I. TRANSPORT

Electrons don't just sit around. They also move. In fact, their motion is enormously important. It is reflected by the conductivity. Let us start with the conductivity. We would want to know both the AC and DC part.

A. AC conductivity of free 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:

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

and immediately change to Fourier transform:

$$-i\omega p_\omega = eE_\omega \to v_\omega = i\frac{eE_\omega}{m\omega} \tag{2}$$

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:

$$j_\omega = i\frac{e^2 E_\omega}{m\omega} n \to \sigma_\omega = i\frac{e^2}{m\omega} n \tag{3}$$

is the ac conductivity. Looks a bit strange - looks like the DC conductivity is going to diverge. Furhtermore - it is imaginary as frequency tends to zero! What is missing in this story? Relaxation.

B. Drude formula

Electrons are resistive because they keep bumping into things. Impurities, phonons, lattice atoms and each other - and I'm mentioning these last two together because every one on its own would 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. This mean we should add a term to eq. (1), which induces relaxation:

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

which quickly becomes

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

So

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

C. Boltzmann Transport Eqation

This analysis can be enhanced by thinking of distributions of electronic occupations. This motivated the development of an evolution equation for the distribution function of electrons. This is called the Boltzman 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:

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \frac{\partial \vec{r}}{\partial t}\cdot\nabla_{\vec{r}} f + \frac{\partial \vec{p}}{\partial t}\cdot\nabla_{\vec{p}} f. \tag{7}$$

To be precise, $f(\vec{r},\vec{p})$ is the occupation of momentum state with momentum $\vec{p}$, at location $\vec{r}$. In the absence of scattering this complete time derivative has to vanish by Liouville theorem.

Let us now consider an electron gas driven out of equilibrium. Scattering should create a restoring force on the distribution towards its equilibirum. In principle we should calculate the entire effects of collisions between electrons, and collisions of electrons with impourities and phonons not included in the single-particle description of the electronic momentum and energy states, on the distribution function time derivative, which is the LHS of Eq. (7). This is tough, however.

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 equilibruium distribution f_0, which is just the Fermi distribution. And then, the collision integral, which is taken to be:

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

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:

$$f - f_0 = \delta f \ll f,\, f_0 \tag{9}$$

Let's see if this pans out by setting up the Boltzmann equation. We assum etha 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:

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

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.

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

Now,

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

And finally, we obtain:

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

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:

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

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 eletrons (or at least isotropic) we can write:

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

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

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

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: $\int dk\frac{\partial f(\epsilon_k)}{\partial k} \to -1$ when the integral covers the vicinity of k_F. From there it is easy to see that what we get is:

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

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

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

and recall that:

$$n = \frac{k_F^3}{3\pi^2} \tag{19}$$

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

$$\sigma = e^2\tau\frac{n}{m} \tag{20}$$

[Below less edited]

D. 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:

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

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:

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

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

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

And we get the conductivity as:

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

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

E. 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:

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

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 localy to:

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

Then we would have, to first order in τ:

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

Extracting f we obtain:

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

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 intrested in the heat current, or the energy current. In the phrasing above I used heat. Indeed, the porper defnition of thermal conductivity involves the heat current:

$$j_S = j_n \cdot s \tag{29}$$

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

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

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

$$T dS = dU - \mu dN \tag{31}$$

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

$$T dS = dN(\epsilon_p - \mu) \tag{32}$$

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:

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

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

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

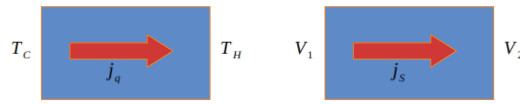
And the only difference is that the integral now has an extra factor of $\frac{(\epsilon-\mu)^2}{T^2}$ in the integrand.

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:

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

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

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



And as final answer we get:

$$j_S = -\kappa \frac{dT}{dx} \tag{37}$$

with

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

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

$$\frac{3}{\pi^2} \frac{\kappa}{T} = \frac{\sigma}{e^2} \tag{39}$$

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

F. Seebeck/Peltier Effect

As a bonus we can also calculate the the amount of electrical current that flows due to a temperature difference. Indeed, when a temperature difference appears, we it's going to move the electrons just because the electrons are the carriers of energy, and more importantly, entropy.

The calculation follows pretty closely to the calclation of the thermal conductivity, except, instead of multiplying the emergent distribution by energy, we multiply by the charge of the electrons:

$$\hat{x} \cdot \vec{j} = \frac{dT}{dx} \tau \int d\epsilon \rho(\epsilon) \langle (\hat{x} \cdot \nabla_{\vec{p}} \epsilon_{\vec{p}})^2 \rangle_{direction} \frac{\partial f_0(\epsilon)}{\partial \epsilon} \frac{(\epsilon - \mu)}{T} e \tag{40}$$

Which yields a Peltier coefficient:

$$\vec{j} = -\lambda \nabla T, \; \lambda = -e\tau \int d\epsilon \rho(\epsilon) \langle (\hat{x} \cdot \nabla_{\vec{p}} \epsilon_{\vec{p}})^2 \rangle_{direction} \frac{\partial f_0(\epsilon)}{\partial \epsilon} \frac{(\epsilon - \mu)}{T} \tag{41}$$

We are tempted to just take the same steps that we had before, and write:

$$\hat{x} \cdot \vec{j} \approx T \frac{dT}{dx} \tau \rho(\epsilon_F) \langle (\hat{x} \cdot \nabla_{\vec{p}} \epsilon_{\vec{p}})^2 \rangle_{direction} \int d\epsilon \frac{\partial f_0(\epsilon)}{\partial \epsilon} \frac{(\epsilon - \mu)}{T^2} \tag{42}$$

But this would result in zero - since $\frac{\partial f_0(\epsilon)}{\partial \epsilon}$ is symmetric about the fermi surface. For this we need the full expression for the denisty of states as well as the group velocity as a function of energy.

Let's as an example calculate this for a free electron gas in 3d.

First, we recall that (see Eq. **??** above)

$$\rho(\epsilon) = 2 \cdot 4\pi \left(\frac{\sqrt{2m}}{2\pi\hbar} \right)^3 \sqrt{\epsilon} \tag{43}$$

and that

$$\frac{\partial \epsilon_k}{\partial k} = \frac{\hbar^2 k}{m} = \sqrt{2\epsilon/m} \tag{44}$$

putting this into the formula we obtain:

$$\lambda = -e\tau \int d\epsilon \frac{2^{3/2}}{3\sqrt{m}\pi^2\hbar^3}\epsilon^{3/2}\frac{\partial f_0(\epsilon)}{\partial\epsilon}\frac{(\epsilon-\mu)}{T} \tag{45}$$

Now, the $\frac{\partial f_0(\epsilon)}{\partial\epsilon}$ is symmetric about μ, so in order to extract the non-vanishing contribution we can expand:

$$\epsilon^{3/2} = (\mu + (\epsilon-\mu))^{3/2} \approx \mu^{3/2} + \frac{3}{2}\mu^{1/2}(\epsilon-\mu) \tag{46}$$

The constant piece vanishes, but the second one teams up with the $\epsilon - \mu$ in the integrand to give:

$$\lambda = -e\tau \frac{2^{1/2}}{\sqrt{m}\pi^2\hbar^3}\mu^{1/2}\int d\epsilon \frac{\partial f_0(\epsilon)}{\partial\epsilon}\frac{(\epsilon-\mu)^2}{T} = e\tau\frac{(2\mu/m)^{1/2}}{3\hbar^3}T \tag{47}$$

G. Onsager relations

Wait - there is another coefficient we could calculate. We could ask how much heat current results from a potential difference. We can take the equation that we had before for the charge current:

$$\hat{x}\cdot\vec{j} = e\tau\int d\epsilon\rho(\epsilon)\langle(\hat{x}\cdot\nabla_{\vec{p}}\epsilon_{\vec{p}})^2\rangle_{direction}\frac{\partial f(\vec{p})}{\partial x} = e^2E\tau\int d\epsilon\rho(\epsilon)\langle(\hat{x}\cdot\nabla_{\vec{p}}\epsilon_{\vec{p}})^2\rangle_{direction}\frac{\partial f(\epsilon)}{\partial\epsilon} \tag{48}$$

but instead of multiplying by e in the middle segment of the equation, we need to multiply by the amount of heat that is carried by the electrons:

$$\rightarrow \hat{x}\cdot\vec{j}_S = \int d\epsilon\rho(\epsilon)\langle(\hat{x}\cdot\nabla_{\vec{p}}\epsilon_{\vec{p}})\rangle_{direction}\frac{\partial f(\epsilon)}{\partial\epsilon}\cdot(\epsilon-\mu) \tag{49}$$

which ends up giving:

$$\hat{x}\cdot\vec{j}_S = eET\tau\int d\epsilon\rho(\epsilon_F)\langle(\hat{x}\cdot\nabla_{\vec{p}}\epsilon_{\vec{p}})^2\rangle_{direction}\frac{\partial f_0(\epsilon)}{\partial\epsilon}\frac{(\epsilon-\mu)}{T} \tag{50}$$

and it seems:

$$\hat{x}\cdot\vec{j}_S = \lambda TE \tag{51}$$

which λ? The same one from the Peltier effect!

This is actually a general result, which is referred to as the Onsager relations. Onsager is one of the sages of statistical mechanics, and is responsible for the 2d solution of the Ising model. But his contributions are everywhere. In this case he organized the transport coefficients we had as follows:

$$\begin{pmatrix}\vec{j}_q\\ \vec{j}_S\end{pmatrix} = \begin{pmatrix}L_{qq} & L_{qs}\\ TL_{sq} & L_{ss}\end{pmatrix}\begin{pmatrix}\nabla\mu/e\\ \nabla T\end{pmatrix} \tag{52}$$

and then showed that:

$$\lambda = L_{qs}(B) = L_{sq}(-B) \tag{53}$$

with B the magnetic field. There is a good sketch of the proof in wikipedia, actually, and I would recommend you looking at it.

Note: One could have gone through the dervation considering the response to gradients $\nabla\frac{1}{T}$, $\nabla\frac{\mu}{T}$. This would result in a similar relation to Eq. (54), but with the *energy* current replacing the heat current:

$$\begin{pmatrix}\vec{j}_q\\ \vec{j}_u\end{pmatrix} = \begin{pmatrix}L_{qq} & L_{qu}\\ L_{uq} & L_{uu}\end{pmatrix}\begin{pmatrix}\nabla\frac{\mu}{T}\\ \nabla\frac{1}{T}\end{pmatrix} \tag{54}$$

with $L_{qu}(B) = L_{uq}(-B)$.

H. Seebeck effect and coefficient

If we have a current as a result of a temperature difference, we can guess that we will also have a voltage drop. Roughly:

$$\sigma \Delta V = \lambda \Delta T \tag{55}$$

At least the units are clear:

$$\frac{\lambda}{\sigma} = \alpha \frac{k_B}{e} \tag{56}$$

In fact, we could calculate this ratio for the 3d electron gas we were obsessing about:

$$\sigma = \frac{ne^2\tau}{m} = \frac{p_F^3}{3\pi^2\hbar^3} e^2 \frac{\tau}{m} \tag{57}$$

and we recall the expression for $\lambda = e\tau \frac{(2\mu/m)^{1/2}}{3\hbar^3} k_B^2 T$. Note that I added to Boltzmann constants so that we can count temperature in Kelvin again. One came from the T coefficient in λ, and the second comes from the ∇T. We see that:

$$\frac{\lambda}{\sigma} = \frac{k_B}{e} \pi^2 \frac{k_B T}{E_F} \tag{58}$$

What is this number - $k_B T/E_F$? It is the entropy per electron of the Fermi gas. The following discussion shows that this is quite general.

Actually, this ratio is anotoher manifestation of thermo-electric effect - the Seebeck effect. A temperature different results in a voltage difference:

$$S_{TE} = \frac{\Delta V}{\Delta T} \tag{59}$$

To finish this discussion and allow the qualitative discussion I would like to have, I would like to bring back memories from Thermodynamics for you. Can you recall the Gibbs-Duhem relation? It is the consequnce of the following identity associated with the grand canonical potential (or the Gibbs free energy for that matter):

$$-pV = \Omega(T, \mu, V) = U - TS - \mu N \tag{60}$$

In differential form it is:

$$V dp = -S dT - N d\mu \tag{61}$$

Now do the following rather ill advised step: divide by dx, and assume $dp/dx = 0$ no pressure gradient, at least that. . . We get:

$$\nabla \mu = \frac{S}{N} \nabla T \tag{62}$$

but this is the same as:

$$e \nabla V = k_B \frac{S}{N} \nabla T \tag{63}$$

and we added k_B for good dimensions. But thi gives:

$$S_{TE} = k_B/e \cdot \frac{S}{N} \tag{64}$$

so the k_B/e ratio, times entropy per particle. That is the baseline for the seebeck coefficient.