Free electron gas

Free electrons in metals give rise to the important properties of electrical and thermal conductivity. These electrons are considered free primarily because they feel nearly no forces due to the nuclei (other than collisions) and are largely not bound to any atom. Thus it is quite appropriate to consider them as a gas of free electrons. The energy of any electron will be their kinetic energy.
We will obtain the energy distribution of free electrons in a metal. Electrons are fermions and hence the distribution has to be Fermi-Dirac distribution. We only have to write the FD distribution in a form suitable for describing free electrons. To this end, we note that the energy of free electron takes a continuous set of values. Therefore it would make sense to talk about an occupation number $n(E)dE$ for a given energy interval, say, $(E, E + dE)$. The second aspect is, for the free electron gas the density of states $\rho(E)dE$ plays the role of the degeneracy factors g_i. This is so because $\rho(E)dE$ gives us the number of phase space points (configurations) for a fermion that correspond to an energy range $(E, E + dE)$.

$$n(E)dE = \frac{\rho(E)}{e^{\frac{E-E_F}{k_B T}} + 1} dE \tag{1}$$

We must find out $\rho(E)$. A free electron has all its energy due to kinetic energy.

$$E = \frac{\mathbf{p}^2}{2m}$$

where the $\mathbf{p}^2 = \mathbf{p}\cdot\mathbf{p}$ gives the square of the magnitude of the momentum vector $\mathbf{p}$. Henceforth we will denote this magnitude with just $p = |\mathbf{p}| = \sqrt{\mathbf{p}^2}$. Thus the energy of the electron is

$$E = \frac{p^2}{2m} \tag{2}$$

From this we see that

$$dE = \frac{p\ dp}{m} \Longrightarrow dp = m\frac{dE}{\sqrt{2mE}} \tag{3}$$

The allowed configurations in phase space for a free particle are all of the phase space. Volume of the phase space is given by the integral

$$\int dx \int dy \int dz \left(4\pi \int p^2 dp\right) = V\left(4\pi \int (2mE)m\frac{dE}{\sqrt{2mE}}\right) = 4\pi m V \int \sqrt{2mE}dE \tag{4}$$

Electron, in addition to being a free particle inside a metal, has two possible spins. It could be in any one of the configurations mentioned above in two ways. Thus for electrons the allowed configurations become

$$2 \times 4\pi m V \int \sqrt{2mE}dE = 8\pi m V\sqrt{2mE}dE \tag{5}$$

In the second step above, we have used equations (2) and (3). From this we get the density of states that gives the configurations in the energy range $(E, E+dE)$ to be

$$\rho(E)dE = 8\pi mV\sqrt{2mE}dE \tag{6}$$

Now, according to quantum mechanics, a position coordinate x and the corresponding momentum coordinate p_x of a particle can never be determined more accurately than allowed by the uncertainty relation

$$\Delta x \; \Delta p_x \geq \hbar \tag{7}$$

This implies that in eqn(4) a product of each coordinate, and its corresponding momentum will have a smallest size $\hbar$. The entire phase space can be thought to be filled up by boxes whose edges (or faces) have area $\hbar$. The number of configurations in phase space can now be counted - it is the total volume by the volume of the box $\hbar^3$ giving us,

$$\frac{8\pi mV\sqrt{2mE}dE}{\hbar^3} \tag{8}$$

Using this the FD distribution for the free electron gas turns out to be

$$n(E)dE = \frac{8\pi mV}{\hbar^3}\frac{\sqrt{2mE}}{e^{\frac{E-E_F}{k_BT}}+1}dE \tag{9}$$

We can now use this FD distribution to find the Fermi energy for the metal in terms of the parameters of the metal. At absolute zero temperature $T = 0K$, we have learnt that the set of free electrons fill up all energy levels up to the Fermi energy E_F. The integral of the occupation number up to Fermi energy must give the total number N of free electrons

$$\int_0^{E_F} n(E)dE = N \tag{10}$$

From the RHS of eqn(9), at $T = 0K$ the FD distribution for $E < E_F$ becomes

$$\lim_{T\to 0}\frac{8\pi mV}{\hbar^3}\frac{\sqrt{2mE}}{e^{\frac{E-E_F}{k_BT}}+1} = \frac{8\pi mV}{\hbar^3}\frac{\sqrt{2mE}}{0+1} = \frac{8\pi mV}{\hbar^3}\sqrt{2mE} \tag{11}$$

If we integrate the FD distribution at $T = 0K$ up to E_F we must get the total number of electrons N.

$$\int_0^{E_F}\frac{8\pi mV}{\hbar^3}\sqrt{2mE}\;dE = N$$

$$\Rightarrow \frac{8\sqrt{2}\pi V}{\hbar^3}m^{\frac{3}{2}}\frac{2E_F^{\frac{3}{2}}}{3} = N$$

$$\Rightarrow E_F = \left(\frac{N}{V}\frac{3\hbar^3}{16\sqrt{2}\pi m^{\frac{3}{2}}}\right)^{\frac{2}{3}} = \frac{\hbar^2}{8m}\left(\frac{3N}{\pi V}\right)^{\frac{2}{3}} \tag{12}$$

Eqn(12) provides the Fermi energy in terms of the electron density $\frac{N}{V}$, often a known number for most metals, and the mass of electron m.