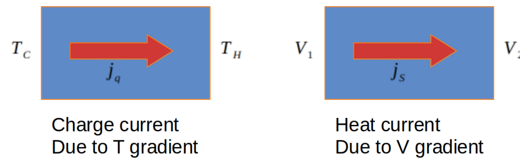

I. THERMOELECTRIC EFFECTS

A. 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:

$$\hat{x} \cdot \vec{j} = \frac{dT}{dx} \tau \int d\epsilon \rho(\epsilon) \langle (\hat{x} \cdot \nabla_{\vec{p}} \epsilon_{\vec{p}})^2 \rangle_{direction} \frac{\partial f_0(\epsilon)}{\partial \epsilon} \frac{(\epsilon - \mu)}{T} e \tag{1}$$

Which yields a Peltier coefficient:

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

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

$$\hat{x} \cdot \vec{j} \approx T \frac{dT}{dx} \tau \rho(\epsilon_F) \langle (\hat{x} \cdot \nabla_{\vec{p}} \epsilon_{\vec{p}})^2 \rangle_{direction} \int d\epsilon \frac{\partial f_0(\epsilon)}{\partial \epsilon} \frac{(\epsilon - \mu)}{T^2} \tag{3}$$

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)

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

and that

$$\frac{\partial \epsilon_k}{\partial k} = \frac{\hbar^2 k}{m} = \sqrt{2\epsilon/m} \tag{5}$$

putting this into the formula we obtain:

$$\lambda = -e\tau \int d\epsilon \frac{2^{3/2}}{3\sqrt{m}\pi^2\hbar^3} \epsilon^{3/2} \frac{\partial f_0(\epsilon)}{\partial \epsilon} \frac{(\epsilon - \mu)}{T} \tag{6}$$

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:

$$\epsilon^{3/2} = (\mu + (\epsilon - \mu))^{3/2} \approx \mu^{3/2} + \frac{3}{2} \mu^{1/2} (\epsilon - \mu) \tag{7}$$

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

$$\lambda = -e\tau \frac{2^{1/2}}{\sqrt{m}\pi^2\hbar^3} \mu^{1/2} \int d\epsilon \frac{\partial f_0(\epsilon)}{\partial \epsilon} \frac{(\epsilon - \mu)^2}{T} = e\tau \frac{(2\mu/m)^{1/2}}{3\hbar^3} T \tag{8}$$

B. 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:

$$\hat{x} \cdot \vec{j} = e\tau \int d\epsilon \rho(\epsilon) \langle (\hat{x} \cdot \nabla_{\vec{p}} \epsilon_{\vec{p}})^2 \rangle_{direction} \frac{\partial f(\vec{p})}{\partial x} = e^2 E\tau \int d\epsilon \rho(\epsilon) \langle (\hat{x} \cdot \nabla_{\vec{p}} \epsilon_{\vec{p}})^2 \rangle_{direction} \frac{\partial f(\epsilon)}{\partial \epsilon} \tag{9}$$

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:

$$\rightarrow \hat{x} \cdot \vec{j}_S = \int d\epsilon \rho(\epsilon) \langle (\hat{x} \cdot \nabla_{\vec{p}} \epsilon_{\vec{p}}) \rangle_{direction} \frac{\partial f(\epsilon)}{\partial \epsilon} \cdot (\epsilon - \mu) \tag{10}$$

which ends up giving:

$$\hat{x} \cdot \vec{j}_S = eET\tau \int d\epsilon \rho(\epsilon_F) \langle (\hat{x} \cdot \nabla_{\vec{p}} \epsilon_{\vec{p}})^2 \rangle_{direction} \frac{\partial f_0(\epsilon)}{\partial \epsilon} \frac{(\epsilon - \mu)}{T} \tag{11}$$

and it seems:

$$\hat{x} \cdot \vec{j}_S = \lambda T E \tag{12}$$

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:

$$\begin{pmatrix} \vec{j}_q \\ \vec{j}_S \end{pmatrix} = \begin{pmatrix} L_{qq} & L_{qs} \\ TL_{sq} & L_{ss} \end{pmatrix} \begin{pmatrix} \nabla \mu / e \\ \nabla T \end{pmatrix} \tag{13}$$

and then showed that:

$$\lambda = L_{qs}(B) = L_{sq}(-B) \tag{14}$$

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. (15), but with the *energy* current replacing the heat current:

$$\begin{pmatrix} \vec{j}_q \\ \vec{j}_u \end{pmatrix} = \begin{pmatrix} L_{qq} & L_{qu} \\ L_{uq} & L_{uu} \end{pmatrix} \begin{pmatrix} \nabla \frac{\mu}{T} \\ \nabla \frac{1}{T} \end{pmatrix} \tag{15}$$

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

C. 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:

$$\sigma \Delta V = \lambda \Delta T \tag{16}$$

At least the units are clear:

$$\frac{\lambda}{\sigma} = \alpha \frac{k_B}{e} \tag{17}$$

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

$$\sigma = \frac{ne^2\tau}{m} = \frac{p_F^3}{3\pi^2\hbar^3} e^2 \frac{\tau}{m} \tag{18}$$

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:

$$\frac{\lambda}{\sigma} = \frac{k_B}{e}\pi^2\frac{k_B T}{E_F} \tag{19}$$

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:

$$S_{TE} = \frac{\Delta V}{\Delta T} \tag{20}$$

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):

$$-pV = \Omega(T, \mu, V) = U - TS - \mu N \tag{21}$$

In differential form it is:

$$V dp = -SdT - Nd\mu \tag{22}$$

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

$$\nabla\mu = \frac{S}{N}\nabla T \tag{23}$$

but this is the same as:

$$e\nabla V = k_B\frac{S}{N}\nabla T \tag{24}$$

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

$$S_{TE} = k_B/e \cdot \frac{S}{N} \tag{25}$$

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