# 2. Drude theory

A Kinetic theory of electrons in a metal explains several results

- Ohm's law

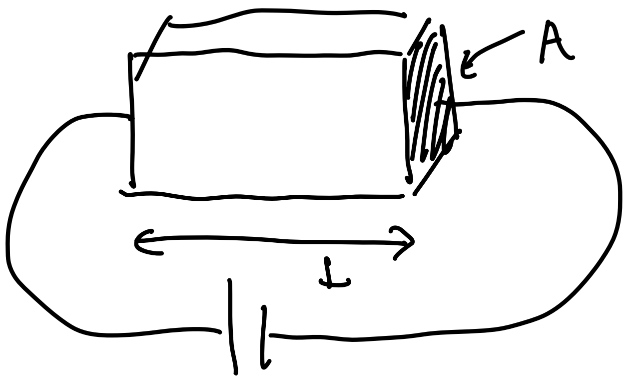
$V = IR \qquad V = EL \qquad I = JA$

electric field

current density

length

area



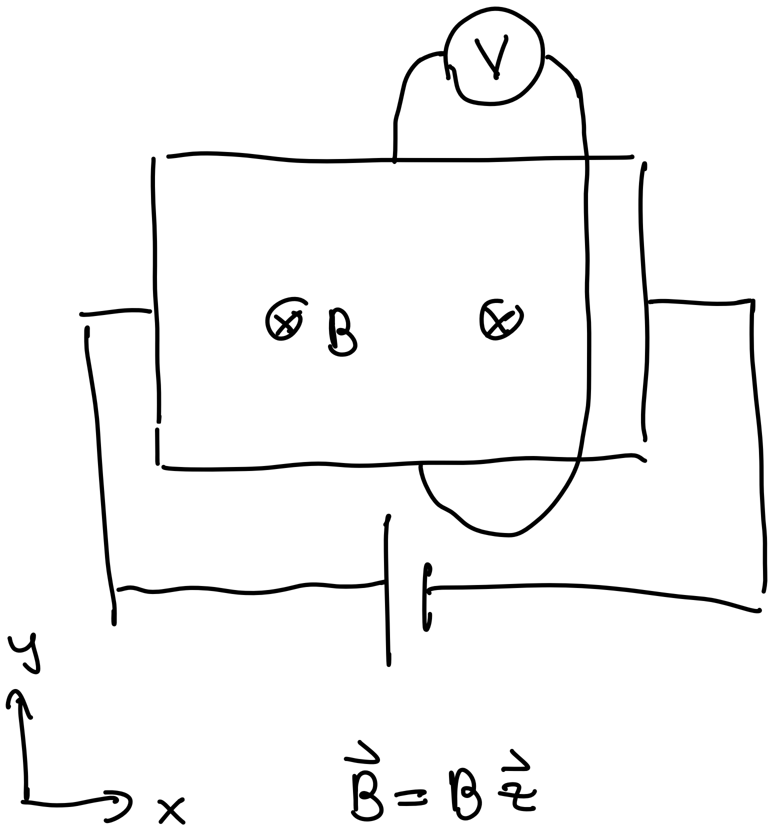

$EL = JAR$

$\therefore J = \frac{L}{AR} E = \sigma E \qquad \sigma = \frac{1}{\rho} = \frac{L}{AR}$

conductivity

resistivity

- Hall Effect (2D Metal in B field)




$\vec{B} = B\hat{z}$

$E_y \propto J_x B_z$

$E_x$ independent of $B_z$

the surprise was these results taken together

it was known that a mag field placed a force on electrons

Hall's explanation: mag field → pushes electrons to one side → reduces effective area

– Weidemann Franz Law (Metals)

$$\vec{J} = \sigma \vec{E} \quad \text{and} \quad \vec{J}_q = -K \vec{\nabla} T$$

electrical current — heat current

$$\frac{K}{\sigma T} = \text{const.}$$

– Transparency:

$\omega \ll \omega_p$ metal opaque

$\omega \gg \omega_p$ metal transparent

– Universality – again these effects applied across wide range of material

2.1 <u>Drudes model</u>

– Following thompsons/maxwell/joule's success with gasses, and Boltzmann with solids Drude is motivated to develop a kinetic theory of electron

- Established via Electrolysis that one could, at reasonably low energies, remove integre # of electrons per atom

1) Atoms $\Longrightarrow$ Ions + Valence electrons

Z per atom

fixed in place

+ve charge

free to wander around

−ve charge

$$n = Z\, n_{ions}$$

- Now we know that

Ion = nucleus + core electrons

this was only established later by X-ray measurements

2) Independent electron approx

1. Electrons undergo free ballistic motion until

$$\frac{d\vec{p}}{dt} = \vec{F}_{Loretz} = q\left(\vec{E} + \vec{v} \times \vec{B}\right) \qquad q = -e$$

2. Electrons scatter with ions

- mean scattering time $\tau$

avg time between collision

- when they scatter their momentum resets to

$$\vec{p} \to 0$$

its sufficient to require that this happens on avg.

$\therefore$ On. avg in interval $dt$, a fraction $\frac{dt}{\tau}$ reset

$$\therefore \quad p(t+dt) = \underbrace{\left[1 - \frac{dt}{\tau}\right]\left[p(t) + F\,dt\right]}_{\text{dont scatter}} + \underbrace{\left[\frac{dt}{\tau}\right]}_{\text{scatter}} \cdot 0$$

expand both sides to $O(dt)$

$$\frac{d\vec{p}}{dt} = -e\left(\vec{E} + \frac{1}{m}\vec{p} \times \vec{B}\right) - \frac{\vec{p}}{\tau}$$

## 2.2 Ohms Law $(\vec{B}=0)$

Ingredients

- At eqm $\frac{d\vec{p}}{dt}=0$
- Current density $\vec{j}=qn\vec{v}$
  - $q$ carrer charge $(-e)$
  - $n$ carrier density

$$\vec{j}=qn\vec{v}=-\frac{en}{m}\vec{p}=-\frac{en}{m}\left(-e\tau\vec{E}\right)=\sigma_0\vec{E}$$

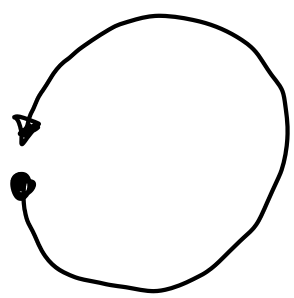
$$\boxed{\text{Drude Conductivity} \quad \sigma_0=\frac{e^2 n\tau}{m}}$$

2.3 <u>Hall Effect</u>

– Cyclotron frequency $\omega_c = \frac{eB}{m}$

for $E = 0$ $\tau = 0$

$$\frac{dp}{dt} = -\frac{e}{m}\,\vec{p} \times B$$



cyclotron motion

period $T = \frac{2\pi}{\omega_c}$

– Same with finite B ; $\frac{d\vec{p}}{dt} = 0$

$$0 = -eE_x - \omega_c p_y - \frac{p_x}{\tau}$$

$$0 = -eE_y + \omega_x p_x - \frac{p_y}{\tau}$$

$$\vec{p} = \frac{-e\tau}{1+(\omega_c\tau)^2}\begin{pmatrix} 1 & -\omega_c\tau \\ \omega_c\tau & 1 \end{pmatrix}\vec{E}$$

$$\therefore \vec{j} = \underbrace{\frac{\sigma_0}{1+\omega_c^2\tau^2}\begin{pmatrix} 1 & -\omega_c\tau \\ \omega_c\tau & 1 \end{pmatrix}}_{\sigma} \vec{E}$$

$\sigma_0$ = scalar $\quad$ $\sigma$ = matrix

similar form for resistivity

$$\vec{E} = \rho\,\vec{j} \quad \therefore \rho = \sigma^{-1} = \rho_0 \begin{pmatrix} 1 & \omega_c\tau \\ -\omega_c\tau & 1 \end{pmatrix}$$

$$\rho_0 = \sigma_0^{-1}$$

– In Hall expt there is no transverse current

Solve for $j_y = 0$

$$\therefore E_y = -\omega_c\tau E_x$$

matrix!

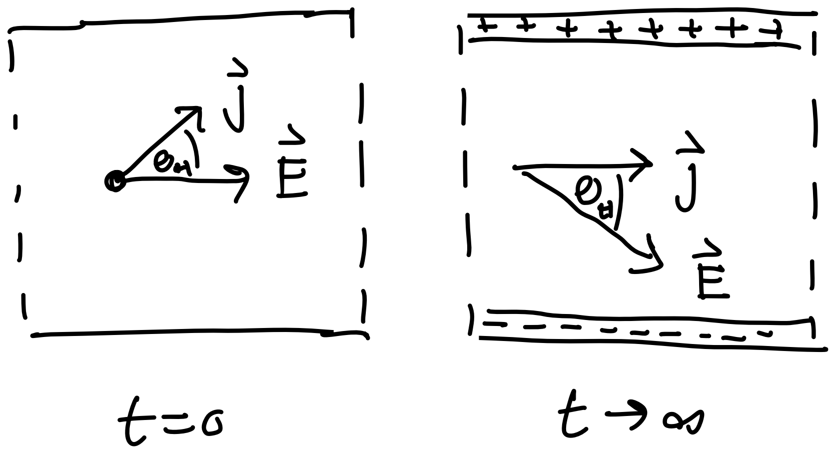
$$\therefore \vec{j} = \sigma \begin{pmatrix} E_x \\ -\omega_c\tau E_x \end{pmatrix} = \sigma_0 \begin{pmatrix} E_x \\ 0 \end{pmatrix}$$

$\dfrac{j_x}{E_x} = \sigma_0$ independent of B //

surprising — contradicts Hall's intuition

— where does $E_y$ come from

suppose B turned on at $t=0$




$\theta_H$ : hall angle $\tan\theta_H = \omega_c \tau$

— Hall Coefficient

note that $\rho$ and $\sigma$ both depend on $\tau$

we don't have an independent measure of that parameter — not so useful

$\rho, \sigma$ vary with $\tau \to$ no independent measurement of $\tau$

$$R_H = \frac{E_y}{j_x B_z} = -\frac{\omega_c \tau E_x}{j_x B_z}$$

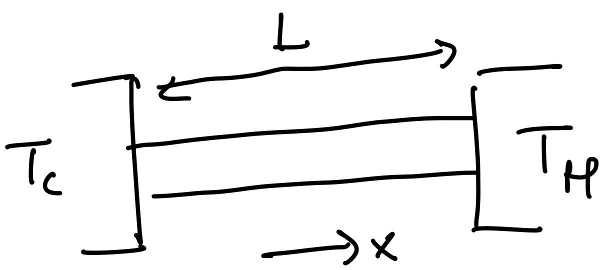
$$= -\frac{\omega_c \tau}{\sigma_0 B} = -\frac{\left(\frac{\cancel{e}\cancel{B}}{\cancel{m}}\right)\cancel{\tau}}{\left(\frac{e^2 n \cancel{\tau}}{\cancel{m}}\right)\cancel{B}}$$

$$= -\frac{1}{en} = -\frac{1}{eZn_{ions}}$$

independent of $\tau$!

## 2.4 Weidermann Franz law

Heat transport




$$= \frac{T_H - T_c}{L} = [K m^{-1}]$$

$$\vec{j}_q = -K \vec{\nabla} T = [J \cdot s^{-1} \cdot m^{-2}] = [W \cdot m^{-2}]$$

$\kappa = [W \cdot m^{-1} \cdot K^{-1}]$

ingredients

- $u(T)$ = avg. energy of electron @ temp $T$
- $T(x)$ be temp @ position $x$ → here we assume independent of $y, z$
- total heat current $j_q = j_L + j_R$

  - left movers
    - initial pos $x_0 = x - v_x \tau$
    - density $\frac{n}{2}$
    - energy $u(T(x_0))$
    - velocity $v_x$

$$\therefore \; j_L = \left(\frac{n}{2}\right) v_x \, u(T(x - v_x t))$$

density of left movers

velocity of left movers

energy carried by left movers

– right movers $V_x \to -V_x$

$$j_R = \left(\frac{n}{2}\right)(-V_x)\, u(T(x+V_x t))$$

$$j_q = j_L + j_R = n v_x^2 \tau \frac{du}{dT}\left(-\frac{dT}{dx}\right) = -K\frac{dT}{dx}$$

$$K = n v_x^2 \tau \frac{du}{dT} = n\left(\frac{k_B T}{m}\right)\tau\, c_{el} \quad //$$

generalising to generic $T(\vec{x})$

more generally – $\vec{J}_q = -K\vec{\nabla}T$

use that $c_{el} = \frac{3}{2}k_B$ ← $\frac{1}{2}k_B$ per mode

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

$$\frac{K}{\sigma T} = \frac{\frac{n\tau}{m}\cdot k_B T \cdot c_{el}}{\frac{ne^2\tau}{m}\cdot T} = \frac{k_B c_{el}}{e^2} = \frac{3}{2}\left(\frac{k_B}{e}\right)^2$$

intuition – electrons carry both the charge and the current

→ two independently measurable quantities

→ electric current response to voltage

→ heat current response to thermal gradient

Implication

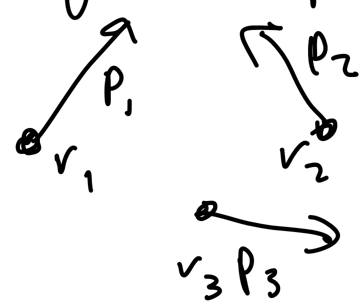
→ Same mobile carriers responsible for $\vec{j}$ and $\vec{J_q}$

→ Both processes limited by same scattering time.

## 2.5 Thermo Electric transport

- Lorentz Electron gas
- Transport coefficients

Consider a system of classical electrons




$$\frac{d\vec{r}_i}{dt} = \vec{V}(r_i, p_i) \overset{\text{here}}{=} \frac{p_i}{m}$$

$$\frac{d\vec{p}_i}{dt} = \vec{F}(r_i, p_i) \overset{\text{here}}{=} -e\vec{E}$$

- Distribution function : central object of theory

$$f(\vec{r}, \vec{p}) = \sum_{n=1}^{N} \delta(\vec{r} - \vec{r}_n)\,\delta(\vec{p} - \vec{p}_n)$$

average, not a vector!

$$\frac{1}{V}\int d^3r \int d^3p\, f(r,p) = \bar{n}$$ density of particles

$$\frac{1}{V}\int d^3r\, f(r,p) = f(p)$$ momentum distribution

$$\int d^3p\, f(r,p) = n(r)$$ particle density at $r$

we will only consider $n(r)=\bar{n}$ unifor distributions due to coulomb

observables then described by integrals

$$\underbrace{\vec{j}(r)}_{\text{current density at } \vec{r}} = \int d^3p\, f(\vec{r},\vec{p}) \underbrace{\left(-\frac{e\vec{p}}{m}\right)}_{\text{current per particle}}$$

## Equilbrium

external potential

- For Drude electrons $V(r) = 0$

$$\text{Eqm state} = f_0(\vec{r}, \vec{p}) = \frac{\bar{n}\, e^{-\beta \epsilon_p}}{(2\pi k m T)^{3/2}} \qquad \epsilon_p = \frac{p^2}{2m}$$

## Dynamics

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \sum_n \Big[ \underbrace{-\frac{d\vec{r}_n}{dt} \cdot \nabla_r \delta(\vec{r} - \vec{r}_n)}\, \delta(\vec{p} - \vec{p}_n) + (\vec{r} \leftrightarrow \vec{p}) \Big]$$

$$= \vec{V}(\vec{r}_n, \vec{p}_n) \cdot \vec{\nabla}_r \delta(\cdots$$

$$= \vec{V}(\vec{r}, \vec{p}) \cdot \vec{\nabla}_r \delta(\cdots$$

$$\underbrace{\left( \frac{d}{dt} + \vec{V} \cdot \vec{\nabla}_r + \vec{F} \cdot \nabla_p \right) f}_{\text{Free propagation}} = \underbrace{\frac{\partial f}{\partial t}}_{\text{collisions}} \Big|_{\text{collisions}}$$

## Collision term

1. Only ion-electron $\Longrightarrow$ linear in $f$

2. Change $p$ only $\Longrightarrow$ $\Delta r = 0$

3. uniform in space $\Rightarrow$ $\vec{r}$ - independent process
(on macroscopic scales)

4. Detailed balance

$$\therefore (r, p) \rightarrow (r, q) \text{ with rate } W_{p\to q}\, dt$$

$$\frac{W_{p\to q}}{W_{q\to p}} = e^{-\beta(\epsilon_q - \epsilon_p)} \qquad \epsilon_p = \frac{p^2}{2m}$$

$$\left.\frac{\partial f(r,p)}{\partial t}\right|_{\text{collisions}} = \int d^3q \left[ f(r,q)\, W_{q\to p} - f(r,p)\, W_{p\to q} \right]$$

Simplifying: Single relaxation time approx

$$W_{p\to q} = \frac{f_0(r,q)}{n\tau}$$

↳ straightforwardly satisfies detailed balance

# Transport via Linear response

Current response to an external force

eg $\quad j = \sigma E \qquad j_q = K \nabla T$

Response

- Electric current

$$j_{el} = -e v \quad \text{per electron}$$

- Heat current

momentum of this electron

$$j_{q,el} = (\epsilon_p - \mu) v \quad \text{per electron}$$

to see this

$$dU = T dS - p dV + \mu dN$$

$\therefore$ at fixed volume $dV = 0$

$$dQ = T dS = dU - \mu dN$$

$$\therefore \quad \vec{j}_q = T \vec{j}_s = \vec{J}_\epsilon - \mu \vec{J}_n$$

since energy and number are both conserved is easy to write down equations for them

$$\vec{j}_{q,el} = (\vec{\epsilon}_p - \vec{\mu})\vec{v}$$

Forces

- Electrochemical force

$$\vec{F} = -\vec{\nabla}\tilde{\mu} \qquad \tilde{\mu} = \mu - e\phi \qquad \vec{\nabla}\phi = -\vec{E}$$

combines electric pontential + chemical potential

- Temperature gradient

$$\vec{F}_q \propto -\vec{\nabla}(k_B T)$$

we will see exactly how this leads to a force

- A subtlety from Charge neutrality:

coulomb force from background ions ensures that charge is always spatially uniform

$$\therefore n(r) = \bar{n}$$

→ enforced by chemical potential

$\mu(T, V, N)$ ← normally $N$ → not important as $V$ fixed

fixed, fixed

$$\therefore \quad d\mu = \left.\frac{d\mu}{dT}\right|_{V,N} dT$$

$$\therefore \quad \vec{\nabla}\mu = \left.\frac{d\mu}{dT}\right|_{V,N} \vec{\nabla} T$$

↳ temperature gradient shows up in EC potential too!

$$\vec{F} = -e\vec{\mathcal{E}} = -\vec{\nabla}\mu - e\vec{E} = -\left.\frac{d\mu}{dT}\right|_{V,N}\vec{\nabla}T - e\vec{E}$$

electrochemical field

in short

$-e\vec{\mathcal{E}}$ is the force on electrons

$V_{AB} = -\int_A^B \vec{\mathcal{E}} \cdot d\vec{l}$ is what you measure with a voltmeter.

# Transport Coeffs

recall Ohms law

conductivity

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

charge current

electrochemical force

in einstein notation $\vec{A} \cdot \vec{B} = A_\alpha B_\alpha$

repeated indices are summed

$$j_\alpha = \sigma_{\alpha\beta} \mathcal{E}_\beta + \sigma_{\alpha\beta\gamma} \mathcal{E}_\beta \mathcal{E}_\gamma + \ldots$$

higher order terms

can still uniquely define conductivity

$$\sigma_{\alpha\beta} = \left. \frac{\partial j_\alpha}{\partial \mathcal{E}_\beta} \right|_{\vec{\mathcal{E}}=0}$$

$$= \frac{\partial}{\partial \mathcal{E}_\beta} \int d^3\vec{p} \int d^3\vec{r}\, f(\vec{r}, \vec{p})\, j_{el,\alpha} \Big|_{\mathcal{E}=0}$$

$$= \int d^3p\, \dot{j}_{el,\alpha} \frac{\partial f}{\partial \mathcal{E}_\beta}\Big|_{\mathcal{E}=0}$$

Equilibrium condition

$$\frac{1}{m}\vec{p}\cdot\vec{\nabla}_r f - e\,\mathcal{E}\,\vec{\nabla}_p f = \frac{1}{\tau} f$$

differentiat $\frac{\partial}{\partial \mathcal{E}_\beta}$

uniform $\qquad\qquad$ $\mathcal{E}=0$

$$\frac{1}{m}\vec{p}\cdot\cancel{\nabla_r \frac{\partial f}{\partial \mathcal{E}_\beta}} - e\left(\frac{\partial f}{\partial p_\beta} + \cancel{\vec{\mathcal{E}}}\cdot\vec{\nabla}_p \frac{\partial f}{\partial \mathcal{E}_\beta}\right) = \frac{1}{\tau}\frac{\partial f}{\partial \mathcal{E}_\beta}$$

set $\mathcal{E}=0$

use maxwell boltzmann

$$\frac{\partial f}{\partial \mathcal{E}_\beta} = -\tau e \frac{\partial f}{\partial p_\beta} = (-\tau e)\left(-\frac{\beta p}{m}\right) f$$

$$\sigma_{\alpha\beta} = \int d^3p\, d^3r\, \underbrace{\left(-\frac{e p_\alpha}{m}\right)}_{J}\left(-\frac{\beta\tau e p_\beta}{m}\right) f = \frac{ne^2\tau}{m}\delta_{\alpha\beta}$$

Similarly for

$$j_\alpha = L^{12}_{\alpha\beta} \frac{\partial T}{\partial x_\beta} \quad \therefore \text{ let } T'_\beta = \frac{\partial T}{\partial x_\beta}$$

$$L^{12}_{\alpha\beta} = \int d^3p\, d^3r\; j_{el,\alpha} \frac{\partial f}{\partial T'_\beta}$$

charge response to a thermal gradient

differentiate Eqm condition for $\vec{\mathcal{E}}=0$

$$\frac{p_\alpha}{m} \frac{\partial f}{\partial r_\alpha} = \frac{1}{\tau} f$$

chain rule $\frac{\partial f}{\partial r_\alpha} = \frac{\partial T}{\partial r_\alpha} \frac{\partial f}{\partial T} = T'_\alpha \frac{\partial f}{\partial T}$

do the rest in the homeworks

temperature is the only spatially dependent quantity

$$\therefore \left.\frac{\partial f}{\partial T'_\beta}\right|_{T'=0} = \frac{\tau p_\alpha}{m} \frac{\partial f}{\partial T} = \frac{\tau p_\alpha}{m} \frac{\partial \log f}{\partial T} f$$

calculable in MB

# Thermo-Electric transport coefficients

$$\begin{pmatrix} \vec{j} \\ \vec{j}_q \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} \begin{pmatrix} \vec{\mathcal{E}} \\ -\vec{\nabla} T \end{pmatrix}$$

- Conductivity $(\vec{\nabla} T = 0)$

$$\vec{j} = \sigma \vec{\mathcal{E}} \qquad \sigma = L_{11} = \frac{ne^2\tau}{m}$$

intuition $\quad \vec{F}_{EC} \equiv -e\vec{\mathcal{E}} = \vec{F}_{scatter} \equiv \frac{\vec{p}}{\tau} = \frac{m\vec{v}}{\tau}$

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

$$\vec{j} = \underbrace{n}_{\text{density}} \underbrace{(-e)}_{\text{charge}} \underbrace{\left(-\frac{e\vec{E}\tau}{m}\right)}_{\text{drift velocity}}$$

• Electronic heat conductivity ($\vec{j}=0$)

$$\vec{J}_q = -K\,\vec{\nabla} T \qquad K = L_{22} - \frac{L_{12}L_{21}}{L_{22}} = \frac{5}{2}\,\frac{k_B^2 n T \tau}{m}$$

<u>intuition</u>

$$\vec{F}_{T'} \sim -k_B \vec{\nabla} T \qquad \vec{v} = \frac{\tau F}{m} = -\frac{\tau k_B \vec{\nabla} T}{m}$$

$$\vec{J}_q = \underbrace{\frac{5}{3}}_{\text{correlations}}\, n \underbrace{\left(\frac{3}{2} k_B T\right)}_{\text{energy an electron carries}} \underbrace{\left(-\frac{\tau k_B \vec{\nabla} T}{m}\right)}_{\text{drift velocity}}$$

→ faster electrons actually have more energy and travel further before scattering.

- Wiedemann-Franz Law

$$\frac{K}{\sigma} \sim \text{cons @ Room } T \qquad (\text{WF})$$

$$\frac{K}{\sigma T} = \text{const} \qquad (\text{Lorenz})$$

from this analysis

$$\frac{K}{\sigma T} = \underbrace{\frac{5}{2}} \cdot \frac{k_B^2}{e^2}$$

$\frac{5}{2}$ depends on calculation framework

→ depends on precise calculation scheme

→ here we assumed $\tau(\epsilon) = \text{const}$.

intuition: $\vec{J}$ and $\vec{J}_q$ due to electrons

⟹ scattering details cancel

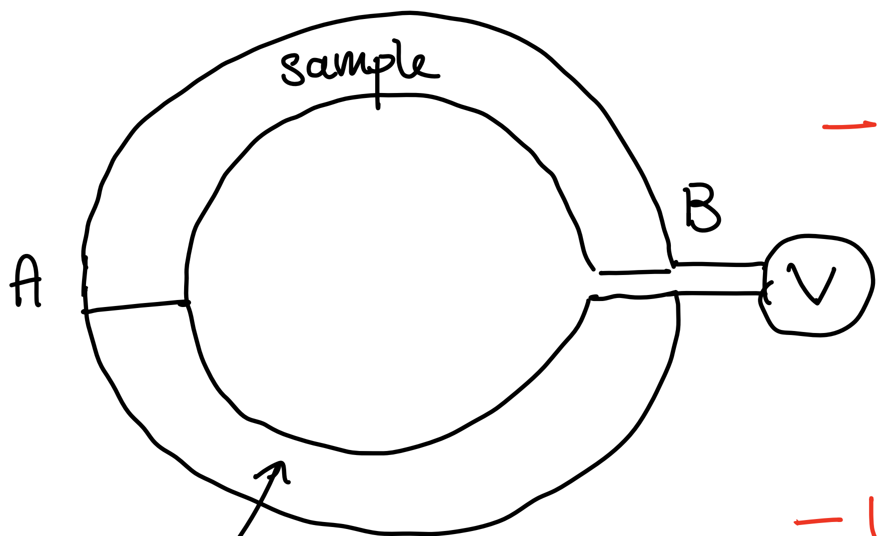
→ this is about right

↪ before we go to slides mention a few other props

• thermo power / Seebeck coefficient ($\vec{j}=0$)

$$\vec{\mathcal{E}} = S\vec{\nabla}T \qquad S = \frac{L_{12}}{L_{11}} = -\frac{k_B}{e}$$

$$V = -\int_A^B \mathcal{E}\cdot dl = S\Delta T_{AB}$$




either sc ($Q=0$) or Pt (ref)

Careful

- cannot have leads at diff temp – as also lead to thermelectric effect
- Use superconductors have $Q=0$

intuition $F_{EC} + F_T = 0 \Rightarrow (-e\vec{\mathcal{E}}) + (-k\vec{\nabla}T) = 0$

$$\therefore \quad \mathcal{E} = -\frac{k_B}{e}\vec{\nabla}T$$

• Peltier Effect $\nabla T = 0$ "heat drag"

$$\vec{J}_q = \Pi \vec{J} \qquad \frac{L_{21}}{L_{11}} = ST \quad \text{(Kelvin)}$$

intuition: $\vec{J} = -en\vec{v}$

$$\vec{J}_q \sim \left(\frac{3}{2}k_B T\right) n\vec{v}$$

$$\therefore \Pi \sim \frac{k_B T}{e}$$

→ however Drude Lorentz theory gets these guys wildly wrong

Summary

→ WF law correct $\frac{K}{\sigma T} \sim \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2$ – about right

→ Seebeck wrong $S = \frac{\Pi}{T} \sim \frac{k_B}{e}$ – off by 10–100

→ heat capacity wrong

→ Boltzmann heat capacity for free electrons

ie. $u_{el} = \frac{3}{2} k_B T$

$$\therefore C_{el,mol} = \underbrace{N_A Z}_{\substack{\#\text{ free electrons} \\ = \#\text{ atoms} \times \text{valence}}} \frac{du_{el}}{dT} = \frac{3}{2} R$$

→ this contribution is not observed

Recall Dulong Petit $C \sim 3R$

→ no significant correction at room temp.