

Lecture 36 Highlights

We are now interested in the macroscopic thermodynamic properties of many identical Fermions with overlapping wavefunctions. The classic example is the problem of electrons in a metal. Each atom in a metal gives up n valence electrons when it joins a metal crystal lattice. These electrons are free to roam all over the crystal, once again considered to be a box of sides $a \times a \times a = V$. As such, these electrons have strongly overlapping wavefunctions. The positive ion cores are left behind in a fixed position, except for small lattice vibrations.

Classically we might expect the “free” electrons to make a substantial contribution to the total heat capacity of the solid. If the electrons have a Hamiltonian

$H = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}$, then they should each acquire $\frac{3}{2}k_B T$ of energy on average, by equipartition of energy. This would lead to a total internal energy of the “electron gas” at temperature T of $U_{electrons} = nN \frac{3}{2}k_B T$, where N is the total number of atoms in the

crystal. This gives rise to an electronic heat capacity of $C_V = \left. \frac{dU}{dT} \right|_V = \frac{3}{2}k_B nN$. However

the measured heat capacity of the electrons is linear in temperature and much smaller than this in magnitude. This dilemma can be understood only after a quantum mechanical description of electrons in a metal is constructed.

Fermi-Dirac statistics predicts for the most likely occupation numbers:

$$n_s = \frac{g_s}{e^{(E_s - \mu)/k_B T} + 1}$$

Take the continuum approximation (not a bad approximation because the ground state is not that important here), and consider the “occupation index” $n(E)/g(E)$:

$$\frac{n(E)}{g(E)} = \frac{1}{e^{(E - \mu)/k_B T} + 1}$$

Recall that for Fermions the occupation number can never exceed the degeneracy. Hence the occupation index is a number between 0 and 1, inclusive. Note from the above formula that the occupation index when $E = \mu$ is simply $n(\mu)/g(\mu) = 1/2$. Also in the limit of temperature $T \rightarrow 0$ one finds that;

$$\frac{n(E)}{g(E)} = \begin{cases} 1 & \text{for } E < \mu \\ 0 & \text{for } E > \mu \end{cases} \quad (T = 0)$$

The Fermi distribution occupation index shows that at $T = 0$ all the states below the chemical potential are filled, while all those above are un-occupied. The Fermi energy is defined as the energy of the highest occupied state at $T = 0$. The collection of filled states below the chemical potential is known as the “Fermi sea.”

Note that for Cu, the Fermi energy is $E_F = 7.0 \text{ eV}$, and the thermal energy at room temperature ($k_B T$ with $T = 300 \text{ K}$) is only 25 meV. Because Fermions can only be excited by making a transition from an occupied state to an un-occupied state (Pauli exclusion principle), only a very small fraction of the electrons can actually be excited out of the Fermi sea! In this case a fraction on the order of $k_B T / E_F \sim 0.004$ of the

electrons can actually make their way to excited states outside the Fermi sea. The remaining electrons are “frozen” in place. Note that the electrons are not frozen in space, they are frozen in their assigned states in momentum space, and thus are actually moving about the crystal at high speeds.

The small number of electrons that can actually accept thermal energy and move into un-occupied states accounts for the very small heat capacity of the electrons.

How do we calculate the Fermi energy? The problem again is to determine the states of the system “s”, the energy levels E_s , and the degeneracies of those levels g_s . We shall make the same rough approximation as with ${}^4\text{He}$ and assume that the electrons are “free” but confined to a cube (3D infinite square well) of sides $a \times a \times a = V$. This leads to the same wavefunctions, eigen-energies, and degeneracies (except for a factor of 2 due to spin) as we obtained for ${}^4\text{He}$. Recall from the ${}^4\text{He}$ case that the total number of states up to energy E is given by;

$$G(E) = \frac{\pi V}{3} \left(\frac{8m_e E}{h^2} \right)^{3/2},$$

where a factor of 2 was thrown in for the two different spin states of the electron. At zero temperature, all states up to the Fermi energy are occupied, accounting for all N of the electrons (note that this N was previously called nN above);

$$G(E_F) = N = \frac{\pi V}{3} \left(\frac{8m_e E_F}{h^2} \right)^{3/2}.$$

Note also that the mass appearing in this equation is that of a single electron. Solving for the Fermi energy we get:

$$E_F = \frac{h^2}{8m_e} \left(\frac{3N/V}{\pi} \right)^{2/3}$$

Here is a table of calculated Fermi energies for some elemental metals:

Metal	Valence (n)	E_F (eV)
Cu	1	7.0
Ag	1	5.5
Au	1	5.5
Li	1	4.7
Be	2	14.4
Al	3	11.66
Pb	4	9.4