

## Lecture 25 Highlights

### Phys 402

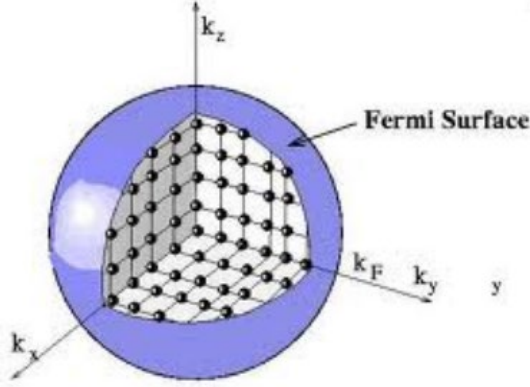
We are now interested in the macroscopic properties of many identical Fermions with overlapping wavefunctions. The classic example is the problem of electrons in a metal. Each atom in a metal gives up one or more valence electrons when it joins a metal crystal lattice. These electrons are **itinerant** (free to roam all over the crystal), as opposed to those electrons that stay with their original nucleus, which are said to be **localized**. The metal itself is considered to be a box of sides  $L_x \times L_y \times L_z = V$ , the volume of the metal. As such, these itinerant electrons have strongly overlapping wavefunctions. The positive ion cores, and the localized electrons, are left behind in a fixed position, except for small lattice vibrations.

We will start with a single particle quantum problem of a particle in 3 dimensions. Later we will consider what happens when more electrons are added to the metal. We will

assume a Hamiltonian of the form  $H = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} + V(x, y, z)$ , where  $V(x, y, z) = \begin{cases} 0 & \text{if } 0 < x < L_x \text{ and } 0 < y < L_y \text{ and } 0 < z < L_z \\ \infty & \text{otherwise} \end{cases}$  is the 3D infinite square well potential. We shall

assume that the electron-ion and electron-electron interactions can be ignored for now. This is the free-electron Fermi gas model of a metal. Condensed matter physics is concerned with what happens when these other interactions are included.

The solution to the 3D Schrodinger equation proceeds by separation of variables in Cartesian coordinates. We shall use running wave solutions (as opposed to standing wave solutions) of the form  $\psi(x, y, z) \sim \frac{1}{\sqrt{V}} e^{ik_x x} e^{ik_y y} e^{ik_z z}$ , where the total energy is  $E = \frac{\hbar^2 k_x^2}{2m} + \frac{\hbar^2 k_y^2}{2m} + \frac{\hbar^2 k_z^2}{2m}$ , where the waves can run in either the  $\pm x$ ,  $\pm y$ , or  $\pm z$  directions. We now apply periodic boundary conditions (or Born-von Karmen boundary conditions), such that  $\psi(x + L_x, y, z) = \psi(x, y, z)$ ,  $\psi(x, y + L_y, z) = \psi(x, y, z)$ , and  $\psi(x, y, z + L_z) = \psi(x, y, z)$ . Given solutions of the form  $\psi \sim e^{ik_x x}$ , this demands that  $e^{ik_x(x+L_x)} = e^{ik_x x}$ , which requires  $k_x L_x = 2\pi n_x$ , with  $n_x = 0, \pm 1, \pm 2, \pm 3, \dots$ , with similar results for the y and z-directions. The total energy of the particle can now be written as  $E = \frac{\hbar^2 (2\pi)^2}{2m} \left( \left( \frac{n_x}{L_x} \right)^2 + \left( \frac{n_y}{L_y} \right)^2 + \left( \frac{n_z}{L_z} \right)^2 \right)$ , which depends on 3 integers. Note that the solution to the TISE  $\psi(x, y, z) \sim \frac{1}{\sqrt{V}} e^{ik_x x} e^{ik_y y} e^{ik_z z}$  is also an eigenstate of the 3D momentum operator  $\vec{p} = -i\hbar \vec{\nabla}$  with eigenvalue  $\hbar \vec{k} = \hbar(k_x, k_y, k_z)$ . Hence the energy eigenstates are also momentum eigenstates. It turns out that labeling the states by their momentum is very convenient. We can treat each eigenstate as a point in k-space labelled by a triplet of integers:  $\vec{k} = 2\pi \left( \frac{n_x}{L_x}, \frac{n_y}{L_y}, \frac{n_z}{L_z} \right)$ . These points make up a regular lattice in k-space.



Note that each individual state takes up a volume of  $\frac{2\pi}{L_x} \times \frac{2\pi}{L_y} \times \frac{2\pi}{L_z} = \frac{(2\pi)^3}{V}$  in k-space.

We have now found all of the single-particle states of an electron in a 3D infinite square well. What happens when we add the next electron? The first electron will occupy the lowest energy state, say  $(n_x, n_y, n_z) = (0,0,0)$  and spin up. By the Pauli exclusion principle, the next electron must go into a state with a different list of quantum numbers. In this case, it would be the state  $(0,0,0)$  and spin down. The next electron would have to go into a higher energy state such as  $(1,0,0)$ . There are many electrons to add, a total of  $qN$ , where  $q$  is the number of electrons that each atom gives up, and  $N$  is a number on the order of Avogadro's number. The occupied electron states will reside inside a sphere in k-space, which represent all the states that are equidistant from the origin, hence they all have the same energy since  $E = \frac{\hbar^2 k^2}{2m}$ . The radius of this sphere that accounts for all  $Nq$  electrons in the metal is called the Fermi momentum  $p_F = \hbar k_F$ . The volume of the sphere must accommodate  $Nq$  electrons, with 2 electrons going in to each integer-labeled state (because of spin). We can write the total volume of the sphere in k-space as the product of the number of electrons and the volume per electron in k-space:

$$\frac{4}{3} \pi k_F^3 = \frac{Nq}{2} \frac{(2\pi)^3}{V}.$$

Solving for  $k_F = (3\pi^2 \rho)^{1/3}$ , where  $\rho \equiv Nq/V$  is the number density of electrons in the metal. The corresponding energy of the highest occupied state is called the Fermi energy, and is defined as  $E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m} (3\pi^2 \rho)^{2/3}$ . The Fermi momentum can also be interpreted in terms of a Fermi velocity  $v_F = \frac{\hbar k_F}{m}$ .

Metals have a number density on the order of  $\rho \sim 10^{23}/\text{cm}^3$ . Typical values for the Fermi energy are in the range of 1 to 10 eV. Here is a table of calculated Fermi energies for some elemental metals:

Metal	Valence ( $q$ )	$E_F$ (eV)
<b>Cu</b>	<b>1</b>	<b>7.0</b>
<b>Ag</b>	<b>1</b>	<b>5.5</b>
<b>Au</b>	<b>1</b>	<b>5.5</b>
<b>Li</b>	<b>1</b>	<b>4.7</b>
<b>Be</b>	<b>2</b>	<b>14.4</b>
<b>Al</b>	<b>3</b>	<b>11.66</b>
<b>Pb</b>	<b>4</b>	<b>9.4</b>

The Fermi wavenumber is typically  $k_F \sim 10^8 \text{ cm}^{-1}$ . The Fermi velocity is typically about  $v_F \sim 10^6 \text{ m/s}$ . One can also define a Fermi temperature as  $T_F = \frac{E_F}{k_B} \sim 10^5 \text{ K} \gg 300 \text{ K}$ .

We can calculate the total energy in the Fermi electron gas by integrating over all of the occupied states,  $U_{Total} = \int_0^{k_F} U_{Shell}(k) dk$ , where  $U_{Shell}(k) dk$  is the energy of all the electrons in the shell between radii  $k$  and  $k + dk$ . A shell of radius  $k$  and thickness  $dk$  has a volume of  $4\pi k^2 dk$  in  $k$ -space. The number of states in that shell is the ratio of its volume to the volume of a single state in  $k$ -space:  $\frac{4\pi k^2 dk}{\frac{(2\pi)^3}{V}/2} = \frac{V}{\pi^2} k^2 dk$ . The energy of

all the states in the shell is  $U_{Shell}(k) dk = \frac{\hbar^2 k^2}{2m} \frac{V}{\pi^2} k^2 dk$ . The total energy is then  $U_{Total} = \int_0^{k_F} \frac{\hbar^2 k^2}{2m} \frac{V}{\pi^2} k^2 dk = \frac{\hbar^2}{2m} \frac{V}{\pi^2} \frac{1}{5} k_F^5$ .

The Fermi gas exerts a pressure on the walls of the metal box. The total energy decreases as the volume of the box increases:  $dU_{Total} = -\frac{2}{3} U_{Total} \frac{dV}{V}$ . Notice that if  $dV > 0$ , the total energy decreases. This energy shows up as work done on the environment,  $dW = PdV$ , showing that  $P = \frac{2}{3} \frac{U_{Total}}{V} = \frac{\hbar^2}{5m} (3\pi^2)^{2/3} \rho^{5/3}$ . This is called the degeneracy pressure of the electron gas. It is the pressure that keeps the metal from collapsing at low temperatures. Note that it is independent of the electron-electron repulsion, which has been ignored! This pressure also stabilizes objects such as white dwarfs and neutron stars.

As an aside, we considered the idea of a density of states (DOS). This arises when we convert a sum over all the points representing solutions to the Schrodinger equation in  $k$ -space to a continuous integral on energy:  $\sum_{n_x, n_y, n_z} \rightarrow \int D(E) dE$ , where  $D(E)$  is the density of states. The number of states in the Fermi sphere between radius  $k$  and  $k + dk$  is the ratio of the volume of that shell in  $k$ -space, divided by the volume per state in  $k$ -space:  $\# \text{ states} = \frac{4\pi k^2 dk}{\frac{(2\pi)^3}{V}/2}$ . Now we know how to convert  $k$  into energy  $E$ :  $k = \sqrt{2mE}/\hbar$ , hence  $dk = \frac{1}{2\hbar} \sqrt{2m/E} dE$ . Now write the number of states in the shell as  $\# \text{ states} = D(E) dE$  by converting from  $k$  to  $E$ :  $D(E) dE = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{E} dE$ . Three dimensional systems typically have a density of states that increases as the square root of energy.

See Prof. Appelbaum's [lecture notes](#) for an alternative derivation of the particle in a box in three dimensions.

If we naively assume the electrons act like free particles in an ideal gas, 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  $U_{electrons} = N \frac{3}{2} k_B T$ , where  $N$  is the total number of atoms in the crystal. This gives rise to an electronic heat capacity

of  $C_V = \left. \frac{dU}{dT} \right|_V = \frac{3}{2} k_B N$ . However the measured heat capacity of the electrons is linear in temperature and much smaller (by orders of magnitude) than this in magnitude. This dilemma can be understood only after a quantum mechanical description of electrons in a metal is constructed.

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, and essentially act like vegetables. 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. A simple estimate of the energy acquired by the electron gas due to thermal excitation is:  $U \sim (\# \text{ electrons in excited states}) \times (\text{energy acquired per electron}) = \left( N \frac{k_B T}{E_F} \right) \times (k_B T)$ . The heat capacity of the electrons is therefore  $C_{V, \text{electrons}} = 2Nk_B \frac{k_B T}{E_F}$ , which is reduced in magnitude from the “free electron” result above and linear in temperature. In metals at low temperatures one expects two main contributions to the heat capacity: that from electrons and from phonons (lattice vibrations). As a result one expects  $C_{V, \text{Total}} = C_{V, \text{electrons}} + C_{V, \text{phonons}} = aT + bT^3$ . Therefore plotting  $C_{V, \text{Total}}/T$  vs.  $T^2$  should be a straight line and the intercept is the electronic heat capacity coefficient while the slope is the phonon heat capacity coefficient.