FREE ELECTRON MODEL Lecture 16

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6.4.4 Experimental results

For our typical metal, with $n \approx 6 \times 10^{28} \mathrm{m}^{-3}$ and $\sigma \approx 6 \times 10^7 \,\Omega^{-1} \mathrm{m}^{-1}$ this gives $\tau \approx 3 \times 10^{-14}$ s. Putting this together with the Fermi velocity $v_{\mathrm{F}} \approx 10^6 \mathrm{m s}^{-1}$ gives $\Lambda \approx 3 \times 10^{-8} \mathrm{m}$ or about 100 interatomic distances. *Historical note:* Drude's theory of metals used a *classical* free electron model. This had electron speeds which were classically thermal $(\frac{1}{2}mv^2 = \frac{3}{2}k_{\mathrm{B}}T)$, i.e. much slower than the v_{F} of the Fermi gas. Drude also assumed that the electrons would be scattered by every atom (i.e. his Λ was about 100 times too small). As a result of these cancelling errors, his estimate of the electrical conductivity was not too bad.

6.5 Electronic Thermal Conductivity

We can use exactly the same expression as we used for phonons:

$$\kappa = \frac{1}{3}c_V v\Lambda,$$

only now c_V is the electronic specific heat per unit volume, v is the electron velocity, which we take as the Fermi velocity v_F , and Λ is the electronic mean free path, $\Lambda = v_F \tau$. We know that

$$c_V = \frac{\pi^2 n k_{\rm B}^2 T}{2E_{\rm F}},$$

(Note that we have converted from N_e to $n = N_e/V$ to get specific heat per volume) and so

$$\kappa = \frac{1}{3} \frac{\pi^2 n k_{\rm B}^2 T}{2E_{\rm F}} v_{\rm F} \times v_{\rm F} \tau.$$

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 $\kappa = \frac{1}{3} \frac{\pi^2 n k_{\rm B}^2 T}{2E_{\rm F}} v_{\rm F} \times v_{\rm F} \tau,$

$$E_{\rm F} = \frac{1}{2}m v_{\rm F}^2,$$

gives

with

$$\kappa = \frac{\pi^2 n k_{\rm B}^2 T \tau}{3m}.$$

If we take $n = 6 \times 10^{28} \text{ m}^{-3}$ and $\tau = 3 \times 10^{-14} \text{ s}$ we have at 300 K that $\kappa = 370 \text{ W} \text{ m}^{-1} \text{K}^{-1}$. The measured thermal conductivity of Copper is $400 \text{ W} \text{ m}^{-1} \text{K}^{-1}$ In pure metals, most of the thermal conductivity arises from the electrons: in impure metals (or random alloys, which amounts to the same thing) the vibrational contribution can be similar.

6.5.1 The Wiedemann-Franz law

At metals at temperatures that are not very low, the ratio of thermal to electrical conductivity is directly proportional to temperature.

$$\frac{\kappa}{\sigma} = \frac{\pi^2 n k_{\rm B}^2 T \tau / 3m}{n e^2 \tau / m} = \frac{\pi^2}{3} \left(\frac{k_{\rm B}}{e}\right)^2 T.$$

The constant of proportionality is called the Lorenz number:

$$L = \frac{\kappa}{\sigma T} = \frac{\pi^2}{3} \left(\frac{k_{\rm B}}{e}\right)^2 = 2.45 \times 10^{-8} \,{\rm W}\,\Omega\,{\rm K}^{-2}.$$

A temperature-independent Lorenz number depends on the relaxation processes for electrical and thermal conductivity being the same – which is not true at all temperatures.

Experimental Lorenz numbers:					
$\underline{\qquad} L \times 10^8 W \ \Omega \ K^{-2}$		$\frac{1}{L \times 10^8 W \Omega K^{-2}}$			
Element	L at 273 K	L at 373 K	Element	L at 273 K	L at 373 K
Ag	2.31	2.37	Pb	2.47	2.56
Au	2.35	2.40	Pt	2.51	2.60
Cd	2.42	2.43	Sn	2.52	2.40
Cu	2.23	2.33	W	3.04	3.20
Mo	2.61	2.79	Zn	2.31	2.33

6.6 Conductivity – the view from reciprocal space

6.6.1 Electrical conductivity

The effect of a force \mathcal{F} is to alter the *momentum*, $\hbar k$. We can ask what this will do to the Fermi sphere. For every electron

$$\frac{\mathrm{d}\mathbf{k}}{\mathrm{d}t} = \frac{\mathcal{F}}{\hbar},$$

so the Fermi sphere is displaced sideways.



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Note that there is a nett flow of electrons.

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If the field acts for a time τ

$$\delta k = \mathbf{k}(\tau) - \mathbf{k}(0) = \frac{\mathcal{F}\tau}{\hbar} - \frac{e\mathcal{E}\tau}{\hbar},$$

If $\mathcal{E} = 1000 \text{ V m}^{-1}$ and $\tau = 10^{-14} \text{ s then}$
$$\delta k = \frac{1.6 \times 10^{-19} \times 1000 \times 10^{-14}}{1.05 \times 10^{-34}} \approx 10^4 \text{ m}^{-1} \approx 10^{-6} k_{\text{F}},$$

the alteration in the Fermi surface is small.

6.6.2 Thermal conductivity

There is no nett electric current – but electrons travelling in one direction have on average higher energy than those travelling in the opposite direction.





The scattering processes are different:

- to reduce electric current requires large change in wavevector phonon contribution falls off quickly at low T.
- \bullet to reduce thermal current requires change in thermal energy by definition, energy $\approx k_{\rm B}T$

6.6.3 Contributions to scattering

Impurities contribution independent of temperature *Electron-phonon scattering*

- High T: plenty of large-k phonons, so effect on σ and κ similar
 - number of phonons $\propto T$ so $\Lambda \propto 1/T$
 - $-\,c_{\rm V}\propto T$
 - $\sigma \propto 1/T$, κ independent of T
- \bullet Low $T{:}$ few large-k phonons, so phonons less effective at limiting σ than κ
 - number of phonons $\propto T^3$ so $\Lambda \propto 1/T^3$ for κ
 - number of large-k phonons $\propto \exp(-\theta/T)$ so $\Lambda \propto \exp(\theta/T)$ for σ

$$-\sigma \propto \exp(\theta/T), \kappa \propto T^{-2}$$

• Very low T: very few phonons, so impurities dominate

$$-c_{\rm V} \propto T$$

– σ independent of T, $\kappa \propto T$

As we saw before, different processes give resistances in series:

$$\rho = \sum_{i} \rho_i$$

Resistivity of potassium - different purities.



Note that this means the Lorenz number $L=\kappa/(\sigma T)$ is not constant with temperature.



Schematic variation of thermal resistance (a), thermal conductivity (b) with T at low T.



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