Lecture 15: free electron gas

Up to this point we have not discussed electrons explicitly, but electrons are the first offenders for most useful phenomena in materials. When we distinguish between metals, insulators, semiconductors, and semimetals, we are discussing conduction properties of the electrons. When we notice that different materials have different colors, this is also usually due to electrons. Interactions with the lattice will influence electron behavior (which is why we studied them independently first), but electrons are the primary factor in materials' response to electromagnetic stimulus (light or a potential difference), and this is how we usually use materials in modern technology.

Electrons as particles

A classical treatment of electrons in a solid, called the Drude model, considers valence electrons to act like billiard balls that scatter off each other and off lattice imperfections (including thermal vibrations). This model introduces important terminology and formalism that is still used to this day to describe materials' response to electromagnetic radiation, but it is not a good physical model for electrons in most materials, so we will not discuss it in detail.

Electrons as waves

In chapter 3, when we discussed metallic bonding, the primary attribute was that **electrons are delocalized**.

In quantum mechanical language, when something is delocalized, it means that its position is ill defined which means that its **momentum** is more well defined. An object with a well defined momentum but an ill-defined position is a plane-wave, and in this chapter we will treat electrons like plane waves, defined by their momentum.

Another important constraint at this point is that electrons **do not** interact with each other, except for pauli exclusion (that is, two electrons cannot be in the same state, where a state is defined by a momentum and a spin).

To find the momentum and energy of the available quantum states, we solve a particle-in-a-box problem, where the box is defined by the boundaries of the solid.

Particle in a Box in one dimension

An electron of mass m is confined to a one-dimensional box of length L with infinitely high walls.

We need to solve Schrodinger's equation with the boundary conditions determined by the box

$$\mathcal{H}\psi_n = \frac{-\hbar^2}{2m}\frac{d^2\psi_n}{dx^2} = \epsilon_n\psi_n$$

Here, ψ_n is the wavefunction of the n-th solution, and ϵ_n is the energy associated with that eigenstate.

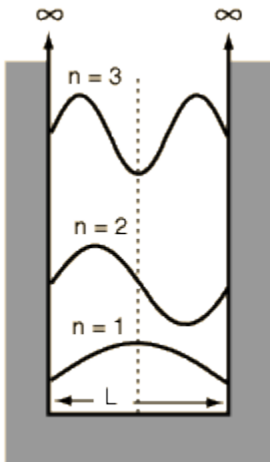The boundary conditions (infinitely high walls) dictate that:

$$\psi_n(x = 0) = 0$$
$$\psi_n(x = L) = 0$$

For all n.

A solution for the wavefunction which satisfies Schrodinger's equation and the boundary conditions is:

$$\psi_n = Asin(\frac{n\pi x}{L})$$

Where A is a constant. Here, each solution wavefunction corresponds to an integer number of half-wavelengths fitting inside the box: $\frac{1}{2}n\lambda_n = L$

x = 0 at left wall of box.

Now, plug our 'guess' back into Schrodinger's equation to get the eigenenergies:

$$\frac{\hbar^2}{2m}\frac{d^2\psi_n}{dx^2} = A\frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2 \sin\left(\frac{n\pi x}{L}\right) = A\epsilon_n \sin\left(\frac{n\pi x}{L}\right)$$

$$\epsilon_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2$$

Each energy level, n, defines a 'state' in which we can put two electrons into, one spin up and one spin down. Here is where the approximation/assumption comes in. We are assuming that our one-particle wavefunction is applicable to a many-electron system—that we do not change the wavefunction of one electron when we add others to the box. It turns out that this approximation works reasonably well for some simple metals like sodium or copper, and the formalism developed here is an excellent framework for describing real many-electron systems where our hopeful assumption doesn't necessarily hold. For now, we are also assuming that the lattice is not there.

Lets say we have N electrons and we want to place them into available eigenstates, defined by N. There are two rules we need to follow.

- Only two electrons per n, one spin up and one spin down (pauli exclusion) (note: if we were not using electrons but some other fermion with a different spin, the number of electrons in each energy eigenstate would change accordingly)

- Lower energy levels get filled up first, sort of like pouring water into a container. We are looking to describe the *ground state* configuration, and you won't get to the ground state if you fill up higher energy levels first.

The **Fermi level** (ϵ_F) is defined as the highest energy level you fill up to, once you have used up all your electrons.

$$\epsilon_F = \frac{\hbar^2}{2m}\left(\frac{N\pi}{2L}\right)^2$$

(we simply plugged in N/2 for n, since we use up two electrons for each state)

Effect of temperature

What has been described thus far is the zero-temperature ground state of a collection of electrons confined to a box in 1D. What finite temperature does is it slightly modifies the occupation probability for energies close to the Fermi level, and this is encompassed in the Fermi-Dirac distribution (also called the Fermi function). The probability that a given energy level, ϵ, is occupied by electrons at a given temperature is given by:

$$f(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/k_B T} + 1}$$

The quantity μ is the **chemical potential** and it ensures that the number of particles come out correctly. At T=0, $\mu = \epsilon_F$, and at temperatures we typically encounter in solid state physics, it does not differ too much from that value.
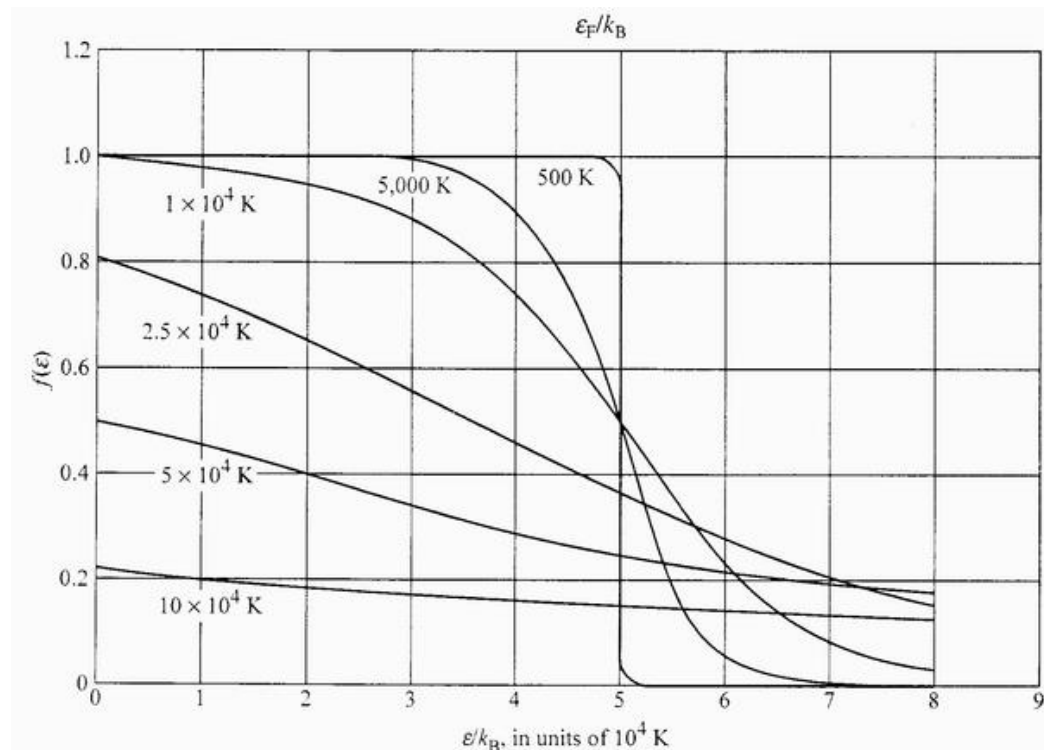
At zero temperature, the Fermi-Dirac distribution represents a sharp cutoff between states that are occupied by electrons and states that are unoccupied. At higher temperature, the Fermi-Dirac function introduces a small probability that states with energy higher than the chemical potential contain an electron and a symmetric small probability that states below the chemical potential lack an electron.

Free electron gas in three dimensions

This toy problem turns out to be applicable to many simple metals such as sodium or copper, and it is a generalization of the infinite potential well to three dimensions.

In three dimensions, the free particle Schrodinger equation is:

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi_k(r) = \epsilon_k \psi_k(r)$$

that the wavefunctions are marked by k instead of by n, and we will see why in a moment.

If we use boundary conditions that are a 3D generalization of the boundary conditions in 1D, we get standing wave solutions of the form:

$$\psi_n(\boldsymbol{r}) = A sin(\frac{\pi n_x x}{L}) sin(\frac{\pi n_y y}{L}) sin(\frac{\pi n_z z}{L})$$

$$\epsilon_{n_x, n_y, n_z} = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2)$$

Where n_x, n_y, n_z are positive integers, and every eigenstate is defined by a unique number of half-periods of a sine wave in each of the x, y, and z direction (but not necessarily by a unique energy, because for example $(n_x, n_y, n_z) = (1,0,0)$ will have the same energy as $(n_x, n_y, n_z) = (0,1,0)$.

At this point, it is helpful to start over with a different formalism.

We consider plane wave wavefunctions of the form

$$\psi_k(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$$

And periodic boundary conditions of the form

$$\psi(x + L, y, z) = \psi(x, y, z)$$

$$\psi(x, y + L, z) = \psi(x, y, z)$$

$$\psi(x, y, z + L) = \psi(x, y, z)$$

Plugging the first one into the wavefunction we get:

$$e^{i(k_x(x+L)+k_y y+k_z z)} = e^{i(k_x x+k_y y+k_z z)}$$

$$e^{ik_x L} = 1$$

$$k_x = 0, \pm\frac{2\pi}{L}, \pm\frac{4\pi}{L}, \dots$$

And similar for ky and kz.

Plugging the plane wave wavefunction into schrodinger's equation we get:

$$\frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right) = \epsilon_k = \frac{\hbar^2 k^2}{2m}$$

This is almost equivalent to the version of the eigenenergies that we had earlier, as that the values that kx can take on can be expressed as $2n_x\pi/L$ (and similar for ky and kz). The factor of 2 comes from the fact that only the even sine wave solutions satisfy periodic boundary conditions. On the surface it seems like these two solutions give contradictory results, but what really matters for a materials electronic properties is what happens close to the Fermi energy, and you can work out that you make up the factor of 4 (in energy) with a factor of 2 shorter k_F (which will be defined shortly…)

As before, we take our N electrons and put them into the available states, filling lowest energy first. In 3D this is trickier because multiple states may have the same energy, even though they are marked by different k_x, k_y, k_z. In 3D, our rules for filling up electrons are:

- Every state is defined by a unique quantized value of (k_x, k_y, k_z)
- Every state can hold one spin up and one spin down electrons
- Fill low energy states first. In 3D, this corresponds to filling up a sphere in k space, one 'shell' at a time. Each shell is defined by a radius k, where $k^2 = k_x^2 + k_y^2 + k_z^2$, and every state in the shell has the same energy, although different combinations of k_x, k_y, k_z
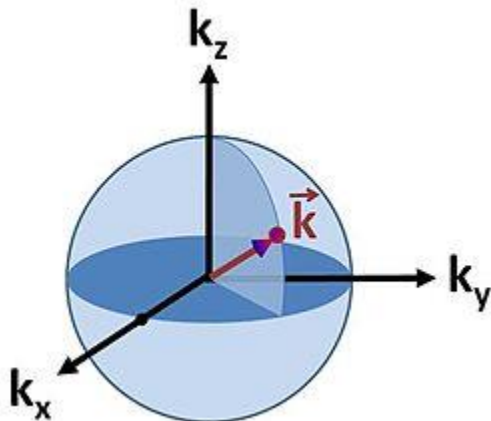
When we have used up all our electrons, we are left with a filled sphere in k space with radius k_F (called the Fermi momentum) such that

$$\epsilon_F = \frac{\hbar^2}{2m}k_F^2$$

This sphere in k-space has a volume $\frac{4}{3}\pi k_F^3$ and it is divided into voxels of volume $\left(\frac{2\pi}{L}\right)^3$

If we divide the total volume of the sphere by the volume of each 'box' and account for the fact that each box holds 2 electrons, we get back how many electrons we put in:

$$2 * \frac{\frac{4}{3}\pi k_F^3}{\left(\frac{2\pi}{L}\right)^3} = N = V k_F^3/3\pi^2$$

Here, $V = L^3$ is the volume of the solid. We can use this relationship to solve for k_F and show that it depends on electron density (N/V)

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

Plugging this back into the expression for ϵ_F we get:

$$\epsilon_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

As with phonons, the density of states is a useful quantity for electrons.

It is defined as:

$$D(\epsilon) \equiv \frac{dN}{d\epsilon}$$

We can find it by expressing N in terms of ϵ and taking a derivative. We begin by considering a sphere in k-space with an arbitrary radius k and asking how many electrons that will hold

$$N(k) = Vk^3/3\pi^2$$

The relationship between energy and momentum in a free electron gas is pretty straightforward too (unlike with phonons):

$$\epsilon = \frac{\hbar^2 k^2}{2m}$$

Solving for k, and plugging in above we get

$$N(\epsilon) = \frac{V}{3\pi^2}\left(\frac{2m\epsilon}{\hbar^2}\right)^{3/2}$$

Now we can just take the derivative with respect to energy and get:

$$D(\epsilon) \equiv \frac{dN}{d\epsilon} = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\epsilon^{1/2}$$

Thus, the density of electron states in 3D is a function of energy. If you have more electrons, you will end up with a higher density of states **at the Fermi energy**. It should be noted that as with phonons, the functional form of the density of states will depend on if you are thinking of a 1D, 2D, or 3D system.

At absolute zero, the Fermi sphere has a hard boundary between occupied and unoccupied states. At higher temperature, this boundary becomes fuzzier with increasing occupation permitted outside the initial boundary. The width of this fuzziness is determined by the width of the Fermi-Dirac distribution at that temperature, and it is roughly proportional to $k_B T$. Notably, the vast majority of electrons in the Fermi gas are completely inert because they are buried deep inside the sphere. Only electrons close to the Fermi level are affected by temperature and participate in conduction. This is quite contrary to the conclusions of particle-like treatments of electrons in a metal which assume that all valence electrons participate in electronic properties.

Electron velocity

There are two ways of extracting an electrons' velocity in a Fermi gas.

- From the derivative of the energy vs k (equivalent to what we did for phonons): $v_g = \frac{1}{\hbar}\frac{\partial \epsilon_k}{\partial k} = \hbar k/m$
- By representing the linear momentum operator as $\boldsymbol{p} = -i\hbar\nabla$ and applying this to the plane-wave wavefunction to get $\boldsymbol{p} = \hbar\boldsymbol{k}$ and equating to m$\boldsymbol{v}$ to get $\boldsymbol{v} = \hbar\boldsymbol{k}/m$

The velocity of electrons at the fermi energy is called the Fermi velocity (v_F) and it is given by:

$$v_F = \frac{\hbar k_F}{m} = \frac{\hbar}{m}\left(\frac{3\pi^2 N}{V}\right)^{1/3}$$

Example: Sodium metal

Sodium metal is one electron beyond a full shell, so it has one valence electron per atom that becomes delocalized and contributes to the sea of conduction electrons that we have been representing as plane waves. Lets calculate some of the parameters we have discussed here

Fermi momentum: $k_F = \left(\frac{3\pi^2 N}{V}\right)^{1/3}$

This depends on the electron concentration. Sodium takes on a BCC structure with a conventional (cubic) unit cell dimension of 4.29Å.

There are 2 valence electrons in this conventional cell, so N/V=$2.53 \times 10^{28}/m^3$

This gives $k_F = 9.1 \times 10^9 m^{-1}$

From this, we can get the Fermi energy: $\epsilon_F = \frac{\hbar^2}{2m}k_F^2$

$$\epsilon_F = 5.03 \times 10^{-19} \ joules$$

It is convenient to divide by a factor of the electron charge to put energy in units of **electron volts (eV).**

$$\epsilon_F = 3.1 \ eV$$

For comparison, $k_B T$ at room temperature (300K) is $4.14 \times 10^{-21} Joules$ or 0.026 eV. Thus, the energy scale of the temperature fuzzing is <1% of the highest energy level at room temperature.

Another way to think about this is to convert the Fermi energy to a Fermi temperature (T_F) by dividing by the Boltzmann constant.

$$T_F = \frac{\epsilon_F}{k_B} = 36{,}342 \ K$$

Physically, the Fermi temperature for a fermi gas is the temperature when the fermions begin to act like classical particles because they do not have to worry about available states already being occupied by electrons. For sodium, the Fermi temperature is waaaay above the melting temperature.

Finally, let's calculate the Fermi velocity for sodium:

$$v_F = \frac{\hbar}{m}\left(\frac{3\pi^2 N}{V}\right)^{1/3} = 1.05 \times 10^6 m/s$$

This is ~1/300 the speed of light, so electrons would get places quite quickly if they didn't scatter.