

Lecture 18

Thermoelectric effects

Thermoelectric effect - generation of electric current or ~~voltage~~ voltage due to temperature gradients.

Reason: if temperature is nonuniform, electrons will flow from hot to cold parts of the sample, thus creating electric current.
This can also be described using Boltzmann equation:

$$\vec{\nabla} f \cdot \vec{v} + \frac{f - f_0}{\tau} = 0$$

No external forces $\Rightarrow \vec{\nabla}_k f \cdot \vec{v}$ term is absent.

Allow the temperature to be nonuniform.
Then ~~the~~ the equilibrium distribution f_0 will depend on \vec{r} :

$$f_0(\vec{k}, \vec{r}) = \frac{1}{e^{\frac{E_k - E_F}{k_B T(\vec{r})}} + 1}$$

$$\vec{\nabla} f \approx \vec{\nabla} f_0 = \frac{\partial f_0}{\partial T} \vec{\nabla} T = - \frac{E_k - E_F}{T} \frac{\partial f_0}{\partial E_k} \vec{\nabla} T$$

2
We obtain:

$$-\frac{E_k - E_F}{T} \frac{\partial f_0}{\partial E_k} \vec{\nabla} T \cdot \vec{v} + \frac{f_1}{T} = 0$$

$$f_1 = T \frac{\partial f_0}{\partial E_k} \frac{E_k - E_F}{T} \vec{\nabla} T \cdot \vec{v}$$

Electric current density is given by:

$$\vec{j} = -e \int \frac{d\vec{k}}{4\pi^3} f_1 \vec{v} =$$

$$= -\frac{eT}{4\pi^3} \int d\vec{k} \frac{\partial f_0}{\partial E_k} \frac{E_k - E_F}{T} (\vec{\nabla} T \cdot \vec{v}) \vec{v}$$

Note: now we can't simply take

$$\frac{\partial f_0}{\partial E_k} = -\delta(E_k - E_F), \text{ need to be more careful.}$$

Again, assume lightly filled band and use effective mass approximation:

$$E_k = \frac{\hbar^2 k^2}{2m^*}$$

$$\text{let } \vec{\nabla} T = |\vec{\nabla} T| \hat{z}$$

The current will be in the same direction, since the Fermi surface is spherical.

$$\vec{j} = -\frac{e\tau}{4\pi^3} 2\pi \int_0^\pi d\theta \sin\theta \cos^2\theta \int_0^\infty dk k^2 \frac{\partial f_0}{\partial \epsilon_k}.$$

$$\cdot \frac{\epsilon_k - \epsilon_F}{T} v_k^2 \vec{\nabla} T$$

$$\text{let } \vec{j} = L \vec{\nabla} T$$

$$dk \cdot k^4 = \frac{m^*}{\hbar^2} \left(\frac{2m^*}{\hbar^2} \epsilon \right)^{3/2} d\epsilon$$

$$L = -\frac{e\tau}{3\pi^2 m^*} \int_0^\infty d\epsilon \left(\frac{2m^* \epsilon}{\hbar^2} \right)^{3/2} \frac{\partial f_0}{\partial \epsilon}.$$

$$\cdot \frac{\epsilon - \epsilon_F}{T}$$

~~Need to expand~~ $\frac{\partial f_0}{\partial \epsilon}$ is sharply peaked and symmetric around ϵ_F . Thus we need to expand $\epsilon^{3/2}$ around ϵ_F .

$$\begin{aligned} \epsilon^{3/2} &= (\epsilon_F + \epsilon - \epsilon_F)^{3/2} = \epsilon_F^{3/2} \left(1 + \frac{\epsilon - \epsilon_F}{\epsilon_F} \right)^{3/2} \\ &\approx \epsilon_F^{3/2} \left(1 + \frac{3}{2} \frac{\epsilon - \epsilon_F}{\epsilon_F} \right) = \epsilon_F^{3/2} + \frac{3}{2} \epsilon_F^{1/2} (\epsilon - \epsilon_F) \end{aligned}$$

Then we obtain:

$$L = - \frac{e\tau}{2\pi^2 m^* T} \left(\frac{2m^*}{\hbar^2} \right)^{3/2} E_F^{1/2} \int_0^\infty d\varepsilon (\varepsilon - E_F)^2 \frac{\partial f_0}{\partial \varepsilon}$$

As in the calculation of the electronic specific heat, change integration variable to:

$$x = \frac{\varepsilon - E_F}{k_B T}$$

$$\frac{\partial f_0}{\partial \varepsilon} = \frac{1}{k_B T} \frac{\partial f_0}{\partial x}$$

$$\frac{\partial f_0}{\partial x} = - \frac{e^x}{(e^x + 1)^2}$$

then we obtain:

$$L = \frac{e\tau (k_B T)^2}{2\pi^2 m^* T} \left(\frac{2m^*}{\hbar^2} \right)^{3/2} E_F^{1/2} \int_{-\infty}^{\infty} dx \cdot x^2 \frac{e^x}{(e^x + 1)^2}$$

$\frac{\pi^2}{3}$

$$L = \frac{\pi^2}{3} k_B^2 T \frac{e\tau}{2\pi^2 m^*} \left(\frac{2m^*}{\hbar^2} \right)^{3/2} E_F^{1/2}$$

To rewrite this in a more illuminating way, first go back to the expression for conductivity from lecture 16.

When we calculated conductivity in the effective mass approximation we obtained:

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

let us rewrite this in a different way.

Start from one of the intermediate expressions:

$$\sigma = \frac{e^2 \tau}{3 \pi^2 m^*} \underbrace{\frac{2 m^* E_F}{\hbar^2}}_{k_F^2} \sqrt{\frac{2 m^* E_F}{\hbar^2}}$$

Recall the expression for the density of states:

$$g(\epsilon) = \frac{m^*}{\pi^2 \hbar^2} \sqrt{\frac{2 m^* \epsilon}{\hbar^2}}$$

Then we obtain; using $v_F = \frac{\hbar k_F}{m^*}$:

$$\sigma = \frac{1}{3} e^2 v_F^2 \tau g(\epsilon_F) \quad \text{— conductivity is proportional to the density of states at Fermi energy.}$$

let us write L in a similar form.

$$\begin{aligned} L &= \frac{\pi^2}{3} k_B^2 T \frac{e \tau}{\pi^2 m^*} \frac{2 m^* E_F}{\hbar^2} \sqrt{\frac{m^*}{2 \hbar^2 E_F}} = \\ &= \frac{\pi^2}{3} k_B^2 T e \tau v_F^2 \left. \frac{dg(\epsilon)}{d\epsilon} \right|_{\epsilon = E_F} \end{aligned}$$

Usually, what is measured in experiment is voltage in response to $\vec{\nabla} T$, not current.

$$\vec{J} = L \vec{\nabla} T$$

$$\vec{E} = \rho \vec{J} = \frac{1}{\sigma} \vec{J}$$

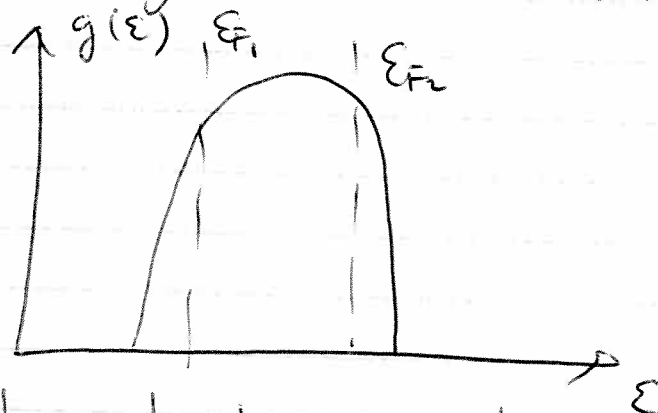
Thus we have:

$$\vec{E} = \frac{1}{\sigma} L \vec{\nabla} T$$

$$\text{Define } S = \cancel{L/\sigma} = \frac{\pi^2 k_B^2 T}{e g(\epsilon_F)} \left. \frac{dg(\epsilon)}{d\epsilon} \right|_{\epsilon=\epsilon_F}$$

S is the thermopower.

Unlike conductivity S is proportional to the derivative of the ~~density~~ density of states at Fermi energy, not the density of states itself.



Clearly $\left. \frac{dg}{d\epsilon} \right|_{\epsilon=\epsilon_F}$ will generally have opposite sign for lightly-filled or almost-filled band.

This can also be seen from the fact that

$$S \sim \frac{1}{e}.$$

Thus ~~the sign of the thermopower is~~ sensitive to the type of conduction - electron or hole.

Another important transport property of metals is ~~thermal~~ conductivity. Metals are generally good conductors of heat as well as electricity and there is in fact a very close relation between ~~thermal~~ conductivity and electrical conductivity.

~~Thermal~~ conductivity is defined as:

$$\vec{J}_q = -\kappa \vec{\nabla} T$$

\vec{J}_q is the heat current.

Physically, when there is a temperature gradient in the sample, electrons will flow from the hot to the cold part ~~to equalize the temperature~~ to equalize the temperature, hence the heat flow.

To write explicit expression for the heat current note the following thermodynamic identity:

$$dQ = T dS = dE - \mu dN$$

This means that:

$\vec{J}_q = \vec{J}_\varepsilon - \mu \vec{J}_n$, where \vec{J}_ε is the energy current and \vec{J}_n is the electron number current.

$$\vec{J} = -e \vec{J}_n$$

Then we obtain:

$$\vec{J}_q = \int \frac{d\vec{k}}{4\pi^3} (\varepsilon_k - \varepsilon_F) \Phi_1 \vec{v}$$

Use our solution for Φ_1 :

$$\Phi_1 = T \frac{\partial f_0}{\partial \varepsilon_k} \frac{\varepsilon_k - \varepsilon_F}{T} \vec{\nabla} T \cdot \vec{v}$$

Again, assume effective mass approximation is valid,

$$\varepsilon_k = \frac{\hbar^2 k^2}{2m^*}$$

$$\vec{J}_q = \frac{T}{4\pi^3} \cdot 2\pi \int_0^\pi d\theta \sin\theta \cos^2\theta \int_0^\infty dk \cdot k^2 \frac{\hbar^2 k^2}{m^{*2}}$$

$$\frac{\partial f_0}{\partial \varepsilon_k} \frac{(\varepsilon_k - \varepsilon_F)^2}{T} \vec{\nabla} T$$

Thus for the ~~band~~^{thermal} conductivity we obtain:

~~$$\mathcal{R} = - \frac{T}{3\pi^2 m^* T} \int_0^\infty d\varepsilon \left(\frac{2m^* \varepsilon}{\hbar^2} \right)^{3/2} \frac{\partial f_0}{\partial \varepsilon} (\varepsilon - \varepsilon_F)^2 \approx$$~~

$$\mathcal{R} = - \frac{T}{3\pi^2 m^* T} \int_0^\infty d\varepsilon \left(\frac{2m^* \varepsilon}{\hbar^2} \right)^{3/2} \frac{\partial f_0}{\partial \varepsilon} (\varepsilon - \varepsilon_F)^2 \approx$$

$$\approx - \frac{T}{3\pi^2 m^* T} \left(\frac{2m^* \varepsilon_F}{\hbar^2} \right)^{3/2} \int_0^\infty d\varepsilon (\varepsilon - \varepsilon_F)^2 \frac{\partial f_0}{\partial \varepsilon}$$

Change integration variable to $x = \frac{\varepsilon - \varepsilon_F}{k_B T}$
 and use $\varepsilon_F = \frac{\hbar^2}{2m^*} (3\pi^2 n)^{2/3}$.

Then we obtain:

$$\mathcal{R} = \bullet \frac{T}{3\pi^2 m^* T} 3\pi^2 n \cdot (k_B T)^2 \int_{-\infty}^{\infty} dx x^2 \frac{e^x}{(e^x + 1)^2} =$$

$$= \frac{\pi^2 T n k_B^2 T}{3 m^*}$$

Calculate the ratio of thermal and electrical conductivity:

$$\frac{\mathcal{R}}{\sigma T} = \frac{\pi^2 T n k_B^2 T}{3 m^*} \cdot \frac{m^*}{n e^2 T} = \frac{\pi^2 k_B^2}{3 e^2}$$

$\frac{\kappa}{\sigma T}$ is called Wiedemann-Franz ratio and is a universal number in ordinary metals.

Violation of Wiedemann-Franz law is a signal that electron-electron interactions are so strong that lead to qualitative changes in the character of the electron liquid and cannot be ignored.