



Lecture 5

Free Electron Model

It sounds obviously wrong and much too simple, but to eventually appreciate this time-honored and indispensable model for metals is to learn what electron really means.

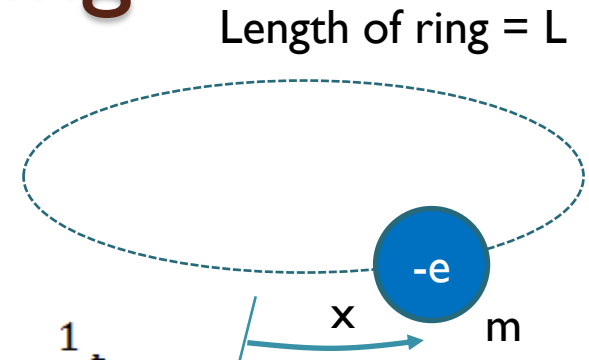
Free electron on a ring

$$\psi(x) = \psi(x + L) \quad \text{Born - von Karman boundary condition}$$

$$\psi(x) = \frac{1}{\sqrt{L}} e^{ikx}, \quad k = \frac{2\pi n}{L}, \quad n = \text{integer}$$

Quantum Numbers

$$p = \hbar k, \quad \varepsilon = \frac{\hbar^2 k^2}{2m}, \quad S_z = \frac{1}{2} \hbar$$



Free electron on a “hyper-ring”

Generalize ring to a torus (2d), a cube with periodic boundary (3d) etc. Define D as spatial dimension.

$$\psi(\mathbf{x}) = \psi(\mathbf{x} + \mathbf{L}) \quad \mathbf{L} = (L, L, \dots, L) \quad D - \text{vector}$$

$$\psi(\mathbf{x}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k} \cdot \mathbf{x}}, \quad k_i = \frac{2\pi n_i}{L}, \quad i = 1..D, \quad n_i = \text{integer}, \quad V = L^D$$

Quantum Numbers

$$\mathbf{p} = \hbar \mathbf{k}, \quad \varepsilon = \frac{\hbar^2 k^2}{2m}, \quad S_z = \frac{1}{2} \hbar$$

Will consider only D=3, from now on in this note.

Free electrons: Fermi Sea at T=0

DOS $dN = 2 \frac{4\pi k^2 dk}{(2\pi/L)^3} = V \frac{k^2 dk}{\pi^2} = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \sqrt{\varepsilon} d\varepsilon = g(\varepsilon) d\varepsilon$

$$g(\varepsilon) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \sqrt{\varepsilon} \propto \sqrt{\varepsilon} \quad \text{in 3d}$$

Fermi-Dirac Statistics and Number of particle numbers

give the energy cutoff (μ): $N = \int_0^{\varepsilon_F} g(\varepsilon) d\varepsilon = \frac{V}{3\pi^2} \left(\frac{2m\varepsilon_F}{\hbar^2}\right)^{\frac{3}{2}}$

Fermi energy

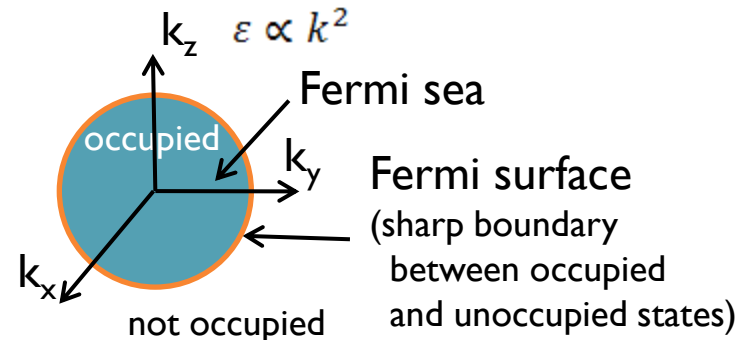
$$\varepsilon_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V}\right)^{2/3} \equiv \frac{\hbar^2 k_F^2}{2m}$$

Fermi momentum

$$k_F = \left(\frac{3\pi^2 N}{V}\right)^{\frac{1}{3}}$$

Fermi temperature

$$T_F \equiv \frac{\varepsilon_F}{k_B}$$



Check before you swim ... W²TGS

Q1: For a given phonon mode in the harmonic potential, which of the following distinguishes between many phonon states and few phonon states?

- A. Spring constant B. Amplitude of Oscillation C. Phase of Oscillation

Q2: Imagine that there are two systems of free quantum particles with the same mass, one of Fermions and the other of Bosons. Ignoring all non-spatial quantum numbers, such as spin and “color,” the density of states (DOS) for the two systems are:

- A. The Same B. Different C. Depends

Q3: In three dimension, energy of a particle is proportional to k^2 . DOS $g(\omega)$ is proportional to

- A. ω B. $\omega^{0.5}$ C. ω^2

Q4: In three dimension, energy of a particle is proportional to k . DOS $g(\omega)$ is proportional to

- A. ω^0 B. ω C. ω^2

Q5: In two dimension, energy of a particle is proportional to k^2 . DOS $g(\omega)$ is proportional to

- A. ω^0 B. ω C. ω^2

$$r_s = \left(\frac{3V}{4\pi N} \right)^{\frac{1}{3}}, \quad \frac{4\pi r_s^3}{3} = \frac{V}{N}$$

Size of “room” for each electron
 ~ inter-electron distance
 Characterizes electron density

$$k_F = \left(\frac{3\pi^2 N}{V} \right)^{\frac{1}{3}} = \left(\frac{9\pi}{4} \right)^{\frac{1}{3}} \frac{1}{r_s} = \frac{1.92}{r_s}$$

$$\varepsilon_F = \frac{\hbar^2 k_F^2}{2m} = \frac{(\hbar c)^2}{2mc^2} k_F^2 \sim \frac{(2000 \text{ eV}\text{\AA})^2}{1e6 \text{ eV}} k_F^2 \sim 4k_F^2 (= 3.8 k_F^2) \quad \text{if } k_F \text{ in } \text{\AA}^{-1} \text{ and } \varepsilon_F \text{ in eV}$$

Numbers, numbers ... for typical metals (Au, Cu, Al, Na ...)

Q1: For typical metals, there is O(1) electron per unit cell. What would be r_s ?

- A. O(a/100) B. O(a) C. O(100a)

Q2: What would be the typical Fermi momentum?

- A. O(1/100a) B. O(1/a) C. O(100/a)

Q3: What would be the typical Fermi energy?

- A. O(eV) ~ 10000 K B. O(100eV) ~ 1e6 K C. O(10 meV) ~ 100K

Q4: What would be the typical Fermi velocity = $v_F \sim E_F/k_F$

- A. O(c) B. O(c/100) C. O(c/10000)

$$r_s = \left(\frac{3V}{4\pi N} \right)^{\frac{1}{3}}, \quad \frac{4\pi r_s^3}{3} = \frac{V}{N}$$

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Numbers, numbers ... for typical metals (Au, Cu, Al, Na ...)

$$r_s = 1 \sim 2 \text{ \AA}$$

$$r_s \sim a \sim \frac{1}{k_F}$$

$$k_F = 1 \sim 2 \text{ \AA}^{-1}$$

$$v_F \sim \frac{\hbar k_F}{m} = \frac{\hbar c}{mc^2} k_F \sim \frac{2000 \text{ eV}\text{\AA}}{0.5e6 \text{ eV}} \times (1 - 2) \text{ \AA}^{-1} \times c \sim 10^{-2} c$$

$$v_F \sim \frac{c}{100}$$

$$v_s \sim \frac{c}{10,000}$$

$$v_s \sim \frac{\omega_D}{\pi/a} \sim 10 - 100 \frac{\text{meV}}{\text{\AA}^{-1}} \frac{c}{\hbar c} \sim 10^{-2} - 10^{-1} \frac{c}{1000} \sim \frac{c}{10,000 - 100,000}$$

$$\varepsilon_F = 1 \sim 10 \text{ eV}$$

$$T_F = 10,000 \sim 100,000 \text{ K} \quad k_B * 300 \text{ K} = 25 \text{ meV}$$

(In comparison, recall $\theta_D \sim 100 \text{ K}$)

Finite Temperature – Math

Apply standard stat. mech. techniques

$$\text{Fermi-Dirac function } f(\varepsilon, T) = \frac{1}{e^{\beta(\varepsilon - \mu)} + 1} \quad \beta = \frac{1}{k_B T}$$

$$\text{Determine chemical potential } \mu \text{ using } N = \int_0^{\infty} g(\varepsilon) f(\varepsilon, T) d\varepsilon$$

$$\text{Obtain energy from } E = \int_0^{\infty} \varepsilon g(\varepsilon) f(\varepsilon, T) d\varepsilon$$

After some tricky math (Sommerfeld expansion for small T/T_F ; see A&M):

$$\mu \approx \varepsilon_F \left[1 - \frac{1}{3} \left(\frac{\pi k_B T}{2\varepsilon_F} \right)^2 \right] \quad \mu(T=0) = \varepsilon_F$$

$$E \approx \frac{3}{5} N \varepsilon_F + \frac{\pi^2}{6} (k_B T)^2 g(\varepsilon_F) \quad g(\varepsilon_F) = \frac{3N}{2\varepsilon_F}$$

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = \frac{\pi^2}{3} k_B (k_B T) g(\varepsilon_F)$$

Corrections to $T=0$

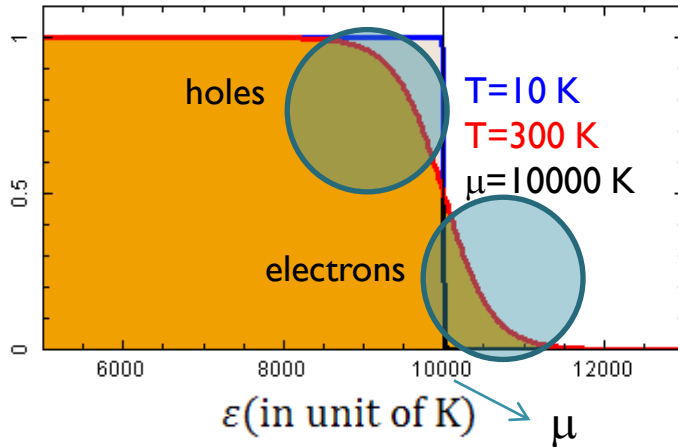
results are

of the order, $O\left(\left\{\frac{T}{T_F}\right\}^2\right)$

i.e. very small (10^{-4}) if $T \sim RT$, compared to $T=0$ values.

Finite Temperature – Physics

FD function: electron and hole excitation relative to vacuum (i.e. Fermi sea at $T = 0$)



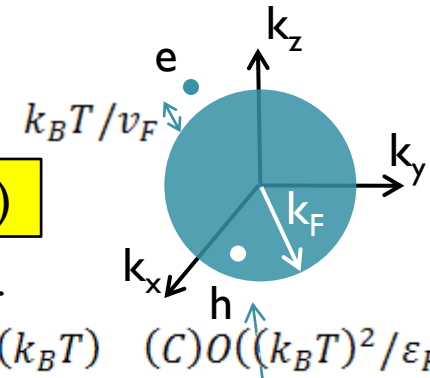
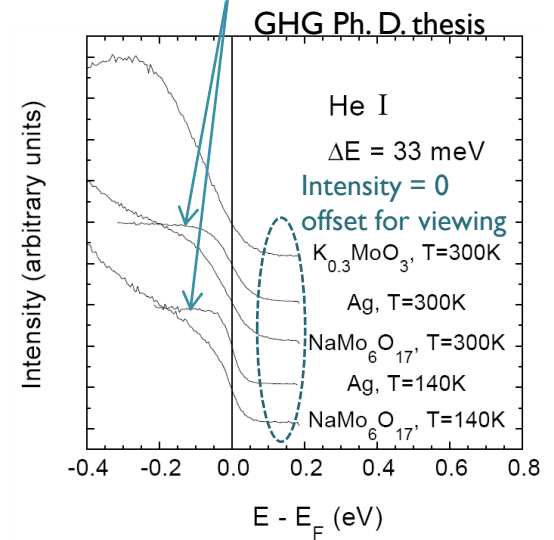
Deviation from step function ($T=0$) occurs within the energy range of $\sim k_B T$

Physics (expressions good up to numerical factors)

Think of excitation rel. to vacuum, not absolute energy.

- | | | | |
|--|---------------------------|-------------------------------|--|
| (1) Energy per excited particle | (A) $O(\epsilon_F)$ | (B) $O(k_B T)$ | (C) $O((k_B T)^2 / \epsilon_F)$ |
| (2) $k_B T / \epsilon_F$ for T near RT | $\sim (A) O(1)$ | $(B) O(100)$ | $(C) O(0.01)$ |
| (3) Number of particles excited | (A) $g(\epsilon_F) k_B T$ | (B) N_F | (C) $g(\epsilon_F) (k_B T)^2 / \epsilon_F$ |
| (4) $E - E(T=0)$ | (A) $N \epsilon_F$ | (B) $g(\epsilon_F) (k_B T)^2$ | (C) $g(\epsilon_F) (k_B T)^3 / \epsilon_F$ |
- (only one shown for clarity)

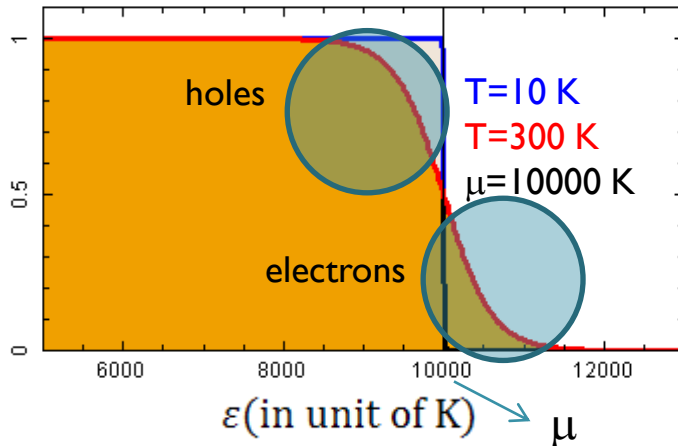
Measured FD function



Fermi surface becomes blurry due to many e-h pairs.

Finite Temperature – Physics

FD function: electron and hole excitation relative to vacuum (i.e. Fermi sea at $T = 0$)



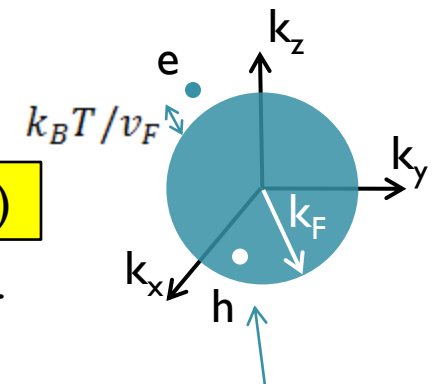
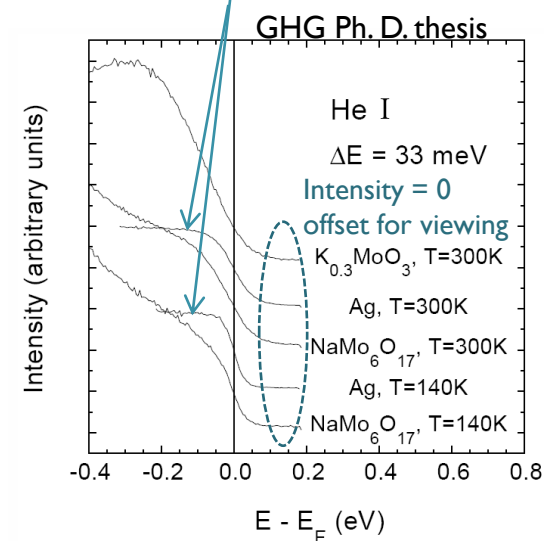
Deviation from step function ($T=0$) occurs within the energy range of $\sim k_B T$

Physics (expressions good up to numerical factors)

Think of excitation rel. to vacuum, not absolute energy.

- (1) Energy per excited particle $\sim k_B T$
- (2) Number of particles $\sim k_B T g(\epsilon_F)$
- (3) $E(T) - E(T=0) \sim (1) \times (2) \sim (k_B T)^2 g(\epsilon_F)$
- (4) $C(T) = dE/dT \sim k_B (k_B T) g(\epsilon_F)$

Measured FD function



Fermi surface becomes blurry due to many e-h pairs.
(only one shown for clarity)

Heat Capacity due to e-'s and lattice

(Often used “specific heat”, = heat capacity per volume or mole)

$$C_V(e^-) \approx \frac{\pi^2}{3} k_B (k_B T) g(\epsilon_F) = \frac{\pi^2}{2} N_e \frac{T}{T_F} k_B \quad C_V(\text{phonon}) \approx \frac{12\pi^4}{5} N_{\text{lattice}} \left(\frac{T}{\theta_D}\right)^3 k_B$$

$$C_V \approx \gamma T + \beta T^3$$

same order in metals

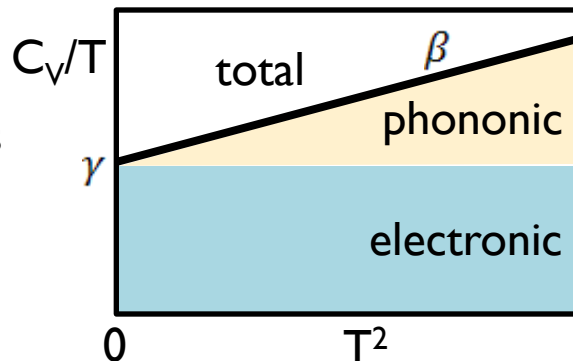
Differences are here!

Phonon term (cube term) is dominant at high (~ room) temperature (θ_D).
 Electron term (linear term) is dominant at low temperature.

Rough estimate of the boundary temperature:

$$\frac{T}{T_F} \sim \left(\frac{T}{\theta_D}\right)^3 \quad T \sim \theta_D \sqrt{\frac{\theta_D}{T_F}} \sim 100 \text{ K} \sqrt{\frac{1}{100}} \sim 10 \text{ K}$$

Many
 Researchers
 Plot C_V
 Like this:



$$\frac{C_V}{T} \approx \gamma + \beta T^2$$

$\gamma \sim 1 \text{ mJ mol}^{-1} \text{ K}^{-2}$
 \sim free electron value

Many exceptions:

γ can be 1000 times larger!

“Heavy Fermion” system

$$\gamma \sim \frac{k_B}{T_F} \sim \frac{1}{m} \quad m: \text{effective mass}$$

Conduction of Electricity

Source for finite conductivity

NOT ions in static crystal, but impurity, jittering ions (i.e. phonons), and other electrons (but only umklapp process in this case)

A simple model (relaxation time approx.)

- Relaxation time τ (time between scattering)
- Scattering events wipe out electron's memory (i.e. restores equilibrium)
- Conduction due to a tiny push by electric field between collisions

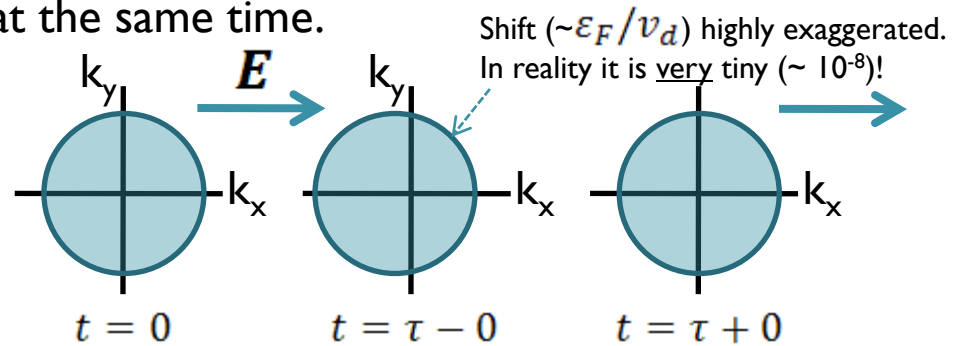
Quasi-elastic scattering in random directions



As all electrons are considered free (i.e. independent), we can think as though all electrons go through scattering at the same time.

$F = eE = ma = mv_d/\tau$
(only magnitude considered)

v_d Drift velocity
NOT electron velocity
Only a small added velocity



Ohm's law

$$j = nev_d = \frac{ne^2\tau}{m} E = \sigma E$$

$$\sigma = \frac{ne^2\tau}{m}$$

Drude conductivity=1/Drude resistivity

This solution can be thought of as a steady state solution for an equation.

$$m \left[\frac{dv_d}{dt} + \frac{v_d}{\tau} \right] = F$$

Keep in mind that microscopically, electrons are jittering fast (v_F), and the drift velocity is a tiny fraction ($10^{-8} v_F$) added to it, but it is what makes a difference since drifting adds up while jittering sums to zero.

We will learn later why $\hbar dk/dt = F$ which is the reason why we can write like this (just like Newton's law)

Conduction of Electricity

- Two common sources of scattering: e-ph and e-im (ph=phonon, im=impurity)

$$\frac{1}{\tau} = \frac{1}{\tau_{ph}} + \frac{1}{\tau_{im}}$$

$$= \frac{1}{\tau_{ph}(T)} + \frac{1}{\tau_{im}}$$

Impurity: no T dependence, elastic
 Phonon: T dependence, inelastic
 (absorption or emission of phonons)

Mattheisen's rule $\rho = \frac{m}{ne^2\tau} = \rho_{ph}(T) + \rho_{im}$

- Units, Time scale, drift velocity etc. in typical metals

$$n \sim \frac{10^{23}}{cm^3} \sim \frac{0.1}{\text{\AA}^3}$$

$$\sigma \sim (\mu\Omega \text{ cm})^{-1} = 10^6 (\Omega \text{ cm})^{-1} = 9.000e17 (\text{stat}\Omega\text{m} - \text{cm})^{-1} = 9.000e17 \text{ s}^{-1}$$

$$\tau = \frac{m\sigma}{ne^2} = \frac{m\sigma\hbar c}{n\hbar ce^2} \sim \frac{mc^2\sigma\hbar c}{n\hbar cc^2 e^2} = \frac{\text{\AA}^3 0.5e6 \text{ eV } 9e17 \text{ s}^{-1}}{0.1 2e3 \text{ eV } \text{\AA} 9e36 \text{\AA}^2 \text{ s}^{-2}} 137 \sim 3 \times 10^{-14} \text{ s}$$

$\tau \sim \text{femtosecond (R.T.)} - 10 \text{ nanosecond (low } T)$

$$l = v_F \tau = 1e16 \frac{\text{\AA}}{\text{s}} \times \tau \sim 10 \text{\AA} - 1 \text{ mm}$$

Mean free path \sim typically $100 \text{\AA} - 1 \mu\text{m}$

$$v_d = \frac{j}{ne} \sim 1000 \frac{\text{A}}{\text{cm}^2 ne} = \frac{10^3 \text{ A cm}}{10^{23} \times 1.6 \times 10^{-19} \text{ C}} \sim 1 \frac{\text{mm}}{\text{s}} \sim 10^{-11} c \sim 10^{-9} v_F$$

Drift Velocity – Slow!

Conduction of Heat

$$\text{Heat current} = -\frac{1}{3} v l \frac{d\left(\frac{E}{V}\right)}{dz} = -\frac{1}{3} v l \frac{dE}{V} \frac{dT}{dz} \equiv -\kappa \frac{dT}{dz}$$

Thermal conductivity

$$\kappa = \frac{1}{3} v l \frac{C}{V}$$

Fermi velocity
 $v = v_F$

Electron heat capacity $k_B T_F = \varepsilon_F = \frac{1}{2} m v_F^2$

Electron mean free path $l = v_F \tau$

$$C = \frac{\pi^2}{2} N \frac{k_B T}{k_B T_F} k_B$$

$$\kappa = \frac{1}{3} v l \frac{C}{V} = \frac{1}{3} v_F^2 \tau \frac{\pi^2}{2} \frac{N}{V} \frac{k_B T}{\frac{1}{2} m v_F^2} k_B = \frac{\pi^2}{3} n \tau \frac{k_B^2 T}{m} = \frac{\pi^2}{3} \frac{n \tau}{m} k_B^2 T \quad n = \frac{N}{V}$$

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

Physics: transport efficiency is high if there are many carriers (n) with long relaxation time (τ), light mass (m^{-1}).

So, it may not come as a surprise ...

Wiedemann-Franz Law

$$\frac{\kappa}{\sigma T} = \frac{\pi^2}{3} \left(\frac{k_B}{e}\right)^2 \equiv \text{Lorenz number}$$

“Universal” constant

Holds as long as scattering is elastic or quasi-elastic (energy change $\ll k_B T$). Ok for impurity scattering (low T) or when $T \gg \theta_D$ (high T).
It breaks down at intermediate T (read p. 92-96)