Electrical conductivity in metals

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Paul Karl Ludwig Drude (July 12, 1863 – July 5, 1906) was a German physicist specializing in optics. He wrote a fundamental textbook integrating optics with Maxwell's theories of electromagnetism.

http://en.wikipedia.org/wiki/Paul_Karl_Ludwig_Drude

In 1897 J.J. Thomson presented the experiments which embody the "discovery of the electron, and to Drude (1900) we owe the concept of a metal as a framework of atoms permeated by a more or less "free electron gas." Drude took a particular kinetic model for the behavior of these free electrons, assuming that the electron in equilibrium were moving randomly as a classical gas but making frequent collisions with the atomic lattice. (D.K.C. MacDonald).

1. Classical theory of DC electrical conductivity (Drude model): Maxwell-Boltzmann statistics

In the presence of an electric field E, the motion of electron (mass m and charge $-e$) can be governed by a Newton's second law,

$$m(\frac{dv}{dt}+\frac{v}{\tau}) = F = -eE,$$

where τ is a relaxation time and -e is the charge of electron; e>0. In the steady state, we have

$$v = -\frac{eE\tau}{m}, \qquad \text{(terminal velocity)}$$

The current density J is given by

$$J = n(-e)v = \frac{ne^2\tau}{m}E = \sigma E,$$

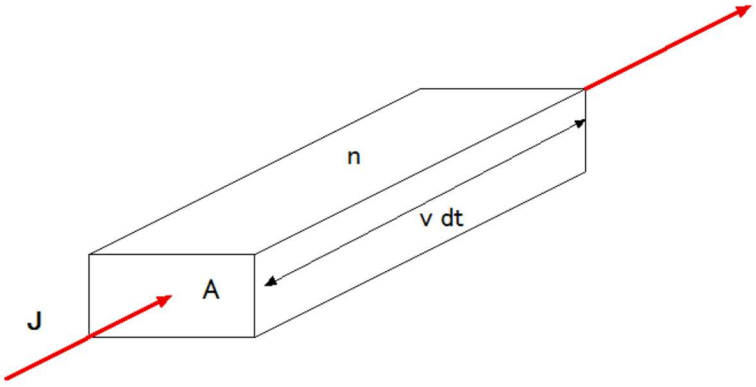


Fig. Current density (current passing through a unit area): $\Delta Q = (-e)nvAdt$;

$$J = \frac{I}{A} = \frac{\Delta Q}{A\Delta t} = (-e)nv$$

The conductivity σ is defined by

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

where n is the number density. The unit of σ is

$$[\sigma] = \frac{\frac{1}{cm^3} \cdot erg \cdot cm \cdot s}{erg \cdot \frac{s^2}{cm^2}} = \frac{1}{s}$$

((**Note**)) In the Drude model at the beginning of the 20th century, the conduction electrons are treated as a classical particle. The electrons, like the molecules of a gas, undergo *collisions*.

2. Change in Fermi sphere due to the presence of electric field (Fermi-Dirac statistics)

We consider the equation of motion,

$$\dot{\boldsymbol{p}} = \hbar \dot{\boldsymbol{k}} = -eE$$

From this, we get

$$\boldsymbol{k}(t) - \boldsymbol{k}(0) = -\frac{e\boldsymbol{E}}{\hbar} t$$

At $t = 0$, the field $\boldsymbol{E}$ is applied to an electron gas that fills the Fermi sphere centered at the origin of $\boldsymbol{k}$-space. At time t, the Fermi sphere will be displaced to a new center at

$$\delta \boldsymbol{k} = -\frac{e\boldsymbol{E}t}{\hbar}.$$

Because of collisions with impurities, lattice imperfections, and phonons, the displaced sphere may be maintained in a steady state in an electric field;

$t = \tau$ collision time

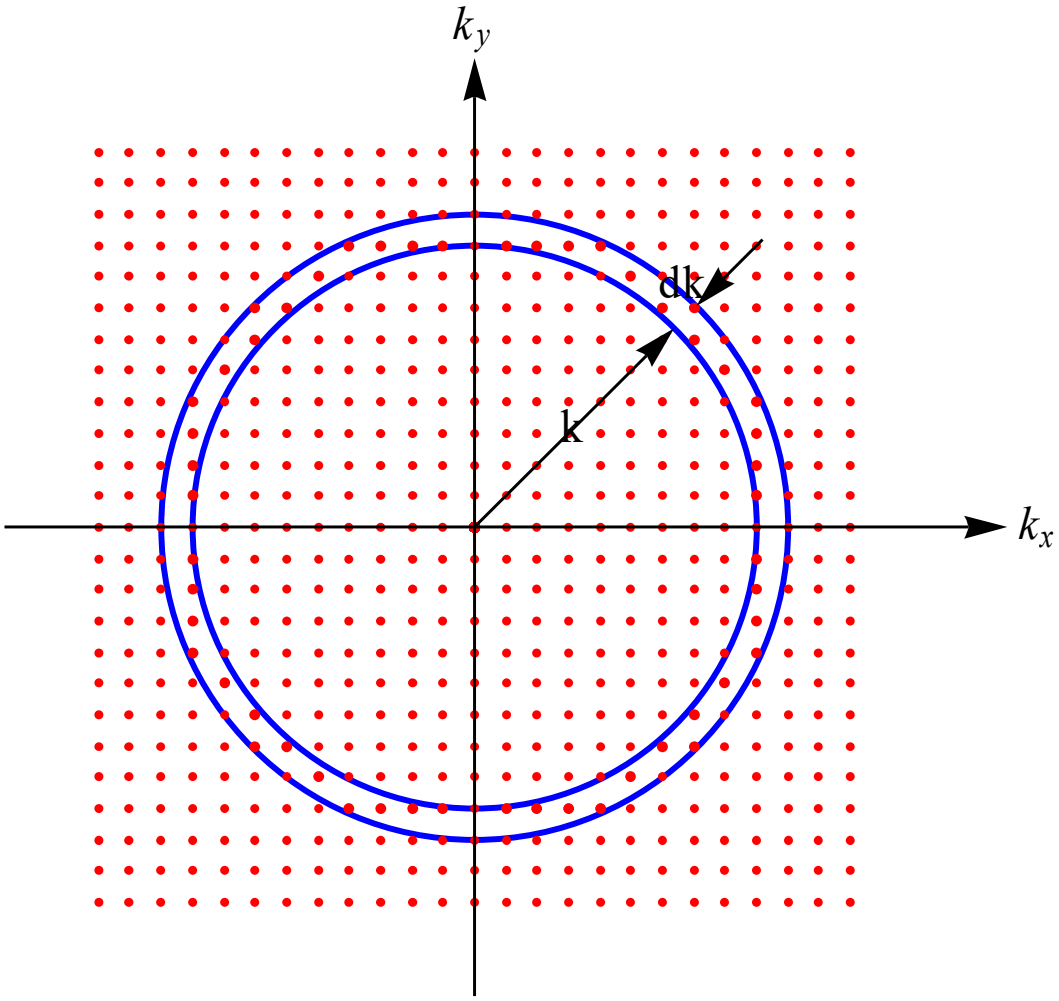
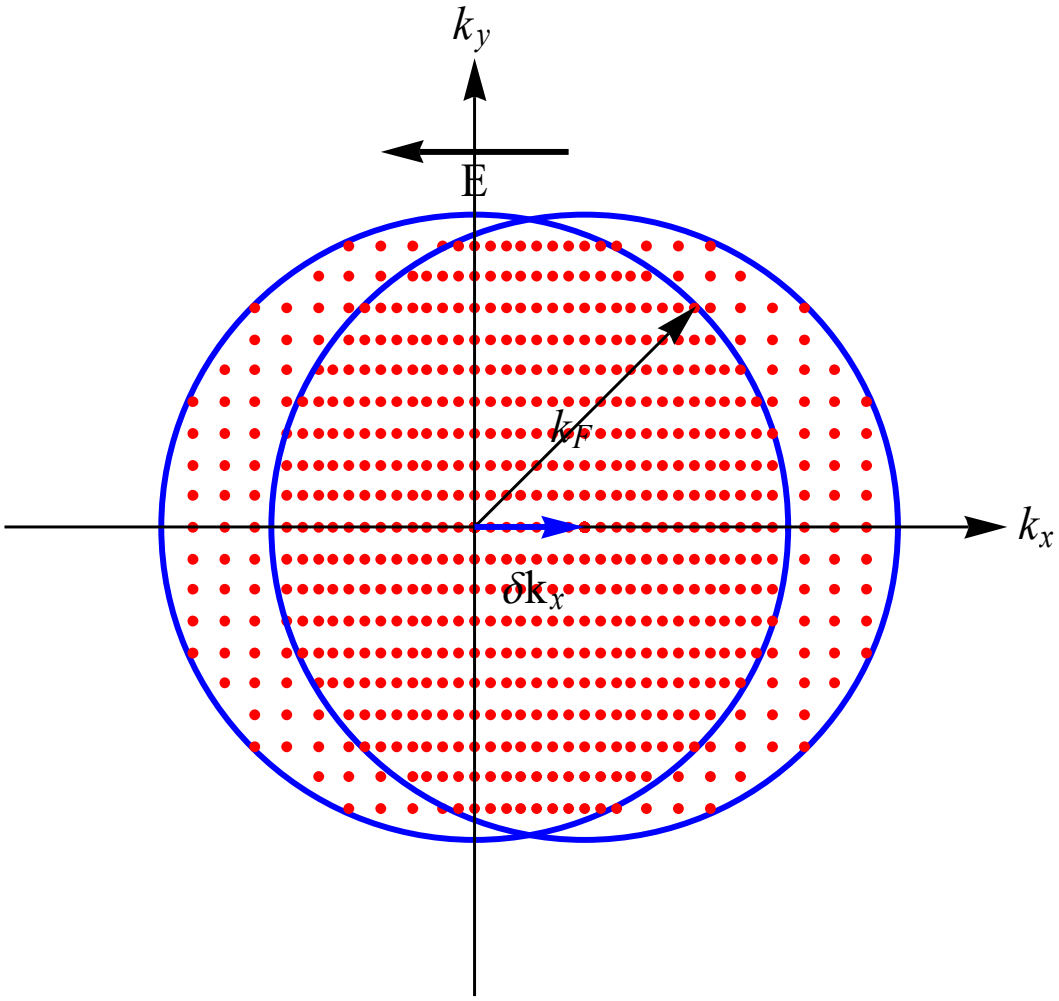


Fig. Fermi sphere with radius k_F.


k_y
E
k_F
k_x
δk_x

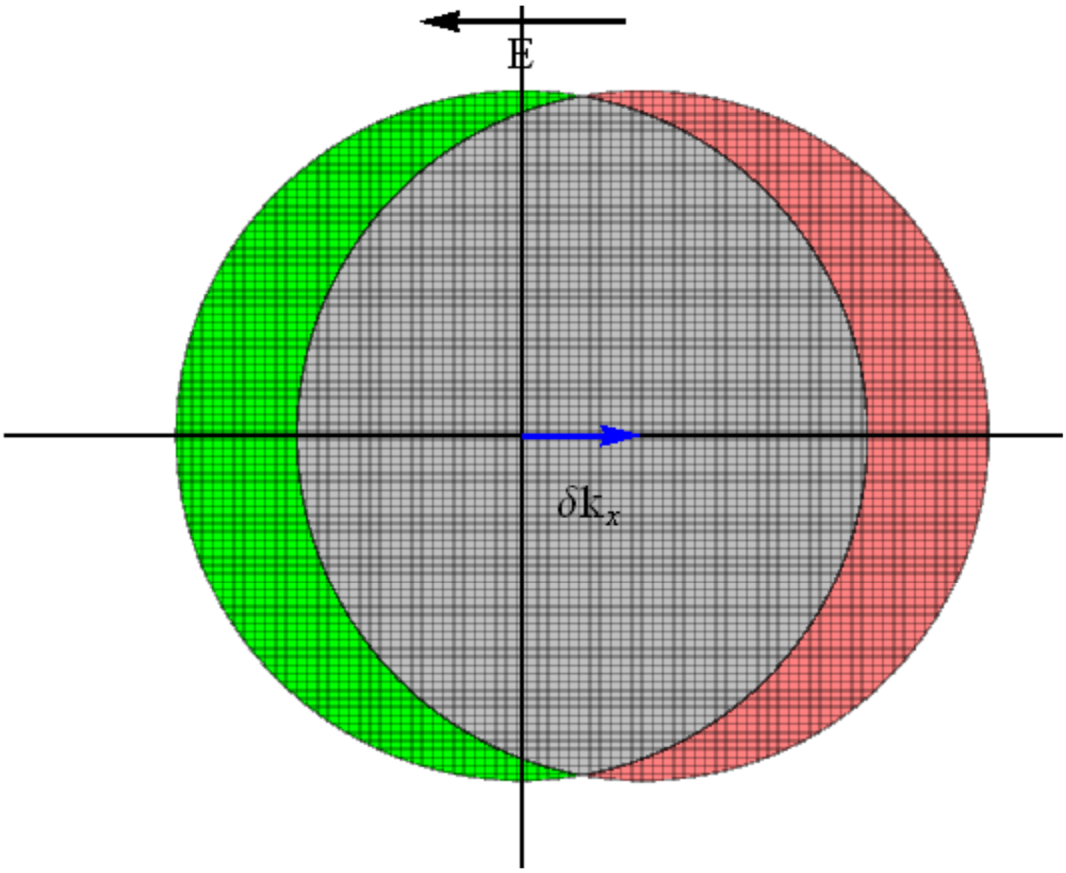


Fig. The shift of the Fermi sphere in the presence of an electric field along the negative x direction.

Then we have

$$\boldsymbol{v} = \frac{\hbar \delta \boldsymbol{k}}{m} = -\frac{\hbar}{m}\frac{e\boldsymbol{E}\tau}{\hbar} = -\frac{e\boldsymbol{E}\tau}{m}.$$

The current density $\boldsymbol{J}$ is given by

$$\boldsymbol{J} = n(-e)\boldsymbol{v} = \frac{ne^2\tau}{m}\boldsymbol{E} = \sigma \boldsymbol{E}$$

which is the Ohm's law. The electrical conductivity σ is defined by

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

The electrical resistivity ρ is defined by

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

The unit of ρ is [s].

((**Note**))

The expression of σ is practically the same as the one derived by Drude. However, the relaxation time τ_e has a completely different meaning. Indeed, for a classical gas, the electrons can all undergo collisions whatever their kinetic energy, and τ_e is a collision time which affects all the electrons equally. According to the Pauli exclusion principle, the collisions can only transfer electrons from occupied states to unoccupied states. If k_F is the radius of the Fermi surface when there is no field, these collisions can therefore only bring states with $k > k_F$ | on the right back to states with $k < k_F$ on the left of **Fig**.(the shift of the Fermi sphere). Only collision processes involving electrons with energy close to ε_F can therefore contribute to establishing the stationary state and the corresponding redistribution of the velocities. *Pauli's principle thus restricts the kind of collision that can occur*, and the collision time τ_e only concerns electrons at the Fermi level, with speed v_F. Likewise, the mean free path concerns only these electrons, which can undergo collisions. The mean free path is given by $l_e = v_F\tau_e$.

3. Relaxation time of electron for Cu at 300 K

It is instructive to estimate from the observed conductivity the order of magnitude of the relaxation time τ. We observe Cu at 300 K,

$\rho = 1.7\,\mu\Omega cm$ or $\sigma = 6.0\times10^5(\Omega cm)^{-1}$ (practical units)

We note that

$$\Omega cm = \frac{V}{A} cm = \frac{\frac{1}{300} statV}{3\times10^{9}\, statA} cm = \frac{1}{9\times10^{11}} esu$$

Then we have

$$\rho = \frac{1}{9\times10^{11}} \times 1.7\times10^{-6} = 1.89\times10^{-18} \text{ [s]}$$

or

$$\sigma = 5.29\times10^{17} \text{ s}^{-1}$$

((Note)) 1 statV = 300 V, 1A = 2.997924536.8431 x 10^9 = 3 x 10^9 statA

Using the number density of electron in Cu,

n = 8.47 x 10^{22}/cm^3.

$$\tau = \frac{\sigma m}{ne^2} = 2.47 \text{ x } 10^{-14} \text{ s} \qquad T = 300 \text{ K}.$$

4. Units of resistivity in SI units and cgs units

We consider the Bohr model for a hydrogen atom, where charge q undergoes a circular motion around the proton. The current I is obtained as

$$I = \frac{q}{T} = q\nu$$

where T is a period and $T = 1/\nu$. ν is the frequency. If we assume that

$$h\nu = qV$$

The resistance R can be expressed by

$$R = \frac{V}{I} = \frac{h\nu}{q}\frac{1}{q\nu} = \frac{h}{q^2} \qquad (\Omega \text{ in the units of SI}).$$

For electron $q = -e$, we get

$$R = \frac{h}{e^2} = \frac{2\pi\hbar}{e^2}$$

which depends only on the fundamental physical constants *e* and *h*. This resistance is called the von Klitzing constant, given by

$$R_K(SI) = \frac{h}{e^2} = 25812.807449\ \Omega$$

Note that

$$\frac{h}{e^2} = \frac{[J \cdot s]}{[e^2]} = \frac{[eV \cdot s]}{[e^2]} = \frac{[\frac{eV}{e}]}{\left[\frac{e}{s}\right]} = \frac{[V]}{[I]} = [\Omega]$$

where we use the relation $W=qV$ (energy) and $I = \frac{\Delta Q}{\Delta t}$.

Using the fine structure constant (in cgs)

$$\alpha = \frac{e^2}{\hbar c} = \frac{1}{137.036}$$

the von Klitzing constant can be

$$R_K(cgs) = \frac{h}{e^2} = \frac{2\pi\hbar c}{e^2 c} = \frac{2\pi}{c\alpha} = \frac{2\pi}{c}137.036 = 2.87206\times10^{-8}\ \text{(s/cm)}$$

In cgs units, we note that

$$\frac{h}{e^2} = \frac{[erg \cdot s]}{[erg \cdot cm]} = [\frac{s}{cm}]$$

$$\frac{R_K(SI)}{R_K(cgs)} = \frac{\Omega}{s/cm} = \frac{25.9128075518\times10^3}{2\pi\dfrac{137.036}{c}} = 30.0954c = 9.02236\times10^{11}$$

or

$$\frac{\Omega}{s/cm} = \frac{\Omega cm}{s} = 9.02236\times10^{11}$$

or

$$\Omega cm = 9.02236\times10^{11} s$$

which is a very important factor for the conversion of resistivity between cgs and SI units.

((**Mathyematica**)) **Klitzing constant R_K**: R_K = 25,812.807449(86) Ω,

Calculation of the Klitzing constant in SI Units and cgs units

```
Clear["Global`*"];
SIrule1 = {me → 9.1093821545 × 10^-31, eV → 1.602176487 × 10^-19,
  qe → 1.602176487 × 10^-19, ge → 2.0023193043622,
  c → 2.99792458 × 10^8, h → 6.62606896 × 10^-34,
  ħ → 1.05457162853 × 10^-34};
CGSrule1 = {c → 2.99792 × 10^10, ħ → 1.054571628 10^-27,
  h → 6.62606957 10^-27, me → 9.10938215 10^-28, qe → 4.8032068 × 10^-10,
  eV → 1.602176487 × 10^-12};
```

$$\text{RKSI} = \frac{h}{qe^2} \text{ /. SIrule1}$$

$$25\,812.8$$

$$\text{RKCGS} = \left(\frac{h}{qe^2} \text{ /. CGSrule1}\right)$$

$$2.87206 \times 10^{-8}$$

$$\text{ratio} = \frac{\text{RKSI}}{\text{RKCGS}}$$

$$8.98756 \times 10^{11}$$

Note that
1 s/cm (cgs units) = 8.98752 x 10^{11} Ω (SI units)

5. Number density

(a)

ρ: density (g/cm^3)
A: mass of atom (g/mol)

Suppose that there are Z electrons per atom. Then the number density is

$$n = \frac{Z\rho}{A} N_A$$

where N_A is the Avogadro number.

(b) Number density of electrons in metal

What is the number density of conduction electrons in metals?

For Cu (fcc), there are 4 Cu atoms per conventional SC unit cell with a lattice constant a; $a = 3.61$ Å. Each Cu atom has one conduction electron. Thus the number density is

$$n = \frac{4}{a^3} = n = 8.50 \times 10^{22} / \text{cm}^3.$$

	Z	n (10^{22}/cm^3)
Li	1	4.7
Na	1	2.65
K	1	1.40
Rb	1	1.15
Cs	1	0.91
Cu	1	8.47
Ag	1	5.86
Au	1	5.90
Be	1	24.7
Mg	2	8.61
Ca	2	4.61
Sr	2	3.55
Ba	2	3.15

6. Mean free path

$$l = v_F \tau$$

where v_F is the Fermi velocity. The conductivity of Cu at 4 K is nearly 10^5 times that at 300 K.

$$\sigma(4K) = 5.29 \times 10^{17} \times 10^5 = 5.29 \times 10^{22}$$

$$\tau = \frac{\sigma m}{ne^2} = 2.47 \text{ x } 10^{-9} \text{ s} \qquad T = 4 \text{ K.}$$

When v_F = 1.57 x 10^8 cm/s for Cu, then the mean free path l is

$$l(4K) = 1.57 \times 10^8 \times 2.47 \times 10^{-9} = 0.3 \text{ cm}$$

and

$$l(300K) = 1.57 \times 10^8 \times 2.47 \times 10^{-14} = 3 \times 10^{-6} \text{cm}$$

7. Temperature dependence of electrical resistivity of metals

The relaxation time τ is described as

$$\frac{1}{\tau} = \frac{1}{\tau_L} + \frac{1}{\tau_i}$$

where τ_L and τ_i are the collision times for scattering by phonons (lattice vibration) and by imperfections, respectively. The net resistivity is given by

$$\rho = \rho_L + \rho_i$$

((**Matthiessen's rule**))

ρ_L is the resistivity caused by thermal phonons. ρ_i is the resistivity caused by scattering of the electron waves by static defects that disturb the periodicity of the lattice.

8. Residual resistivity

The residual resistivity $\rho_i(T = 0 \text{ K})$, is the extrapolated resistivity at $T = 0$ K.

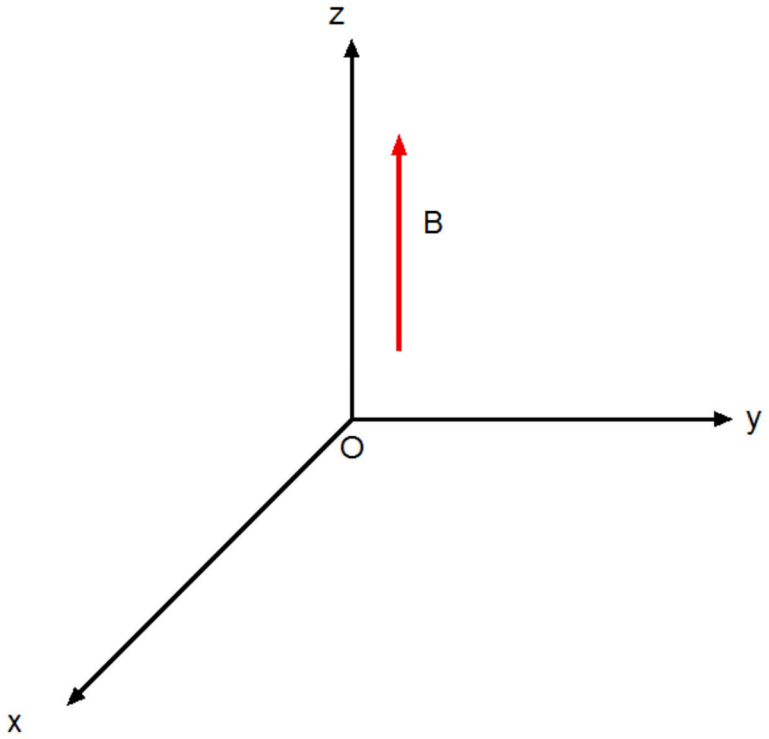
$$\rho_L(T) \to 0 \qquad \text{as } T \to 0.$$

$$\rho_i \to \rho_i(0) \qquad \text{as } T \to 0.$$

Often ρ_i is independent of T.

Residual resistivity ratio = $\frac{\rho(T=300K)}{\rho_i}$, which is a convenient approximate indicator of sample purity.

9. Conductivity in the presence of magnetic field



We consider the motion of an electron (charge q = -e, mass m) in the presence of a magnetic field $\boldsymbol{B}$ directed along the z axis. E is the electric field which lies in the x-y plane.

$$m(\frac{d}{dt}+\frac{1}{\tau})v_x = -e(E_x + \frac{B}{c}v_y)$$

$$m(\frac{d}{dt}+\frac{1}{\tau})v_y = -e(E_y - \frac{B}{c}v_x)$$

where τ is a relaxation time. In the steady state ($\frac{dv_x}{dt} = \frac{dv_y}{dt} = 0$), we get

$$v_x = -\frac{e\tau}{m} E_x - \omega_c \tau v_y$$

$$v_y = -\frac{e\tau}{m} E_y + \omega_c \tau v_x$$

where

$$\omega_c = \frac{eB}{mc} \qquad \text{(cyclotron frequency)}$$

Then we have the velocity $\boldsymbol{v}$ as

$$\boldsymbol{v} = \begin{pmatrix} v_x \\ v_y \end{pmatrix} = \frac{-\frac{e\tau}{m}}{1+\omega_c{}^2\tau^2} \begin{pmatrix} 1 & -\omega_c\tau \\ \omega_c\tau & 1 \end{pmatrix} \begin{pmatrix} E_x \\ E_y \end{pmatrix}$$

The current density is

$$\boldsymbol{J} = \begin{pmatrix} J_x \\ J_y \end{pmatrix} = -ne\boldsymbol{v} = \frac{\sigma_0}{1+\omega_c{}^2\tau^2} \begin{pmatrix} 1 & -\omega_c\tau \\ \omega_c\tau & 1 \end{pmatrix} \begin{pmatrix} E_x \\ E_y \end{pmatrix} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} \\ \sigma_{yx} & \sigma_{yy} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \end{pmatrix} = \sigma \boldsymbol{E},$$

with the conductivity without magnetic field

$$\sigma_0 = \frac{ne^2\tau}{m}$$

and

$$\sigma_{xx} = \sigma_{yy} = \frac{\sigma_0}{1+\omega_0{}^2\tau^2}, \qquad \sigma_{xy} = -\sigma_{yx} = -\frac{\sigma_0\omega_0\tau}{1+\omega_0{}^2\tau^2}$$

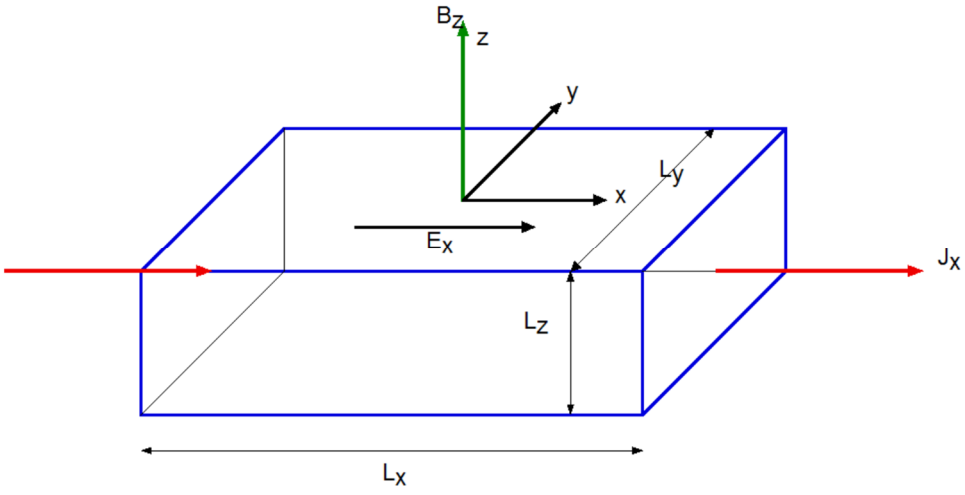
10. Measurement of Hall effect

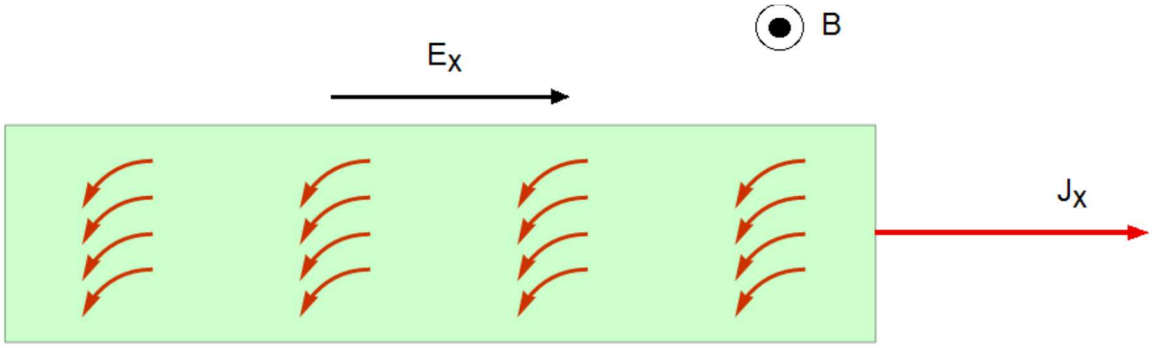
Experimentally we need the following expression

$$\begin{pmatrix} E_x \\ E_y \end{pmatrix} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} \\ -\sigma_{xy} & \sigma_{xx} \end{pmatrix}^{-1} \begin{pmatrix} J_x \\ J_y \end{pmatrix}$$
$$= \begin{pmatrix} \rho_{xx} & \rho_{xy} \\ \rho_{yx} & \rho_{yy} \end{pmatrix} \begin{pmatrix} J_x \\ J_y \end{pmatrix}$$

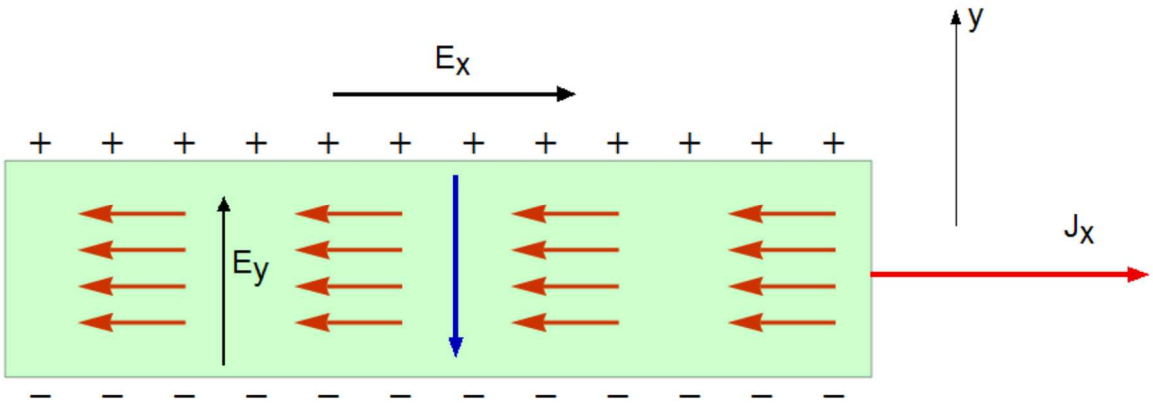
with

$$\rho_{xx} = \rho_{yy} = \frac{\sigma_{xx}}{{\sigma_{xx}}^2 + {\sigma_{xy}}^2}, \qquad \rho_{xy} = -\rho_{yx} = -\frac{\sigma_{xy}}{{\sigma_{xx}}^2 + {\sigma_{xy}}^2}$$





(a)



(b)

Fig. Top view of the configuration for the Hall effect measurement. (a) The drift of electrons immediately after the electric field is applied. (b) The steady state.

In the measurement of the Hall effect, $J_y = 0$. Then we get

$$\begin{pmatrix} J_x \\ 0 \end{pmatrix} = \frac{\sigma_0}{1+\omega_c{}^2\tau^2} \begin{pmatrix} 1 & -\omega_c\tau \\ \omega_c\tau & 1 \end{pmatrix} \begin{pmatrix} E_x \\ E_y \end{pmatrix}$$

From this, we have

$$E_y = -\omega_c \tau E_x = -\frac{eB\tau}{mc} E_x$$

$$J_x = \frac{\sigma_0}{1+\omega_c{}^2\tau^2}(E_x - \omega_c\tau E_y) = \frac{\sigma_0}{1+\omega_c{}^2\tau^2}(1+\omega_c{}^2\tau^2)E_x = \sigma_0 E_x$$

The Hall coefficient R_H is defined by

$$R_H = \frac{E_y}{BJ_x} = \frac{1}{n(-e)c}$$

So we can obtain the sign and the concentration of the charge carriers simply by measuring E_y, J_x, and B_z. Using conventional definitions for the directions of E_y, J_x, and B_z, R_H will be negative for free electrons.

11. Definition of thermal conductivity in metal (Feremi-Dirac statistics)

The contribution to thermal conductivity from conduction electrons is given by

$$\kappa_{el} = \frac{1}{3} c_e v_F l ,$$

where and l (= $v_F \tau$) is a mean free path of electron, c_e is the heat capacity of electrons per unit volume,

$$c_e = \frac{C_e}{V} = \frac{\pi^2 {k_B}^2}{2\varepsilon_F} \frac{N}{V} T = \frac{\pi^2 {k_B}^2}{2\varepsilon_F} nT ,$$

and n is the number density (concentration). Note that C_e is given by

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

with

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

Then the thermal conductivity in metal is derived as

$$\kappa_{el} = \frac{1}{3} \frac{\pi^2 {k_B}^2 nT}{2\varepsilon_F} {v_F}^2 \tau = \frac{1}{3} \frac{\pi^2 {k_B}^2}{m {v_F}^2} nT {v_F}^2 \tau = \frac{\pi^2 n {k_B}^2 T \tau}{3m}$$

where

$$\varepsilon_F = \frac{1}{2} m {v_F}^2$$

In pure metals the electronic contribution is dominant at all temperatures, compared with the lattice contribution.

12. Wiedermann-Franz law

Here we discuss the ratio of the thermal conductivity to the electrical conductivity in metals.

$$\frac{\kappa_e}{\sigma} = \frac{\pi^2 n k_B{}^2 T\tau}{3m}\frac{m}{ne^2\tau} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 T$$

which does not involves neither n or m (the universal relation). This relation is called the **Widermann-Franz law**. The Lorentz number L is defined as

$$L = \frac{\kappa_e}{\sigma T} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 = 2.44301 \text{ x } 10^{-8} \text{ W.}\Omega/\text{K}^2. \qquad \text{(SI units)}$$

or

$$L = \frac{\kappa_e}{\sigma T} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 = 2.71821 \text{ x } 10\text{-}13 \text{ erg/(esu K)}^2. \qquad \text{(cgs units)}$$

This value of L agrees remarkably well with the results of experiments around room temperature on a considerable number of metals. This means that the general concepts of a free electron gas is valid.

((**Note**)) http://en.wikipedia.org/wiki/File:Ohmsketch.gif

This empirical law is named after Gustav Wiedemann and Rudolph Franz, who in 1853 reported that κ/σ has approximately the same value for different metals at the same temperature. The proportionality of κ/σ with temperature was discovered by Ludvig Lorenz in 1872. Qualitatively, this relationship is based upon the fact that the heat and electrical transport both involve the free electrons in the metal.

13. Contribution of phonons and electrons to thermal conductivity

Thermal conductivity from electrons can be expressed by

$$\kappa_e = \frac{1}{3} c_e v_F l_e ,$$

where v_F is the Fermi velocity and l_e is the mean free path of electrons. The thermal conductivity from phonons can be expressed as

$$\kappa_g = \frac{1}{3} c_g v l_g ,$$

where v is the velocity of sound and l_g is the mean free path of phonons. For simplicity, we assume that there is one electron per atom. For $N = N_A$, the number of electrons is N_A. Then the specific heat from lattice and electrons can be expressed as

$$C_g = 9N_A k_B \left(\frac{T}{\theta}\right)^3 \int_0^{\Theta/T} \frac{x^4 e^x}{\left(e^x - 1\right)^2} dx$$
$$\approx 9N_A k_B \left(\frac{T}{\theta}\right)^3 \int_0^{\Theta/T} x^2 dx = 3N_A k_B = 3R$$

$$C_e = \frac{\pi^2 N_A k_B}{2\varepsilon_F} T = R \frac{\pi^2}{2} \frac{T_0}{T_F}$$

at high temperatures (such as room temperature $T_0 = 300$ K). The ratio of κ_e to κ_g is obtained as

$$\frac{\kappa_e}{\kappa_g} = \frac{c_e v_F l_e}{c_g v l_g} = \frac{R}{3R} \frac{\pi^2}{2} \frac{T_0}{T_F} \frac{v_F}{v} \frac{l_e}{l_g} = \frac{\pi^2}{6} \frac{T_0}{T_F} \frac{v_F}{v} \frac{l_e}{l_g}$$

For Na, $T_F = 3.75 \times 10^4$ K, $v_F = 1.07 \times 10^8$ cm/s and $l_e = 350$ Å. The velocity of phonon is v is on the order of 10^5 cm/s and l_g is typically on the order of 40 Å. The we have

$$\frac{\kappa_e}{\kappa_g} \approx \frac{T_0}{T_F} \frac{v_F}{v} \frac{l_e}{l_g} = \frac{300}{3.75 \times 10^4} \frac{1.07 \times 10^8}{10^5} \frac{350}{40} = 75$$

In other words, in metal the conduction electrons mainly contribute to the heat conduction.