The electronic properties of metals

- What is a metal, anyway?
- A metal conducts electricity (but some non-metals also do).
- A metal is opaque and looks shiny (but some non-metals also do).
- A metal conducts heat well (but some non-metals also do).

We will come up with a reasonable definition!

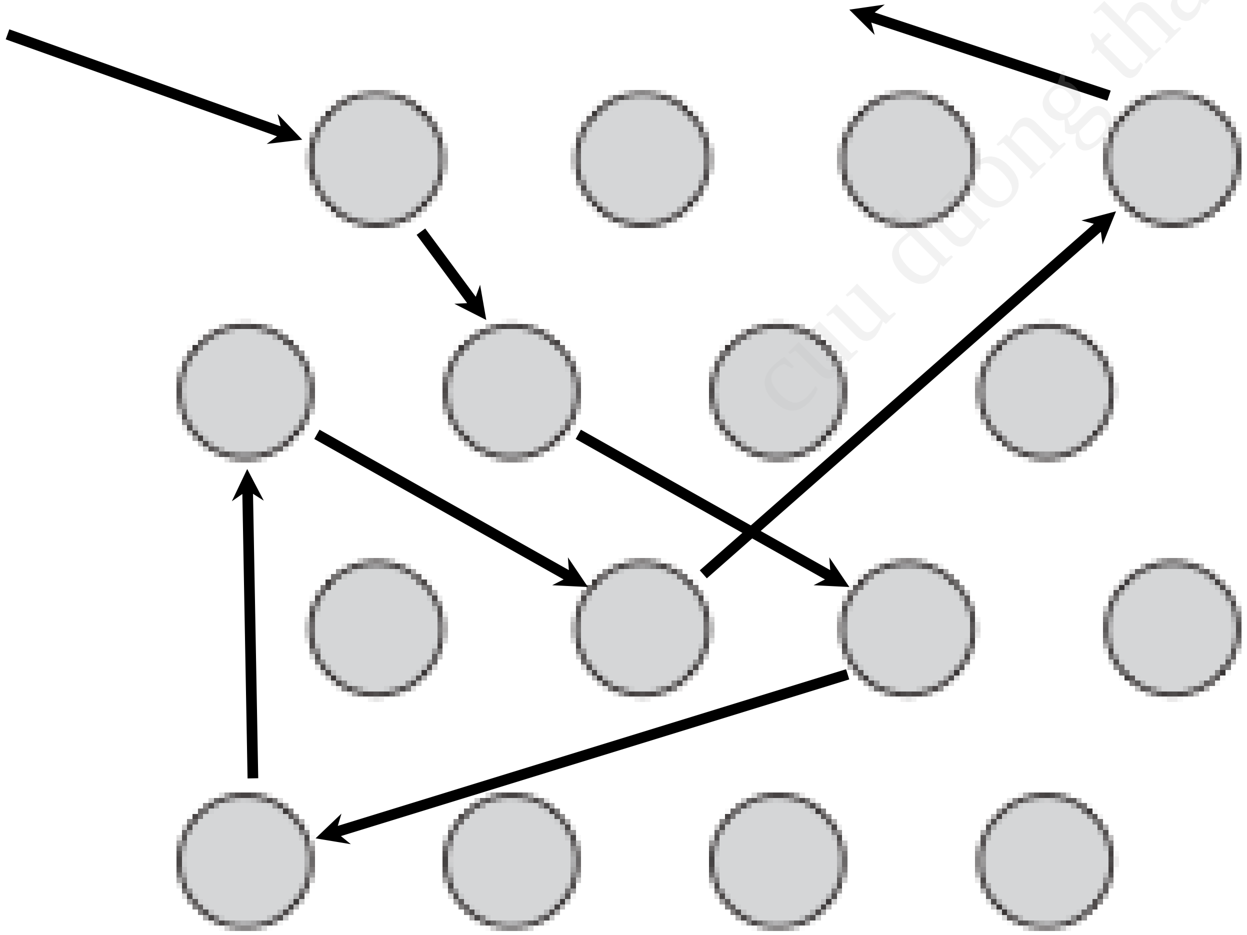
Electrical properties of metals: Classical approach (Drude theory)

at the end of this lecture you should understand....

- Basic assumptions of the classical theory
- DC electrical conductivity in the Drude model
- Hall effect
- Plasma resonance / why do metals look shiny?
- thermal conduction / Wiedemann-Franz law
- Shortcomings of the Drude model: heat capacity...

Drude's classical theory

- Theory by Paul Drude in 1900, only three years after the electron was discovered.
- Drude treated the (free) electrons as a classical ideal gas but the electrons should collide with the stationary ions, not with each other.



average rms speed

$$\frac{1}{2}mv_t^2 = \frac{3}{2}k_BT$$

$$v_t = \sqrt{\frac{3k_BT}{m}}$$

so at room temp.

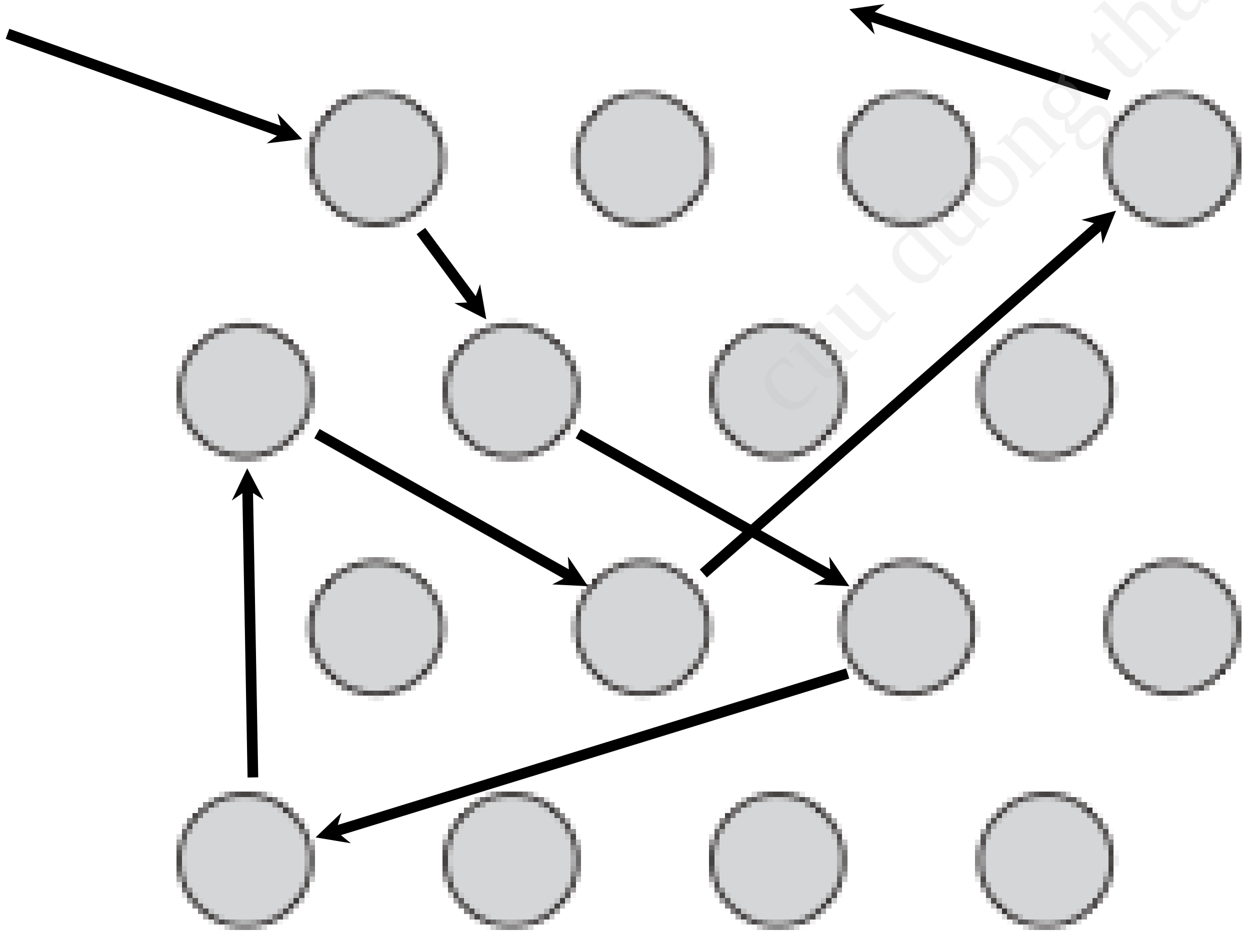
$$v_t \approx 10^5 \mathrm{ms}^{-1}$$

Drude's classical theory

relaxation time τ

(average time between scattering events)

mean free path $\lambda = \tau v_t$



$\lambda \approx 1\text{nm}$

$v_t \approx 10^5 \text{ms}^{-1}$

$\tau \approx 1 \times 10^{-14}$ s

Conduction electron Density *n*

#atoms per volume

calculate as $Z_V \rho_m / A$

#valence electrons per atom

density

atomic mass

metal	Z_V	$n(10^{28}\ \mathrm{m}^{-3})$
Li	1	4.7
Na	1	2.65
K	1	1.4
Rb	1	1.15
Cs	1	0.91
Cu	1	8.47
Ag	1	5.86
Au	1	5.9
Be	2	24.7
Mg	2	8.61
Ba	2	3.15
Fe	2	17
Al	3	18.1
Pb	4	13.2
Sb	5	16.5
Bi	5	14.1

...this must surely be wrong....

- The electrons should strongly interact with each other. Why don't they?
- The electrons should strongly interact with the lattice ions. Why don't they?
- Using classical statistics for the electrons cannot be right. This is easy to see:

condition for using classical statistics

$\lambda \ll l$ $\qquad$ l is some Å

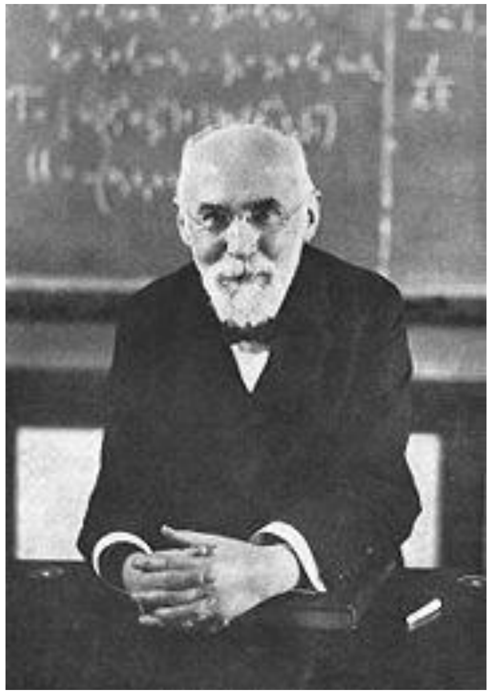
de Broglie wavelength of an electron:

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE_{tr}}} = \frac{h}{\sqrt{2m\frac{3}{2}k_B T}}$$ for room T $\lambda \approx 6 \times 10^{-9}\mathrm{m}$

but:

In a theory which gives results like this, there must certainly be a great deal of truth.

Hendrik Antoon Lorentz



So what are these results?

Drude theory: electrical conductivity

we apply an electric field. The equation of motion is

$$m_e \frac{d\mathbf{v}}{dt} = -e\boldsymbol{\mathcal{E}}$$

integration gives

$$\mathbf{v}(t) = \frac{-e\boldsymbol{\mathcal{E}}t}{m_e}$$

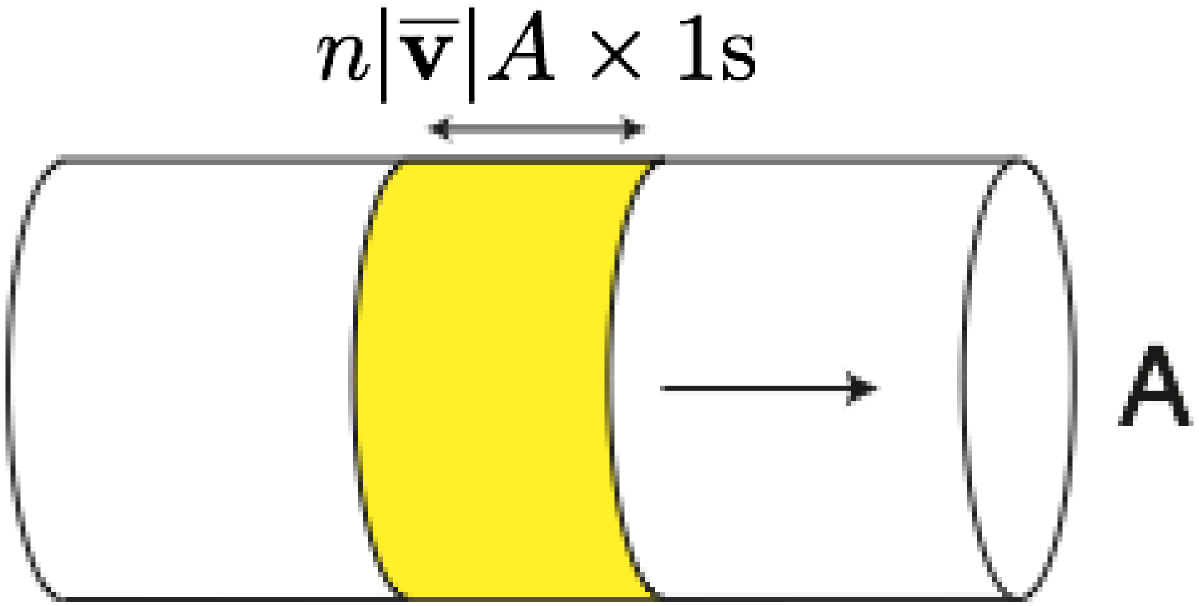
and if τ is the average time between collisions then the average drift speed is

$$\bar{\mathbf{v}} = \frac{-e\boldsymbol{\mathcal{E}}\tau}{m_e}$$

for $\mathcal{E} \approx 10\mathrm{Vm}^{-1}$ we get $\bar{v} = 10^{-2}\mathrm{ms}^{-1}$

remember: $v_t = 10^5\mathrm{ms}^{-1}$

Drude theory: electrical conductivity



number of electrons passing in unit time

$$n|\overline{\mathbf{v}}|A$$

current of negatively charged electrons

$$-en|\overline{\mathbf{v}}|A$$

current density

$$\mathbf{j} = n\overline{\mathbf{v}}(-e)$$

and with $\overline{\mathbf{v}} = \frac{-e\mathcal{E}\tau}{m_e}$ we get

Ohm's law

$$\mathbf{j} = \frac{ne^2\tau}{m_e}\mathcal{E}$$

Drude theory: electrical conductivity

Ohm's law

$$\mathbf{j} = \frac{ne^2\tau}{m_e}\mathcal{E}$$

$$\mathbf{j} = \sigma\mathcal{E} = \frac{\mathcal{E}}{\rho}$$

and we can define the conductivity

$$\sigma = \frac{ne^2\tau}{m_e} = n\mu e$$

and the resistivity

$$\rho = \frac{m_e}{ne^2\tau} = \frac{1}{n\mu e}$$

and the mobility

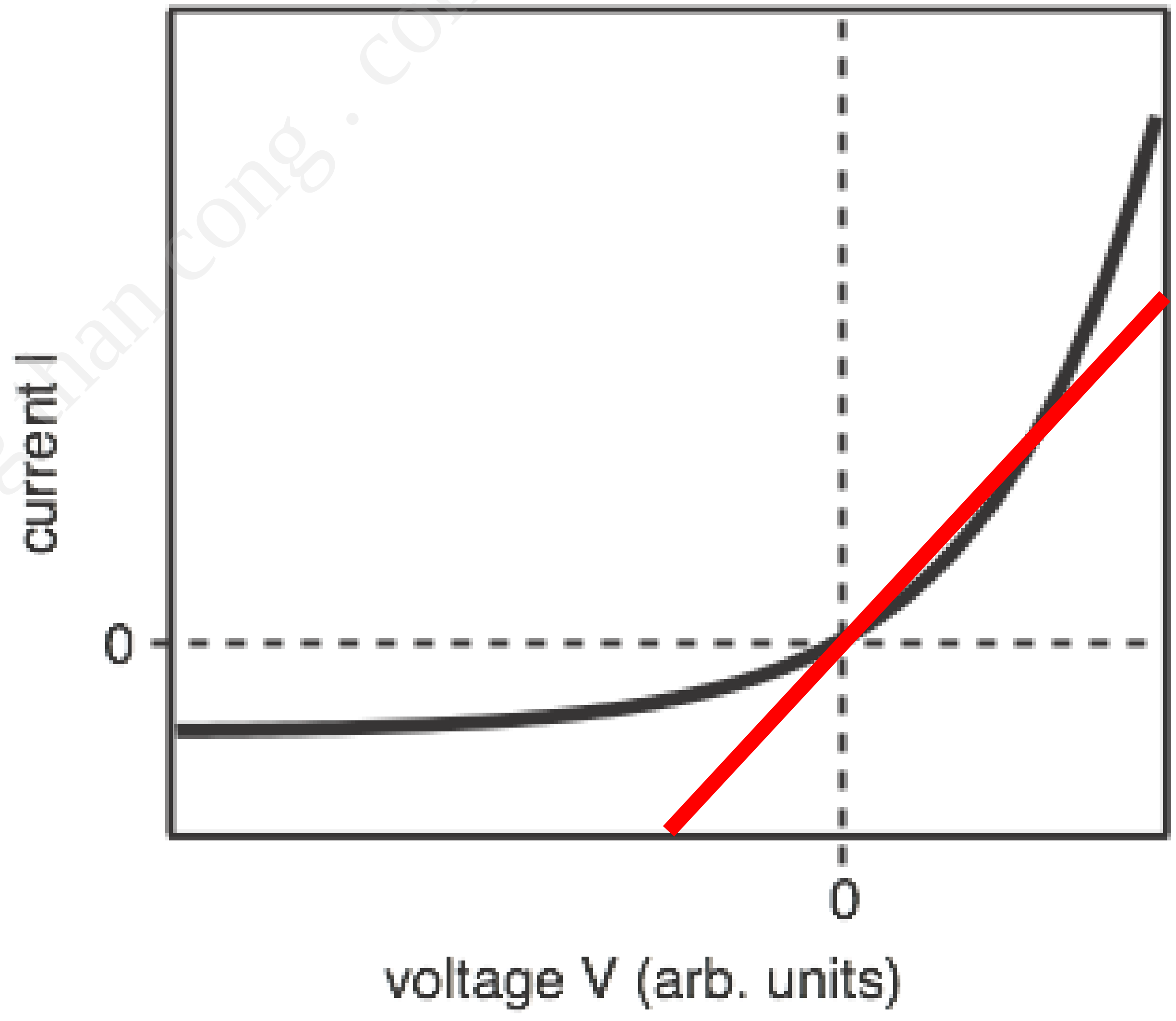
$$\mu = \frac{e\tau}{m_e}$$

$$|\mathbf{v}| = \mu|\mathcal{E}|$$

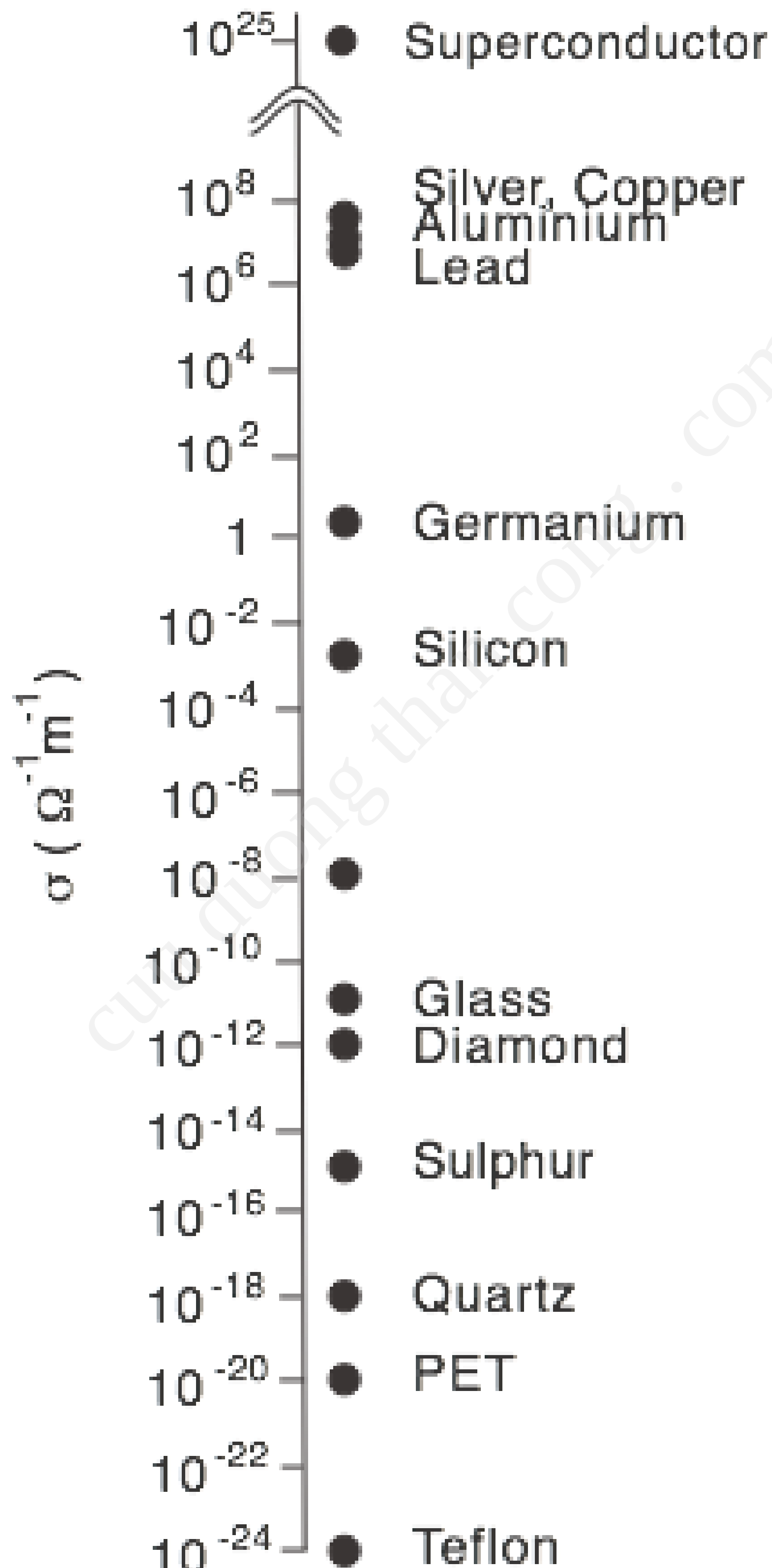
Ohm's law

$$\mathbf{j} = \frac{ne^2\tau}{m_e}\boldsymbol{\mathcal{E}}$$

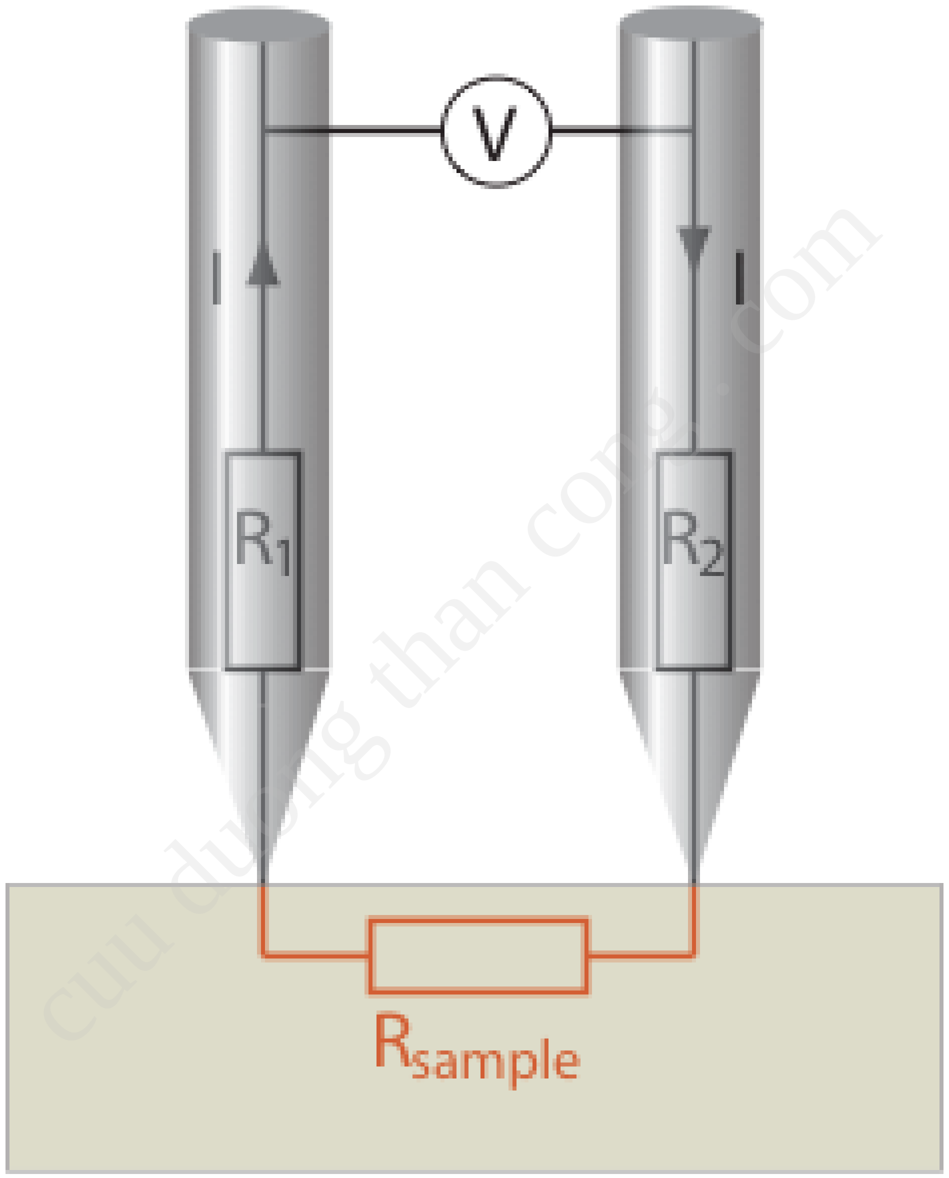
- valid for metals
- valid for homogeneous semiconductors
- not valid for inhomogeneous semiconductors
- not valid for metal contacts to semiconductors



Electrical conductivity of materials

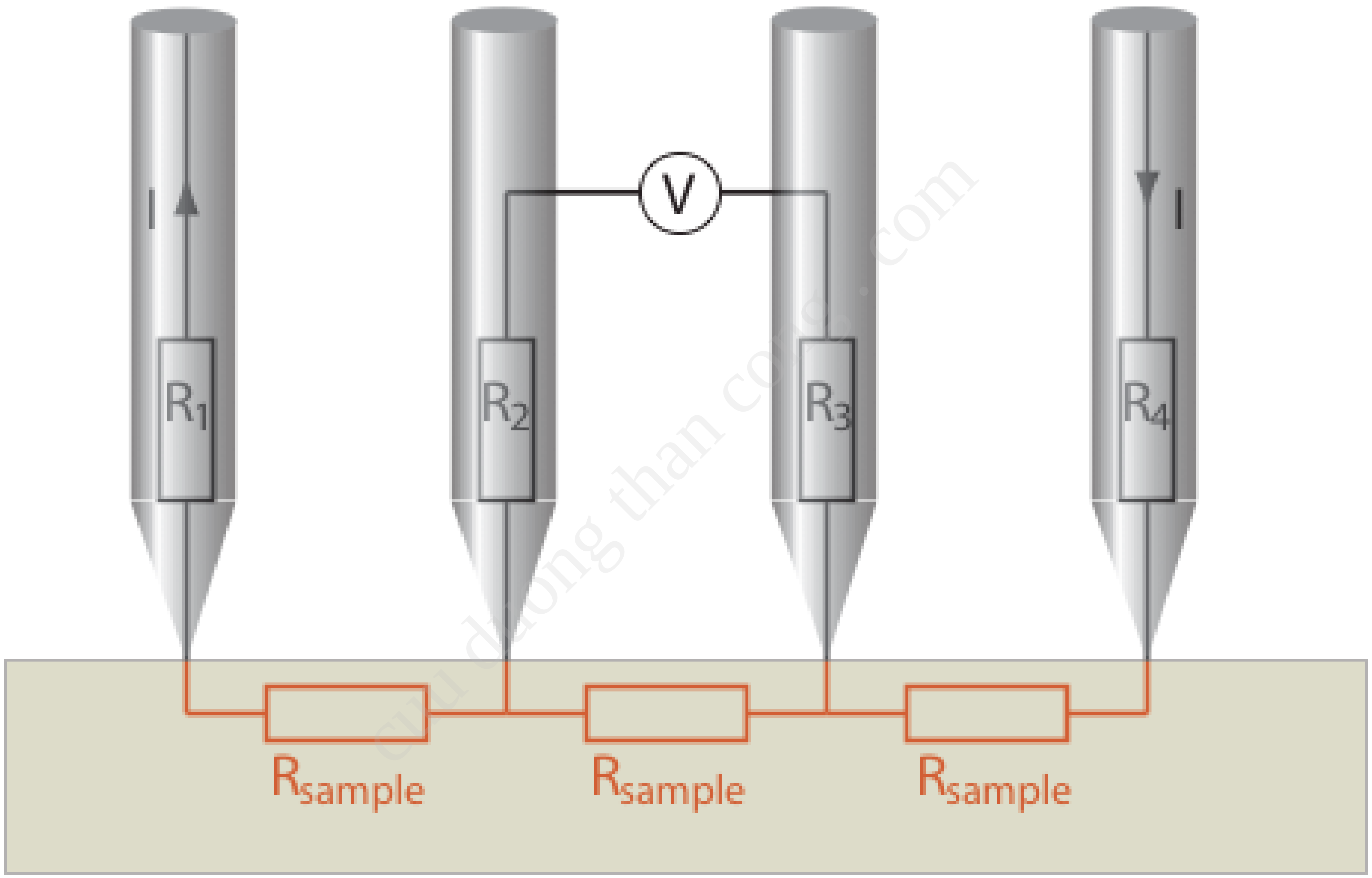


How to measure the conductivity / resistivity



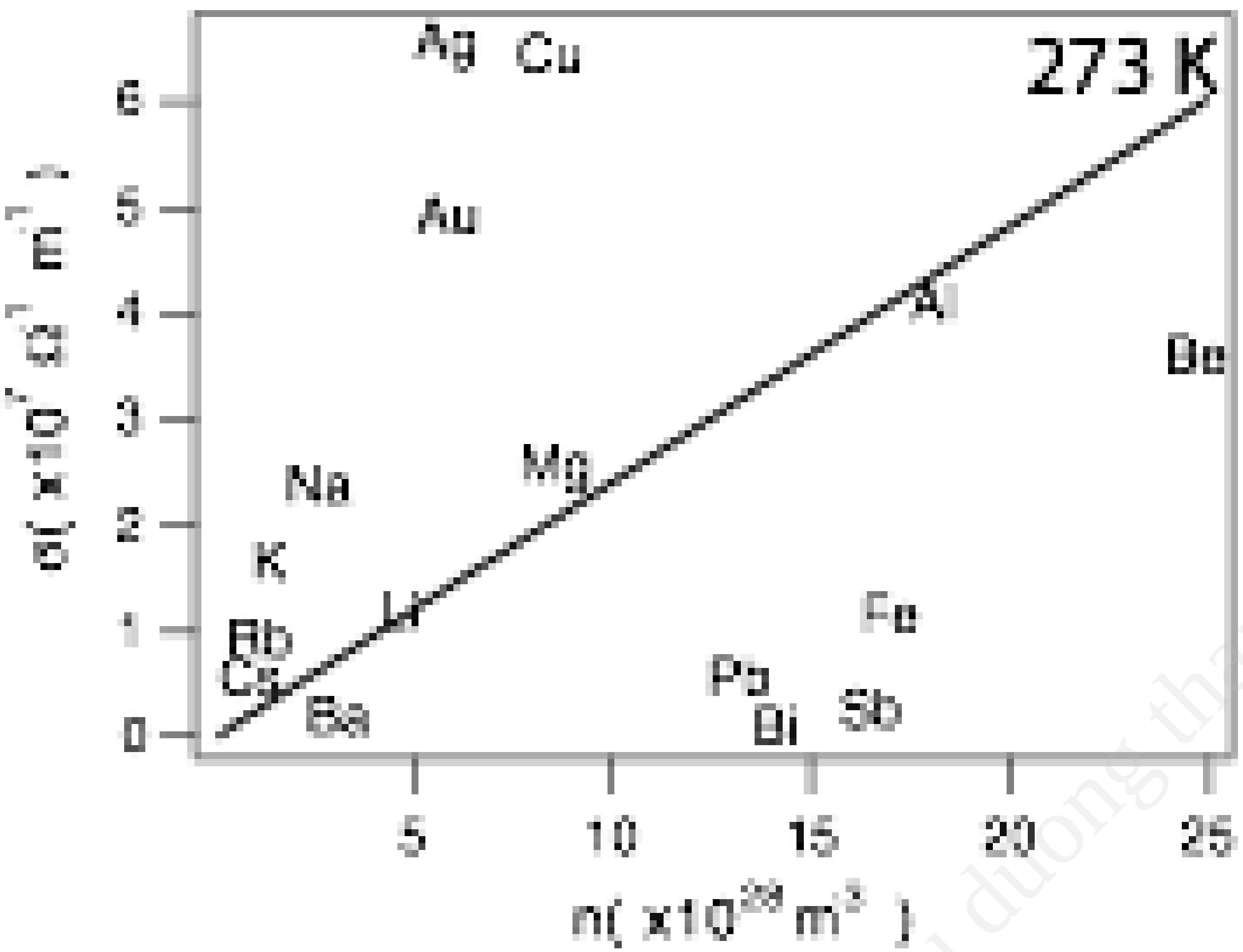
- A two-point probe can be used but the contact or wire resistance can be a problem, especially if the sample has a small resistivity.

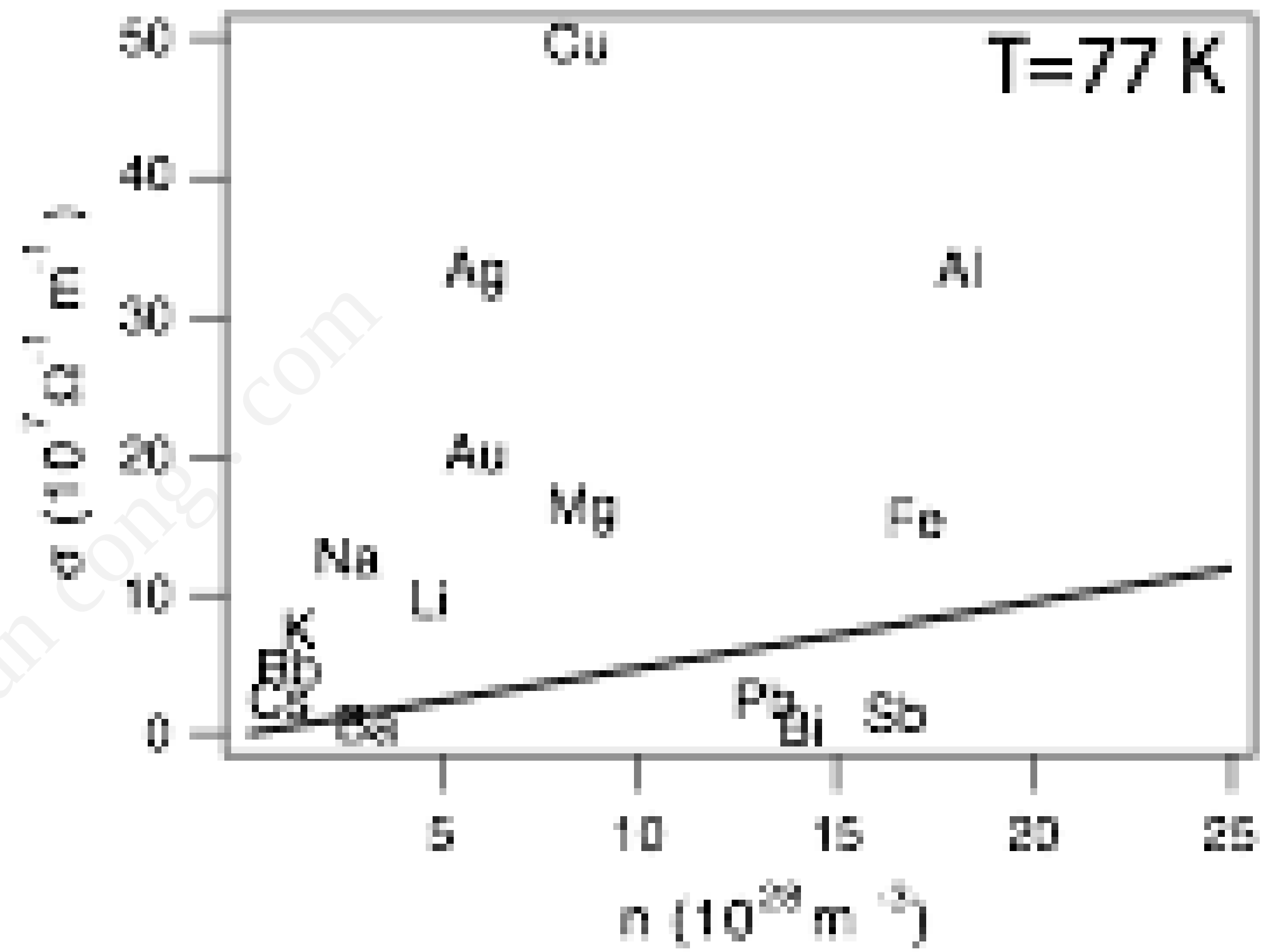
How to measure the conductivity / resistivity



- The problem of contact resistance can be overcome by using a four point probe.

Drude theory: electrical conductivity





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

line

$$\lambda \approx 1\text{nm}$$

$$\tau = \lambda / v_t$$

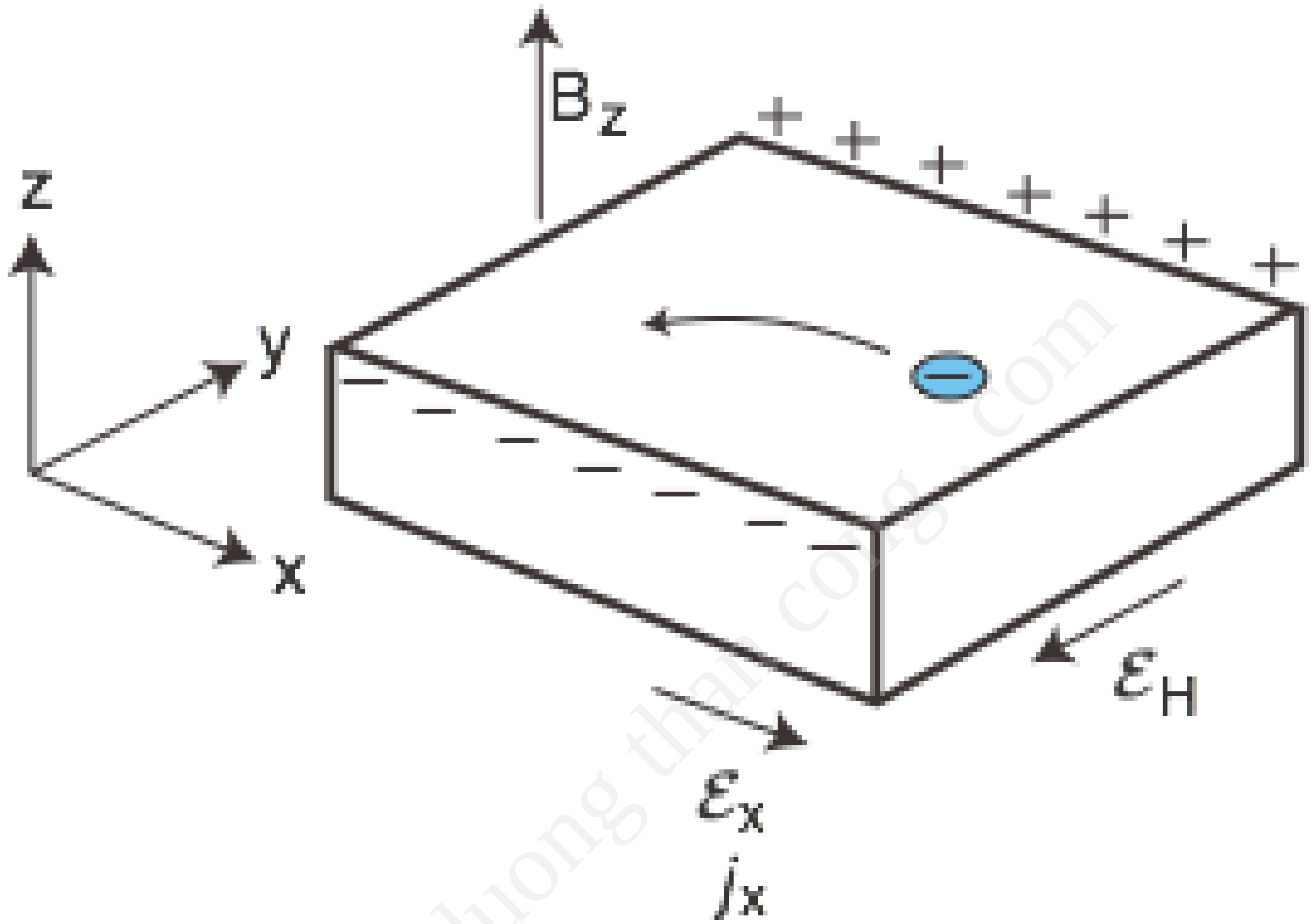
$$\frac{1}{2}mv_t^2 = \frac{3}{2}k_B T$$

$$v_t = \sqrt{\frac{3k_B T}{m}}$$

Drude theory: electrical conductivity

- Drude's theory gives a reasonable picture for the phenomenon of resistance.
- Drude's theory gives qualitatively Ohm's law (linear relation between electric field and current density).
- It also gives reasonable quantitative values, at least at room temperature.

The Hall Effect

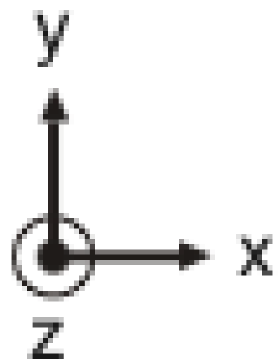


- Accumulation of charge leads to Hall field E_H.
- Hall field proportional to current density and B field

$$\mathcal{E}_H = R_H j_x B_z$$

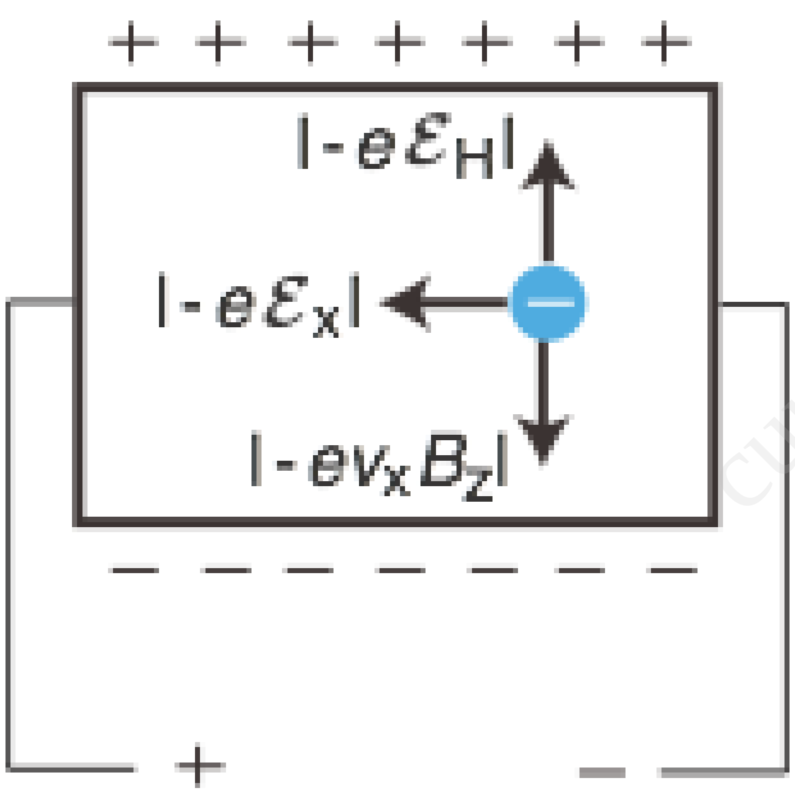
R_H is called Hall coefficient

The Hall coefficient



$$\mathbf{F} = -e\mathbf{v} \times \mathbf{B}$$

$$\mathbf{F} = -e\mathcal{E}_H$$



$$e\mathcal{E}_H = eB_z v_x$$

and definition $\mathcal{E}_H = R_H j_x B_z$

for the steady state we get

$$R_H = \frac{\mathcal{E}_H}{j_x B_z} = \frac{\mathcal{E}_H}{-env_x B_z}$$

$$= \frac{v_x B_z}{-env_x B_z} = \frac{-1}{ne}$$

electron density form Ohm's law? $\mathbf{j} = \frac{ne^2\tau}{m_e}\mathcal{E}$

The Hall coefficient

metal	measured R_H in units of $-1/ne$
Li	0.8
Na	1.2
K	1.1
Rb	1.0
Cs	0.9
Cu	1.5
Ag	1.3
Au	1.5
Be	-0.2
Mg	-0.4
Al	-0.3
Bi	38,923

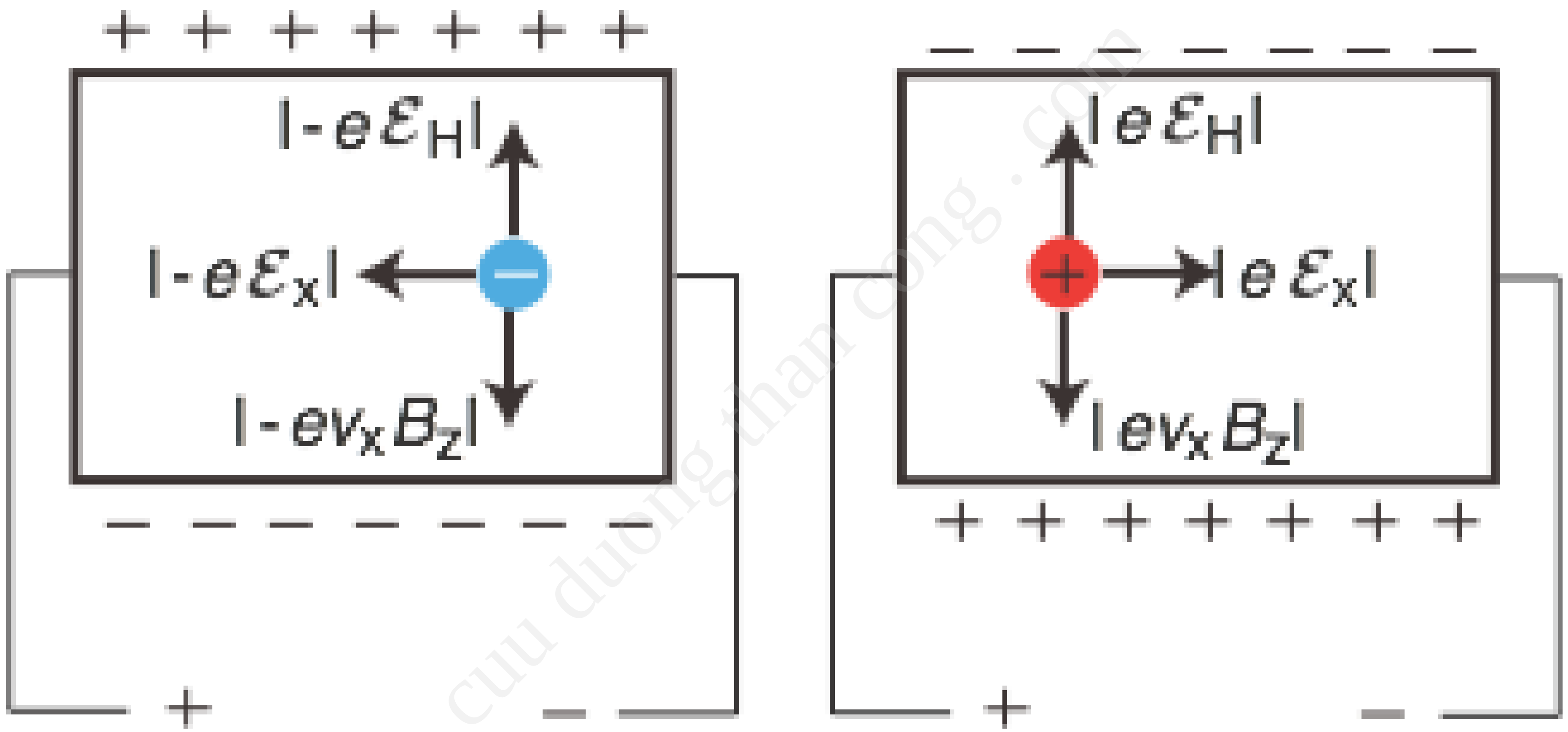
Ohm's law contains e^2

$$\mathbf{j} = \frac{ne^2\tau}{m_e}\boldsymbol{\mathcal{E}}$$

But for R_H the sign of e is important.

$$R_H = \frac{vB_z}{-envB_z} = \frac{-1}{ne}$$

What would happen for positively charged carriers?



$$R_H = \frac{-1}{ne}$$

$$R_H = \frac{1}{pe}$$

Drude theory: why are metals shiny?

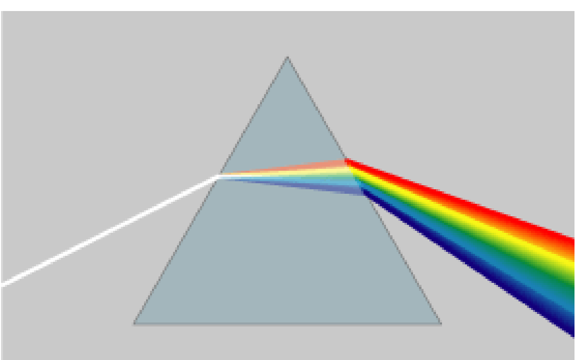
- Drude's theory gives an explanation of why metals do not transmit light and rather reflect it.

Some relations from basic optics wave propagation in matter

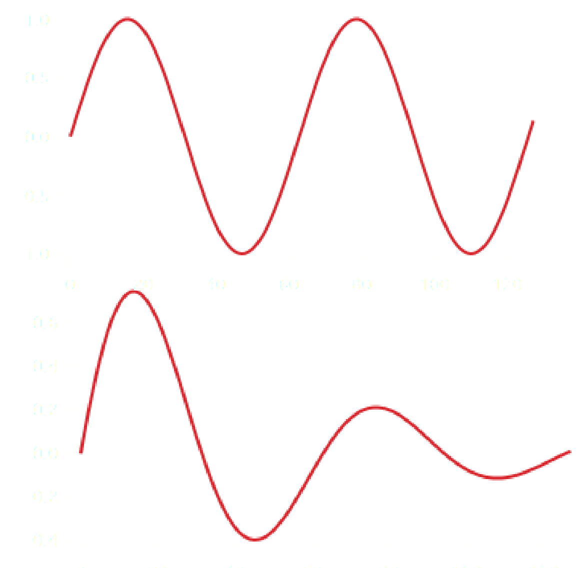
plane wave $$\mathcal{E}(z,t) = \mathcal{E}_0 e^{i(kz-\omega t)}$$

$$k = \frac{2\pi N}{\lambda_0}$$

complex index of refraction $$N = n + i\kappa$$



$$\mathcal{E}(z,t) = \mathcal{E}_0 e^{i\left(\frac{2\pi n}{\lambda_0} z - \omega t\right)} e^{-\frac{2\pi\kappa}{\lambda_0} z}$$



$$N = N(\omega)$$

Maxwell relation $$N = \sqrt{\epsilon} = \sqrt{\epsilon_r + i\epsilon_i}$$

$$\mathcal{E}(z,t) = \mathcal{E}_0 e^{i((2\pi N/\lambda_0)z - \omega t)} = \mathcal{E}_0 e^{i((\omega\sqrt{\epsilon}/c)z - \omega t)}$$

all the interesting physics in in the dielectric function!

Free-electron dielectric function

one electron in time-dependent field

$$m_e \frac{d^2x(t)}{dt^2} = -e\mathcal{E}_0 e^{-i\omega t}$$

Ansatz

$$x(t) = Ae^{-i\omega t}$$

and get

$$A = \frac{e\mathcal{E}_0}{m_e \omega^2}$$

the dipole moment for one electron is

$$P(t) = -ex(t)$$

and for a unit volume of solid it is

$$P(t) = -nex(t) = -neAe^{-i\omega t} = -\frac{ne^2\mathcal{E}_0 e^{-i\omega t}}{m_e\omega^2}$$

Free-electron dielectric function

$$P(t) = -\frac{ne^2\mathcal{E}_0 e^{-i\omega t}}{m_e\omega^2}$$

we use

$$D = \epsilon\epsilon_0\mathcal{E} = \epsilon_0\mathcal{E} + P$$

to get

$$\epsilon = 1 + \frac{P(t)}{\epsilon_0\mathcal{E}_0 e^{-i\omega t}}$$

so the final result is

$$\epsilon = 1 - \frac{ne^2}{\epsilon_0 m_e\omega^2} = 1 - \frac{\omega_P^2}{\omega^2}$$

$$\omega_P^2 = \frac{ne^2}{m_e\epsilon_0}$$

is called the plasma frequency

Meaning of the plasma frequency

the dielectric function in the Drude model is

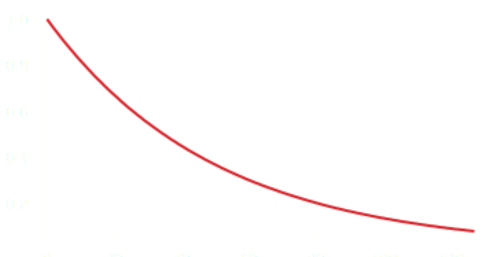
$$\epsilon(\omega) = (1 - \frac{\omega_P^2}{\omega^2})$$

with

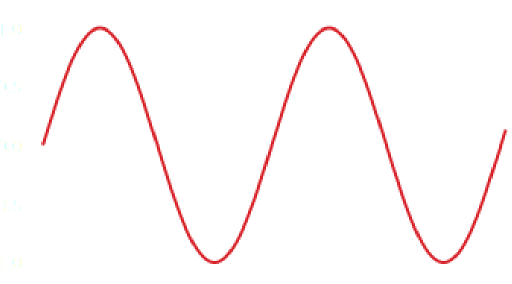
$$\omega_P^2 = \frac{ne^2}{m_e \epsilon_0}$$

remember

$$\mathcal{E}(z,t) = \mathcal{E}_0 e^{i((\omega\sqrt{\epsilon}/c)z - \omega t)}$$

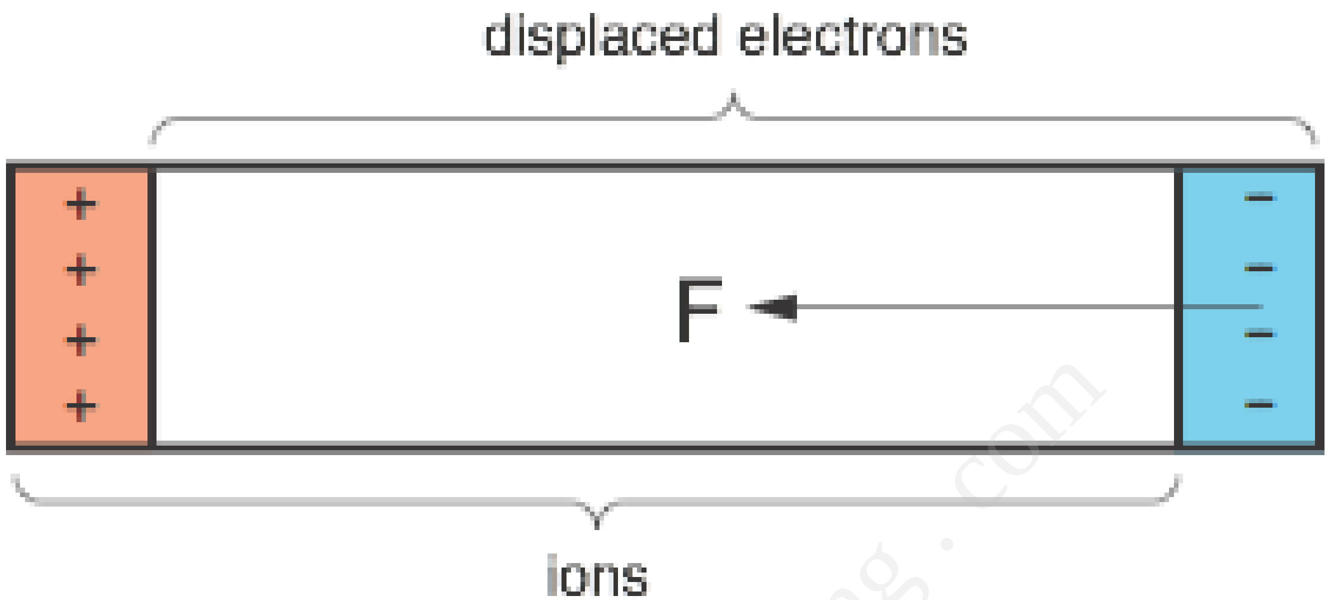


$\omega < \omega_P$ ε real and negative, no wave propagation
metal is opaque



$\omega > \omega_P$ ε real and positive, propagating waves
metal is transparent

plasma frequency: simple interpretation



$$\omega_P = \sqrt{\frac{ne^2}{m_e \epsilon_0}}$$

values for the plasma energy $\hbar\omega_P$

	measured	calculated
K	3.72 eV	4.29 eV
Mg	10.6 eV	10.9 eV
Al	15.3 eV	15.8 eV
Si	16.6 eV	16.0 eV
Ge	16.2 eV	16.0 eV

- longitudinal collective mode of the whole electron gas

the Wiedemann-Franz law

$$\frac{\kappa}{\sigma} = constant$$

$$\frac{\kappa}{\sigma} = LT$$

- Wiedemann and Franz found in 1853 that the ratio of thermal and electrical conductivity for ALL METALS is constant at a given temperature (for room temperature and above). Later it was found by L. Lorenz that this constant is proportional to the temperature.
- Let's try to reproduce the linear behaviour and to calculate L here.

The Wiedemann Franz law

estimated thermal conductivity
(from a classical ideal gas)

$$\kappa = \frac{1}{3} v_t^2 \tau c_v$$

$$\frac{\kappa}{\sigma} = \frac{3}{2}\frac{k_B^2}{e^2} T = LT$$

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

the actual quantum mechanical result is

$$\frac{\kappa}{\sigma} = \frac{\pi^2}{3}\frac{k_B^2}{e^2} T = LT$$

this is 3, more or less....

Comparison of the Lorenz number to experimental data

at 273 K

metal	10^{-8} Watt Ω K^{-2}
Ag	2.31
Au	2.35
Cd	2.42
Cu	2.23
Mo	2.61
Pb	2.47
Pt	2.51
Sn	2.52
W	3.04
Zn	2.31

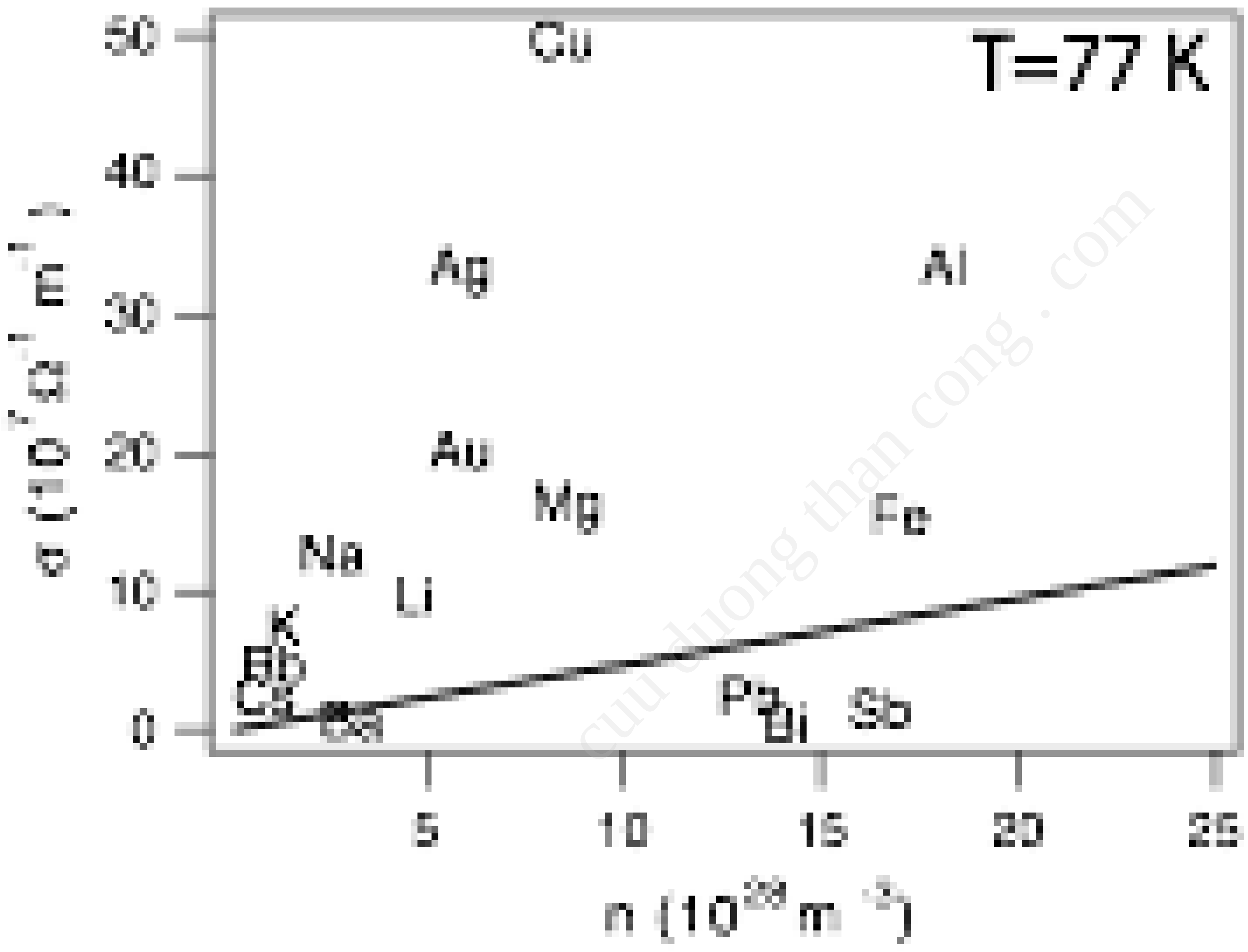
$$\frac{\kappa}{\sigma} = \frac{\pi^2}{3}\frac{k_B^2}{e^2}T = LT$$

L = 2.45 10^{-8} Watt Ω K^{-2}

Failures of the Drude model

- Despite of this and many other correct predictions, there are some serious problems with the Drude model.

Drude theory: electrical conductivity



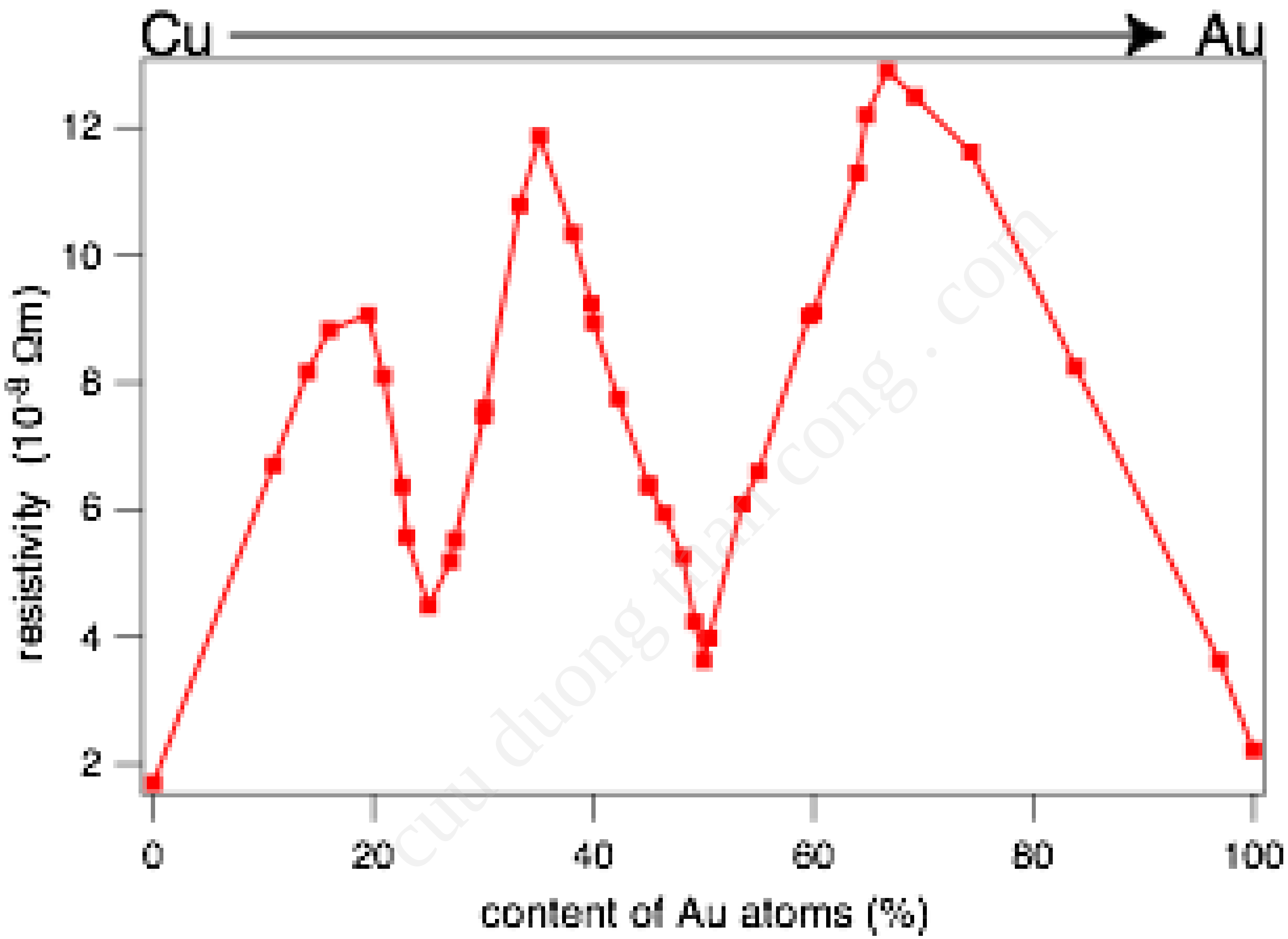
line

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

$$\lambda \approx 1\text{nm}$$

$$\lambda = \tau v_t$$

Failures of the Drude model: electrical conductivity of an alloy



- The resistivity of an alloy should be between those of its components, or at least similar to them.
- It can be much higher than that of either component.

Failures of the Drude model: heat capacity

consider the classical energy for one mole of solid in a heat bath: each degree of freedom contributes with $\frac{1}{2}k_B T$

	energy	heat capacity
monovalent	$3 \times \frac{1}{2}N_{\rm A}k_{\rm B}T + 6 \times \frac{1}{2}N_{\rm A}k_{\rm B}T = \frac{9}{2}N_{\rm A}k_{\rm B}T$	$\frac{9}{2}N_{\rm A}k_{\rm B}$
divalent	$6 \times \frac{1}{2}N_{\rm A}k_{\rm B}T + 6 \times \frac{1}{2}N_{\rm A}k_{\rm B}T = 6N_{\rm A}k_{\rm B}T$	$6N_{\rm A}k_{\rm B}$
trivalent	$9 \times \frac{1}{2}N_{\rm A}k_{\rm B}T + 6 \times \frac{1}{2}N_{\rm A}k_{\rm B}T = \frac{15}{2}N_{\rm A}k_{\rm B}T$	$\frac{15}{2}N_{\rm A}k_{\rm B}$

el. transl. ions vib.

- Experimentally, one finds a value of about $3N_{\rm A}k_{\rm B}$ at room temperature, independent of the number of valence electrons (rule of Dulong and Petit), as if the electrons do not contribute at all.

Many open questions:

- Why does the Drude model work so relatively well when many of its assumptions seem so wrong? In particular, the electrons don't seem to be scattered by each other. Why?
- How do the electrons sneak by the atoms of the lattice?
- Why do the electrons not seem to contribute to the heat capacity?
- Why is the resistance of an disordered alloy so high?