$$\langle v^2 \rangle = u^2$$

- Current density carried by electrons:

$$\vec{j} = n(-e)\vec{v}_d = 0$$

where n is number density of electrons



Apply electric field

- Electron starts at past time $t = -t_0$ with random velocity $\vec{v}_0$
- Force on electron is $\vec{F} = (-e)\vec{E}$
- Solve equation of motion till present time $t = 0$:

$$m\frac{\mathrm{d}\vec{v}}{\mathrm{d}t} = (-e)\vec{E}$$

$$\vec{v} = \vec{v}_0 - \frac{e\vec{E}t_0}{m}$$

- Need to average over all electrons
- Probability that electron started at $-t_0$ and did not scatter till $t = 0$ is

$$P(t_0) \propto e^{-t_0/\tau} = e^{-t_0/\tau}/\tau \text{ (normalized)}$$

- Probability distribution of initial velocities satisfies

$$\int \mathrm{d}\vec{v}_0 P(\vec{v}_0) = 1 \qquad \text{(normalized)}$$

$$\int \mathrm{d}\vec{v}_0 P(\vec{v}_0)\vec{v}_0 = 0 \qquad \text{(random)}$$

Drift velocity in electric field

- Drift velocity is the average velocity of all electrons

$$
\begin{aligned}
\vec{v}_d &\equiv \langle \vec{v} \rangle \\
&\equiv \int \mathrm{d}\vec{v}_0 P(\vec{v}_0) \int_0^\infty \mathrm{d}t_0 P(t_0) \left(\vec{v}_0 - \frac{e\vec{E}t_0}{m} \right) \\
&= \int \mathrm{d}\vec{v}_0 P(\vec{v}_0)\vec{v}_0 \int_0^\infty \mathrm{d}t_0 P(t_0) - \int \mathrm{d}\vec{v}_0 P(\vec{v}_0) \int_0^\infty \mathrm{d}t_0 P(t_0) \frac{e\vec{E}t_0}{m} \\
&= 0 \cdot 1 - 1 \cdot \int_0^\infty \mathrm{d}t_0 \frac{e^{-t_0/\tau}}{\tau} \frac{e\vec{E}t_0}{m} \\
&= \frac{-e\vec{E}}{m\tau} \cdot \int_0^\infty t_0 \mathrm{d}t_0 e^{-t_0/\tau} \\
&= \frac{-e\vec{E}}{m\tau} \cdot \tau^2 \qquad \left(\int_0^\infty x^n \mathrm{d}x e^{-ax} = \frac{n!}{a^{n+1}} \right) \\
&= \frac{-e\vec{E}\tau}{m}
\end{aligned}
$$

Drude conductivity

- Current density carried by electrons:

$$\vec{j} = n(-e)\vec{v}_d = n(-e)\left(-\frac{e\vec{E}\tau}{m}\right) = \frac{ne^2\tau}{m}\vec{E}$$

- Which is exactly the local version of Ohm's law with conductivity

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

- For a given metal, n is determined by number density of atoms and number of 'free' electrons per atom
- e and m are fundamental constants
- Predictions of the model come down to τ (discussed next)
- Later: quantum mechanics changes τ, but above classical derivation remains essentially correct!

Classical model for scattering

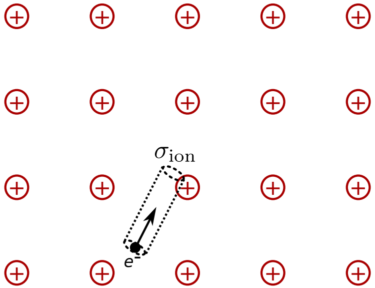
- Electrons scatter against ions (nuclei + fixed core electrons)
- Scattering cross-section σ_{ion}: projected area within which electron would be scattered
- WLOG assume electron travelling along z
- Probability of scattering between z and $\mathrm{d}z$ is

$$-\mathrm{d}P(z) = P(z)\underbrace{\sigma_{\text{ion}}\mathrm{d}z}_{\mathrm{d}V_{\text{eff}}} n_{\text{ion}}$$

  where n_{ion} is number density of ions and $\mathrm{d}V_{\text{eff}}$ is the volume from which ions can scatter electrons

- This yields $P(z) \propto e^{-\sigma_{\text{ion}} n_{\text{ion}} z}$
- $\Rightarrow$ Mean free path

$$\lambda = \frac{1}{n_{\text{ion}}\sigma_{\text{ion}}}$$



Classical estimate of scattering time

- From Drude model, $\tau = \sigma m/(ne^2)$
- Experimentally, $\sigma \propto T^{-1} \Rightarrow \tau \propto T^{-1}$
- From classical model, $\tau = \lambda/u$, where u is average electron speed
- $\lambda = 1/(n_{\text{ion}}\sigma_{\text{ion}})$ should be T-independent
- Kinetic theory: $\frac{1}{2}mu^2 = \frac{3}{2}k_BT \Rightarrow u = \sqrt{3k_BT/m}$
- Therefore classical scattering time

$$\tau = \frac{\lambda}{u} = \frac{1}{n_{\text{ion}}\sigma_{\text{ion}}\sqrt{3k_BT/m}} \propto T^{-1/2}$$

gets the temperature dependence wrong

Comparisons for copper

- Experimentally:

$$\sigma = 6 \times 10^7 \ (\Omega\mathrm{m})^{-1} \text{ (at 293 K)}$$

$$n = n_{\mathrm{ion}} = \frac{4}{(3.61\ \text{Å})^3} = 8.5 \times 10^{28}\ \mathrm{m}^{-3}$$

$$\tau = \frac{\sigma m}{n e^2} = \frac{6 \times 10^7\ (\Omega\mathrm{m})^{-1} \cdot 9 \times 10^{-31}\ \mathrm{kg}}{8.5 \times 10^{28}\ \mathrm{m}^{-3} (1.6 \times 10^{-19}\ \mathrm{C})^2} = 2.5 \times 10^{-14}\ \mathrm{s}$$

- Classical model:

$$\sigma_{\mathrm{ion}} \sim \pi (1\ \text{Å})^2 \sim 3 \times 10^{-20}\ \mathrm{m}^2$$

$$\lambda = \frac{1}{n_{\mathrm{ion}} \sigma_{\mathrm{ion}}} \sim \frac{1}{8.5 \times 10^{28}\ \mathrm{m}^{-3} \cdot 3 \times 10^{-20}\ \mathrm{m}^2} \sim 4 \times 10^{-10}\ \mathrm{m}$$

$$u = \sqrt{\frac{3 k_B T}{m}} = \sqrt{\frac{3 \cdot 1.38 \times 10^{-23}\ \mathrm{J/K} \cdot 293\ K}{9 \times 10^{-31}\ \mathrm{kg}}} = 1.2 \times 10^5\ \mathrm{m/s}$$

$$\tau = \frac{\lambda}{u} \sim 3 \times 10^{-15}\ \mathrm{s}$$

- Need σ_{ion} to be 10x smaller to match experiment

What changes in quantum mechanics?

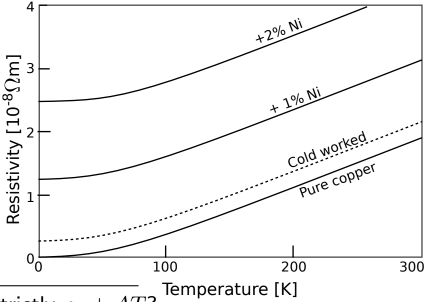
1. Electron velocity in metals is (almost) independent of temperature
   - Pauli exclusion principle forces electrons to adopt different velocities
   - 'Relevant' electrons have Fermi velocity v_F ($=1.6 \times 10^6$ m/s for copper)
2. Electrons don't scatter against ions of the perfect crystal
   - Electrons are waves which 'know' where all the ions of the crystal are
   - They only scatter when ions deviate from ideal positions!
   - Crude model $\sigma_{\text{ion}} = \pi x^2$ for RMS displacement x
   - Thermal displacements $\frac{1}{2}kx^2 = \frac{1}{2}k_B T$
   - Spring constant $k \sim Ya \sim$ (120 GPa)(3.6Å$/\sqrt{2}$) ~ 30 N/m
   - $$\sigma_{\text{ion}} = \frac{\pi k_B T}{k} \sim 4 \times 10^{-22}\ \text{m}^2 \text{ (at room } T\text{)}$$
   - $$\tau = \frac{1}{n_{\text{ion}}\sigma_{\text{ion}}v_F} = \frac{k}{n_{\text{ion}}\pi k_B T v_F} \sim 1.7 \times 10^{-14}\ \text{s (at room } T\text{)}$$
   - Correct $1/T$ dependence and magnitude at room T (expt: 2.5×10^{-14} s)!

Matthiessen's rule

- Perfect metal: $\tau_T \propto T^{-1}$ due to scattering against thermal vibrations (so far)
- Impurity and defect scattering contribute $\tau_I \propto T^0$
- Scattering rates (not times) are additive, so net τ given by

$$\tau^{-1} = \tau_T^{-1} + \tau_I^{-1} + \cdots$$

- Resistivity $\rho \propto \tau^{-1} \sim \rho_0 + AT$ with residual resistivity ρ_0 due to τ_I



Is the experimental data strictly $\rho_0 + AT$?

Mobility

- Drude conductivity in general

$$\sigma = \frac{nq^2\tau}{m} = n|q|\mu$$

where n is the number density of charge carriers q with mobility

$$\mu = \frac{|q|\tau}{m}$$

effectively measuring the conductivity per unit (mobile) charge

- In metals, $q = -e$ since charge carried by electrons (so far)
- In semiconductors, additionally $q = +e$ for holes and

$$\sigma = e(n_e\mu_e + n_h\mu_h)$$

- Semiconductors have typically higher μ, substantially lower n and σ

Hall effect

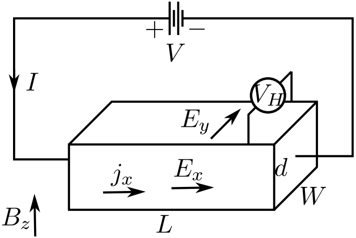
- Apply magnetic field perpendicular to current: voltage appears in third direction
- Hall coefficient defined by

$$R_H = \frac{E_y}{j_x B_z} = \frac{V_H/W}{I/(Wd)B_z} = \frac{V_H d}{I B_z}$$

- Simple explanation in Drude model
- Average driving force on carriers now

$$\vec{F} = q(\vec{E} + \vec{v}_d \times \vec{B}) \\ = q(E_x \hat{x} - (v_d)_x B_z \hat{y})$$

- Steady-state current only in $\hat{x}$
- $\Rightarrow E_y = (v_d)_x B_z$ develops to cancel F_y



Hall coefficient in metals

- Note $E_y = (v_d)_x B_z$, while $j_x = nq(v_d)_x$
- Eliminate $(v_d)_x$ to get

$$R_H \equiv \frac{E_y}{j_x B_z} = \frac{1}{nq}$$

- In particular, $q = -e$ for electronic conduction $\Rightarrow R_H = -1/(ne)$
- Compare to experimental values:

Metal	Experiment R_H [m^3/C]	Drude R_H [m^3/C]
Cu	-5.5×10^{-11}	-7.3×10^{-11}
Ag	-9.0×10^{-11}	-10.7×10^{-11}
Na	-2.5×10^{-10}	-2.4×10^{-10}
Cd	$+6.0 \times 10^{-11}$	-5.8×10^{-11}
Fe	$+2.5 \times 10^{-11}$	-2.5×10^{-11}

- Good agreement for 'free-electron' metals
- Wrong sign for some (transition metals)!

Hall coefficient in semiconductors

- Remember: conductivities due to electrons and holes add $\sigma = e(n_e\mu_e + n_h\mu_h)$
- Different drift velocities for electrons and holes
- For each of electrons and holes
  - Given driving force $\vec{F}$, drift velocity $\vec{v}_d = \vec{F}\tau/m$
  - Mobility $\mu \equiv |q|\tau/m$, so $\vec{v}_d = \vec{F}\mu/|q|$
  - Driving force $F_y = q(E_y - (v_d)_x B_z)$
  - Corresponding drift velocity $(v_d)_y = F_y\mu/|q|$
  - And corresponding current $j_y = nq(v_d)_y = nqF_y\mu/|q| = nq^2(E_y - (v_d)_x B_z)\mu/|q|$
  - Substitute $(v_d)_x = (qE_x)\mu/|q|$ to get $j_y = n\mu(|q|E_y - qE_x\mu B_z)$
- Net j_y must be zero (that's how we got Hall coefficient before):

$$0 = n_e\mu_e(eE_y + eE_x\mu_e B_z) + n_h\mu_h(eE_y - eE_x\mu_h B_z)$$

Hall coefficient in semiconductors (continued)

- Net zero j_y yields:

$$\begin{aligned} 0 &= n_e\mu_e(eE_y + eE_x\mu_e B_z) + n_h\mu_h(eE_y - eE_x\mu_h B_z) \\ &= (n_e\mu_e + n_h\mu_h)E_y + (n_e\mu_e^2 - n_h\mu_h^2)E_x B_z \\ \Rightarrow R_H &= \frac{E_y}{j_x B_z} = \frac{E_y}{\sigma E_x B_z} \\ &= -\frac{n_e\mu_e^2 - n_h\mu_h^2}{(n_e\mu_e + n_h\mu_h)\sigma} \\ &= \frac{-n_e\mu_e^2 + n_h\mu_h^2}{e(n_e\mu_e + n_h\mu_h)^2} \end{aligned}$$

- Reduces to metal result if $n_h = 0$
- Note holes conrtibute positive coefficient, while electrons negative (not additive like conductivity)
- Transition metals can have positive Hall coefficients for the same reason! (Explained later with band structures.)

Frequency-dependent conductivity

- So far, we applied fields $\vec{E}$ constant in time
- Now consider oscillatory field $\vec{E}(t) = \vec{E}e^{-i\omega t}$ (such as from an EM wave)
- Same Drude model: free electron between collisions etc.
- Only change in equation of motion:

$$\frac{\mathrm{d}\vec{v}}{\mathrm{d}t} = \frac{q\vec{E}}{m}e^{-i\omega t}$$

$$\vec{v} = \vec{v}_0 + \int_{-t_0}^{0} \mathrm{d}t \frac{q\vec{E}}{m}e^{-i\omega t}$$

$$= \vec{v}_0 + \frac{q\vec{E}}{m}\left[\frac{e^{-i\omega t}}{-i\omega}\right]_{-t_0}^{0}$$

$$= \vec{v}_0 + \frac{q\vec{E}}{m} \cdot \frac{e^{i\omega t_0} - 1}{i\omega}$$

Frequency-dependent conductivity: drift velocity

- Drift velocity is the average velocity of all electrons

$$
\begin{aligned}
\vec{v}_d \equiv \langle \vec{v} \rangle &\equiv \int \mathrm{d}\vec{v}_0 P(\vec{v}_0) \int_0^\infty \mathrm{d}t_0 P(t_0) \left(\vec{v}_0 + \frac{q\vec{E}}{m} \cdot \frac{e^{i\omega t_0} - 1}{i\omega} \right) \\
&= \int_0^\infty \mathrm{d}t_0 P(t_0) \frac{q\vec{E}}{m} \frac{e^{i\omega t_0} - 1}{i\omega} \\
&= \int_0^\infty \mathrm{d}t_0 \frac{e^{-t_0/\tau}}{\tau} \frac{q\vec{E}}{m} \frac{e^{i\omega t_0} - 1}{i\omega} \\
&= \frac{q\vec{E}}{im\omega\tau} \int_0^\infty \mathrm{d}t_0 \left(e^{-t_0(1/\tau - i\omega)} - e^{-t_0/\tau} \right) \\
&= \frac{q\vec{E}}{im\omega\tau} \left(\frac{1}{1/\tau - i\omega} - \tau \right) \qquad \left(\int_0^\infty x^n \mathrm{d}x e^{-ax} = \frac{n!}{a^{n+1}} \right) \\
&= \frac{q\vec{E}}{im\omega\tau} \cdot \frac{1 - (1 - i\omega\tau)}{1/\tau - i\omega} \\
&= \frac{q\vec{E}\tau}{m} \cdot \frac{1}{1 - i\omega\tau}
\end{aligned}
$$

Frequency-dependent conductivity: Drude result

- As before, $\vec{j} = nq\vec{v}_d$, which yields conductivity

$$\sigma(\omega) = \frac{nq^2\tau}{m(1 - i\omega\tau)} = \frac{\sigma(0)}{1 - i\omega\tau}$$

- Same as before, except for factor $(1 - i\omega\tau)$ (which $\rightarrow 1$ for $\omega \rightarrow 0$ as expected)
- What does the phase of the complex conductivity mean?
- Current density has a phase lag relative to electric field
- When field changes, collisions are needed to change the current, which take average time τ
- From constitutive relations discussion, complex dielectric function

$$\epsilon(\omega) = \epsilon_0 + \frac{i\sigma(\omega)}{\omega} = \epsilon_0 - \frac{nq^2/m}{\omega(\omega + i/\tau)}$$

Plasma frequency

- Displace all electrons by x
- Volume xA containing only electrons with charge $-xAne$
- Counter charge $+xAne$ on other side due to nuclei
- Electric field by Gauss's law:

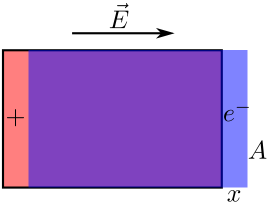
$$\vec{E} = \frac{xne}{\epsilon_0}\hat{x}$$

- Equation of motion of electrons:

$$m\frac{\mathrm{d}^2x}{\mathrm{d}t^2} = (-e)E_x = -x\frac{ne^2}{\epsilon_0}$$

- Harmonic oscillator with frequency ω_p given by

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



Drude dielectric function of metals

- Simple form in terms of plasma frequency

$$\epsilon(\omega) = \epsilon_0 - \frac{nq^2/m}{\omega(\omega + i/\tau)} = \epsilon_0 \left(1 - \frac{\omega_p^2}{\omega(\omega + i/\tau)}\right)$$

- For $\omega \ll 1/\tau$,

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

imaginary dielectric, real conductivity (Ohmic regime)

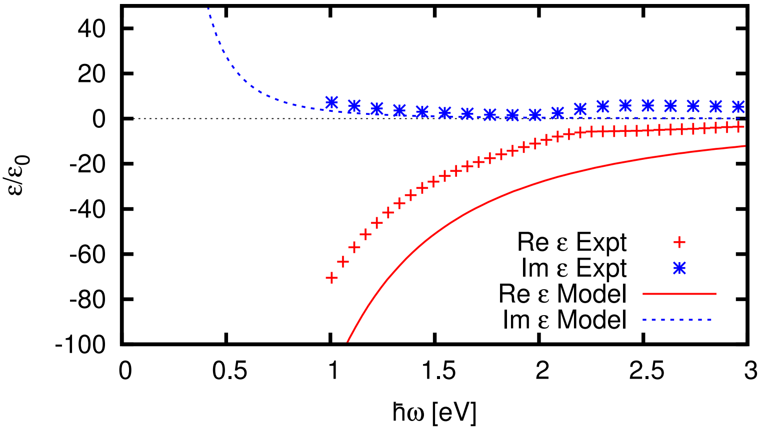
- For $1/\tau \ll \omega < \omega_p$,

$$\epsilon(\omega) \approx \epsilon_0 \left(1 - \frac{\omega_p^2}{\omega^2}\right)$$

negative dielectric constant (plasmonic regime)

- For $\omega > \omega_p$, positive dielectric constant (dielectric regime)

Copper dielectric function



- For copper, $\omega_p = 10.8$ eV and $\tau = 25$ fs
- Note 1 eV corresponds to $\omega = 1.52 \times 10^{15}$ s^{-1} and $\nu = 2.42 \times 10^{14}$ Hz