

I. TRANSPORT

Electrons don't just sit around.. They also move. In fact, their motion is how they are most important to our technology. There is one number is most important to us. The conductivity. We would want to know both the AC and DC part.

[Diagram of pulled electrons]

The Jellium model is a great starting point. Let's think of electrons subject to an electric field. If the electrons are completely free, we can write:

$$\frac{d\vec{p}}{dt} = eE(t) \quad (1)$$

and immediately change to Fourier transform:

$$-i\omega p_\omega = eE_\omega \rightarrow v_\omega = i\frac{eE_\omega}{m\omega} \quad (2)$$

The current density is really what we are after. It is simply the density of electrons multiplied by this velocity and the electron charge. We obtain:

$$j_\omega = i\frac{e^2 E_\omega}{m\omega} n \rightarrow \sigma_\omega = i\frac{e^2}{m\omega} n \quad (3)$$

is the ac conductivity. Looks a bit strange - looks like the DC conductivity is going to diverge. in an imaginary way! Indeed it will. What is missing in this story? Relaxation.

Electrons are resistive because they keep bumping into things. Impurities, phonons, lattice atoms and each other - and I'm saying these two together because every one on its own should not be enough to cause resistance. But more on that later. Let's make a crude approximation. Suppose electrons get scattered on average after time τ . With this we can add a term to eq. (1) which gives relaxation:

$$\frac{d\vec{p}}{dt} = eE(t) - \frac{\vec{p}}{\tau} \quad (4)$$

which quickly becomes

$$(-i\omega + \frac{1}{\tau})p_\omega = eE_\omega \rightarrow p_\omega = i\frac{eE_\omega}{\omega + i/\tau}. \quad (5)$$

So

$$\sigma(\omega) = \frac{ne^2/m}{1/\tau - i\omega} \quad (6)$$

This analysis is really fine but in practice we must think of distributions of electronic occupations. This motivated the development of an evolution equation for the distribution function of electrons. This is called the Boltzmann transport equation. The equation is supposed to describe the evolution of the density function. So why not start with the time derivative of the electronic density, as a function of both space and momentum:

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \frac{\partial \vec{r}}{\partial t} \cdot \nabla_{\vec{r}} f + \frac{\partial \vec{p}}{\partial t} \cdot \nabla_{\vec{p}} f \quad (7)$$

In the absence of scattering this has to vanish by .. theorem. But scattering should create a restoring force on the distribution. In principle we should calculate the entire effects of collisions on the distribution function. Luckily there is an effective approximation for the collision integral. The approximation on par with Eq. (4) is, surprisingly, the relaxation time approximation. We assume that there is an equilibrium distribution f_0 , which is just the Fermi distribution. And then, the collision integral is taken to be:

$$\frac{df}{dt} = -\frac{1}{\tau}(f - f_0) \quad (8)$$

How do we get the conductance from this? Let's think about what a field is going to do to the distribution. It is going to move it up momentum. We expect something along the lines of:

$$f - f_0 = \delta f_0(\cos\theta) \quad (9)$$

Let's see if this pans out by setting up the Boltzmann equation. We assume that the density function reaches a steady state, so $\frac{\partial f}{\partial t} = 0$. If there is only an electric field, we also don't expect any nonuniformity in space. So we expect $\nabla_{\vec{r}} f = 0$. The only thing we have left then is:

$$\frac{\partial \vec{p}}{\partial t} \nabla_{\vec{p}} f = eE \nabla_{\vec{p}} f = -\frac{1}{\tau} (f - f_0) \quad (10)$$

Next, we have another approximation. Let's assume that the deviation from equilibrium is small. So on the LHS we only need whatever comes from f_0 , and this automatically defines the perturbation.

$$e\vec{E} \nabla_{\vec{p}} f_0 = -\frac{1}{\tau} (f - f_0) \quad (11)$$

Now,

$$e\vec{E} \nabla_{\vec{p}} f_0 = e\vec{E} \cdot \hat{p} \frac{\partial f_0}{\partial p} = eE \cos \theta \frac{\partial f_0}{\partial p} \quad (12)$$

And finally, we obtain:

$$f = f_0 - \tau eE \cos \theta \frac{\partial f_0}{\partial p} \quad (13)$$

From this we need to extract the current. No problem. Each state has a velocity $\vec{v} = \nabla_{\vec{p}} \epsilon_{\vec{p}}$. For the entire current, we just need to average over the entire momentum space:

$$\vec{j} = 2e \int \frac{d^d \vec{p}}{(2\pi\hbar)^d} \nabla_{\vec{p}} \epsilon_{\vec{p}} f(\vec{p}) \quad (14)$$

By symmetry, we can see that the response will be along the direction of \vec{E} . Setting this in the x direction, and assuming the dispersion of free electrons (or at least isotropic) we can write:

$$\hat{x} \cdot \vec{j} = -2 \int \frac{d^d \vec{p}}{(2\pi\hbar)^d} |\nabla_{\vec{p}} \epsilon_{\vec{p}}| \tau e^2 \tau E \cos^2 \theta \frac{\partial f_0}{\partial p} \quad (15)$$

And the calculation is straight forward. Let's carry it out in 3d:

$$\vec{j} = -2\tau e^2 \vec{E} \int \frac{k^2 dk}{(2\pi)^3} \left| \frac{\partial \epsilon_p}{\partial p} \right| \int_0^{2\pi} \phi \int_0^{\pi/2} \sin \theta d\theta \cos^2 \theta \frac{\partial f_0}{\partial p} = -\vec{E} e^2 \tau \frac{1}{2\pi^2} \frac{2}{3} \int k^2 dk \frac{\partial \epsilon_p}{\partial p} \frac{\partial f(\epsilon_p)}{\partial p} \quad (16)$$

Now, the derivative of the Fermi function $f(\epsilon_p)$ at $T = 0$ is a delta-function no matter how you parse it. Namely, $\frac{\partial f(\epsilon_k)}{\partial k}$ is only substantial near $k = k_F$, and the integral: $\int dk \frac{\partial f(\epsilon_k)}{\partial k} \rightarrow -1$ when the integral covers the vicinity of k_F . From there it is easy to see that what we get is:

$$\vec{j} = e^2 \tau \vec{E} \frac{k_F^2}{3\pi^2} \frac{v_F}{\hbar} \quad (17)$$

but $v_F = \hbar k_F / m$ so we obtain the conductivity:

$$\sigma = e^2 \tau \frac{k_F^3}{3\pi^2} \frac{1}{m} \quad (18)$$

and recall that:

$$n = \frac{k_F^3}{3\pi^2} \quad (19)$$

so we get an answer that corresponds exactly to the Drude model:

$$\sigma = e^2 \tau \frac{n}{m} \quad (20)$$

A. Recasting in terms of density of states

Let's look back at Eqs. (14) and (15). Let's recast it in terms of the density of states:

$$\hat{x} \cdot \vec{j} = e \int d\epsilon \rho(\epsilon) \langle \hat{x} \cdot \nabla_{\vec{p}} \epsilon_{\vec{p}} f(\vec{p}) \rangle_{direction} = e^2 E \tau \int d\epsilon \rho(\epsilon) \langle (\hat{x} \cdot \nabla_{\vec{p}} \epsilon_{\vec{p}})^2 \rangle_{direction} \frac{\partial f(\epsilon)}{\partial \epsilon} \quad (21)$$

Where we used the fact that:

$$\nabla_{\vec{p}} f(\epsilon_p) = \nabla_{\vec{p}} \epsilon_p \frac{\partial f(\epsilon_p)}{\partial \epsilon_p}$$

and added the average over direction, which the DOS can't do on its own. At low temperature, this results in:

$$\hat{x} \cdot \vec{j} = e^2 E \rho(\epsilon_F) \langle (\hat{x} \cdot \nabla_{\vec{p}} \epsilon_{\vec{p}_F})^2 \rangle_{direction} \tau \int d\epsilon \frac{\partial f(\epsilon)}{\partial \epsilon} \quad (22)$$

Namely everything except the Fermi function take the Fermi surface value. By the way:

$$\int d\epsilon \frac{\partial f(\epsilon)}{\partial \epsilon} = -1 \quad (23)$$

And we get the conductivity as:

$$\sigma = e^2 \rho(\epsilon_F) \langle (\hat{x} \cdot \nabla_{\vec{p}} \epsilon_{\vec{p}_F})^2 \rangle_{direction} \tau \quad (24)$$

Why is this so helpful? Because now we can easily ask questions about different gradients with the same formalism.

B. Thermal conductivity

In order to consider the thermal conductivity, we think of a temperature that depends on location: $T(\vec{r})$. And let's even assume that the thermal gradient is along the x axis. We can use the Boltzmann equation again in the relaxation time approximation. The distribution function f could become a function of space through the temperature dependence, and we expect:

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \frac{\partial \vec{r}}{\partial t} \cdot \nabla_{\vec{r}} f + \frac{\partial \vec{p}}{\partial t} \cdot \nabla_{\vec{p}} f = \frac{\partial \vec{r}}{\partial t} \cdot \nabla_{\vec{r}} T \frac{\partial f}{\partial T}. \quad (25)$$

We would then like to write the relaxation part, Eq. (8). But that's not so easy! What is the relaxed distribution function? What is f_0 ? We could make the naive, but excellent, assumption that the distribution equilibrates locally to:

$$f_0 = \frac{1}{e^{(\epsilon - \mu)/T(\vec{r})} + 1} \quad (26)$$

Then we would have, to first order in τ :

$$\frac{\partial \vec{r}}{\partial t} \cdot \nabla_{\vec{r}} T \frac{\partial f}{\partial T} \approx \frac{\partial \vec{r}}{\partial t} \cdot \nabla_{\vec{r}} T \frac{\partial f_0}{\partial T} = -\frac{f - f_0}{\tau}. \quad (27)$$

Extracting f we obtain:

$$f = f_0 - \tau \frac{\partial \vec{r}}{\partial t} \cdot \nabla_{\vec{r}} T \frac{\partial f_0}{\partial T} = f_0 - \tau \frac{\partial \vec{r}}{\partial t} \cdot \nabla_{\vec{r}} T \frac{\partial f_0(\epsilon)}{\partial \epsilon} \left(-\frac{\epsilon - \mu}{T} \right) \quad (28)$$

If next, we would like to calculate the heat current density, we need to multiply the phase-space density not be $e\vec{v}$ as we done for the charge current. Rather, we need to multiply by the heat times the velocity (recall that multiplying the phase-space density by the velocity gives a probability current, and then we multiply by the stuff that the particles carry. It could be charge, or it could be heat):

$$(\epsilon_p - \mu) \vec{v}_p$$

and integrate.

Now, there is a subtle point to consider. Do we multiply by ϵ_p or $\epsilon_p - \mu$? it really depends if we are interested in the heat current, or the energy current. In the phrasing above I used heat. Indeed, the proper definition of thermal conductivity involves the heat current:

$$j_S = j_n \cdot s \quad (29)$$

with s being entropy per particle. Similarly, the definition of heat capacity is not (du/dT) but rather:

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_{N,V}. \quad (30)$$

What is the entropy per particle? We can find out by recalling from the first law of Thermodynamics that:

$$TdS = dU - \mu dN \quad (31)$$

And we are adding an electron at a particular state, we can write:

$$TdS = dN(\epsilon_p - \mu) \quad (32)$$

Again, we assume that we will only have a current in the direction of the gradient, and integrate of all states through the density of states. We obtain:

$$\hat{x} \cdot \vec{j}_S = \frac{dT}{dx} \tau \int d\epsilon \rho(\epsilon) \langle (\hat{x} \cdot \nabla_{\vec{p}} \epsilon_{\vec{p}})^2 \rangle_{direction} \frac{\partial f_0(\epsilon)}{\partial \epsilon} \frac{(\epsilon - \mu)^2}{T} \quad (33)$$

But this we can concisely write with only dimensionless quantities as:

$$\hat{x} \cdot \vec{j}_S = T \frac{dT}{dx} \tau \rho(\epsilon_F) \langle (\hat{x} \cdot \nabla_{\vec{p}} \epsilon_{\vec{p}})^2 \rangle_{direction} \int d\epsilon \frac{\partial f_0(\epsilon)}{\partial \epsilon} \frac{(\epsilon - \mu)^2}{T^2} \quad (34)$$

And the only difference is that the integral now has an extra factor of $\frac{(\epsilon - \mu)^2}{T^2}$ in the integrand.

If this is not glaringly a numerical factor, which also appears in the Sommerfeld expansion, I'm going to have to assign some Taylor expansions as a disciplinary measure. We can write the integral as:

$$\int d\epsilon \frac{\partial f_0(\epsilon)}{\partial \epsilon} \frac{(\epsilon - \mu)^2}{T^2} = \int dx \frac{df_0(x)}{dx} x^2 \quad (35)$$

with $x = (\epsilon - \mu)/T$, and $f_0(x) = 1/(e^x + 1)$. This is Temperature independent, and even mathematica can calculate it to be:

$$\int dx \frac{df_0(x)}{dx} x^2 = -\frac{\pi^2}{3} \quad (36)$$

And as final answer we get:

$$j_S = -\kappa \frac{dT}{dx} \quad (37)$$

with

$$\kappa = \tau T \frac{\pi^2}{3} \rho(\epsilon_F) \langle (\hat{x} \cdot \nabla_{\vec{p}} \epsilon_{\vec{p}})^2 \rangle_{direction} \quad (38)$$

We must compare this to Eq. (24). We quickly see that they are essentially the same:

$$\frac{3}{\pi^2} \frac{\kappa}{T} = \frac{\sigma}{e^2} \quad (39)$$

This is known as the Wiedemann-Franz law, and is generally true whenever thermal and electric conduction happens through the same quasi-particles.