ELECTRON GAS - A CRUDE MODEL OF A SOLID

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Solids are complex structures, and a full quantum theory of solids is a vast subject. In this post, we'll have a look at the simplest model of solids, known as the *electron gas*.

In a solid, typically the outer electrons of an atom become detached from their parent atom and wander more or less freely thoughout the solid. Obviously, the potential felt by such a wandering electron is complex, as it depends on the positions of the various nuclei and on the positions of all the other electrons. A very crude model can be constructed, in which all of these influences on the free electrons are ignored, and the free electrons move in what is effectively a 3-d infinite square well, where the potential is $V = 0$ everywhere inside the solid and $V = \infty$ at the boundaries.

If we consider the 3-d box to be rectangular with side lengths l_x, l_y and l_z, then the solution is a straightforward generalization of the 1-d case (since the Schrödinger equation separates into 3 equations, one for each dimension), giving a wave function of

$$\psi_{n_x n_y n_z} = \sqrt{\frac{8}{l_x l_y l_z}} \sin\left(\frac{n_x \pi x}{l_x}\right) \sin\left(\frac{n_y \pi y}{l_y}\right) \sin\left(\frac{n_z \pi z}{l_z}\right) \tag{1}$$

where the ns are positive integers. The energies are also a generalization of the 1-d case:

$$E_{n_x n_y n_z} = \frac{\pi^2 \hbar^2}{2m} \left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2}\right) \tag{2}$$

For any macroscopic quantity of solid, the number of free electrons is enormous (remember that one mole of a substance contains Avogadro's number of 6.02×10^{23} atoms, and each atom can contribute more than one electron in many cases). Since electrons are fermions, no more than 2 electrons can occupy any single spatial state (one with spin up and the other spin down). Thus the number of quantum numbers (the number of values of the three ns) required to accommodate all the electrons is going to be huge.

One way of thinking about this is to define the quantity

$$k^2 \equiv \frac{\pi^2 n_x^2}{l_x^2} + \frac{\pi^2 n_y^2}{l_y^2} + \frac{\pi^2 n_z^2}{l_z^2} \equiv k_x^2 + k_y^2 + k_z^2 \tag{3}$$

In the ground state, the electrons will fill the individual states starting from $n_x = n_y = n_z = 1$ and working upwards. We can think of these states as occupying the lattice points in a 3-d rectangular coordinate system with the k_is as the axes. Each particular combination of the k_is can be assigned the rectangular cell adjacent to it. Since the distance between lattice points is π/l_i the volume of each cell is $\pi^3/l_x l_y l_z = \pi^3/V$, where V is the volume of the solid.

The states will be filled out to a maximum value of k_F and since $k_F^2 = k_x^2 + k_y^2 + k_z^2$ is the equation of a sphere of radius k_F, and we're taking all the k_is to be positive, the filled states in the ground state of the solid occupy the first octant of this sphere. The number of lattice points within this octant is the volume of the octant divided by the volume of each cell, so

$$N_{points} = \frac{1}{8}\frac{4\pi}{3}k_F^3\frac{V}{\pi^3} = \frac{Vk_F^3}{6\pi^2} \tag{4}$$

If N is the total number of atoms in the solid and q is the number of free electrons per atom, the number of spatial states required for these electrons is $Nq/2$, so

$$\frac{Nq}{2} = N_{points} \tag{5}$$

$$= \frac{Vk_F^3}{6\pi^2} \tag{6}$$

$$k_F = \left(\frac{3\pi^2 Nq}{V}\right)^{1/3} \tag{7}$$

If we define $\rho \equiv Nq/V$ as the density of free electrons, then we get

$$k_F = \left(3\pi^2\rho\right)^{1/3} \tag{8}$$

with corresponding energy, known as the *Fermi energy*:

$$E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m}\left(3\pi^2\rho\right)^{2/3} = \frac{\hbar^2}{2m}\left(3\pi^2 Nq\right)^{2/3} V^{-2/3} \tag{9}$$

This is the maximum energy that a free electron in the ground state will have.

The total energy can be found from an integral. All states with a given value of k have the same energy $E = \hbar^2 k^2/2m$, and these states lie in a spherical shell in the first octant. The number of states with this energy

in a volume element is the volume element $k^2 \sin\theta dk d\theta d\phi$ divided by the volume of a cell π^3/V times 2 spin states per spatial state, so

$$E_{tot} = \frac{2\hbar^2 V}{2m\pi^3} \int_0^{k_F} \int_0^{\pi/2} \int_0^{\pi/2} k^4 \sin\theta d\phi d\theta dk \tag{10}$$

$$= \frac{\hbar^2 V}{10\pi^2 m} k_F^5 = \frac{\hbar^2 \left(3\pi^2 Nq\right)^{5/3}}{10\pi^2 m} V^{-2/3} \tag{11}$$

The average energy per electron is then

$$E_{av} = \frac{E_{tot}}{Nq} \tag{12}$$

$$= \frac{\hbar^2 \left(3\pi^2\right)^{5/3} (Nq)^{2/3}}{10\pi^2 m} V^{-2/3} \tag{13}$$

$$= \frac{3}{5} \frac{\hbar^2}{2m} \left(3\pi^2 Nq\right)^{2/3} V^{-2/3} \tag{14}$$

$$= \frac{3}{5} E_F \tag{15}$$

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