Physics 228, Lecture 17
Monday, March 28, 2005
Free-Electron Model, Conductivity, Metals, Insulators and Semiconductors. Ch. 42:4-6

1 Independent Electron Model

We have seen that the quantum states an electron can occupy when in the presence of a large number of positive ions form energy bands, each arising from the mixing of one atomic state from each ion. The state of the full system is then described[1] by which electronic states are occupied (have an electron in them) and which are not. This is just what we did for atoms.

As for atoms, the ground state, or lowest energy state, of the whole system is the state for which all the electrons have occupied the lowest energy available states, and left the higher energy electronic states unoccupied. Unlike isolated atoms, however, a crystal of metal is so complex, with so many available states, that it is very unlikely to be in its ground state, and in fact it is not useful to discuss the system as being in any single state, but rather to think of it as a thermal system in equilibrium at some temperature. We will use absolute temperatures T.

At any given temperature, there is a probability that a given electronic state will be occupied. That probability is given by the **Fermi-Dirac distribution function**:

$$f(E) = \frac{1}{e^{(E-E_F)/k_BT} + 1},$$

where E is the energy of the state for which we want the probability, E_F is a parameter called the **Fermi energy**, and k_B is Boltzmann's constant, which we have seen before, in

$f(E)$ 42.24
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[1] This is an approximation in which we ignore the interactions between electrons, because we are assuming the state of one electron is independent of which states the other electrons are in. It also assumes the ions are behaving in a way independent of where the electrons are. These approximations work surprisingly well.

thermal physics, is the natural scale for comparing temperatures to energies on an atomic level. Note the behavior depends on the energy difference $E - E_F$ compared to $k_B T$. If $E - E_F \gg k_B T$, the exponential is very large, and $f(E)$ is essentially zero, and the state is almost certainly not occupied. On the other hand, if E is less than E_F by an amount much greater than $k_B T$, the exponent is a large negative number and the exponenial is very small, so that the state is almost certainly occupied; the probability is near one. As $T \to 0$ these limits apply to all states; those with energies less than E_F are occupied and those above are empty. This is what determines the parameter E_F, for the number of electrons in a given hunk of metal is fixed[2]. For finite temperature, those states with energies close to the Fermi energy have some probability of being occupied and of not being occupied, while those further away are almost certainly occupied or not according to which side of E_F the energy lies. Here is a plot of $f(E)$.

2 Free Electron Theory

Knowing the possible electronic states of a substance and knowing which are occupied is what determines the behavior of the substance. The Fermi-Dirac distribution tells us the latter, but we need a model to describe the states of the system. We will first use a surprisingly simple model, treating the electrons as if they were totally free within the box formed by the crystal. Free means there are no forces on each electron, which seems very strange, but in fact we get a quite good first approximation with this assumption.

When we considered a one dimensional box confining a particle to $0 \leq x \leq L$, we found that the states were given by standing waves

$$\psi(x) = A \sin(n\pi x/L),$$

where the sin and the quantization of the wave number came from the necessity for $\psi(x) = 0$ at $x = 0$ and $x = L$. For simplicity we will consider a metal cube with each coordinate, x, y, z confined to the interval $[0, L]$. Then the wave function is

$$\psi(x, y, z) = A \sin(n_x \pi x/L) \sin(n_y \pi y/L) \sin(n_z \pi z/L),$$

[2]We are not considering letting the metal gain or lose charge. Coulomb forces are so large that any change in total charge that involved a substantial fraction of the electrons would cause electric fields that would produce lightening!

where each of the quantum numbers n_x, n_y, and n_z are positive integers. Schrödinger's equation (in three dimensions) then picks up a contribution to p^2 from each direction, and

$$E = \frac{\hbar^2\pi^2}{2m_eL^2}(n_x^2 + n_y^2 + n_z^2).$$

Thus the energy depends on the length of a three dimensional vector of integers, with

$$|\vec{n}| = \sqrt{n_x^2 + n_y^2 + n_z^2} = \sqrt{2m_e}\frac{L}{\pi\hbar}\sqrt{E} = \sqrt{8m_e}\frac{L}{h}\sqrt{E}.$$

We need to know the number of states per unit energy range. It will turn out proportional to the volume of the crystal, so we define $g(E)$ to be the number of states per unit volume per unit energy range. Thus the number of states with energies between E and $E + dE$ is $g(E)L^3dE$. But that is just twice the number of triplets of positive integers (n_x, n_y, n_z) with $|\vec{n}|$ in a certain range,

$$\sqrt{8m_e}\frac{L}{h}\sqrt{E} \le |\vec{n}| \le \sqrt{8m_e}\frac{L}{h}\sqrt{E + dE}.$$

The reason we need to double the number of triplets is that each one gives one state with spin up and one state with spin down. The triplets of integers are uniformly spread out in three dimensions, so the number with $|\vec{n}|$ in a range $\Delta|\vec{n}|$ is just the number in a spherical shell of radius $|\vec{n}|$ and thickness $\Delta|\vec{n}|$, so as long as we don't look closely enough to see that these points are discrete. The number of triplets of positive integers in the right range is

$$\text{number of triplets } = 4\pi\vec{n}^{\,2}d|\vec{n}| \times 1/8 = \frac{1}{2}\pi\vec{n}^{\,2}d|\vec{n}|,$$

where the factor of 1/8 came because only the octant of all positive values counts. From

$$|\vec{n}| = \sqrt{8m_e}\frac{L}{h}\sqrt{E}, \quad \vec{n}^{\,2} = \frac{8m_eL^2}{h^2}E, \quad d|\vec{n}| = \sqrt{8m_e}\frac{L}{h} \times \frac{1}{2}\frac{dE}{\sqrt{E}},$$

we have

$$\begin{aligned} \text{number of states} &= 2 \times \frac{1}{2}\pi \times \frac{8m_eL^2}{h^2}E \times \sqrt{8m_e}\frac{L}{h} \times \frac{1}{2}\frac{dE}{\sqrt{E}} \\ &= CL^3\sqrt{E}\,dE, \qquad \text{with } C = \frac{8\sqrt{2}\pi m_e^{3/2}}{h^3}. \end{aligned}$$

The function $g(E) = C\sqrt{E}$ is the **density of states**.

With this information, we now know the number of electrons we can expect to have in every energy range, $N(E)dE$, where $N(E) = f(E)g(E)$, the number of states times the probability for each to be occupied. The total number of electrons per unit volume is

Show S&B 43.22 $N(E) = f(E)g(E)$ 3 3/4" × 3"

$$n_e = \int_0^\infty N(E)\,dE \underset{T\to 0}{\longrightarrow} C\int_0^{E_F} E^{1/2}\,dE = \frac{2}{3}CE_F^{3/2},$$

so at zero temperature,

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

The model we have just described is best used to describe only the valence electrons, which are not tightly bound to their individual atoms. For gold, there is one valence electron per atom, and from the density of gold (19,300 kg/m^3) and the atomic mass, 197 u, we can verify there are 5.90×10^{28} free electrons/cubic meter, and E_F works out to 5.53 eV, which corresponds to k_BT for $T = 64,000$ K. So we see that only a very small fraction of the states are within k_BT of E_F for a metal at room temperature.

2.1 Reconciling the two models of electronic states

The free electron model clearly ignores some important effects, such as the regular arrangement of nuclear charges in which the electrons move, rather than being in a force-free box. If we think of the free electron model as describing all of the electrons, including the tightly bound ones in low energy atomic states, these interactions are clearly important and will surely cause significant deviations from the free electron model. These states are much better described by the energy band picture of section 4. A better model is to think of the free electron model as describing only the valence electrons, with the tightly bound electrons and the nuclei approximated by the constant potential of the box. But if we are only considering the $3s$ electrons in sodium, for example, then the free electron model can work as long as we don't run out of states. There are only $2N$ states available from the $3s$ electrons, while we have one valence electron from each atom, or N electrons, and our free electron model should be okay. If, however,

Show S&B 43.20 Energy Bands 2 3/4" × 4 1/2"

we are considering magnesium instead of sodium, we would have $2N$ electrons filling this band of $2N$ states, and the free electron model would be misleading, implying there were more available states when these are really of a different nature, $3p$ rather than $3s$.

3 Metals, Insulators, and Semiconductors

Current flows in a solid in response to an applied electric field when electrons can move from the states they were in when there was no field to other states. In the absence of a field, states moving left and states moving right are equally occupied, but if some electrons can hop from left moving to right moving states, they can support a net current. This requires there to be available unoccupied states which don't require too much extra energy.

There is a Fermi level even when the states occur in bands, as discussed in the last lecture. The conductivity of the solid depends crucially on whether that energy level is in the middle of an allowed band or within an energy gap. For a half-filled band, the Fermi energy is at a level where the density of states $g(E_F)$ is big, and so there are many occupied and unoccupied states close together in energy, and the transitions necessary for current to flow are easily made. Then we have a conductor. If, however, the Fermi energy lies within a forbidden band with an energy gap large compared to k_BT, there will be almost no occupied states which can be excited into unoccupied states, no current will flow, and we have an insulator.

S&B 43.23
E_F inside band
2 3/4" × 1 1/4"

S&B 43.24
E_F in big gap
3 1/8" × 3 3/4"

In semiconductors, the Fermi energy is in the forbidden region between two bands, but the gap is smaller than in an insulator. While the probability of any level in the valence band (below the gap) being empty, or any in the conduction band (above the gap) being occupied, is small, as there are a large number of states there are enough transitions to make for a small conductivity. Conduction can take place due to occupied states in the conduction band, because they can easily move to nearby empty states. It can also occur due to **holes** in the valence band — that is, empty states in the valence band can cause current flow because electrons in nearby occupied states can make a transition into the unoccupied hole. It leaves a new hole behind, so a succession of transitions can cause a current.

S&B 43.25
E_F in semiconductor
3 1/4" × 2 1/2"

In a pure semiconductor in which the Fermi energy lies between bands, each hole in the valence band must have contributed an electron to the conduction band, and both will conduct. These are called **intrinsic semiconductors**. But of great technological importance are **doped** semiconductors. An impurity in the semiconductor which has one more electron will create one state in the middle of the gap, and one extra the electron, but the electron is very likely to be in a valence band state rather than the one extra state, and can carry current. Semiconductors doped in this way are called n-type, because the extra carrier is the negatively charged electron.

42.27, S&B 43.27 donor level 7" × 4 1/4"

Another form of doped semiconductor contains in impurity with one fewer electrons than the bulk material. There is a single state within the gap due to his atom, without an electron to match, but it is very likely that an electron will fill this state and the unoccupied state will be one of those in the bulk valence band. Again this causes current. This kind of semiconductor is called **p-type** because the charge carrier is a positive hole relative to the sea of electrons. Doped devices are called **extrinsic semiconductors**, while conduction due to spontaneous electron-hole pairs is called intrinsic semiconductivity.

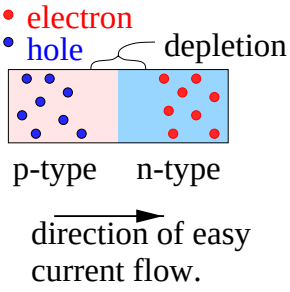
42.28, S&B 43.28 acceptor level 7" × 4 1/4"

4 Semiconductor Devices

Semiconductors play a crucial role in electronics technology. Most of the semiconducting devices available today are based on silicon (Si), but germanium (Ge) and gallium arsenide (GaAs) are also used. Semiconductor devices typically contain junctions between regions with opposite doping. For example, consider a piece of p-type joined to a piece of n-type semiconductor.

Display silicon boule

In the region of the interface the carriers will flow into the opposite region, leaving a region depleted of carries. If a voltage is applied which tries to push electrons from the n region and holes from the p region towards the depletion region, current can flow, from p to n. But if a voltage tries to cause current in the opposite direction, nothing causes carriers to be in the depletion region, and there is very little flow of current. Thus we have a diode, which permits flow of current in one direction but not in the other.



Transitions can be caused by photoabsorption or photoemission as well as by thermal excitations. If the energy gap between the conduction band and the valence band is the energy of a visible or infrared photon, we can produce light emitting diodes and photovoltaic cells, which convert electric current and power into light, and vice-versa.

Display solar energy windmill

A very large part of the technological advance of the last half century has been due to semiconducting devices. Transistors can be built from three regions of doped semiconductor, and they are able to amplify electrical signals as well as rectify them. These transistors fairly quickly took the place of the much larger, less durable, and far less efficient vacuum tubes which did the amplifying earlier. A huge advance came with the idea that transistors could be laid down photographically in large numbers on the surface of a semiconducting wafer, giving birth to the integrated circuit. We can now purchase for a few dollars a "chip" with hundreds of thousands of transistors laid out in a functional circuit.

Display integrated circuit wafer

5 Superconductivity

We discussed superconductivity slightly last term, and we will skip this section now.