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

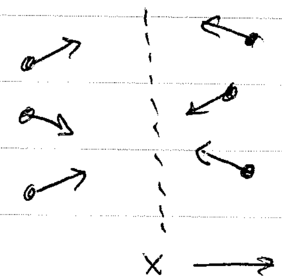
Experiment observed the following empirical relation between κ and the dc conductivity σ

Wiedemann - Franz law

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

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

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



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

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 $\overbrace{\text{crossing}}^{\text{per unit time per unit area}}$ left to right 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)

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

For slow temperature variation $\frac{dT}{dx} < \frac{T_0}{\ell}$ ← ave temp; ← mean free path
we can expand

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

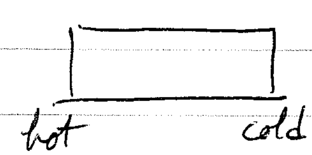
first term: $\tfrac{1}{2}(v_x^L)^2 + \tfrac{1}{2}(v_x^R)^2 \approx \langle v_x^2 \rangle = \tfrac{1}{3}\langle v^2 \rangle$

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

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

2nd term: $v_x^L - v_x^R = \langle v_x \rangle$ at position x

But since thermal conductivity is usually ~~accepted~~ measured in an open circuit



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

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

~~now~~ $\cancel{\frac{d\mathcal{E}}{dT} \cdot n = \frac{1}{V} \frac{d\mathcal{E}}{dT}}$

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

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

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

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

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

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

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

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

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

This is $\sim\frac{1}{2}$ 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 $\frac{3}{2}nk_B$.

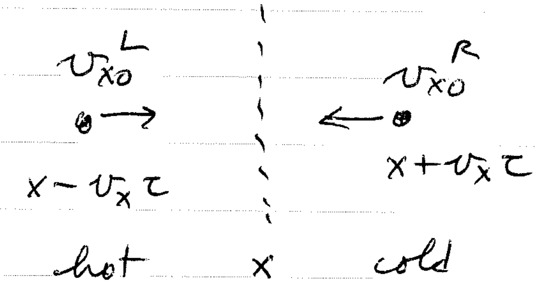
<u>Thermoelectric effect</u>

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 thermoelectric field $\vec{E}$ and it is proportional to $\vec{\nabla} T$. We define the "thermopower" by

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



To estimate Q

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

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

Similarly

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

So $v_x^L - v_x^R = v_{x0}^L - v_{x0}^R - \dfrac{2eE\tau}{m} = 0$
determines value of E

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

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

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

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

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

$\langle v_x^2\rangle = \frac{1}{3}\langle v^2\rangle$

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

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

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

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

$\Rightarrow Q = -\frac{c_v}{3ne}$

Classically $c_v = \frac{3}{2}nk_B \Rightarrow Q = -\frac{k_B}{2e}$

$= -0.4\times10^{-4}\,\frac{\text{volt}}{{}^\circ K}$

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.

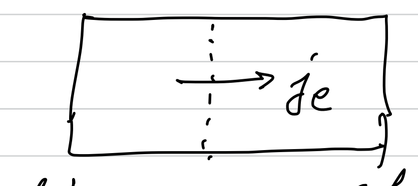
Physical mechanism for the thermoelectric effect

Suppose start with a slab of metal. No $\tilde{E}$, no $\vec{\nabla} T$

$\Rightarrow$ no electric current, no thermal current

Now apply a temperature gradient in an open circuit geometry.

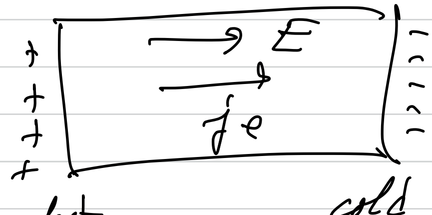
Initially, the electrons on the hot side will have a greater thermal speed than the electrons on the cold side. The result will be a current of electrons j_e flowing from hot to cold, since the electrons traveling



across a crossectional area from $L \to R$ travel faster than those crossing $R \to L$.

(Note, since electrons have charge $-e$, the current of electrons $j_e = -j$ the electric current.

This current of electrons deposits a net negative charge on the right side surface, while leaving a net positive charge on the left side



These surface charges give rise to an electric field pointing L to R. This is the thermo-electric field

When steady state is reached, this thermoelectric field is just the right strength to cancel out the effect of ∇T in driving the initial j_e, and as a result the electron current drops to zero as it must for an open circuit geometry.