Thermal Conductivity of metals

Apply temperature gradient $\vec{\nabla} T$ across sample.
A thermal current (energy current) $\vec{j}^q$ will flow.

From thermodynamics: $dE = TdS - pdV$.
Here $dV = 0$ so $dE = TdS$.
Heat $dQ = TdS$ so $dQ = dE$
$\Rightarrow$ heat current (or thermal current) $=$ energy current

$$\vec{j}^q = -\kappa \vec{\nabla} T \qquad \text{heat equation}$$

defines <u>thermal conductivity</u> κ
heat flows from hot to cold so $\kappa > 0$
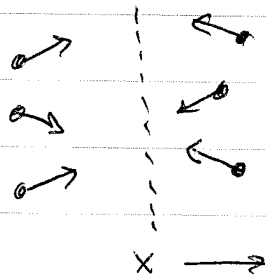(thats why we define κ using a $(-)$ sign in the heat equation)

Experimt observed the following empirical relation between κ and the dc conductivity σ

Wiedemann - Franz law

$$\frac{\kappa}{\sigma} \sim \text{const} \times T$$

where $\text{const} \simeq 2 \times 10^{-8}$ watt-ohm/°K^2
is roughly the same for all metals

Consider the energy flowing through a plane $\perp$ to $\vec{\nabla}T$

suppose $\vec{\nabla}T = \dfrac{dT}{dx}\hat{x}$

$x \longrightarrow$

Electrons crossing from left to right have had their last collision on average a time τ earlier at position $x^L = x - v_x^L \tau$, where v_x^L is the average speed of these electrons in the x direction

The electrons thus have average energy
$\mathcal{E}(T(x - v_x^L \tau))$ where $\mathcal{E}(T)$ is the average energy at temperature T.

Similarly the electrons crossing from right to left have had their last collision at position $x^R = x + v_x^R \tau$ and carry average energy $\mathcal{E}(T(x + v_x^R \tau))$.

The number of electrons crossing left to right (per unit time per unit area) is $\frac{1}{2} n v_x^L$.

The number of electrons per unit time per unit area crossing right to left is $\frac{1}{2} n v_x^R$.

(factor $\frac{1}{2}$ since half of electrons go in $+\hat{x}$ direction and $\frac{1}{2}$ go in $-\hat{x}$ direction)

$$\Rightarrow j^q = \tfrac{1}{2} m v_x^L \, \mathcal{E}\left(T(x - v_x^L \tau)\right)$$

$$- \tfrac{1}{2} m v_x^R \, \mathcal{E}\left(T(x + v_x^R \tau)\right)$$

For slow temperature variation $\dfrac{dT}{dx} < \dfrac{T_0}{\ell}$ $\leftarrow$ ave temp
we can expand $\quad\quad\quad\quad\quad \leftarrow$ mean free path

$$j^q = \tfrac{1}{2} m v_x^L \left[\mathcal{E}(T(x)) - v_x^L \tau \, \frac{d\mathcal{E}}{dT} \frac{dT}{dx} \right]$$

$$- \tfrac{1}{2} m v_x^R \left\{ \mathcal{E}(T(x)) + v_x^R \tau \, \frac{d\mathcal{E}}{dT} \frac{dT}{dx} \right\}$$

$$= \frac{-1}{2} m \tau \, \frac{d\mathcal{E}}{dT} \frac{dT}{dx} \left[(v_x^L)^2 + (v_x^R)^2 \right]$$

$$+ \tfrac{1}{2} m \, \mathcal{E}(T(x)) \left[v_x^L - v_x^R \right]$$

<u>first term</u> : $\quad \tfrac{1}{2}(v_x^L)^2 + \tfrac{1}{2}(v_x^R)^2 \approx \langle v_x^2 \rangle = \tfrac{1}{3}\langle v^2 \rangle$

$$\langle v_x^2 \rangle = \tfrac{1}{3}\langle v^2 \rangle = \tfrac{1}{3} \frac{3 k_B T}{m}$$

(using $\tfrac{1}{2} m \langle v^2 \rangle = \tfrac{3}{2} k_B T$ equipartition theorem)

So first term is $\quad - \tfrac{1}{3} m \tau \langle v^2 \rangle \frac{d\mathcal{E}}{dT} \frac{dT}{dx}$

<u>2nd term</u> : $\quad v_x^L - v_x^R = \langle v_x \rangle \quad$ at position x
But since thermal conductivity is usually
~~computed~~ measured in an <u>open</u> circuit

hot $\quad\quad$ cold

no current flows in x direction $\Rightarrow \langle v_x \rangle = 0$
So 2nd term vanishes! (see more on this later!)

$$\Rightarrow j^Q = -\frac{1}{3} n \tau \langle v^2 \rangle \frac{d\mathcal{E}}{dT} \frac{dT}{dx} = -\kappa \frac{dT}{dx}$$

$$\text{note } \frac{d\mathcal{E}}{dT} \cdot m \cdot m = \frac{1}{V} \frac{d\mathcal{E}}{dT}$$

Now $\mathcal{E}$ is average energy per electron at temp T.

$\Rightarrow N\mathcal{E}$ is total average energy

$\frac{N}{V}\mathcal{E} = n\mathcal{E}$ is average energy density

$$\Rightarrow n\frac{d\mathcal{E}}{dT} = c_v \qquad \text{specific heat per volume}$$
$$\text{at constant volume}$$

$$\kappa = \frac{1}{3} \tau c_v \langle v^2 \rangle = \frac{1}{3} \ell v c_v \qquad \text{where } \ell = \tau v$$
$$v = \sqrt{\langle v^2 \rangle}$$

$$\sigma = \frac{n e^2 \tau}{m}$$

$$\frac{\kappa}{\sigma} = \frac{\ell v \tau c_v n \tau}{3 \left(\frac{n e^2 \tau}{m} \right)}$$

$$\frac{\kappa}{\sigma} = \frac{\frac{1}{3} \tau c_v \langle v^2 \rangle}{\frac{n e^2 \tau}{m}} = \frac{m c_v \langle v^2 \rangle}{3 n e^2} \qquad \text{indep of } \tau !$$

$$\mathcal{E} = \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T \qquad\qquad c_v = \frac{3}{2} n k_B$$

$$\frac{\kappa}{\sigma} = \frac{c_v k_B T}{n e^2} = \boxed{\frac{3}{2} \frac{k_B^2}{e^2} T = \frac{\kappa}{\sigma}}$$

Wiedemann-Franz const is $\frac{3}{2} \frac{k_B^2}{e^2} = 1.11 \times 10^{-8}$ watt-ohm/$°K^2$

This is ~½ the experimental value!

In his calculation Drude made a factor 2 error, so he reported a result 2.22×10^{-8} watt-ohm/$°K^2$ in <u>excellent</u> agreement with experiment!

This success was just luck. We will see, when we treat the ~~gas~~ electron gas quantum mechanically, that the correct $\langle v^2 \rangle$ is ~100 times larger than Drude's classical result, but C_V is ~100 times smaller. So these two factors cancel to give a reasonable result, but just by accident!

Even in Drude's day it was known that something was not right since no electronic contribution to specific heat was ever found as large as $\frac{3}{2} m k_B$.
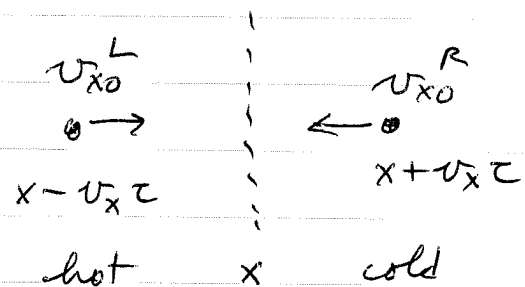
Thermo electric effect

We said that $v_x^L - v_x^R = \langle v_x \rangle = 0$ in our open circuit. But since $T(x_L) > T(x_R)$ one would expect that $v_x^L > v_x^R$.

$\Rightarrow$ In steady state an electric field must be generated, in same direction as $\vec{\nabla} T$, that exactly compensates for the thermal difference in velocities, so that velocities of both right going and left going electrons are equal as they cross the same plane at x.

this is the thermo electric field $\vec{E}$ and it is proportional to $\vec{\nabla}T$. We define the "thermo power" by

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

To estimate Q

$$v_{x0}^{L} \quad \bullet \longrightarrow \qquad \longleftarrow \bullet \quad v_{x0}^{R}$$

$$x - v_x \tau \qquad\qquad x + v_x \tau$$

$$\text{hot} \quad x \quad \text{cold}$$

v_{x0}^{L} is from equilib thermal distrib at $T(x - v_x \tau)$

v_{x0}^{R} is from equilib thermal distrib at $T(x + v_x \tau)$

when the thermo electric field $\vec{E}$ is present the speed of the right going electrons when they pass the plane at x is

$$v_x^{L} = v_{x0}^{L} - \frac{eE\tau}{m} \quad \longleftarrow \quad \text{change in velocity due to acceleration by electric field}$$

Similarly

$$v_x^{R} = v_{x0}^{R} + \frac{eE\tau}{m}$$

So $v_x^{L} - v_x^{R} = v_{x0}^{L} - v_{x0}^{R} - \frac{2eE\tau}{m} = 0$

determines value of E

$$v_{x0}^{L} = v_x(T(x - v_x \tau)) = v_x(T(x)) - \frac{dv_x}{dT}\frac{dT}{dx} v_x \tau$$

$$v_{x0}^{R} = v_x(T(x + v_x \tau)) = v_x(T(x)) + \frac{dv_x}{dT}\frac{dT}{dx} v_x \tau$$

$$v_x^{L} - v_x^{R} = -2\frac{dv_x}{dT}\frac{dT}{dx} v_x \tau - \frac{2eE\tau}{m} = 0$$

use $\left(\frac{dv_x}{dT}\right) v_x = \frac{1}{2}\frac{dv_x^2}{dT}$

So $\quad E = -\dfrac{m}{2e} \dfrac{d\,v_x^2}{dT} \dfrac{dT}{dx}$

$$\langle v_x^2 \rangle = \frac{1}{3} \langle v^2 \rangle \quad , \quad \cancel{\langle v_x^2 \rangle = \frac{\cancel{3}}{m}}$$

$$= \frac{2}{3m} \mathcal{E} \qquad \text{where} \qquad \mathcal{E} = \frac{1}{2} m \langle v^2 \rangle$$

$$E = -\frac{1}{3e} \frac{d\mathcal{E}}{dT} \frac{dT}{dx}$$

$$c_v = m \frac{d\mathcal{E}}{dT}$$

$$E = -\frac{1}{3me} c_v \frac{dT}{dx} = Q \frac{dT}{dx}$$

$$\cancel{c_v = c_v = \frac{3}{2} m k_B \quad classically}$$

$$\cancel{cAvA} \implies Q = -\frac{c_v}{3me}$$

Classically $\quad c_v = \dfrac{3}{2} m k_B \implies Q = -\dfrac{k_B}{2e}$

$$= -0.4 \times 10^{-4} \frac{volt}{{}^\circ K}$$

observed Q is ~100 times smaller
than this classical Drude result

we will get more reasonable value
for Q when we use correct quantum
mechanical result for c_v.