

VIII.2 Wiedemann - Franz law

is a connection between electric conductivity σ , defined by

$$(8.12) \quad \mathbf{j} = -\sigma \frac{\Delta V}{\Delta x} \quad E = -\frac{\Delta V}{\Delta x}$$

and heat conductivity κ , defined by

$$(8.13) \quad \frac{\Delta Q}{A \Delta t} = -\kappa \frac{\Delta T}{\Delta x}$$

This expression relates transport of thermal energy per area and time interval to temperature gradient.

(8.14) Wiedemann - Franz Law (1853)

$\frac{\kappa}{\sigma}$ same for all metals,
depends on T only

reason: in metals both charge and heat is transported mainly via electrons.

units in (8.13): $\left[\frac{\Delta Q}{A \Delta t} \right] = \frac{W}{m^2} \quad [\kappa] = \frac{J}{m \cdot s \cdot K}$

In classical kinetic gas theory, [no derivation]

$$(8.15) \quad \kappa = \frac{1}{3} \bar{C}_v v_{rms} \cdot L_{wfp}$$

where \bar{C}_v denotes heat capacity per unit volume, unit volume = $\frac{N_A}{n}$, Avogadro's number ~~per~~ electron density

$$(8.16) \quad \bar{C}_v = \frac{3}{2} N_A k_B \left(\frac{n}{N_A} \right) = \frac{3}{2} k_B n$$

To understand (8.16), remember $C_{\text{vdW}} = 3R = 3N_A k_B$ written in (2.51) for solid. In solid, each particle has 3 kinetic and 3 potential degrees of freedom. For free electron gas, $C_{\text{vdW}} = \frac{3}{2} N_A k_B$, only kinetic degrees of freedom count.

Inserting (8.16) into (8.15)

$$(8.17) \quad \mathcal{R} = \frac{k_B n v_{\text{rms}} L_{\text{mfp}}}{2}$$

$$(8.18) \quad \stackrel{(8.11)}{\Rightarrow} \frac{\mathcal{R}}{\sigma} = \frac{k_B (v_{\text{rms}})^2 m e}{2 e^2} \stackrel{(8.4)}{=} \frac{3 k_B^2}{2 e^2} T$$

This is the classical version of Wiedemann-Franz law.

Comments on classical results:

- classical derivation (8.18) confirms that $\frac{\mathcal{R}}{\sigma}$ depends on T only and not on material

$$(8.19) \quad \bullet \quad \frac{\mathcal{R}}{\sigma T} = 1.1 \cdot 10^{-8} \frac{\text{W}\Omega}{\text{K}^2} \quad \text{Lorentz number}$$

approximately factor 2 too small, compared to experiment

- classical theory predicts

$$(8.20) \quad \sigma \sim \frac{1}{T} \quad (\text{theory})$$

but experiment shows

$$(8.21) \quad \frac{1}{\sigma} \sim T \quad (\text{experiment}) \quad \Downarrow$$

VIII.3 Quantum aspects of the electron gas in a metal

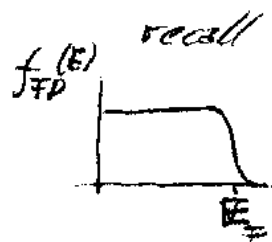
Electrons follow Fermi-Dirac statistics, so they occupy velocities up to essentially up to the Fermi velocity v_F

$$(8.22) \quad v_F = \sqrt{\frac{2E_F}{m_e}}$$

where E_F is the Fermi energy, see (7.15).

Only electrons close to the Fermi energy can move freely.

⇒ replace Maxwell-Boltzmann v_{rms} by Fermi velocity v_F



$$(8.23) \quad \sigma = \frac{n e^2 \bar{v}_{mfp}}{m_e v_F} \quad \text{electric conductivity (quantum)}$$

$$(8.24) \quad \kappa = \frac{1}{3} \bar{c}_v v_F L_{mfp} \quad \text{heat conductivity (quantum)}$$

~~Here~~ Note: $v_{rms} \sim \sqrt{T}$, but v_F is essentially temperature-independent.

This changes the T-dependence of σ
 Temperature dependence of σ is now given by T-dependence of L_{mfp}
 It turns out $\sigma \sim T$

To consider quantum version of Wiedemann-Franz; heat capacity of electron gas depends only on the few electrons near E_F , which transport heat

$$(8.25) \quad C_{\text{electrons}} = \frac{\pi^2}{3} \frac{k_B T}{E_F} \left(\frac{3}{2} R\right) \ll \frac{3}{2} R \quad (\text{no derivation})$$

This allows us to write

$$(8.26) \quad \begin{aligned} \rho & \stackrel{(8.24)}{=} \frac{1}{3} C_{\text{electrons}} \left(\frac{n}{N_A}\right) \cdot v_F L_{\text{mfp}} \\ & = \frac{1}{3} \frac{\pi^2}{3} \frac{k_B^2 T}{E_F} \cdot n \frac{3}{2} \cdot v_F L_{\text{mfp}} \\ & = \frac{\pi^2}{3} \frac{k_B^2 T}{m_e v_F} \cdot n L_{\text{mfp}} \end{aligned}$$

$$(8.27) \quad \begin{aligned} \frac{\rho}{\sigma T} & = \left(\frac{\pi^2}{3} \frac{k_B^2}{m_e v_F} \cdot n L_{\text{mfp}} \right) / \frac{n e^2 L_{\text{mfp}}}{m_e v_F} \\ & = \frac{\pi^2}{3} \frac{k_B^2}{e^2} = 2.45 \cdot 10^{-8} \frac{\text{W}\Omega}{\text{K}^2} \end{aligned}$$

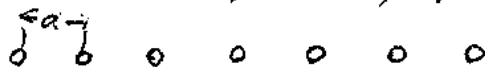
in very good agreement with experiment.

VIII.4 Energy bands in solids (metals)

Consider free electron wave function

$$(8.28) \quad \Psi_{\text{free}} = \text{const} e^{i(kx - \omega t)}, \quad E = \frac{p^2}{2m_e} = \frac{\hbar^2 k^2}{2m_e}$$

In an ordered crystal of positive charges at spacing a



waves propagate freely if they are in-phase with lattice structure, i.e.

(8.29)

$$2a = \pm n\lambda, \quad n=1,2,3,\dots \text{ integer}$$

With the wave number $k = \pm \frac{n\pi}{a}$, corresponding to (8.29), we can write down two ~~static waves~~ standing waves, which move neither to the left nor to the right

(8.30)

$$\begin{aligned} \Psi_- &= B e^{i(kx - \omega t)} - B e^{i(-kx - \omega t)} \\ &= \pm 2B i e^{-i\omega t} \sin \frac{n\pi x}{a} \end{aligned}$$

(8.31)

$$\begin{aligned} \Psi_+ &= B e^{i(kx - \omega t)} + B e^{i(-kx - \omega t)} \\ &= 2B e^{-i\omega t} \cos \frac{n\pi x}{a} \end{aligned}$$

The corresponding Born probabilities are

(8.32)

$$\Psi_-^* \Psi_- = 4|B|^2 \cos^2 \frac{n\pi x}{a} \quad \Psi_+^* \Psi_+ = 4|B|^2 \sin^2 \frac{n\pi x}{a}$$

Ψ_- has lower energy, since occupation probability is the highest at the position of positive charge $x=0$, etc.

\Rightarrow The energy levels between E_+ (corresponding to Ψ_+) and E_- (corresponding to Ψ_-) are not occupied (forbidden band), since there is no wave number k corresponding to them

