

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

$$\vec{j}_q = -\kappa \vec{\nabla}T \quad \text{heat equation}$$

defines thermal conductivity κ

heat flows from hot to cold so $\kappa > 0$

(that's why we define κ using a $(-)$ sign in the heat equation)

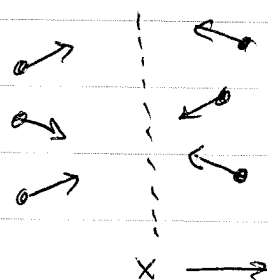
Experiment observed the following empirical relation between κ and the dc conductivity σ

Wiedemann - Franz law

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

where $\text{const} \simeq 2 \times 10^{-8} \text{ watt-ohm}/\text{K}^2$
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 $E(T(x - v_x^L \tau))$ where $E(T)$ is the average energy at temperature T .

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

The number of electrons ^(per unit time per unit area) crossing 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)

$$\Rightarrow \dot{q} = \frac{1}{2} m v_x^L \varepsilon(T(x - v_x^L \tau)) - \frac{1}{2} m v_x^R \varepsilon(T(x + v_x^R \tau))$$

For slow temperature variation $\frac{dT}{dx} < \frac{T_0}{l} \leftarrow \text{ave temp}$
 we can expand $l \leftarrow \text{mean free path}$

$$\begin{aligned} \dot{q} &= \frac{1}{2} m v_x^L \left[\varepsilon(T(x)) - v_x^L \tau \frac{d\varepsilon}{dT} \frac{dT}{dx} \right] \\ &\quad - \frac{1}{2} m v_x^R \left[\varepsilon(T(x)) + v_x^R \tau \frac{d\varepsilon}{dT} \frac{dT}{dx} \right] \\ &= -\frac{1}{2} m \tau \frac{d\varepsilon}{dT} \frac{dT}{dx} \left[(v_x^L)^2 + (v_x^R)^2 \right] \\ &\quad + \frac{1}{2} m \varepsilon(T(x)) [v_x^L - v_x^R] \end{aligned}$$

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

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

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

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

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

But since thermal conductivity is usually ~~measured~~ 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!)

$$\Rightarrow j^0 = -\frac{1}{3} n \tau \langle v^2 \rangle \frac{dE}{dT} \frac{dT}{dx} = -\kappa \frac{dT}{dx}$$

~~$$m n \frac{dE}{dT} = \frac{1}{V} \frac{dE}{dT}$$~~

Now E is average energy per electron at temp T .

$\Rightarrow NE$ is total average energy

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

$$\Rightarrow n \frac{dE}{dT} = c_v \quad \text{specific heat per volume at constant volume}$$

$$\kappa = \frac{1}{3} \tau c_v \langle v^2 \rangle = \frac{1}{3} l v c_v \quad \text{where } l = \tau v$$

$$v = \sqrt{\langle v^2 \rangle}$$

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

~~$$\frac{\kappa}{\sigma} = \frac{l v c_v}{\frac{ne^2 \tau}{m}}$$~~

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

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

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

Weidemann-Frey const is $\frac{3}{2} \frac{k_B^2}{e^2} = 1.1 \times 10^{-8} \text{ watt-ohm/K}^2$

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/ $^{\circ}\text{K}^2$ in excellent agreement with experiment!

This success was just luck. We will see, ~~the~~ 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 $\frac{3}{2} n k_B$.

Thermoelectric effect

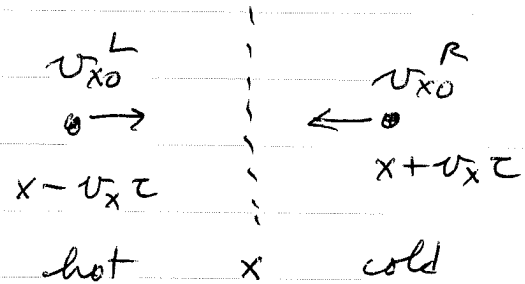
We said that $v_x^L - v_x^R = \langle v_x \rangle = 0$ in our open circuit. But since $T(x_L) > T(x_R)$ one would expect that $v_x^L > v_x^R$.

$\Rightarrow$ 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 thermoelectric field $\vec{E}$ and it is proportional to ~~the~~ $\vec{\nabla} T$. 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

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

Similarly

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

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

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

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

$$\langle v_x^2 \rangle = \frac{1}{3} \langle v^2 \rangle, \quad \cancel{\langle v^2 \rangle = \frac{3k_B T}{m}} \\ = \frac{2}{3m} E \quad \text{where } E = \frac{1}{2} m \langle v^2 \rangle$$

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

$$C_v = m \frac{dE}{dT}$$

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

$$\cancel{C_v} = \frac{3}{2} m k_B \text{ classically}$$

$$\Rightarrow Q = - \frac{C_v}{3me}$$

$$\text{Classically } C_v = \frac{3}{2} m k_B \Rightarrow Q = - \frac{k_B}{2e}$$

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

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 .

Sommerfeld model

Classical Drude model assumed classical statistics for the electron gas:

Maxwell Boltzmann distribution

$$f_{MB}(\vec{v}) = n \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-mv^2/2k_B T}$$

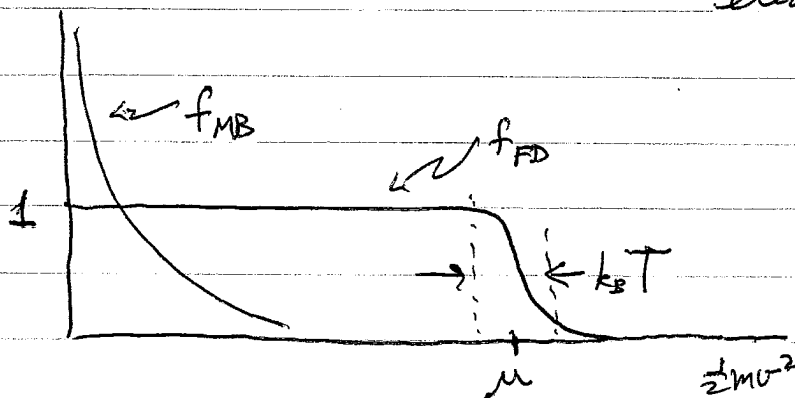
density of electrons per unit volume with velocity $\vec{v}$

Once quantum mechanics was developed, Sommerfeld realized that the electrons, which obey the Pauli exclusion principle, use instead behave according to Fermi-Dirac statistics

$$f_{FD}(\vec{v}) = \frac{(m/\hbar)^3}{4\pi^3} \frac{1}{e^{(\frac{1}{2}mv^2 - \mu)/k_B T} + 1}$$

where μ is the chemical potential (to be discussed in the following)

$$\int d^3N f_{FD}(\vec{v}) = n \quad \text{total conduction electron density}$$



Review of quantum mechanics of a free electron gas

A single electron in a metal will be modeled as a free electron in a box of volume $V = L^3$

The states of the electron are given by the eigenstates of Schrodinger's Equation

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = \epsilon \psi$$

which has solutions

$$\psi_{\mathbf{k}}(\vec{r}) = \underset{\substack{\uparrow \\ \text{normalization constant}}}{A} e^{i\vec{k} \cdot \vec{r}} \quad \text{with energy } \epsilon_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m}$$

This wavefunction is also an eigenstate of momentum

$$-i\vec{\nabla} \psi_{\mathbf{k}} = \vec{p} \psi_{\mathbf{k}} \Rightarrow \vec{p} = \hbar \vec{k}$$

with velocity $\vec{v} = \frac{\hbar \vec{k}}{m}$

For electrons in a finite volume V , we also need to specify the boundary conditions on ψ .
at the walls: $x=0, L$, $y=0, L$, and $z=0, L$

One natural boundary condition is to choose $\psi=0$ on the walls since there is no probability to find the electron outside the box.

The $\psi_k(\vec{r})$ cannot satisfy this boundary condition.
~~except for the trivial case~~

We can make eigenstates which satisfy $\psi=0$ on the walls by taking an appropriate linear superposition of the degenerate eigenstates ψ_k with $|\vec{k}| = \sqrt{2mE/\hbar^2}$ constant. to get

$$\psi_k = (A \sin k_x x)(\sin k_y y)(\sin k_z z)$$

where k_μ must satisfy

$$k_\mu = n_\mu \frac{\pi}{L} \quad \text{with } n_\mu \text{ integer} \\ \mu = x, y, \text{ or } z$$

But this ψ_k is not an eigenstate of momentum. It describes a "standing wave" whose expectation value of momentum is always

$$\langle \psi_k | \vec{p} | \psi_k \rangle = 0$$

Since we will want to describe states of a metal that carry a current, these standing wave solutions corresponding to the $\psi=0$ boundary condition are not convenient.

Instead we use periodic boundary conditions requiring the wavefunction ψ to equal itself on opposite walls of the box, i.e.

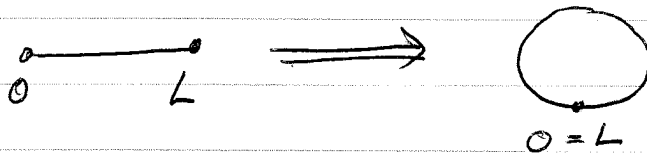
$$\psi(x+L, y, z) = \psi(x, y, z)$$

$$\psi(x, y+L, z) = \psi(x, y, z)$$

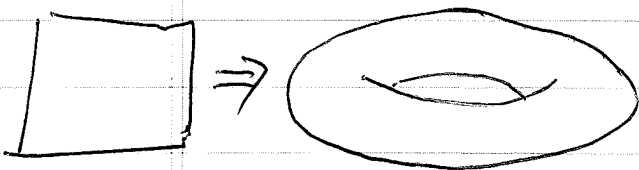
$$\psi(x, y, z+L) = \psi(x, y, z)$$

These are also known as the Born-von Karman boundary conditions.

In 1-d, this boundary condition is equivalent to describing the system by a loop of length L .



In 2-d, it is equivalent to making the system the surface of a torus



In 3-d, it is the surface of a 3d torus (I won't try to sketch it!)

An electron hitting the wall at, say, $x=L$ leaves the metal and simultaneously comes

back in at the corresponding point on the opposite wall at $x=0$. This, therefore, is a convenient boundary condition to ~~describe~~ allow for situations in which a current can be flowing.

The periodic boundary conditions restrict the solutions

$$\psi_{\vec{k}} = A e^{i\vec{k} \cdot \vec{r}}$$

to values of $\vec{k}$ that obey the conditions

$$e^{ik_x L} = e^{ik_y L} = e^{ik_z L} = 1$$

since, for example,

$$\begin{aligned}\psi(x+L, y, z) &= A e^{i[(k_x+L)x + k_y y + k_z z]} \\ &= A e^{ik_x L} e^{i(k_x x + k_y y + k_z z)} \\ &= e^{ik_x L} \psi(x, y, z)\end{aligned}$$

The allowed values of $\vec{k}$ therefore satisfy

$$k_\mu = \frac{2\pi n_\mu}{L} \quad \text{with } n_\mu \text{ an integer}$$

$$\vec{k} = \left(\frac{2\pi n_x}{L}, \frac{2\pi n_y}{L}, \frac{2\pi n_z}{L} \right)$$