Lecture 2

Drude Theory of Thermal Conductivity

The thermal conductivity k is defined as the proportionality constant in Fourier's law:

$$\vec{\jmath}_Q = -\kappa \nabla T$$

where $\vec{\jmath}_Q$ = heat current = heat transported across a unit area per unit time.

In Drude's model, electrons transport heat because the electrons thermalized at the "local" temperature of the last collision. (Assume thermalization at each collision.) Thus, the electrons leaving the hotter regions carry more energy. Let's derive Fourier's law and derive an expression for κ. We will use the same approach that we used for deriving σ_0. Look at $\left.\frac{d\vec{\jmath}_Q}{dt}\right|_{total}$. There are 2 contributions - diffusion and collisions (which knock electrons out of the right direction):

$$\left.\frac{d\vec{\jmath}_Q}{dt}\right|_{total} = \left(\frac{d\vec{\jmath}_Q}{dt}\right)_{diffusion} + \left(\frac{d\vec{\jmath}_Q}{dt}\right)_{collision}$$

What is $\left(\frac{d\vec{\jmath}}{dt}\right)_{diffusion}$? Suppose the system has a temperature gradient but no collisions (save those for the other term). Consider the electrons which cross the plane $x = 0$ at a time t after the start of the operation. An electron with velocity $\vec{v}$ will have come from a point $\vec{r} = -\vec{v}t$ away and will therefore have the average energy appropriate for that point, i.e., $\varepsilon(\vec{r})$. The extra energy will be

$$\delta\varepsilon_i = \vec{r}_i \cdot \nabla\varepsilon = \vec{r}_i \cdot \nabla T \left(\frac{\partial\varepsilon}{\partial T}\right) = -t\vec{v}_i \cdot \nabla T \left(\frac{d\varepsilon}{dT}\right)$$

The "extra" energy current is

$$\begin{aligned}
\left.\vec{\jmath}_Q(t)\right|_{diffusion} &= \sum_i \vec{v}_i \delta\varepsilon_i = -t \sum_i \vec{v}_i(\vec{v}_i \cdot \nabla T)\left(\frac{d\varepsilon}{dT}\right) \\
\left(\frac{d\vec{\jmath}_Q}{dt}\right)_{diffusion} &= -\left(\frac{d\varepsilon}{dT}\right) \sum_i \vec{v}_i(\vec{v}_i \cdot \nabla T)
\end{aligned}$$

Since the velocity distribution is approximately isotropic (nothing makes the electrons go in the ∇T direction), the energy diffusion is along ∇T. $\frac{d\vec{\jmath}_Q}{dt}$ has a component only along ∇T and we can replace the v_i's with $\frac{1}{3}\overline{v^2}$. This gives

$$\left(\frac{d\vec{\mathrm{j}}_Q}{dt}\right)_{diffusion} = -\left(\frac{dE}{dT}\right)\frac{1}{3}\overline{v^2}\nabla T$$

where the energy per unit volume $E = n\varepsilon$, and ε is the energy per particle.

Collisions Now put in collisions. We assume that the electrons thermalize at every collision. Thus the extra heat current carried by an electron is annihilated at every collision. $\vec{\mathrm{j}}_Q = \sum_i \vec{v}_i\delta\varepsilon_i$ is also lost and we can simply write

$$\left(\frac{d\vec{\mathrm{j}}_Q}{dt}\right)_{collision} = -\frac{\vec{\mathrm{j}}_Q}{\tau}$$

Thus

$$\left(\frac{d\vec{\mathrm{j}}_Q}{dt}\right)_{total} = -\left(\frac{dE}{dT}\right)\frac{1}{3}\overline{v^2}\nabla T - \frac{\vec{\mathrm{j}}_Q}{\tau}$$

In steady state, $(\frac{d\vec{\mathrm{j}}_Q}{dt})_{total} = 0$. Using $c_v = (\frac{dE}{dt})\Big|_V$ gives the standard Kinetic Theory of Gases result:

$$\boxed{\begin{array}{l} \vec{\mathrm{j}}_Q = -\kappa\nabla T \\ \kappa = \frac{1}{3}c_v\overline{v^2}\tau \end{array}}$$

To the extent that $\overline{v^2}\tau = v\ell$, $\boxed{\kappa = \frac{1}{3}c_v\, v\ell}$

Wiedemann-Franz Law

It is an empirical fact that

$$\begin{aligned} \frac{\kappa}{\sigma T} &\simeq \text{constant that is nearly the same in all metals} \\ &\sim 2\cdot 10^{-8}\text{watt} - \text{ohm}/K^2 \end{aligned}$$

(See Table 1.6 in AM). $(\kappa/\sigma T)$ is called the *Lorenz number.* Can the Drude theory explain this? We have

$$\sigma = \frac{ne^2\tau}{m} \qquad\qquad \kappa = \frac{1}{3}c_v\overline{v^2}\tau$$

Thus

$$\frac{\kappa}{\sigma T} = \frac{1}{3} \quad \frac{c_v \overline{v^2} m\tau}{ne^2 \tau T} = \frac{1}{3}\frac{c_v m\overline{v^2}}{ne^2 T} \qquad (*)$$

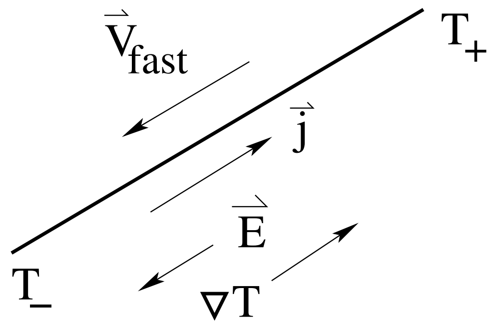
Now if one uses a simple Kinetic Theory of Gases picture for a monatomic gas:

$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}k_B T \qquad \text{and} \quad c_v = \frac{3}{2}nk_B$$

$$\Rightarrow \qquad \boxed{\frac{\kappa}{\sigma T} = \frac{3}{2}\left(\frac{k_B}{e}\right)^2}$$

This is $1.11 \times 10^{-8}\ \frac{W\Omega}{k^2}$, i.e., almost exactly half the experimental value. We will see later that Eq. $(*)$ is in fact approximately right: it is the evaluation of c_v and $m\overline{v^2}$ that is wrong. Fortuitously, the mistakes cancel except for a factor of 2. Incidentally, there was no evidence in Drude's time for an electronic specific heat of $\frac{3}{2}nk_B$. ($\frac{3}{2}nk_B$ is a lot of specific heat.) So it was puzzling as to why the Lorenz number came out correctly when it appeared that there was no c_{el} at room temperature.

Seebeck Effect - Thermopower



The fact that higher energy electrons move faster means that setting up a temperature gradient would give rise to an electric current. So, if we could set up a temperature gradient on a closed circuit, a current would flow *up* the gradient (since electrons are negatively charged). On an open circuit, the flow gives rise to a build-up of charge at the ends, and a steady state is obtained when the field $\vec{E}$ produced is sufficient to cancel the drift. Hence we expect

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

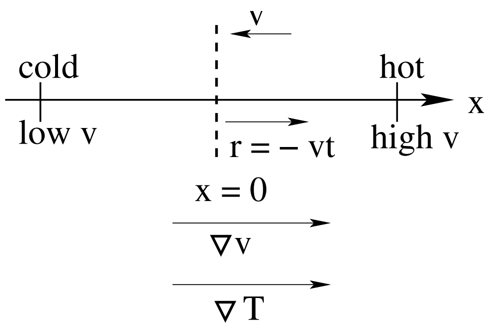
where the thermopower Q should be < 0.

Let's calculate Q in the Drude model.

Strategy: In steady state

$$\left.\frac{d\vec{\jmath}}{dt}\right|_{total} = \left.\frac{d\vec{\jmath}_Q}{dt}\right|_{diffusion} + \left.\frac{d\vec{\jmath}_E}{dt}\right|_{field} = 0$$

Diffusion



Suppose the gradient is along the x-direction. Consider the electrons crossing the $x = 0$ plane a time t after the start of the operation. An electron with velocity $\vec{v}$ will come from a point $\vec{r} = -\vec{v}t$ away and will have a velocity appropriate to $\vec{r}$. Let $\nabla v_x || \nabla T || + \hat{x}$. The excess velocity at $x = 0$ for the x-component is

$$\delta v_x = -t\vec{v} \cdot \nabla v_x = -tv_x \nabla v_x = -\frac{1}{2} t \nabla v_x^2 = -\frac{1}{6} t \nabla \overline{v^2}$$

$$\frac{\partial v_x}{\partial t} = -\frac{1}{6} \nabla \overline{v^2} \Rightarrow \left(\frac{\partial \vec{\jmath}_Q}{\partial t}\right)_{diff} = +\frac{1}{6} ne \nabla \overline{v^2} = +\frac{1}{6} ne \frac{\partial \overline{v^2}}{\partial T} \nabla T$$

where we used $\vec{\jmath} = -nev$. $\vec{\jmath}_Q$ is the electric current due to the thermal gradient.

E-field current

Recall

$$\left(\frac{\partial \vec{\jmath}}{\partial t}\right)_{field} = \frac{ne^2 \vec{E}}{m}$$

Steady-State: (Heat current cancels $\vec{E}$-field current)

$$\left.\frac{d\vec{\jmath}}{dt}\right|_{tot} = \left.\frac{d\vec{\jmath}_Q}{dt}\right|_{diff} + \left.\frac{d\vec{\jmath}}{dt}\right|_{\vec{E}} = 0$$

$$\begin{aligned}\frac{ne^2\vec{E}}{m} &= -\frac{1}{6}ne\frac{\partial\overline{v^2}}{\partial T}\nabla T \\ \vec{E} &= Q\nabla T\end{aligned}$$

where

$$\boxed{Q = -\frac{1}{6e}\frac{\partial}{\partial T}(m\overline{v^2}) = -\frac{1}{3e}\frac{c_v}{n}}$$

In the Kinetic Theory of Gases,

$$c_v = \frac{3}{2}nk_B \Rightarrow Q = -\frac{k_B}{2e} \sim \left(\begin{array}{c}100 \times \text{too} \\ \text{large for expt.}\end{array}\right)$$

Quantum Theory of Electrons in Metals

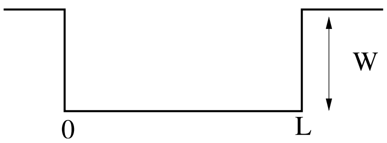
("Free Electrons; Sommerfeld")

(AM, Ch 2)

Now let's put QM into the model.

The most important effect of putting quantum mechanics into the theory of metals is the result of treating electrons as fermions with Fermi-Dirac statistics, rather than as a classical gas of particles obeying the Kinetic Theory of Gases. But let's start at the beginning.

When electrons are treated quantum mechanically, 2 things change: (a) possible states are quantized; (b) particles are indistinguishable.



Consider non-interacting electrons moving (freely) in a constant potential which we take to be zero. Schroedinger's equation in 1D is

$$\frac{\hbar^2}{2m}\frac{d^2\psi_n}{dx^2} = \varepsilon_n\psi_n$$

What boundary conditions do we use? (It doesn't matter all that much because the bulk properties aren't really affected by what goes on at the surface.)

(a) Realistic, i.e., ψ_n finite outside the metal but decaying exponentially ($\to 0$ as $x \to \infty$). This is practically never used for bulk calculations since $r_{decay} \sim$ atomic dimensions.

(b) Box: Standing Wave Solutions $\qquad \psi_n = 0$ at walls

$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right); \qquad \varepsilon_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \quad n > 0.$

We're interested in transport - want traveling waves.

(c) Periodic: $\psi_n(x + L) = \psi_n(x)$

Now traveling wave solutions are allowed.

$$\psi_n(x) = \sqrt{\frac{1}{L}} e^{ik_n x}$$
$$k_n = \frac{2n\pi}{L} \quad n \gtrless 0$$
$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{2n\pi}{L}\right)^2$$

It is easy to generalize this to 3D. Consider a box with sides L_x, L_y, L_z: Schroedinger's equation becomes

$$-\frac{\hbar^2}{2m}\nabla^2\psi_n = -\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi_n}{\partial x^2} + \frac{\partial^2\psi_n}{\partial y^2} + \frac{\partial^2\psi_n}{\partial z^2}\right) = \varepsilon_n\psi_n$$

For periodic b.c.'s, the solution is a product wavefunction

$$\begin{aligned}
\psi_n(x, y, z) &= \frac{1}{\sqrt{V}}(\exp\ ik_x x)(\exp\ ik_y y)(\exp ik_z z) \\
&= \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}} \\
E_n &= \frac{\hbar^2 k^2}{2m}
\end{aligned}$$

with

$$k_x = \frac{2n_x\pi}{L_x} \qquad k_y = \frac{2n_y\pi}{L_y} \qquad k_z = \frac{2n_z\pi}{L_z}$$

The momentum carried in the plane wave state is $\vec{p} = \hbar\vec{k}$ and the velocity $\vec{v} = \frac{\hbar\vec{k}}{m}$. Each state is characterized by $\vec{k}$ and by the spin σ along some chosen axis. There are 2 different states for each allowed value of $\vec{k}$. Note that the probability density $|\psi_n(\vec{r})|^2$ is uniform in space.

Density of States

Suppose we are interested in some property of the one-electron states, such as the total average number of electrons in them. We sum over the states

$$N = \sum_{\vec{k}\sigma} n_{k\sigma} \qquad \begin{array}{c}\text{sum over allowed } \vec{k}'s \\ k_x = \dfrac{2n\pi}{L}, \text{etc.}\end{array}$$

where $n_{k\sigma}$ is the number of electrons in state k with spin σ. Assume that $n_{k\sigma}$ is a rather smoothly varying function of $\vec{k}$. This allows us to transform the sum into an integral.

$$\sum_{\vec{k}\sigma} n_{k\sigma} \to \sum_{\sigma} \int d^3k \; n_{k\sigma}\, \varphi(\vec{k})$$

$\varphi(\vec{k})$ is the density of states per unit volume of $\vec{k}$-space. What is $\varphi(\vec{k})$? $k_x = \dfrac{2n\pi}{L_x}$ implies that the density of allowed k_x values along the k_x-axis is $\frac{1}{2\pi/L_x} = \frac{L_x}{2\pi}$. Similar arguments for k_y and k_z lead to

$$\boxed{\varphi(\vec{k}) = \frac{L_x L_y L_z}{(2\pi)^3} = \frac{V}{(2\pi)^3} = \text{ density of states of one spin in } k\text{-space}}$$

Note that this is independent of the ratio of L_x, L_y, and L_z. In fact, $\varphi(\vec{k})$ is independent of the sample shape in the limit $V \to \infty$, except for the lowest few states.

If spin is included, put in an extra factor of 2. Thus

$$\sum_{\vec{k}\sigma} n_{k\sigma} \longrightarrow \sum_{\sigma} V \int \frac{d^3k}{(2\pi)^3} n_{k\sigma} = \frac{2V}{(2\pi)^3} \int d^3k \, n_k$$

if $n_{k\sigma}$ is independent of σ. In general for any dimension d

$$\sum_{\vec{k}\sigma} \longrightarrow \frac{2V_d}{(2\pi)^d} \int d^dk$$

where V_d is the d-dimensional volume.

Density of States Per Unit Energy

Most of the properties of the electron states are governed by energy, and sometimes, direction of propagation. So it is convenient to write

$$\int d^3k \longrightarrow \int d\Omega \int k^2 dk = \int \frac{d\Omega}{4\pi} \cdot 4\pi \int k^2 dk$$

If the property we are considering does not depend on angle, $\int \frac{d\Omega}{4\pi} = 1$ and we are left with $4\pi \int k^2 dk$.

Often it is more convenient to integrate over energy. Since $\varepsilon = \varepsilon(|k|)$ depends only on the magnitude of $\vec{k}$, $\Delta\varepsilon = (\frac{d\varepsilon}{dk})\Delta k$.

$$\int d^3k \longrightarrow 4\pi \int k^2 dk = 4\pi \int k^2 \frac{dk}{d\varepsilon} d\varepsilon$$

To summarize, for quantities which do not depend on angle or spin, we have

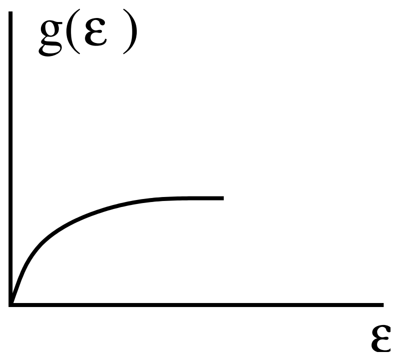
$$\sum_{\vec{k}\sigma} \longrightarrow \frac{2V}{(2\pi)^3} 4\pi \int k^2 \frac{dk}{d\varepsilon} d\varepsilon \equiv \int g(\varepsilon) d\varepsilon$$

where $g(\varepsilon) = \frac{2V}{(2\pi)^3}\, 4\pi k^2\, \frac{dk}{d\varepsilon} = \frac{dn}{d\varepsilon}$ is the number of states in the interval $\Delta\varepsilon$. It is called the *density of states*. This formula is valid in 3D.

For a free electron gas, $\varepsilon(k) = \frac{\hbar^2 k^2}{2m}$, $\frac{d\varepsilon}{dk} = \frac{\hbar^2 k}{m}$

$$\boxed{g(\varepsilon) = V \frac{mk}{\hbar^2\pi^2} = V \frac{m}{\hbar^2\pi^2} \sqrt{\frac{2m}{\hbar^2}}\ \varepsilon^{\frac{1}{2}}}$$

For $\varepsilon < 0$, $g(\varepsilon) = 0$. Note $g(\varepsilon) \propto V$.



Fermi-Dirac Statistics

Electrons are fermions, hence the total wavefunction is antisymmetric. There can be no more than one electron per state $|k\sigma\rangle$. At $T = 0$, the ground state is obtained by filling up the lowest possible energy states (assuming a fixed number of electrons). In this way, we fill up a sphere in k-space. The radius of the sphere is fixed by the condition

$$N = \sum_{k\sigma} n_{k\sigma} = \text{ total number of occupied states}$$

Call the radius of the sphere k_F. Then

$$N = \frac{4}{3}\pi k_F^3 \cdot \frac{2V}{(2\pi)^3} = \frac{V k_F^3}{3\pi^2}$$

Thus the radius of the filled sphere is given by

$$\boxed{k_F^3 = \frac{N}{V} \cdot 3\pi^2}$$

k_F is called the Fermi wavevector. ($k_F = \frac{1.92}{r_s}$) The filled sphere is called the *Fermi sphere*. *Fermi momentum* $= p_F = \hbar k_F$. The *Fermi energy*

$$\varepsilon_F = \frac{p_F^2}{2m} = \frac{\hbar^2}{2m}\left(3\pi^2 \frac{N}{V}\right)^{2/3}$$

Fermi velocity $= v_F = \frac{p_F}{m}$. Note that all these depend only on the density N/V.

Typical values: $k_F \sim 10^8 \text{cm}^{-1}$ ($\sim 1\mathring{A}^{-1}$), $v_F \sim 10^8$ cm/sec (< 0.01c), $\varepsilon_F \sim$ a few eV $\sim$ atomic energies which is no coincidence. We can also define a Fermi temperature $T_F = \frac{\varepsilon_F}{k_B}$. $T_F \sim 10^4 - 10^5 K$. (Note $T \ll T_F$ for all temperatures where substance is a solid or a liquid.)

Ground State Energy and Bulk Modulus of Electron Gas

The total number of electrons $N = \sum\limits_{\vec{k}\sigma} n_{\vec{k}\sigma} = \int\limits_0^{\varepsilon_F} g(\varepsilon) d\varepsilon$. We could check our expression for $g(\varepsilon)$ by plugging it in to see if we get N back. The total energy is

$$E = \sum_{\vec{k}\sigma} \varepsilon_k n_{k\sigma} = \int_0^{\varepsilon_F} \varepsilon g(\varepsilon) d\varepsilon$$

Now $g(\varepsilon) = A\varepsilon^{1/2}$ (It won't matter what A is.)

$$\Rightarrow N = \frac{2}{3}A\,\varepsilon_F^{3/2} \quad \text{and} \quad E = \frac{2}{5}A\varepsilon_F^{5/2}.$$

Thus $\boxed{\frac{E}{N} = \frac{3}{5}\varepsilon_F}$ (no dependence on A)

(Contrast w/ classical gas $\frac{E}{N} = \frac{3}{2}kT$)

Pressure: Note ε_F is proportional to $(\frac{N}{V})^{2/3}$, i.e., it depends on V. If V is changed, the electron gas should exert a pressure. At $T = 0$,

$$P = -\left(\frac{\partial E}{\partial V}\right)_N = \frac{2}{3}\frac{E}{V} = \frac{2}{5}\left(\frac{N}{V}\right)\varepsilon_F \qquad \left(\text{use} \quad E = \frac{3}{5}N\varepsilon_F\right)$$

Aside: Dimensions or units dictate $-(\partial E/\partial V)_N = 2E/3V$:

$$\begin{aligned}
\varepsilon_F &\sim k_F^2 \sim n^{2/3} \sim \left(\frac{N}{V}\right)^{2/3} \\
E &= A\varepsilon_F \qquad \left(A = \frac{3}{5}N\right) \\
&= \tilde{A}\left(\frac{N}{V}\right)^{2/3} \\
\frac{dE}{dV} &= \frac{2}{3}\tilde{A}N^{2/3}V^{-5/3} \\
&= \frac{2}{3}\frac{E}{V}
\end{aligned}$$

where $\tilde{A}$ is a constant. The inverse compressibility (or bulk modulus B) is defined as $-V(\frac{dP}{dV})$. (At $T = 0$, the derivative is taken with $N = const.$) Since

$$P \propto \frac{\varepsilon_F}{V} \propto V^{-5/3}, \quad B = -V\frac{\partial P}{\partial V} = \frac{5}{3}P$$

Using $P = \frac{2}{3}\frac{E}{V}$, we obtain $B = \frac{10}{9}\frac{E}{V} = \frac{2}{3}(\frac{N}{V})\varepsilon_F$.

We would not expect B to represent the total bulk modulus (ions contribute, too!), but the fact that this gives the right order of magnitude means that the electronic contribution is substantial.