Free Electrons in Metals

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Metals are known for their electrical conductivity, thermal conductivity, magnetism, and other useful properties. The valence electrons (or free electrons) are often responsible for these properties. However, the classical free electron theory was inadequate to explain the experimental observations until the discovery of the Fermi-Dirac distribution of electrons which are fermions with +1/2 and -1/2 spins. This article provides a brief summary of the free electron theory of metals.

Fermi-Dirac Distribution

The grand canonical ensemble partition function for fermion has only two terms: either the state, r, is not occupied ($n_r = 0$) or the state is occupied ($n_r = 1$):

$$Z(r) = e^{-\beta 0(E_r-\mu)} + e^{-\beta 1(E_r-\mu)} = 1 + e^{-\beta(E_r-\mu)} = \frac{1}{z^{-1}e^{\beta E_r}+1}$$

This is the Fermi-Dirac distribution where $z = e^{\beta\mu}$ is called *fugacity*. For wave vectors k_i in an energy well of L, using the periodic boundary condition:

$$k_i = \frac{2\pi n_i}{L} \qquad n_i \in \mathbb{Z}$$

$$\int d^3n = \left(\frac{L}{2\pi}\right)^3 \int d^3k = \frac{4\pi V}{(2\pi)^3}\int dk k^2 = \frac{V}{2\pi^2}\int dE\sqrt{\frac{2mE}{\hbar^2}}\frac{m}{\hbar^2} = \int dE g(E)$$

where $g(E)$ is the density of states. The variable substitution from k to E utilizes the relations:

$$E = \frac{\hbar^2 k^2}{2m}$$

$$dE = \frac{\hbar^2 k}{m}dk$$

For electrons, each state is occupied by two electrons, one with spin up and the other spin down. The density of states becomes:

$$g(E) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$$

Therefore,

$$N = \int \frac{g(E)dE}{z^{-1}e^{\beta E}+1}$$

$$E = \int \frac{g(E)EdE}{z^{-1}e^{\beta E}+1}$$

Sommerfeld Approximation

At absolute zero, the Fermi-Dirac distribution becomes a step function where an energy state is either occupied ($E < \mu$) or not ($E > \mu$). The chemical potential, $\mu(T = 0)$, is the Fermi energy E_F. As such, the above integrations can be evaluated between 0 and E_F since only these states are occupied:

$$N = \int_0^{E_F} g(E)dE = \frac{V}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E_F^{3/2}$$

$$E = \int_0^{E_F} g(E)EdE = \frac{3}{5}NE_F$$

At temperatures above absolute zero but still low relative to E_F, the integrations (per unit volume) must be carried throughout the energy range instead of stopping at E_F. Let λ as the thermal *de Broglie* wavelength:

$$\lambda = \sqrt{\frac{2\pi\hbar^2}{mk_BT}}$$

$$\frac{N}{V} = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^{\infty} dE\frac{\sqrt{E}}{z^{-1}e^{\beta E}+1} = \frac{2}{\lambda^3}f_{3/2}(z)$$

$$\frac{E}{V} = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^{\infty} dE\frac{\sqrt{E^3}}{z^{-1}e^{\beta E}+1} = \frac{3}{\lambda^3}k_BTf_{5/2}(z)$$

where $f_n(z)$ is the poly-logarithmic function:

$$f_n(z) = \frac{1}{\Gamma(n)}\int_0^{\infty} dx\frac{x^{n-1}}{z^{-1}e^{x}+1}$$

For a large z (or small z^{-1}), $f_n(z)$ can be approximated by the *Sommerfeld expansion*:

$$f_n(z) = \frac{(logz)^n}{\Gamma(n+1)}\left(1+\frac{\pi^2}{6}\frac{n(n-1)}{(logz)^2}+\dots\right)$$

Heat Capacity

The heat capacity of a solid is the change in energy by change in unit temperature, mostly in thermal phonon activations. At temperatures less than the material’s Derby temperature, the heat capacity follows a “cubic law” in terms of temperature. Metals, however, at very low temperatures, their heat capacities follow a linear relationship with temperature. This part of the thermal energy is attributed to free electrons in metals; specifically electrons on the “Fermi surface”. Using the Sommerfeld expansion, one can derive the free electron energy as follows:

$$\frac{E}{V} = \frac{(2m)^{3/2}\mu^{5/2}}{5\pi^2\hbar^3}\left(1 + \frac{5\pi^2}{8}\left(\frac{k_BT}{\mu}\right)^2 + \ldots\right)$$

$$\frac{E}{N} = \frac{3E_F}{5}\left(1 + \frac{5\pi^2}{12}\left(\frac{k_BT}{E_F}\right)^2 + \ldots\right)$$

The heat capacity at constant volume indeed follows a linear relation with T.

$$C_V = \left.\frac{\partial E}{\partial T}\right|_{N,V} = Nk_B\frac{\pi^2}{2}\left(\frac{T}{T_F}\right)$$

Paramagnetism

In a magnetic field, B, free electrons have extra energies. One is the energy resulting from the *Lorentz force*, the other is the coupling of the electron spin to the magnetic field. An electron can have two different spin states, up and down, noted as $s = 1$ and $s = -1$ where s is the spin index.

$$E_{spin} = \mu_B Bs$$

where μ_B is the Bohr magneton. The number of electrons at the $s = 1$ and $s = -1$ states follow the Fermi-Dirac distribution:

$$\frac{N(s=1)}{V} = \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty dE\frac{\sqrt{E}}{e^{\beta(E+\mu_BB-\mu)}+1} = \frac{1}{\lambda^3}f_{3/2}(ze^{-\beta\mu_BB})$$

$$\frac{N(s=-1)}{V} = \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty dE\frac{\sqrt{E}}{e^{\beta(E-\mu_BB-\mu)}+1} = \frac{1}{\lambda^3}f_{3/2}(ze^{+\beta\mu_BB})$$

Magnetization, M, is a measure of energy response to a magnetic field:

$$M = -\frac{\partial E}{\partial B} = -\mu_B(N(s=1) - N(s=-1)) = -\frac{\mu_BV}{\lambda^3}\left(f_{3/2}(ze^{-\beta\mu_BB}) - f_{3/2}(ze^{+\beta\mu_BB})\right)$$

As $z \to 0$, $f_{3/2}(z) \approx z$:

$$M \approx \frac{2\mu_BVz}{\lambda^3}\sinh(\beta\mu_BB)$$

One can also compute N as

$$N = N(s=1) + N(s=-1) \approx \frac{2Vz}{\lambda^3}\cosh(\beta\mu_BB)$$

Combining the two equations, one has:

$M \approx \mu_B N \tanh(\beta \mu_B B)$

The magnetic susceptibility, χ, is a measure of how easy to magnetize a metal:

$$\chi = \frac{\partial M}{\partial B} = \frac{N\mu_B^2}{k_B T} sech^2(\beta \mu_B B)$$

At small B or high temperature (small β), $sech(\beta \mu_B B) \approx 1$. This inverse behavior with temperature is known as the *Curie's law*. At low temperatures, however, an additional term in the Sommerfeld expansion must be included:

$$M \approx \frac{\mu_B V}{6\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left[(E_F + \mu_B B)^{3/2} - (E_F - \mu_B B)^{3/2}\right] \approx \frac{\mu_B^2 V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E_F}B$$

Using the density of states, $g(E)$ expression,

$$M \approx \mu_B^2 g(E_F) B$$

$$\chi \approx \mu_B^2 g(E_F)$$

Note that $\chi > 0$; therefore in the presence of a magnetic field, paramagnetic materials are attracted to the magnetic field.

Poly-logarithmic Function

Poly-logarithmic function $f_n(z)$ used in this article is often expressed as $Li_s(z)$ in mathematics where n is replaced by s:

$$Li_s(z) = \sum_{k=1}^{\infty} \frac{z^k}{k^s} = z + \frac{z^2}{2^s} + \frac{z^3}{3^s} + \dots$$

It can also be expressed in the familiar integral form:

$$Li_s(z) = \frac{1}{\Gamma(s)} \int_0^\infty \frac{t^{s-1}}{e^t/z - 1} dt$$

At small z,

$$\lim_{z \to 0} \frac{Li_s(z)}{z} = \frac{1}{\Gamma(s)} \int_0^\infty t^{s-1} e^{-t} dt = 1$$
