

## ELECTRONS

### FYS3410: PROBLEM SET 3

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CANDIDATE 33

#### 1. DRUDE MODEL

One of the basic assumptions of the free electron gas (FEG), or Drude model for electrons in solids, is that the mean free path is of the order of the inter-atomic distance. If this assumption is questionable, it challenges interpretations of all transport properties in terms of FEG, specifically thermal ( $\kappa$ ) and electrical ( $\sigma$ ) conductivities.

The Drude theory makes three assumptions

- (1) Electrons have a scattering time  $\tau$ . The probability of scattering within a time interval  $dt$  is  $dt/\tau$ .
- (2) Once a scattering event occurs, we assume the electron returns to momentum  $\mathbf{p} = 0$ .
- (3) In between scattering events, the electrons, which are charge  $-e$  particles, respond to the externally applied electric field  $\mathbf{E}$  and magnetic field  $\mathbf{B}$ .

The failures of the Drude theory:

- The Hall coefficient frequently is measured to have the wrong sign, indicating a charge carrier with charge opposite to that of the electron.
- There is no  $\frac{3}{2}k_B$  heat capacity per particle measured for electrons in metals. This then makes the Peltier and Seebeck coefficients come out wrong by a factor of 100.

**A. Prediction of Wiedemann-Franz.** The most impressive success of the Drude model at the time it was proposed was its explanation of the empirical law of Wiedemann and Franz.

Firstly, the Lorentz force on an electron is given by

$$(1) \quad \mathbf{F} = -e(\mathbf{E} + \mathbf{v} \times \mathbf{B})$$

Now, consider an electron with momentum  $\mathbf{p}$  at a time  $t$ . What will the momentum of the electron be at a time  $t + dt$ ? There is a probability  $dt/\tau$  that it will scatter to momentum zero. If it does not scatter, it will be accelerated as dictated by Newton's second law of motion<sup>1</sup> at probability

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*Date:* April 20, 2017.

<sup>1</sup> $\mathbf{F} = \frac{d\mathbf{p}}{dt}$

$1 - dt/\tau$ . The expected value of the momentum becomes

$$(2) \quad \langle \mathbf{p}(t + dt) \rangle = \left(1 - \frac{dt}{\tau}\right) (\mathbf{p}(t) + \mathbf{F}dt) + \mathbf{0} \frac{dt}{\tau}.$$

This can be rearranged if one keeps the terms in linear order of  $dt$

$$(3) \quad \frac{d\langle \mathbf{p} \rangle}{dt} = \mathbf{F} - \frac{\langle \mathbf{p} \rangle}{t},$$

where  $\mathbf{F}$  is the Lorentz force from equation 1, of course. Assuming that the electric field is non-zero, the magnetic field is zero, and writing  $\langle \mathbf{p} \rangle$  as  $\mathbf{p}$  we get

$$(4) \quad \frac{d\mathbf{p}}{t} = -e\mathbf{E} - \frac{\mathbf{p}}{\tau}.$$

In a steady state  $d\mathbf{p}/dt = 0$  which gives

$$(5) \quad m\mathbf{v} = \mathbf{p} = -e\tau\mathbf{E} \quad \rightarrow \quad \mathbf{v} = -\frac{e\mathbf{E}\tau}{m},$$

where  $m$  is the mass of the electron and  $\mathbf{v}$  is its velocity.

If there is a density of  $n$  of electrons in the metal each with charge  $-e$ , and they are all moving at velocity  $\mathbf{v}$ , the electrical current is given by

$$(6) \quad \mathbf{j} = -en\mathbf{v} = \frac{e^2\tau n}{m}\mathbf{E}.$$

The electrical conductivity of the metal, defined via  $\mathbf{j} = \sigma\mathbf{E}$ , is given by

$$(7) \quad \sigma = \frac{e^2\tau n}{m}.$$

From the kinetic theory of gas we have that the thermal conductivity is

$$(8) \quad \kappa = \frac{1}{3}nC_v \langle v \rangle \lambda,$$

where  $\langle v \rangle$  is the average thermal velocity and  $\lambda = \langle v \rangle \tau$  is the scattering length. For a monatomic gas the heat capacity per particle is

$$(9) \quad C_v = \frac{3}{2}k_B,$$

and

$$(10) \quad \langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}}.$$

Inserting 9 and 10 into equation 8 yields

$$(11) \quad \kappa = \frac{4}{\pi} \frac{n\tau k_B^2 T}{m}.$$

While this quantity has the unknown parameter  $\tau$  in it, equation 7 contains the same quantity. Thus, we may look at the ratio of thermal conductivity to electrical conductivity, known as the Lorenz number

$$(12) \quad L = \frac{\kappa}{T\sigma} = \frac{4}{\pi} \left( \frac{k_B}{e} \right)^2.$$

A slightly different prediction is obtained by realising that  $\langle v \rangle^2$  was used in this calculation, whereas one can use  $\langle v^2 \rangle$  instead<sup>2</sup>. This gives

$$(13) \quad L = \frac{\kappa}{T\sigma} = \frac{3}{2} \left( \frac{k_B}{e} \right)^2.$$

This result was seen as a big success for the Drude model, because it was known for a long time that almost all metals have roughly the same value for this ratio. This fact is called the Wiedemann-Franz law.

**B. Free electron Fermi gas.** For a free electron Fermi gas, the heat capacity is given as

$$(14) \quad C_{\text{el}} = \frac{\pi^2}{2} \frac{Nk_B T}{T_F}$$

and the Fermi velocity is given as

$$(15) \quad v_f = \frac{\hbar k_F}{m},$$

where  $k_F$  is the Fermi wavevector. This gives a new expression for the heat conductivity

$$(16) \quad \kappa = \frac{\pi^2}{6} \frac{Nn k_B T \hbar^2 k_F^2 \tau}{T_F m^2},$$

while the electrical conductivity ( $\sigma$ ) is the same and given by equation 7. The Lorenz factor becomes

$$(17) \quad L = \frac{\kappa}{T\sigma} = \frac{\pi^2}{6} \frac{Nk_B k_F^2 \hbar^2}{e^2 T_F m},$$

which is somewhat of a mess, but replacing the Fermi temperature with

$$T_F = \frac{E_F}{k_B} = \frac{N \hbar^2 k_F^2}{2mk_B}$$

turns the expression in 17 into

$$(18) \quad L = \frac{\kappa}{T\sigma} = \frac{\pi^2}{3} \frac{k_B^2}{e^2}.$$

This is somewhat similar to what I obtained in equation 13.

### 3. FREE ELECTRON FERMION GAS

**A. The Chemical Potential at Absolute Zero.** In a one-dimensional sample, the number of electrons will be

$$(19) \quad N_e = 2 \int \frac{d\epsilon}{2\pi\hbar/L} f(\epsilon_k) = \frac{L}{\pi\hbar} \int d\epsilon \frac{1}{e^{(\frac{k^2}{2m} - \mu)/k_B T} + 1},$$

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<sup>2</sup>From kinetic theory:  $C_v T = \frac{1}{2} m \langle v^2 \rangle$

dividing by  $L$  on both sides give

$$(20) \quad \frac{N_e}{L} = \frac{1}{\pi\hbar} \int d\epsilon \frac{1}{e^{(\frac{k^2}{2m} - \mu)/k_B T} + 1}.$$

If we know the density of electrons  $N_e/L$ , one can solve this equation to find  $\mu$ . In general,  $\mu$  depends on  $T$  and the electron density.

As the temperature approaches zero, the Fermi-Dirac distribution,  $f(\epsilon_k)$  turns into a step function. At low  $T$ ,  $(\epsilon - \mu)/(k_B T)$  becomes very large. Depending on the sign of  $\epsilon - \mu$

$$(21) \quad \lim_{T \rightarrow 0} \frac{\epsilon - \mu}{k_B T} = \begin{cases} -\infty, & \epsilon < \mu \\ +\infty, & \epsilon > \mu \end{cases}$$

Therefore,

$$(22) \quad \lim_{T \rightarrow 0} f(\epsilon) = \lim_{T \rightarrow 0} \frac{1}{e^{(\epsilon - \mu)/(k_B T)} + 1} = \begin{cases} 1, & \epsilon < \mu \\ 0, & \epsilon > \mu \end{cases}$$

It is therefore easy to see that the chemical potential  $\mu$  plays the role of  $\epsilon_F$  here. In other words  $\mu = \epsilon_F$  at  $T = 0$ . This result generalises to higher dimensions.

**B. FEFG at  $T > 0K$ .** For any  $T$  the Fermi-Dirac distribution becomes  $\frac{1}{2}$  if  $\mu = \epsilon_F$

$$(23) \quad f(\mu) = \frac{1}{e^{(\mu - \mu)/(k_B T)} + 1} = \frac{1}{e^0 + 1} = \frac{1}{2},$$

however, this is only an OK approximation for quite high temperatures. This computation begs the question - at what temperatures is the assumption that  $\mu = \epsilon$  reasonable?

Figure 1 illustrates this problem nicely. One can see that the Fermi-Dirac function only is a true step function at very low temperatures, and as the temperature increases, the distribution will be more and more flat, approaching  $1/2$ .

**C. Chemical Potential Dependence on Temperature.** The total number of orbitals of energy  $\leq \epsilon$  in a Fermi sphere is given by

$$(24) \quad N = \frac{V}{3\pi^2} \left( \frac{2m\epsilon}{\hbar^2} \right),$$

the same quantity is found by way of the following integral

$$(25) \quad n = \int_0^\infty d\epsilon D(\epsilon) f(\epsilon)$$

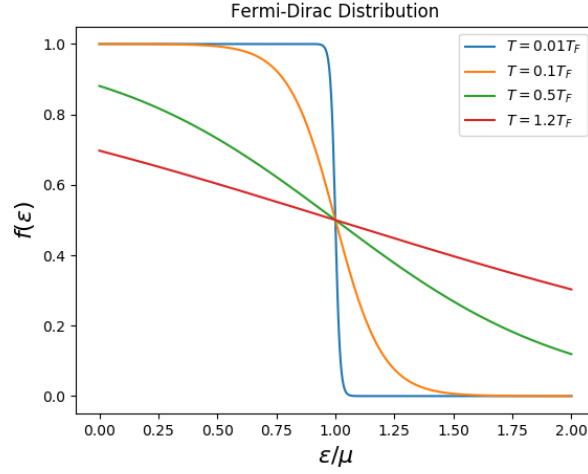


FIGURE 1. The Fermi-Diract Distribution at different temperatures

## 4. FREE ELECTRON FERMI GAS IN LOWER DIMENSIONS

**A. DOS Independent of Energy in Two Dimensions.** It can be showed that the density of states (DOS) is independent of energy in two dimensions.

$$\begin{aligned}
 \text{DOS}_{2D}(k)dk &= 2 \left(\frac{1}{2}\right)^2 \frac{2\pi k}{\frac{\pi}{L_x} \frac{\pi}{L_y}} \frac{1}{V} dk = \frac{\pi k}{\frac{\pi^2 L_x L_y L_z}{L_x L_y}} = \frac{k}{L_z \pi} dk \\
 \text{DOS}_{2D}(E)dE &= \text{DOS}_{2D}(k)dk \\
 \text{DOS}_{2D}(E) &= \frac{\text{DOS}_{2D}(k)}{\frac{dE}{dk}} \\
 &= \frac{k}{L_z \pi} \frac{2m}{\hbar^2} \frac{1}{2k} \\
 &= \frac{m}{\hbar^2 L_z \pi}
 \end{aligned}$$

**B. DOS Proportional to Inverse Square Root of Energy in One Dimension.** It can be showed that the density of states (DOS) is proportional

to  $E^{-\frac{1}{2}}$  in one dimension.

$$\begin{aligned}
\text{DOS}_{1D}(k)dk &= 2 \frac{1}{2} \frac{1}{\frac{\pi}{L_x}} \frac{1}{V} dk = \frac{1}{\pi} \frac{1}{L_y L_z} dk \\
\text{DOS}_{1D}(E) &= \frac{\text{DOS}_{1D}(k)}{\frac{dE}{dk}} \\
&= \frac{1}{\pi} \frac{1}{L_y L_z} \frac{2m}{\hbar^2} \frac{1}{2k} \\
&= \frac{m}{\hbar^2 \pi} \frac{1}{L_y L_z} \frac{1}{k} \\
&\rightarrow k = \left( \frac{2m}{\hbar^2} \right)^{\frac{1}{2}} E^{\frac{1}{2}} \\
\text{DOS}_{1D}(E) &= \left( \frac{m}{E} \right)^{\frac{1}{2}} \frac{1}{2\pi \hbar L_y L_z}
\end{aligned}$$

**C. DOS Trends for Quantum Wells and Wires.** In quantum wells, the function  $\text{DOS}(E)$  has a stair step graph. The wavevector  $k = |\mathbf{k}|$  will lie in a plane with  $z$ -component equal to  $k_{z,1}$  until  $(k_x^2 + k_y^2)$  is large enough for  $k_z$  to be excited. Then the wavevector  $k$  is long enough for  $k_z$  to be excited from  $n_z = 1$  to  $n_z = 2$ , for instance. This implies that for energy eigenvalue  $E < \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_{z,1}^2)$ ,  $\text{DOS}_{2D}(E) = 0$ , and will be increased discretely for higher values of energy  $E$ .

In one dimension, the wavevector  $k$  will only have one degree of freedom. It can only move in one direction, for instance the  $x$ -direction. The wavevector will increase in magnitude in the  $x$ -direction until  $(k_x^2 + k_{y,1}^2 + k_{z,1}^2)$  is large enough to excite  $k_y$  or  $k_z$ . At this point  $\text{DOS}_{1D}(E)$  will jolt upwards and then decrease with  $E^{-1/2}$  until again  $k_y$  or  $k_z$  can be excited.

Figure 2 provides a good illustration of how the density of states depends on energy, for different dimensionality.

**D. Degeneracy in Quantum Wires.** Assuming that the “collapsed” dimensions  $y$  and  $z$  have the same length,  $L = L_y = L_z$ , then the expression for energy is simplified to

$$(26) \quad E(n_x, n_y, n_z) = \frac{\hbar^2}{2m} k_x^2 + \frac{\hbar}{2m} \left( \frac{2\pi}{K} \right)^2 (n_y^2 + n_z^2)$$

which can be simplified further by concatenating the quantum number in  $y$ - and  $z$ -directions, such that  $n = n_x + n_y$ . In this case, the energy will be the same, independently of  $n_y$  and  $n_z$ , assuming that  $n^2 = n_y^2 + n_z^2$  holds. The degeneration will be decided by the number of distributions possible for a particular value of  $n^2$ . For instance  $n^2 = 20$  has degeneracy 2 because the equation  $20 = n_x^2 + n_y^2$  has solutions  $(n_x, n_y) = (2, 4)$  and  $(n_x, n_y) = (4, 2)$ .

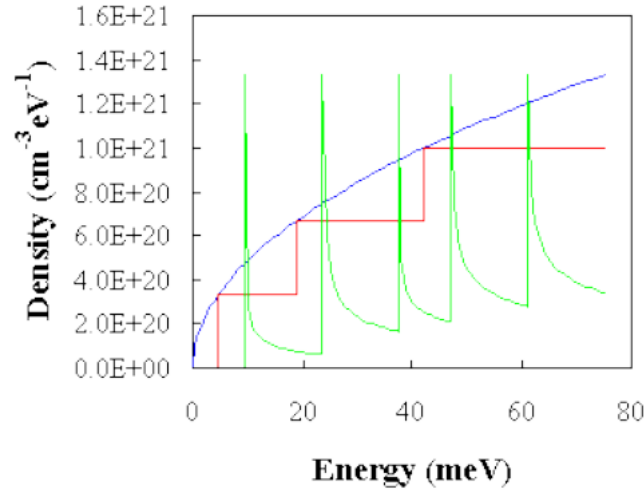


FIGURE 2. Density of states as a function of energy for 3D semiconductor (blue curve), a 10nm quantumwell with infinite barriers (red curve) and a 10nm quantum wire with infinite barriers (green curve).

## 6. MONOVALENT ATOM CRYSTALLISATION

Monovalent atoms are assumed to crystallise in a simple cubic (SC) lattice with lattice parameter  $\alpha$ .

**A. Magnitude of the Fermi Vector.** The Fermi vector is given by

$$(27) \quad k_F = \left( \frac{3\pi^2 N}{V} \right)^{\frac{1}{3}},$$

where the volume is given by the lattice parameter as  $V = a^3$ . Moreover, the wave vector for the first Brillouin zone is  $k_{\text{BZ}, 1\text{D}} = \frac{1}{2}k_{\text{max}} = \frac{\pi}{a}$ . Then, for a SC lattice in 3D,  $k_{\text{BZ}} \approx \frac{\pi}{a}$ .

Setting  $N = 1$  gives

$$(28) \quad k_F = \frac{(3\pi^2)^{\frac{1}{3}}}{a}.$$

By computation we find that  $(3\pi^2)^{1/3} \approx 3.094 < \pi$ . We see that the Fermi vector is shorter, but quite close to the Brillouin zone vector.

**B. Filling of Empty States.** If  $k_F < k_{\text{BZ}}$  there must be unoccupied states available up to  $k = k_{\text{BZ}}$ . How many divalent atoms that must be added in order to fill up these states can be computed numerically. The Python script below contains a function for the Fermi vector which is dependent on the composition of divalent atoms in the crystal. The script runs through

the possible magnitudes of the Fermi vector until the it is the same as the Brillouin zone. The result is printed.

```

import numpy as np
from matplotlib import pyplot as plt

# Parameters
a = 1
N = 1
c = np.linspace(0, 1, 1001)

# Fermi vector function
# Dependent on divalent atom composition
def k_F(x):
    Z = (1 - x) + 2*x
    e_1 = (3*np.pi*np.pi)**(1/3)
    e_2 = ((Z*N)**(1/3)) / (N*a)
    return e_1*e_2

# Brillouin zone
k_BZ = np.pi / a

# Counter
i = 0

# For loop comparing vectors
for value in k_F(c):
    i += 1

    # Printing result and breaking
    if (np.abs(value - k_BZ) < 0.001):
        print("Optimum divalent mix is ", c[i])
        break

```

The script found that when 4.8% of the atoms are divalent, the Fermi vector will reach the edge of the Brillouin zone. The number of unoccupied states will be fewer if this happens, resulting in a decreased electrical conductivity.

C. **Sodium.** Na is one of the best behaving metals. Notably, Na crystallises in a body-centred cubic (BCC) structure with two atoms in each conventional unit cell. A BCC structure can be described as by vectors that give a volume  $V = \frac{1}{2}a^3$ . Moreover,

$$(29) \quad N = V_F \times \text{DOS} = \frac{k_F^3}{3} \frac{V}{\pi^2}.$$



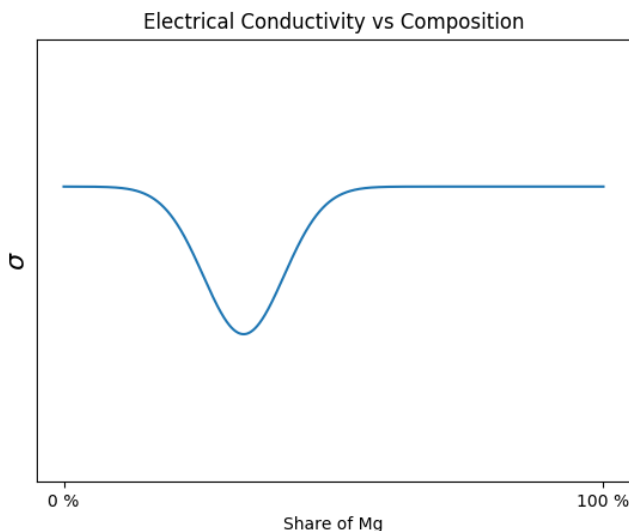


FIGURE 3. Electrical conductivity as a function of crystal composition

By a simple algebraic exercise, this is rewritten to

$$(30) \quad k_F = \left( \frac{3\pi^2 N}{V} \right)^{\frac{1}{3}} = \frac{(\frac{3}{2}\pi^2 N)^{\frac{1}{3}}}{a}.$$

In a BCC unit cell the longest distance to another atom is  $\sqrt{2}a$  which gives

$$(31) \quad k_{BZ} \approx \frac{\sqrt{2}\pi}{a}.$$

A computation gives  $(\frac{3}{2}\pi^2)^{1/3} \approx 2.455 < \sqrt{2}\pi \approx 4.443$ . Again, the Fermi vector is lower in magnitude than the vector defining the Brillouin zone, as expected. But for Na in a BCC structure it is much shorter compared with a regular SC lattice. This means that there are several more unoccupied states!

**D. Mixing the Sodium with Magnesium.** By modifying the script above I find the mix of Na and Mg to have full states when there is 48% Mg, which is much higher, as expected.

**E. Electrical Conductivity as a Function of Composition.** The electric conductivity will be at a minimum when  $k_F = k_{BZ}$ . Moving away from this point, the electrical conductivity will increase before reaching a maximum asymptotic level. This is illustrated in figure 3.

## 7. EFFECTIVE MASS

The general Schrödinger equation is given by

$$(32) \quad \hat{H}\psi = E\psi,$$

where the Hamiltonian is usually the sum of kinetic and potential energy. However, the potential energy is sometimes unknown or difficult to deal with. The problem is circumvented by including the potential in the mass of the electron, by introducing “effective mass”.

An arbitrary energy can be Taylor expanded around  $k_0 = 0$

$$(33) \quad E(k) \approx E_0 + \frac{\partial E}{\partial k} + \frac{1}{2} \frac{\partial^2 E}{\partial k^2} k^2 + \dots,$$

where  $E_0 = 0$  and  $\frac{\partial E}{\partial k} = 0$  and the higher order terms are ignored. This leaves us with

$$(34) \quad E(k) = \frac{1}{2} \frac{\partial^2 E}{\partial k^2} k^2.$$

What remains from the Hamiltonian in equation 32 is the energy eigenvalue

$$(35) \quad E(k) = \frac{\hbar^2}{2m} k^2.$$

Equating 34 and 35 yields

$$(36) \quad \frac{\hbar^2}{m^*} = \frac{\partial^2 E}{\partial k^2} \rightarrow m^* = \hbar^2 \left( \frac{\partial^2 E}{\partial k^2} \right)^{-1}$$

where  $m^*$  is the effective mass.

**A.** The effective mass includes the potential of the electron and is therefore different from the rest mass.

**B.** States of positive effective mass occur near the bottom of a band because positive effective mass means that the band has an upward curvature. States of negative mass occur near the top of a band. These are valence bands, meaning that the electron is removed from the conduction band, creating a “hole”, which is an alternate description of a band with one missing electron. This effect is important in semiconductor physics and solid state electronics.

**C.** The energy of electrons in the vicinity of the conduction band edge is  $E(k) = Ak^2$ , where  $A = 5 \times 10^{-37} \text{ Jm}^2$ . The effective mass of these electrons are

$$\begin{aligned} m^* &= \hbar^2 \left( \frac{\partial^2 E}{\partial k^2} \right)^{-1} = \hbar^2 \frac{1}{2A} = \frac{(1.0545718 \times 10^{-34} \text{ Js})^2}{10 \times 10^{-37} \text{ Jm}^2} \\ &= 1.112 \times 10^{-32} \text{ Js}^2 \text{m}^{-2} \\ &= 1.112 \times 10^{-32} \text{ kg} \approx 0.01 m_e \end{aligned}$$