

Fermi Energy in the Free Electron Model

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1 Assumptions of the Free Electron Model

- Interactions between electrons are negligible
- There are no interactions with the lattice.

Essentially, the electrons are flowing freely through the solid. These approximations can be very accurate in a metal.

2 Fermi energy

2.1 Quantum mechanical model

The possible energy levels for electrons free to move about a volume V are found from the Schrödinger equation. The energy levels are quantized, and each level can be occupied by two fermions, one with spin up and one with spin down.

At $T = 0$, the energy levels will be completely filled up to a certain energy, which we have called the chemical potential, or alternatively, the *Fermi energy*. At $T = 0$, there will be no occupied states with $\epsilon > \epsilon_F$.

2.2 An explicit expression for ϵ_F

2.2.1 Write ϵ_F in terms of n_F

For an electron in a cubic box,

$$\epsilon_n = \frac{\pi^2 \hbar^2 n^2}{2mL^2}$$

where $n^2 = n_x^2 + n_y^2 + n_z^2$

We can then define the Fermi energy in terms of n at the Fermi energy.

$$\epsilon_F = \frac{\pi^2 \hbar^2 n_F^2}{2mL^2}$$

where n_F is the quantum number at the energy level ϵ_F . An explicit expression for n_F has yet to be determined.

2.2.2 Find the density of states

We want the density of states for the electrons in the metal as a function of n , which we will then relate to the energy. The approach is the same as in the case of photons: consider a three-dimensional n space and integrate over the positive octant of a sphere. We consider an octant because $n_i \geq 0$. The radius of the shell is n and the width of the shell is dn . We consider n to be sufficiently large that it is a continuous variable.

The number of states between n and $n + dn$ is given by the density of states per unit n space volume times the volume we are examining.

$$\mathcal{N}(n)dn = 2 \cdot \frac{1}{8} \cdot 4\pi n^2 dn = \pi n^2 dn$$

Note. The factor 2 appears because there are 2 spin directions for spin $\frac{1}{2}$, and thus each energy level can support 2 electrons.

The total number of occupied states, thus electrons in the system, is then

$$N = \int_0^{n_F} \mathcal{N}(n)dn = \pi^2 \int_0^{n_F} n^2 dn = \frac{\pi}{3} n_F^3$$

Thus n_F is defined in terms of N . The expression for ϵ_F contains the square of n_F ,

$$n_F^2 = \left(\frac{3N}{\pi} \right)^{\frac{2}{3}}$$

Substituting,

$$\epsilon_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{\frac{2}{3}}$$

Note. • We have used

$$L^2 = (L^3)^{\frac{2}{3}} = V^{\frac{2}{3}}$$

- The only variable parameter that appears in the expression for ϵ_F is the density of the electrons.

2.3 Numerical example

2.3.1 ϵ_F

Sodium is the canonical example of a free electron gas. It behaves as an ideal electron gas to a very good approximation. Thus we consider sodium to evaluate a standard example of ϵ_F in a metal.

Note. Each sodium atom contributes on average one electron to the free electron gas.

The average mass of sodium is $23 \frac{\text{g}}{\text{mol}}$. Sodium floats, so its density is on the same order as that of water, $\rho \sim 1 \frac{\text{g}}{\text{cm}^3}$. The number density is then,

$$\frac{N}{V} \approx \frac{N_A}{V \text{ per mol}} = \frac{6 \times 10^{23} \frac{\text{particles}}{\text{mol}}}{23 \frac{\text{cm}^3}{\text{mol}}} \approx 2.5 \times 10^{22} \text{ cm}^{-3}$$

Note. This is a good number to remember as an estimation of the density of electrons in a metal in general.

Evaluating the constants in ϵ_F ,

$$\epsilon_F \approx 3 \text{ eV}$$

Expressing a quantity in terms of other units can sometimes be enlightening, so consider...

2.3.2 T_F

Definition (Fermi temperature).

$$T_F = \frac{\epsilon_F}{k_b}$$

Note. This is the temperature equivalent to the energy of the electrons in the highest energy state. This is *not* the temperature of the material. The temperature is an expression of the average of all of the energies of particles in the system. In this case, only one or two electrons obtain the energy level corresponding to T_F , while most of the rest of the electrons are at much lower energy levels, and hence T_F will be much higher than the actual temperature of the metal.

Evaluating T_F in the case of sodium,

$$T_F \approx \frac{3 \text{ eV} \cdot 1.6 \times 10^{-19} \frac{\text{J}}{\text{eV}}}{1.38 \times 10^{-23} \frac{\text{J}}{\text{K}}} \approx 35,000 \text{ K}$$

2.3.3 v_F

Definition (Fermi velocity).

$$\begin{aligned} \epsilon_F &= \frac{1}{2} m v_F^2 \\ \Rightarrow v_F &= \left(\frac{2\epsilon_F}{m} \right)^{\frac{1}{2}} \end{aligned}$$

Note. • There is the implicit assumption that there is no interaction energy in the Free Electron Model, so the potential energy of each of the electrons is 0. Thus all of their energy is kinetic, so the above definition is justified.

- As in the case of the Fermi temperature, only one or two electrons obtain the Fermi velocity, while most of the rest travel much slower.

In the case of sodium,

$$\epsilon_F \approx 10^6 \frac{\text{m}}{\text{s}}$$

Note. • $v_F \ll c$, so relativistic corrections are negligible, as is usually the case in free electrons in a metal.

- Relativistic corrections may not always be negligible, such as in the case of a electrons in a white dwarf star.

2.4 Compare to a classical gas at 300 K

The average velocity of a particle in a classical gas of nitrogen is given by the equipartition theorem,

$$\begin{aligned}\frac{1}{2}mv^2 &= \frac{3}{2}k_bT \\ \Rightarrow v &= \left(\frac{3k_bT}{m}\right)^{\frac{1}{2}}\end{aligned}$$

This is smaller than the Fermi velocity of electrons in sodium by a factor of

$$\left(\frac{\left(\frac{T}{T_F}\right)}{\left(\frac{m_{N_2}}{m_e}\right)}\right)^{\frac{1}{2}} \sim \frac{\frac{1}{10}}{100} = \frac{1}{1000}$$

Thus the velocity of an electron in a metal is much much larger than that of particle in a classical gas.

Note. Changing T from absolute 0 to room temperature will have very little effect on this ratio. The thermal velocity in a classical gas is lower than that of electrons in a metal over a broad range of temperatures.

3 Density of states

3.1 An expression for $D(\epsilon)$

The number of electrons in a small energy range ϵ to $\epsilon + d\epsilon$ can be written similarly to the case of photons,

$$D(\epsilon)d\epsilon$$

where $D(\epsilon)$ is the density of states per unit energy range. The energy density of states is related to the number density of states,

$$D(\epsilon)d\epsilon = \mathcal{N}(n)dn = \pi n^2 \frac{dn}{d\epsilon} d\epsilon$$

These are simply two different expressions for the same distribution.

From the expression for ϵ from the Schrödinger equation,

$$\begin{aligned}\epsilon &= \frac{\hbar^2 \pi^2 n^2}{2mL^2} \\ \Rightarrow n &= \left(\frac{2mL^2}{\hbar^2 \pi^2} \right) \epsilon^{\frac{1}{2}} \\ \Rightarrow \frac{dn}{d\epsilon} &= \left(\frac{mL^2}{2\pi^2 \hbar^2} \right) \epsilon^{-\frac{1}{2}}\end{aligned}$$

Computing the term that appears in $D(\epsilon)$,

$$n^2 \frac{dn}{d\epsilon} = \underbrace{\frac{2m\epsilon L^2}{\pi^2 \hbar^2}}_{n^2} \underbrace{\left(\frac{mL}{2\pi^2 \hbar^2} \right)^{\frac{1}{2}}}_{\frac{dn}{d\epsilon}} \epsilon^{\frac{1}{2}}$$

Multiplying by the π from the original expression for $D(\epsilon)$ and combining like terms,

$$D(\epsilon) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \epsilon^{\frac{1}{2}}$$

Note. $D(\epsilon)$ is directly proportional to the volume of the box. As the volume of the box is increased, the spacing between the the energy levels decreases, so there are more states accessible at a given energy, and thus $D(\epsilon)$ increases.

3.2 $D(\epsilon)$ at ϵ_F

Note that ϵ_F scales as $N^{\frac{2}{3}}$. Writing ϵ_F in terms of a constant A ,

$$\epsilon_F = AN^{\frac{2}{3}}$$

Taking the log of both sides,

$$\log \epsilon_F = \frac{2}{3} \log N + C$$

Differentiating both sides,

$$\frac{d\epsilon_F}{\epsilon_F} = \frac{2}{3} \frac{dN}{N}$$

$$D(\epsilon_F) = \frac{dN}{d\epsilon_F} = \frac{3 N}{2 \epsilon_F}$$

Apart from the numerical factor, this is the answer we would expect from dimensional analysis.

4 Ground state energy

Recall that the Fermi distribution function is a step function that is 1 for $\epsilon < \mu$ and 0 for $\epsilon > 0$. As the temperature is increased, the Fermi function smears out about the value $\epsilon = \mu$.

Combine this knowledge with what we have just learned about the density of states, which scales as the square root of the energy, but is independent of the temperature. The net population is the product of these two.

For $T = 0$, the product is the same as $D(\epsilon)$ for $\epsilon < \mu$, and 0 for $\epsilon > \mu$. As the temperature is increased, the density of states stays the same, but the distribution smears out according to the behavior of the Fermi distribution function. The important point is that the density of states is independent of the temperature.