DEGENERACY PRESSURE IN A SOLID

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References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 5.16.

The electron gas is a crude model of a solid, in which only the free electrons are considered, and all interactions, both between the electrons themselves and between them and the nuclei, are ignored. The total energy of the free electrons in a solid in this model is

$$E_{tot}=\frac{\hbar^{2}\left(3\pi^{2}Nq\right)^{5/3}}{10\pi^{2}m}V^{-2/3} \tag{1}$$

where N is the number of atoms, q is the number of free electrons per atom and V is the volume of the solid. The dependence on the volume is interesting in its own right. As the volume increases, the energy decreases, much as in an ideal gas as studied in classical thermodynamics. The classical explanation of this phenomenon is that an ideal gas exerts a pressure P on its container and if this pressure causes the container to expand, the gas is doing work on its surroundings. This work results in a decrease in the internal energy of the gas.

If the pressure acts on an area A of the container and causes this area to move a distance dx then since pressure is force per unit area, the amount of work done is $PAdx$. The quantity Adx is the change dV in the volume, so the amount of work done, and hence the decrease in energy dE, is PdV.

Taking the differential of the above equation, we get

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

Since the negative sign indicates a decrease in energy, the effective pressure is

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

where ρ is the free electron density (number of free electrons per unit volume). This pressure is known as the *degeneracy pressure*.

This may seem to be a rather curious result, since a real solid sitting on a table doesn't have any container against which this pressure is acting, so if the electron gas model were accurate, we might expect a solid to just expand until it dissipated in the air. Of course, we're neglecting the electrical attraction between the electrons and nuclei which is what holds the solid together. The quantum pressure thus helps to explain the inverse problem of why a solid doesn't contract under the electric force. The Fermi exclusion principle requires a substance with a given number of free electrons to have a minimum size in order for there to be enough states to accommodate all the electrons.

As an example, we can calculate a few numbers for copper. Given its density of 8.96 gm cm^3 and its atomic weight of 63.5 gm mole^{-1} we get, assuming one free electron per atom ($q = 1$) since its outermost electron is a single 4s electron:

(4)
$$\rho = \frac{8.96}{63.5}\left(6.02\times10^{23}\right) = 8.49\times10^{22} \text{ electrons cm}^{-3} = 8.49\times10^{28} \text{ electrons m}^{-3}$$

The Fermi energy is

$$E_F = \frac{\hbar^2}{2m}\left(3\pi^2\rho\right)^{2/3} = 7.04 \text{ eV} \tag{5}$$

If we take this as kinetic energy so that $E_F = \frac{1}{2}mv^2$ then the speed of the electrons at the Fermi energy is (using the mass of the electron as 0.51 MeV$/c^2$):

$$v = \sqrt{\frac{2E_F}{m}} = 1.57\times10^6 \text{m sec}^{-1} \tag{6}$$

This is about 0.5% of the speed of light which isn't solidly relativistic, but fast enough that some relativistic effects might be noticeable in a sensitive experiment.

The characteristic thermal energy of a particle is given by k_BT, where k_B is the Boltzmann constant and T is the absolute temperature. (This comes out of statistical mechanics, which we haven't covered yet, so just take it as given.) Equating this to E_F we get the *Fermi temperature* $T = E_F/k_B =$ 81725 K (in other words, extremely hot). Since the melting point of copper is 1357.77 K and its boiling point is 2835 K, any solid copper will be well below the Fermi temperature and can be considered as 'cold'.

The degeneracy pressure is

$$P=\frac{\hbar^{2}\left(3\pi^{2}\right)^{2/3}\rho^{5/3}}{5m}=3.84\times10^{10}\text{N m}^{-2} \tag{7}$$

This is enormous, and gives you some idea of the strength of the electrical attraction required to counter it.

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