Electronic properties of solids - Drude Model

Lecture 12

CHM 637

Chemistry & Physics of Materials

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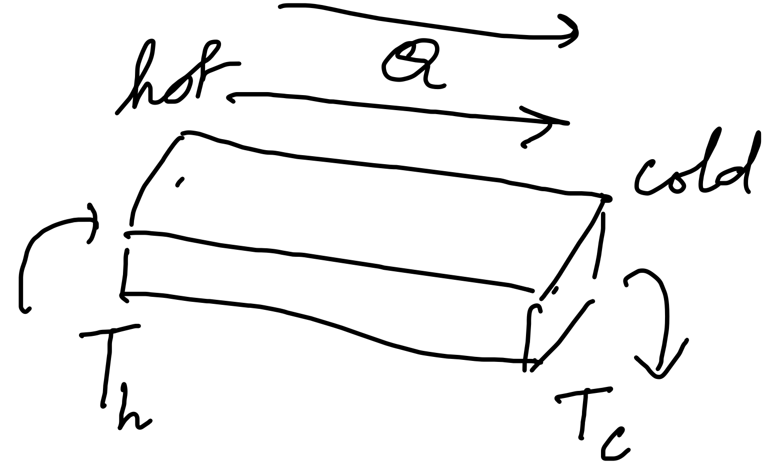
Lecture Plan

- Thermal conductivity and Weidemann-Franz Law
- Seebeck Effect

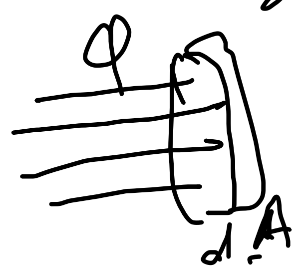
Thermal Conductivity of Metals

Temperature gradient results



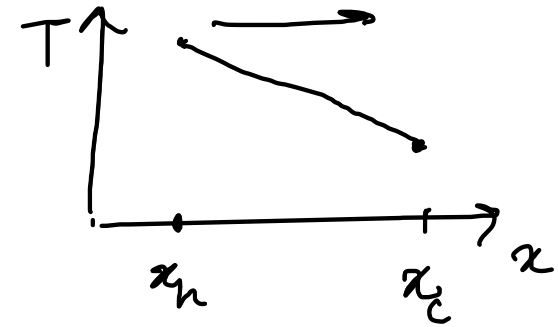
$\Rightarrow$ Steady flow of heat across the metal (bar).

$\vec{j}^{\,q}$ $\longrightarrow$ Amount of heat flowing per second across a unit area (normal to direction of flow)



$$\frac{dQ}{dt} \times \frac{1}{dA} = j^q$$

$$\vec{j}^{\,q} \propto -\vec{\nabla} T$$



$$\boxed{\vec{j}^{\,q} = -K \vec{\nabla} T}$$ (Fourier's Law)

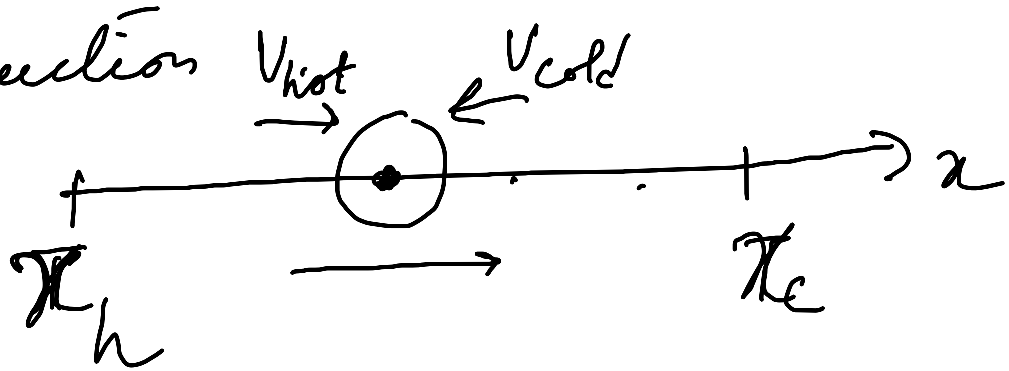
$$\frac{dT}{dx} < 0 \qquad j^q_x > 0$$

Thermal conductivity

Relate K to n, v, e, m, τ

Consider flow of heat along the x axis

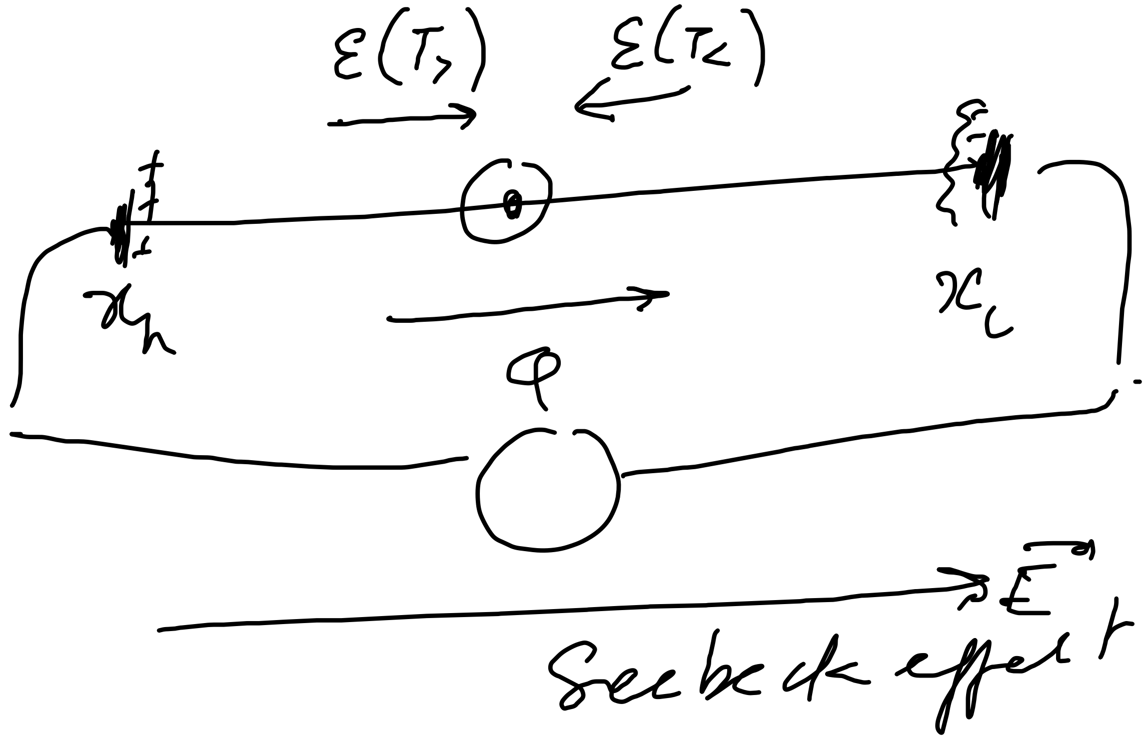
→ Assume that conduction electron are solely responsible for heat flow.



→ Velocities after collision are randomly distributed. But the speeds at any pt. are distributed according to the T at that pt.

→ Let's assume $\mathcal{E}(T)$ → average thermal energy per electron at temp. T.

Since T varies w/ x, $\mathcal{E}(T)$ will also vary w/ x, i.e. $\mathcal{E}(T) \equiv \mathcal{E}(T[x])$



$$j^{q}_{x} = \left(\frac{\text{Average thermal energy per electron flowing across a pt. } x}{}\right)$$

$$\times \underline{n} \times v$$

$$= v \times \underline{\left[\mathcal{E}(T_-) \times n_- - \mathcal{E}(T_+) \times n_+ \right]}$$

Last collision of electrons arriving at x from left end w/d have been at

$$x - v\tau \quad \text{(on an average)}$$

$$\Rightarrow \overline{\mathcal{E}(T_-)} = \mathcal{E}(T[x - v\tau])$$

(iii) electron arriving at x from cold side would have undergone a collision (on an average) at $x+v\tau$

$$\Rightarrow \mathcal{E}(T_-) = \mathcal{E}(T[x+v\tau])$$

We are assuming that v is independent of whether electrons come from hot or cold end.

Since the distribution of velocities at any pt is random, $n_+ = n_- = n/2$

$$\therefore \quad j_x^{\varepsilon} = v_x \times \frac{n}{2}\left[\varepsilon\left(T[x - v\tau]\right) - \varepsilon\left(T[x + v\tau]\right)\right]$$

$$\simeq v_x \times \frac{n}{2} \times \left[\cancel{\varepsilon\left(T[x]\right)} - \frac{d\varepsilon}{dT}\cdot\frac{dT}{dx}\cdot(v\tau) - \cancel{\varepsilon\left(T[x]\right)} - \frac{d\varepsilon}{dT}\cdot\frac{dT}{dx}(v\tau)\right]$$

$$= -v_x \times n \times \frac{d\varepsilon}{dT} \times \frac{dT}{dx} \cdot v\tau$$

$$= -\left(n v_x^2 \tau \frac{d\varepsilon}{dT}\right)\frac{dT}{dx} \quad //$$

Going to the 3-d., we replace v^2 by $\langle v^2 \rangle$ in each direction. But this is just $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3} \langle v^2 \rangle$

$$\vec{j}^{\,q} = \frac{1}{3} v^2 \times \tau \frac{d\varepsilon}{dT} \times n \left(-\vec{\nabla} T \right)$$

$$n \frac{d\varepsilon}{dT} = \frac{N}{V} \frac{d\varepsilon}{dT} = \frac{1}{V} \left(\frac{dE}{dT} \right)_V = \frac{1}{V} C_V = c_V$$

volume specific heat capacity

$$\vec{j}^{\,q} = \frac{1}{3} v^2 \tau c_V \left(-\vec{\nabla} T\right)$$

$$\ell = v\tau$$

$$= \left(\frac{1}{3} \ell v c_V\right)\left(-\vec{\nabla} T\right)$$

$$\hookrightarrow \boxed{K = \frac{1}{3} \ell v c_V}$$

$$\sigma = \frac{ne^2\tau}{m} \Rightarrow \frac{K}{\sigma} = \frac{1/3\, v^2 \cancel{\tau}\, c_V}{ne^2 \cancel{\tau}/m}$$

$$= \frac{2}{3}\left(\underbrace{\frac{1}{2}mv^2}\right)\underset{\downarrow}{C_v} \times \frac{1}{ne^2}$$

Classical ideal gas

$$C_v = \frac{3nk_B}{2} \qquad \frac{1}{2}mv^2 = \frac{3}{2}k_B T$$

$$\Rightarrow \frac{K}{\sigma} = \frac{\cancel{2}}{\cancel{3}} \times \frac{\cancel{3}}{\cancel{2}}k_B T \times \frac{3}{2}\cancel{n}k_B \times \frac{1}{\cancel{n}e^2}$$

$$= \left(\frac{3k_B^2}{2e^2}\right)T \Rightarrow \text{W-F law}$$

$$\Rightarrow \frac{K}{\sigma T} = \frac{3}{2}\left(\frac{k_B}{e}\right)^2 = 1.11 \times 10^{-8}$$

$W\text{-}ohm/K^2$

Weidemann-Franz Law

Table 1.6
EXPERIMENTAL THERMAL CONDUCTIVITIES AND LORENZ NUMBERS OF SELECTED METALS

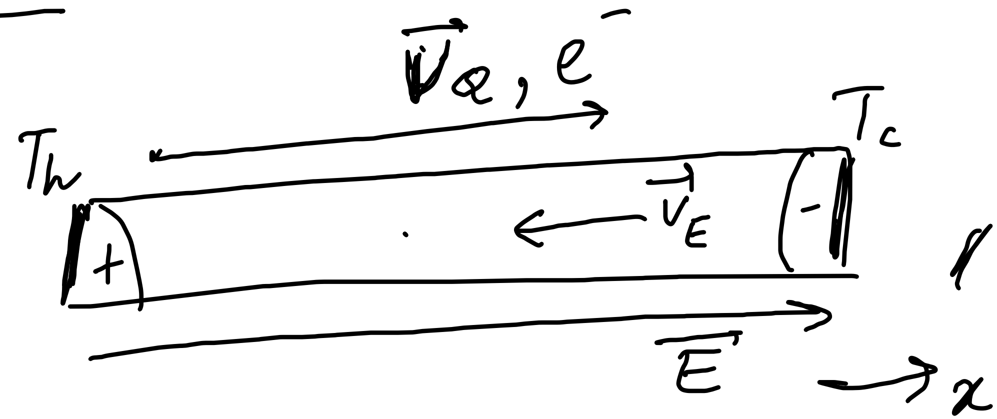
ELEMENT	273 K κ (watt/cm-K)	273 K $\kappa/\sigma T$ (watt-ohm/K^2)	373 K κ (watt/cm-K)	373 K $\kappa/\sigma T$ (watt-ohm/K^2)
Li	0.71	2.22×10^{-8}	0.73	2.43×10^{-8}
Na	1.38	2.12		
K	1.0	2.23		
Rb	0.6	2.42		
Cu	3.85	2.20	3.82	2.29
Ag	4.18	2.31	4.17	2.38
Au	3.1	2.32	3.1	2.36
Be	2.3	2.36	1.7	2.42
Mg	1.5	2.14	1.5	2.25
Nb	0.52	2.90	0.54	2.78
Fe	0.80	2.61	0.73	2.88
Zn	1.13	2.28	1.1	2.30
Cd	1.0	2.49	1.0	
Al	2.38	2.14	2.30	2.19
In	0.88	2.58	0.80	2.60
Tl	0.5	2.75	0.45	2.75
Sn	0.64	2.48	0.60	2.54
Pb	0.38	2.64	0.35	2.53
Bi	0.09	3.53	0.08	3.35
Sb	0.18	2.57	0.17	2.69

Source: G. W. C. Kaye and T. H. Laby, *Table of Physical and Chemical Constants*, Longmans Green, London, 1966

Source: Ashcroft and Mermin

Seebeck Effect

$$\boxed{\vec{v}_Q + \vec{v}_E = 0}$$



$$\vec{E} = Q \vec{\nabla} T$$

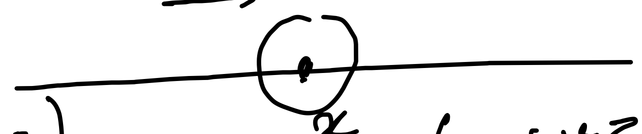
Thermoelectric field

Q → Thermopower

$$\frac{dT}{dx} < 0$$

$$E_x > 0$$

$\bar{v}_{hot}$ → ← v_{cold}



v

$$v_{hot} = v(x - v\tau)$$

$$v_{cold} = v(x + v\tau)$$

$(x - v\tau)$ $(x + v\tau)$

The mean x-velocity per electron at position x

$$V_Q^x = \frac{1}{2}\left[v_x(x - \tau v_x) - v_x(x + \tau v_x)\right]$$

$\rightarrow \leftarrow$

$$\simeq -\tau v_x \frac{dv_x}{dx}$$

$$= -\tau \frac{d}{dx}\left(\frac{v_x^2}{2}\right)$$

Generalizing to 3-d: $\langle v_x^2\rangle = \langle v_y^2\rangle = \langle v_z^2\rangle$

$$= \langle v^2\rangle/3 \equiv v^2/2$$

$$\vec{v}_Q = -\frac{\tau}{3}\vec{\nabla}\left(\frac{v^2}{2}\right) = -\frac{\tau}{6}\frac{dv^2}{dT}\vec{\nabla}T$$

$$\vec{V}_E = -\frac{e\vec{E}\tau}{m} = -\frac{eQ\tau}{m}\vec{\nabla}T$$

$$\vec{V}_Q + \vec{V}_E = 0$$

$$\Rightarrow -\frac{\tau}{6}\frac{dv^2}{dT}\vec{\nabla}T - \frac{eQ\tau}{m}\vec{\nabla}T = 0$$

即

$$Q = -\frac{\cancel{\tau} m}{6e\cancel{\tau}}\frac{dv^2}{dT}$$

$$= \frac{m}{6e}\frac{dv^2}{dT}$$

$$= -\frac{1}{3e}\underbrace{\frac{d}{dT}\left(\frac{mv^2}{2}\right)}$$

$$\simeq -\frac{1}{3e}\left(\frac{C_v}{n}\right) = -\frac{C_v}{3ne}$$

For classical ideal gas : $C_v = \frac{3}{2} n k_B$

$\therefore\ Q = -\frac{k_B}{2e} = -0.43\times10^{-4}\ V/K$

is 100 times larger than measured.