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Lecture 13: Metals

1 Introduction

Fermions satisfy the Pauli-exclusion principle: no two fermions can occupy the same state. This makes fermionic systems act very differently from bosonic systems.

We introduced the non-interacting Fermi gas in Lecture 10, and will continue to discuss it here. We assume the fermions do not interact with each other. This means that the single-particle states of a system are not affected by which states are occupied. So we will fix the states, then fill them from the bottom up, then see what happens when we heat it up. You can think of the possible states as bunch of little shelves and we stack the fermions onto them one-by-one. The exclusion principle implies that once a state is occupied, it cannot be occupied again: the occupancy number of each state is either 0 or 1. This leads to the single-particle grand partition function of state i

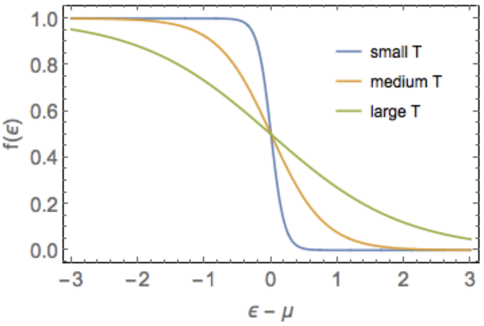
$$\mathcal{Z}_i = \sum_{n=0,1} e^{-\beta(\varepsilon_i - \mu)n} = 1 + e^{-\beta(\varepsilon_i - \mu)} \tag{1}$$

and grand free energy for state i:

$$\Phi_i = -\frac{1}{\beta}\ln \mathcal{Z}_i = -\frac{1}{\beta}\ln[1 + e^{-\beta(\varepsilon_i - \mu)}] \tag{2}$$

The occupation number for state i we then found to be given by

$$\langle n_i \rangle = -\frac{\partial \Phi_i}{\partial \mu} = \frac{1}{e^{\beta(\varepsilon_i - \mu)} + 1} \equiv f(\varepsilon_i) = \tag{3}$$



This is known as the **Fermi-Dirac distribution** or **Fermi function**, $f(\varepsilon)$. As $T \to 0$ the function approaches a step function where all the states below μ are occupied and the staes above μ are unoccupied. The value of μ at $T = 0$ is called the **Fermi energy** and denoted by ε_F. Sometimes the Fermi energy is also called the **Fermi level**.

At any temperature $T > 0$, some fermions will have energies higher than ε_F, and therefore some states with energy less than ε_F will not be occupied. We call the unoccupied states **holes**. You can picture a finite-temperature Fermi gas as having fermions constantly bouncing out of lower-energy states into higher energy states, leaving holes, then other fermions falling out of excited states into those holes. The electron/hole picture gives a useful way to think about finite temperature metals and gives a powerful way to understand the physics of semiconductors, as we will see in this and the next lecture.

We call the temperature corresponding to the Fermi energy the **Fermi temperature**:

$$T_F \equiv \frac{\varepsilon_F}{k_B} \tag{4}$$

This is like how the Debye temperature was related to the Debye energy by $T_D = \frac{\varepsilon_D}{k_B}$ in Lecture 11. Similarly, we can say roughly that for $T < T_F$ quantum effects are important. When the temperature of a system is well below the Fermi temperature, $T \ll T_F$, then $\mu \approx \varepsilon_F$ and the Fermi distribution looks very much like a step function $f(\varepsilon) \approx \theta(\varepsilon_F - \varepsilon)$. In such situations, the lowest states are almost all occupied and we say the system is **degenerate**. So, in a degenerate system, quantum effects are important. Electrons in metals have $T_F > 10000K$, so they are degenerate systems at room temperature and quantum statistical mechanics is necessary to understand their properties.

Generally, Fermi temperatures in metals are very high (for example, T_F for electrons in copper is around 80,000K, as we will see below). So high in fact, that it is generally impossible to heat a system above the Fermi temperature without changing the nature of the system (i.e. melting the metal). Thus, quantum statistics are *always* important for electrons in metals.

The typical picture of a highly degenerate fermionic system is having a relatively small set of energy levels that are relevant, namely those near ε_F. Energy levels with $\varepsilon \ll \varepsilon_F$ require a lot of energy, of order ε_F, to be excited into an empty state, since the first available state is above ε_F. This is nearly impossible when $T \ll T_F$. The set of low-energy states that do not participate in the thermal activity are called the **Fermi sea**. The Fermi sea can be very deep (a lot of states), but its depth is largely irrelevant to the thermal properties of the material. Similarly, the levels with energies much higher than ε_F are impossible to excite when $T \ll T_F$. So only those levels near ε_F matter. Thus degenerate gases have something very close to a symmetry between states above and below ε_F: a symmetry between electrons and holes. We'll use this picture to understand some properties of metals.

2 Free electron gas

The possible single-particle states of the electrons in a free electron gas are the same as for a boson in a box. The allowed wavenumbers are

$$\vec{k} = \frac{\pi}{L}\vec{n}, \quad \vec{n} = \text{triplet of whole numbers} \tag{5}$$

In the non-relativistic limit energies are determined by the usual relation in quantum mechanics

$$\varepsilon_n = \frac{\hbar^2 \vec{k}^2}{2m_e} = \frac{\pi^2 \hbar^2}{2m_e L^2} n^2 \tag{6}$$

with $n = |\vec{n}|$. So

$$n = \frac{L}{\pi}\sqrt{\frac{2m_e}{\hbar^2}}\sqrt{\varepsilon}, \quad dn = \frac{L}{2\pi}\sqrt{\frac{2m_e}{\hbar^2}}\frac{d\varepsilon}{\sqrt{\varepsilon}} \tag{7}$$

For electrons, there are two spins. So we compute the density of states via

$$2\sum_n \to 2 \times \frac{1}{8}\int 4\pi n^2 dn = \frac{V}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2}\int \sqrt{\varepsilon}\, d\varepsilon \tag{8}$$

As before, the $\frac{1}{8}$ accounting for the modes only counting the first octant (i.e. the $\vec{n}$ are whole numbers) while the integral over the sphere includes all 8 octants. We'll also study the relativistic and ultrarelativistic limits when we discuss white dwarf stars in Lecture 15, but in metals the electrons are generally non-relativistic, as we will check shortly. Thus $g(\varepsilon) = \frac{V}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2}\sqrt{\varepsilon}$. This scaling $g(\varepsilon) \sim \sqrt{\varepsilon}$ is the same as for the Bose gas from last lecture, only the constant in $g(\varepsilon)$ is different.

Recall that as $T \to 0$, the Fermi function becomes a step function: $\langle n_\varepsilon \rangle \to \begin{cases} 1, \varepsilon < \varepsilon_F \\ 0, \varepsilon > \varepsilon_F \end{cases}$. The Fermi energy ε_F is the chemical potential at $T = 0$ or equivalently the energy below which all the states are occupied at $T = 0$. So in particular, the number of of states at $T = 0$ is

$$N = \int_0^\infty \langle n_\varepsilon \rangle g(\varepsilon) d\varepsilon \xrightarrow{T=0} \frac{V}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2}\int_0^{\varepsilon_F}\sqrt{\varepsilon}\, d\varepsilon = \frac{V}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2}\frac{2}{3}\varepsilon_F^{3/2} \tag{9}$$

Therefore

$$\boxed{\varepsilon_F = \frac{\hbar^2}{2m_e}\left(3\pi^2\frac{N}{V}\right)^{2/3}} \tag{10}$$

Using this, it's convenient to write the density of states as

$$g(\varepsilon) = \frac{V}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2}\sqrt{\varepsilon} = \frac{3N}{2\varepsilon_F^{3/2}}\sqrt{\varepsilon} \tag{11}$$

The **Fermi temperature** is then

$$T_F = \frac{\varepsilon_F}{k_B} \tag{12}$$

This temperature is the characteristic temperature above which electrons can be readily excited into unoccupied states. Typically $T \ll T_F$ and so the probability of an electron getting excited into a unoccupied state (i.e. $\varepsilon \gtrsim \varepsilon_F$) is very small: $P \sim e^{-\frac{\varepsilon}{k_B T}} \approx e^{-\frac{T_F}{T}} \ll 1$.

The energy of the Fermi gas at zero temperature is

$$E_0 = E(T=0) = \frac{3N}{2\varepsilon_F^{3/2}}\int_0^{\varepsilon_F} \varepsilon\sqrt{\varepsilon}\, d\varepsilon = \frac{3}{5}N\varepsilon_F \tag{13}$$

So the average energy of each electron at zero termperature is $\langle\varepsilon\rangle = \frac{E_0}{N} = \frac{3}{5}\varepsilon_F$.

An important concept in electron gases, or Fermi gases in general, is that of **degeneracy pressure**. Pressure is defined as $P = -\frac{\partial E}{\partial V}$. Normally we associate pressure with the kinetic motion of molecules bombarding the walls of a container. This exerts a force on the walls, so that if the volume increases, the energy would go down. Because the force is due to thermal motion, this ordinary pressure is absent at $T = 0$. Degeneracy pressure, on the other hand, is a contribution to $-\frac{\partial E}{\partial V}$ in Fermi gases that persists even at $T = 0$.

The way to understand degeneracy pressure is by thinking about how the energy levels change as the volume is shrunk, for example under isothermal compression. For a classical gas, isothermal compression does not change the energy of the gas (i.e. $E = C_V k_B T$ is volume independent). What it does is increase the density of molecules, so the number of collisions on the wall of a container goes up, and hence the pressure increases ($P = \frac{N}{V}k_B T$). For a Bose gas, as the volume shrinks, all the energy levels go up, but the occupancies of different levels adjust so that the total energy is the same. Thus, Bose gases behave essentially like classical gases when compressed. For a degenerate Fermi gas, when the volume goes down, the occupancies of states cannot adjust. Instead, the energy levels go up and the total energy simply increases. This contribution to $-\frac{\partial E}{\partial V}$ is called degeneracy pressure.

To see that this pressure really is different from kinetic motion on container walls, consider the $T = 0$ limit. As we saw before, $T = 0$ is often a good approximation when $T \ll T_F$. Since we have been working at $T = 0$ already, all we have to do is differentiate Eq. (13):

$$P = -\frac{\partial E}{\partial V} = -\frac{\partial}{\partial V}\left[\frac{3}{5}N\varepsilon_F\right] = -\frac{3}{5}N\frac{\partial}{\partial V}\left[\frac{\hbar^2}{2m_e}\left(3\pi^2\frac{N}{V}\right)^{2/3}\right] = \frac{2}{3}\frac{E_0}{V} \tag{14}$$

In this limit, the classical pressure goes to zero but the degeneracy pressure persists. Degeneracy pressure is essential to understand white dwarfs and neutron stars, as we'll see in Lecture 15.

3 Sommerfeld free electron model for metals

Sommerfeld proposed that the electrons in a metal can be described by a free electron gas. The basic idea is that each atom in a metal has some number of loosely bound electrons that it contributes to the gas. The alkali metals (first column of periodic table, e.g. potassium) are **monovalent**, contributing one electron each. Some metals contribute more than one electron per atom (we'll see why in Lecture 15). The weakly bound electrons, called the **valence electrons**, are assumed to be free at leading order, so they just bounce around like particles in a box, with the size of the box determined by the size of the metal. This is called the **free electron model**, Before getting into the predictions of the free electron model, it's worth a few comments about why on earth this model should be at all reasonable. At first thought, it seems crazy that we could both ignore the attractive interactions of the electrons to the positively charged nuclei and ignore the repulsive Coulomb interactions among the electrons themselves. On second thought, however, we realize that because of the exclusion principle, electrons like to stay away from each other, so the electron-electron forces may indeed be small. As for the nuclei, we can't forget that metals have not only fairly high nuclear charge ($Z=29$ for copper), but also a whole lot of other electrons more tightly bound to the nucleus than the electron being contributed to the electron gas. Thus the valence electrons are forced to be far away from the nuclei (by the exclusion principle) and moreover, the other electrons screen the nuclear charge. With these considerations, the free electron model at least does not seem horribly wrong, and we can start to study it.[1]

First, let's compute the Fermi energy ε_F and fermi temperature $T_F=\frac{\varepsilon_F}{k_B}$ in the free electron model. Consider copper, which has a density $\rho=9.0\frac{g}{\mathrm{cm}^3}$ and an atomic weight of 63.6 $\frac{\mathrm{g}}{\mathrm{mol}}$, so the number density of atoms is $n=9.0\frac{g}{\mathrm{cm}^3}/63.6\frac{g}{\mathrm{mol}}=0.14\frac{\mathrm{mol}}{\mathrm{cm}^3}$. Treating copper as monovalent (Cu is [Ar]$3d^{10}4s^1$ as we explain next lecture), this is also the number density of valence electrons. So $n_e=0.14\frac{\mathrm{mol}}{\mathrm{cm}^3}=8.4\times10^{28}\frac{\mathrm{electrons}}{m^3}$. The Fermi energy is then

$$\varepsilon_F=\frac{\hbar^2}{2m_e}(3\pi^2 n)^{2/3}=7\,\mathrm{eV} \tag{15}$$

Note that this is much less than the electron rest mass $m_e c^2=511\mathrm{keV}$, so the non-relativistic limit is justified. The Fermi energy is also much higher than $k_B T=25\,\mathrm{meV}$ at room temperature. The corresponding Fermi temperature is

$$T_F=\frac{\varepsilon_F}{k_B}=82000\,K \tag{16}$$

Compared to room temperature $T_0=298K$. We see that $\frac{T_F}{T_0}\approx 270$. Since the Fermi temperature is much higher than room temperature, copper at room temperature is highly degenerate and quantum effects dominate.

Let's next look at the degeneracy pressure in a metal. From Eq. (14) we can write

$$P=\frac{2}{3}\frac{E_0}{V}=\frac{2}{5}\frac{N}{V}\varepsilon_F=\frac{2}{5}\frac{N}{V}k_B T_F \tag{17}$$

Now the Fermi temperature in metals is always well above room temperature, as in Eq. (16), $\frac{T_F}{T_0}\approx 270$. The density of metals is also typically much higher than in gases, by a factor of 1000 or so. Thus the degeneracy pressure is of order $1000\times 270\times 1\,\mathrm{atm}=10^5\,\mathrm{atm}$ – enormous! The electrons really *really* want to get out of the metal; in a larger volume, their energy levels would go down and the degeneracy pressure would be relieved. Fortunately, the electrons cannot leave since the outward force is compensated by strong attractive forces holding the metal together. Thus we are not going to be able to measure degeneracy pressure directly in a metal without understanding those (rather complicated) attractive foces.

Instead of pressure, a more reasonable quantity to look at is the bulk modulus, $B=-V\left(\frac{dP}{dV}\right)_T$. The bulk modulus measures how much a solid will compress when a pressure is applied. It tells how springy a material is. Indeed, as mentioned in Lecture 11, the bulk modulus determines the speed of sound in solids, as $c_s=\sqrt{\frac{dP}{d\rho}}=\sqrt{\frac{B}{\rho}}$ with ρ the density. Thus B plays the role of the spring constant k in Hooke's law. In solids, this constant should be determined by the restoring force when atoms are moved, which is due to the electrons. Thus we expect that B can be computable from a good model of electrons in solids.

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[1] A more formal justification of the free electron model is given by **Fermi liquid theory**. Basically, Fermi liquid theory uses renormalization-group methods to show that when interactions are included in the free electron model, the electron mass changes to an "effective mass" which is slightly different from m_e, but otherwise the interactions can be ignored.

For a free electron gas at $T=0$,

$$B=-V\frac{dP}{dV}=V\frac{d^2}{dV^2}\left[\frac{3}{5}N\frac{\hbar^2}{2m_e}\left(3\pi^2\frac{N}{V}\right)^{2/3}\right]=\frac{2}{3}\frac{N}{V}\varepsilon_F=\frac{10}{9}\frac{E_0}{V}=\frac{5}{3}P \tag{18}$$

Let's compute this for potassium. Solid potassium has an valence electron number density of $n=1.4\times10^{28}\frac{1}{m^3}$. This gives a Fermi energy of $\varepsilon_F=3.4\times10^{-19}J$ and a bulk modulus of $B=3.2\times10^9\frac{N}{m^2}$. The experimental value is $B=3.1\times10^9\frac{N}{m^2}$. Thus our prediction from the free electron gas is in excellent agreement with the measured value. Equivalently using the density of potassium is $\rho=856\frac{\text{kg}}{m^3}$ we predict a speed of sound $c_s=\sqrt{\frac{B}{\rho}}=1933\frac{m}{s}$; the measured value is $c_s=2000\frac{m}{s}$. Apparently, the elasticity of metals is determined by the degeneracy pressure of the electrons within it. This is rather a profound conclusion: when I squeeze a penny in my hand, the penny is fighting back not with the classical Coulomb force, but with the quantum Pauli exclusion principle.

Next, we want to compute the temperature dependence of the energy and heat capacity. To do that, we need to first eliminate the chemical potential. As with bosons, we can trade μ for N by integrating over the density of states. For fermions, using Eq. (11), we find

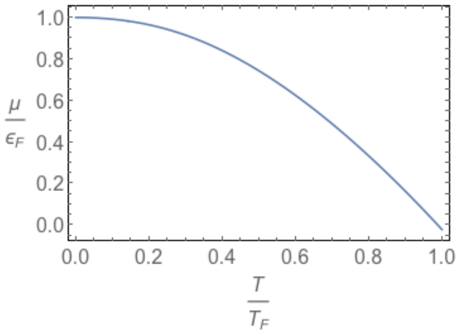
$$N=\int_0^\infty\frac{g(\varepsilon)}{e^{\beta(\varepsilon-\mu)}+1}d\varepsilon=\frac{3N}{2\varepsilon_F^{3/2}}\left(-\frac{\sqrt{\pi}}{2\beta^{3/2}}\right)\text{Li}_{3/2}(-e^{\beta\mu}) \tag{19}$$

where $\text{Li}_{3/2}$ is a polylogarithm function. Thus, we get an equation relating μ to ε_F at a given T:

$$-\frac{4}{3\sqrt{\pi}}(\beta\varepsilon_F)^{3/2}=\text{Li}_{3/2}(-e^{\beta\mu}) \tag{20}$$

Unfortunately, the polylogarithm of an exponential is really hard to work with. So let us start by examining it numerically. Solving this transcendental equation numerically we find a perfectly smooth function $\mu(\varepsilon_F,T)$:

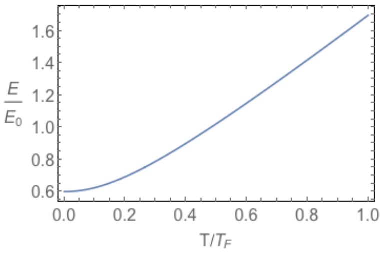
$$\mu(\varepsilon_F,T)= \tag{21}$$



Plugging in some numbers: at room temperature for copper $\frac{T}{T_F}=\frac{298}{82000}=0.0036$ and Eq. (20) gives $\mu=0.9999\varepsilon_F$. At the melting temperature of copper, $T_{\text{melt}}=1358K$, Eq. (20) gives $\mu=0.9996\varepsilon_F$. Thus in the entire range for which copper is a solid, $T=0$ to $T=T_{\text{melt}}$ μ only varies from $1.0\varepsilon_F$ to $0.9997\varepsilon_F$. This justifies the common practice of using the chemical potential and Fermi energy interchangeably when studying metals.

We can also compute the energy of the free electron gas:

$$E=\frac{3N}{2\varepsilon_F^{3/2}}\int_0^\infty\frac{\varepsilon\sqrt{\varepsilon}}{e^{\beta(\varepsilon-\mu)}+1}d\varepsilon=\frac{-15\sqrt{\pi}E_0}{8(\beta\varepsilon_F)^{5/2}}\text{Li}_{5/2}(-e^{\beta\mu})= \tag{22}$$



where $E_0 = \frac{3}{5} N\varepsilon_F$ as in Eq. (13). Thus the total energy, like the chemical potential, is a smooth function of T the nasty polylogarithm in the analytic formula.

Before doing a careful small T expansion, let's think a little about what we expect. The key to small T behavior of the energy is understanding how many states can be excited. Because N is so large, the energy levels near the Fermi surface are essentially continuous: there are generally *a lot* of electrons and a lot of states. Most of the electrons are in the Fermi sea, and it takes a lot of energy to excite an electron out of deep in the sea. Since $k_B T \ll T_F$ for any metal, only the highest energy electrons have any hope of being excited. All of the thermal activity comes from a small number of electrons close to the Fermi surface moving to states slightly above it. The electrons deep in the sea would require energies of order $\varepsilon_F \gg k_B T$ to move into a free state, for which there are exponentially small probabilities, $P \sim e^{-T/T_F}$. In other words, the states that are involved in the thermal activity are essentially only those with energies $\varepsilon_F - k_B T \lesssim \varepsilon \lesssim \varepsilon_F + k_B T$

At a temperature T some states will be excitable and gain energy $\sim k_B T$. So the total energy should be $E \approx E_0 + N_{\text{excitable}} k_B T$. This scaling is the essential content of the equipartition theorem. As a check on this logic, for a *bosonic* gas, we found the density of states to scale like $g(\varepsilon) \sim \varepsilon^2$ so the total number of excitable states are those with $\varepsilon < k_B T$ which is $N_{\text{excitable}} \sim \int_0^{k_B T} g(\varepsilon) d\varepsilon \sim T^3$. Thus $E \sim T^4$ for bosons, as we found through explicit calculation in the Debye model. For a fermionic gas, only those states with energies ε between $\varepsilon_F - k_B T$ and $\varepsilon_F + k_B T$ can be excited, so $N_{\text{excitable}} \sim k_B T$ and therefore $E \approx E_0 + k_B^2 T^2$. Plugging in E_0 from Eq. (13) we get

$$E = \frac{3}{5} N\varepsilon_F + a N \frac{k_B^2 T^2}{\varepsilon_F} + \cdots \tag{23}$$

for some a. The factor of ε_F in the denominator of the T^2 term was included by dimensional analysis – it is the only scale that could possibly appear. Eq. (23) is in qualitative agreement with Eq. (22). This heuristic argument is helpful to understand the quadratic dependence on T, however, it cannot give us the coefficient a. We now turn to computing this coefficient a.

3.1 Small T expansion

In this section, we will discuss how to expand the chemical potential and total energy at small T. These quantities are determined by Eqs. (19) and (22):

$$N = \int_0^\infty g(\varepsilon) f(\varepsilon) d\varepsilon, \qquad E = \int_0^\infty \varepsilon g(\varepsilon) f(\varepsilon) \tag{24}$$

with $g(\varepsilon) = \frac{3N}{2\varepsilon_F^{3/2}} \sqrt{\varepsilon}$ and $f(\varepsilon) = \frac{1}{e^{\beta(\varepsilon - \mu)} + 1}$ the Fermi distribution. Although we can do the integrals analytically, the resulting polylogaritms are not easy to expand around $T = 0$. Of course, you can just look up the polylogarithm limits, but we will learn more about the system by finessing the small T expansion using some tricks developed by Sommerfeld. We'll start with the chemical potential, then do the energy. Don't worry too much if you don't follow everything here, we'll do the calculation in a slicker way in Section 3.2. The reason I include this calculation is that it introduces some useful tricks which you can add to your toolbox to use in other contexts.

The first trick is to integrate by parts:

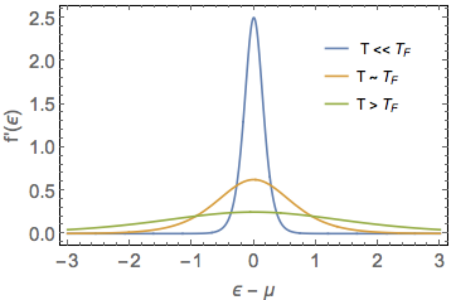
$$N = \frac{3N}{2\varepsilon_F^{3/2}} \int_0^\infty f(\varepsilon) \sqrt{\varepsilon} d\varepsilon = \underbrace{\frac{N}{\varepsilon_F^{3/2}} \varepsilon^{3/2} f(\varepsilon) \Bigg]_0^\infty}_{=0} - \frac{3N}{2\varepsilon_F^{3/2}} \int_0^\infty [f'(\varepsilon)] \left[\frac{2}{3} \varepsilon^{3/2}\right] d\varepsilon \tag{25}$$

The first term on the right vanishes at both boundaries, so it is zero. Then we have

$$1 = \frac{1}{\varepsilon_F^{3/2}} \int_0^\infty [-f'(\varepsilon)] \varepsilon^{3/2} d\varepsilon \tag{26}$$

The derivative of the Fermi distribution is a sharply peaked Guassian-like function centered on μ with width $\sqrt{k_BT}$:

$$-f'(\varepsilon)=\frac{\beta}{2}\frac{1}{1+\cosh(\beta(\varepsilon-\mu))}= \tag{27}$$



The second trick is to observe (as we can from the plot) that when $T\ll T_F$, the support of $f'(\varepsilon)$ is for energies $|\varepsilon-\mu|\lesssim k_BT$. In this region we can Taylor expand the function multiplying $f'(\varepsilon)$ in Eq. (26) around $\varepsilon=\mu$ giving

$$1=\frac{1}{\varepsilon_F^{3/2}}\int_0^\infty[-f'(\varepsilon)]\left[\mu^{3/2}+\frac{3}{2}\sqrt{\mu}(\varepsilon-\mu)+\frac{3}{8\sqrt{\mu}}(\varepsilon-\mu)^2+\cdots\right]d\varepsilon \tag{28}$$

The third trick is to note that since $f'(\varepsilon)$ is exponentially suppressed at small ε we can extend the lower limit of integration to $-\infty$. Once the integral is from $-\infty$ to ∞ the integral is much easier to do. Changing variables to $x=\beta(\varepsilon-\mu)$ makes the integrals doable by Mathematica

$$1=\left(\frac{\mu}{\varepsilon_F}\right)^{3/2}\int_{-\infty}^\infty\frac{dx}{2+2\cosh(x)}\left[1+\frac{3}{2\beta\mu}x+\frac{3}{8\beta^2\mu^2}x^2+\cdots\right]=\left(\frac{\mu}{\varepsilon_F}\right)^{3/2}\left[1+\frac{\pi^2}{8\beta^2\mu^2}+\cdots\right] \tag{29}$$

Now we can solve perturbatively for μ. Substituting $\mu=\varepsilon_F+aT^2+\cdots$ into Eq. (29) and expanding to order T^2 leads us directly to

$$\mu=\varepsilon_F\left[1-\frac{\pi^2}{12}\frac{k_B^2}{\varepsilon_F^2}T^2+\cdots\right] \tag{30}$$

As a check on this, plugging in $T=1358K$ (the melting point of copper), this gives $\mu=0.9997\varepsilon_F$ in excellent agreement with our exact numerical calculation.

We can do a similar expansion for the energy. The only difference is that instead of integrating the Fermi function against $g(\varepsilon)$ we integrate against $\varepsilon g(\varepsilon)$. After integrating by parts and dropping the boundary term, the equation for the total energy, Eq. (22) becomes

$$E=\frac{N}{\varepsilon_F^{3/2}}\int_0^\infty[-f'(\varepsilon)]\left[\frac{3}{5}\mu^{5/2}+\frac{3}{2}\mu^{3/2}(\varepsilon-\mu)+\frac{9}{8}\sqrt{\mu}(\varepsilon-\mu)^2+\cdots\right]d\varepsilon \tag{31}$$

$$=N\left(\frac{\mu}{\varepsilon_F}\right)^{3/2}\mu\int_{-\infty}^\infty\frac{dx}{2+2\cosh(x)}\left[\frac{3}{5}+\frac{3}{2\beta\mu}x+\frac{9}{8\beta^2\mu^2}x^2+\cdots\right] \tag{32}$$

$$=N\left(\frac{\mu}{\varepsilon_F}\right)^{3/2}\mu\left[\frac{3}{5}+\frac{3\pi^2}{8\beta^2\mu^2}+\cdots\right] \tag{33}$$

Substituting the form of μ in Eq. (30) we find that to second order in T

$$E=\frac{3}{5}N\varepsilon_F+N\frac{\pi^2k_B^2T^2}{4\varepsilon_F}+\cdots \tag{34}$$

Thus the unknown coefficient a in Eq. (23) is now known: $a=\frac{\pi^2}{4}$.

What did we learn from all these tricks? First of all, we got the answer $a = \frac{\pi^2}{4}$ without having to expand $\mathrm{Li}_{5/2}(e^{-\beta\mu})$. The second thing we learned was that the expansion was difficult mainly because of the $\varepsilon \geqslant 0$ constraint – we couldn't just integrate $\int_{-\infty}^{\infty} \varepsilon f(\varepsilon) d\varepsilon$ from the start since the integrand blows up at $\varepsilon \to \infty$, so we had to do this integration by parts trick to get the integral in a form where we could extend the limits of integration. The physical reason that the extension works is that the very low energy states and the very high energy states are irrelevant, as we anticipated. In fact, there's a more physical and less mathematical way to isolate these relavant states called the electron/hole picture that we will discuss next.

3.2 Electrons and holes

The electron and hole picture gives a quick way to understand the leading temperature dependence of the energy. Since $T \ll T_F$ for any metal, or equivalently, $k_B T \ll \varepsilon_F$, it is very hard to excite electrons deep in the Fermi sea. As mentioned by Eq. (23) only states within $k_B T$ of $\varepsilon_F \sim \mu$ can contribute to the energy shift $E - E_0$ and to the heat capacity. Thus overall, both excited states (above μ) and states below μ that do not have electrons in them (holes) are rare.

The idea of the electron/hole picture is to replace the original Fermi gas, with its inert Fermi sea, by a symmetric thermal system of electron excitations and the holes. Of course, in reality the electrons and holes are related, since each electron excitation comes from a hole. However, with a large N of electrons, we can treat the electrons and holes as their own statistical mechanical system and ignore the (very small) correlations among them.

To construct the gas, we first define the zero-point of energy in the new system to be at the fermi level. Now, each excited electron in the original system in a state with energy $\varepsilon > \mu$ contributes positive energy $\Delta = \varepsilon - \mu > 0$ to this new gas. Each hole, from a state of energy $\varepsilon < \mu$ in the orignal system, represents the *absence* of a state with negative energy $-\Delta = \varepsilon - \mu < 0$. Thus each hole contributes *positive* energy $\Delta = \mu - \varepsilon$ to the new gas. The positive energy can be understood if we think about an excitation of the original gas from energy $\mu - \Delta_h$ to $\mu + \Delta_e$. This excitation contributes a total of $\Delta_h + \Delta_e$ to the energy, with Δ_e coming from the electron and Δ_h from the hole.

Recall that the probabilities of occupation for each state are independent in a Fermi gas (this is the main reason we use the grand canonical ensemble at fixed μ rather than the canonical ensemble at fixed N). So the probability of finding an electron with excitation energy $\Delta_e = \varepsilon - \mu$ is

$$f_e(\Delta_e) = f(\varepsilon) = f(\mu + \Delta_e) \tag{35}$$

where $f(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)} + 1}$ is the Fermi function.

What is the probability of finding a hole of energy Δ_h? Since any state has either a hole or an electron, the probability of finding a state of energy ε to be empty is $1 - f(\varepsilon)$. Since $\varepsilon = \mu - \Delta_h$ for holes, the probability of finding a hole with energy Δ_h is then

$$f_h(\Delta_h) = 1 - f(\mu - \Delta_h) \tag{36}$$

Now a useful property of the Fermi distribution $f(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)} + 1}$ is that it is symmetric around its midpoint at $\varepsilon = \mu$. More precisely,

$$f(\mu + \Delta) = 1 - f(\mu - \Delta) \tag{37}$$

And therefore

$$\underbrace{f_h(\Delta)}_{\text{prob. of hole with energy } \Delta > 0} = 1 - f(\mu - \Delta) = f(\mu + \Delta) = \underbrace{f_e(\Delta)}_{\text{prob. of electron with energy } \Delta > 0} \tag{38}$$

Thus holes and electrons have identical probability distributions!

This gives us an easy way to calculate the total energy: we just calculate the energy of the electron excitations and double. The electron excitation contributions are like the original electron contributions but shifted to $\mu = 0$. In this region, the density of states is approximately constant

$$g(\mu + \Delta) \approx g(\mu - \Delta) \approx g(\varepsilon_F) = \frac{3N}{2\varepsilon_F} \tag{39}$$

So, the contribution to the total energy from the electron excitations about μ is

$$E_e = \int_\mu^\infty (\varepsilon - \mu) g(\varepsilon) f(\varepsilon) d\varepsilon \approx g(\varepsilon_F) \int_0^\infty \frac{\Delta}{e^{\beta\Delta}+1} d\Delta = \left(\frac{3N}{2\varepsilon_F}\right) \frac{\pi^2}{12\beta^2} = \frac{\pi^2 N}{8\varepsilon_F} k_B^2 T^2 \tag{40}$$

The hole contribution is identical

$$E_h = \int_0^\mu (\mu - \varepsilon) g(\varepsilon) f(\varepsilon) d\varepsilon \approx g(\varepsilon_F) \int_0^\infty \frac{\Delta}{e^{\beta\Delta}+1} d\Delta = \left(\frac{3N}{2\varepsilon_F}\right) \frac{\pi^2}{12\beta^2} = \frac{\pi^2 N}{8\varepsilon_F} k_B^2 T^2 \tag{41}$$

The only additional approximation we must do for holes is take the upper limit of integration on Δ to ∞, since $\varepsilon > 0$ means $\Delta_h < \mu$. Due to the exponential expression at large Δ, taking the upper limit to ∞ has essentially no effect on the integral.

Thus the total energy is

$$E = E_0 + E_e + E_h = E_0 + \frac{\pi^2 N}{4\varepsilon_F} k_B^2 T^2 \tag{42}$$

This is in perfect agreement with Eq. (34). (To get subleading terms in Eq. (34) you can include subleading terms in Eqs. (39)-(41).)

This calculation was certainly simpler than Sommerfeld's from Section 3.1 (although you may not have believed this one without that one as a check). The two are actually equivalent and make the same approximations. In this version, we sidestepped the fact that the energy of the holes is bounded by $\Delta < \varepsilon_F$ by setting the hole contribution equal to electron contribution, and integrating to ∞. In the Sommerfeld calculation, we integrated by parts and dropped the boundary terms to avoid the $\varepsilon_F < \infty$ limit. The electron/hole picture is nice not only because it is simpler but because it gives us a powerful language for discussion fermionic systems. This language is particularly useful for solid-state physics, as we'll see in the next lecture.

3.3 Heat capacity

Having computed the temperature dependence of the energy of a free electron gas, it is now trivial to find the heat capacity

$$C_V^{\text{electons}} = \frac{\partial E}{\partial T} = \frac{\pi^2}{2} N k_B \frac{T}{T_F} + \cdots \tag{43}$$

We computed this as the leading term in the $\frac{T}{T_F}$ expansion, but since $T_F \gtrsim 50000K$ for metals, this expansion can work for any temperature a metal can have – up to the melting point. In particular, it holds even if $T \gg 298K$.

We can compare this to the heat capacity due to phonons (oscillations of the atoms), for example through the law of Dulong and Petit: $C_V^{\text{phonons}} \approx 3Nk_B$. Recall that we derived this behavior in Lecture 11 as the high-temperature limit of the Debye model. Typical Debye temperatures for metals are around 100 K, so $T \gg T_D \sim 100K$ is reasonable at room temperature. Note that high temperature for phonons ($T \gg T_D$) is consistent with low temperature for electrons ($T \ll T_F$), and so we can use both limits to see

$$\frac{C_V^{\text{electrons}}}{C_V^{\text{phonons}}} = \frac{\pi^2}{6} \frac{T}{T_F} \ll 1 \tag{44}$$

This explains why the electrons do not contribute appreciably to the total heat capacity $C_V = C_V^{\text{phonons}} + C_V^{\text{electrons}} \approx C_V^{\text{phonons}}$. Historically, there was a puzzle for some time about why the law of Dulong and Petite should be correct, since the equipartition theorem says that electrons should contribute to the heat capacity just like the atoms. We now understand that because of Fermi-Dirac statistics the valence electrons have very high energy compared to room temperature, so only a small fraction of the electrons can be thermally excited (those near the Fermi level). Thus, at room temperature the electronic contribution is very small and this historical puzzle is thereby resolved by quantum statistics.

At very low temperatures $T \ll T_D$, the law of Dulong and Petite no longer applies. In the Debye model we found that for $T \ll T_D$

$$C_V^{\text{Debye}} = \frac{12\pi^4}{5} N k_B \left(\frac{T}{T_D}\right)^3 \tag{45}$$

where the formula for the Debye temperature is

$$T_D = \frac{\hbar\omega_D}{k_B} = \frac{\hbar}{k_B} c_s \left(6\pi^2 \frac{N}{V}\right)^{1/3} \tag{46}$$

with c_s the speed of sound. Thus the full heat capacity at low temperature is the sum of the electronic and phononic parts

$$C_V = C_V^{\text{electrons}} + C_V^{\text{phonons}} = \frac{\pi^2}{2} N k_B \frac{T}{T_F} + \frac{12\pi^4}{5} N k_B \left(\frac{T}{T_D}\right)^3 + \cdots \tag{47}$$

For copper $T_D = 315K$ and $T_F = 80,000K$. Thus we have to go to very low temperatures to see the electronic contribution. The two contributions are comparable when

$$\frac{T}{T_F} \sim \left(\frac{T}{T_D}\right)^3 \quad \Rightarrow \quad T \sim \sqrt{\frac{T_D^3}{T_F}} \tag{48}$$

For copper this is $T \sim 19K$.

We can see the electronic contribution by measuring the heat capacity at small T and plotting $\frac{C_V}{T}$ as a function of T^2:

$$\frac{C_V}{T} = \frac{\pi^2}{2} N k_B \frac{1}{T_F} + \frac{12\pi^4}{5} N k_B \frac{1}{T_D^3} (T^2) \tag{49}$$

The y-intercept of such a plot gives the electronic contribution and the slope gives the phonon contribution. Here is such a plot for copper:

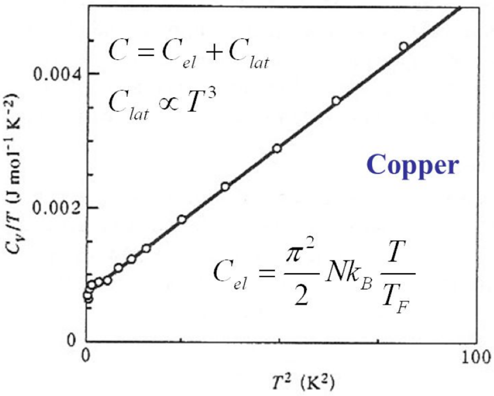


Figure 1. Heat capacity of copper at low temperatures compared to the prediction from the Sommerfeld free electron gas model.

Measurements like this demonstrate an electronic contribution in good agreement with the prediction from the Sommerfeld free electron model.

An obvious limitation of the free electron model is that it is the same model for any metal. Thus it cannot tell us what is a conductor, what is an insulator, or account for any of the interesting structure of the elements in the periodic table. To do that we need to make some improvements.

4 Nearly free electron gas

To improve on the free electron model, we can consider how electrons become free. If the atoms are far apart, then the electrons would have been in orbitals around their atom. There is thus some kind of attractive potential $V(r)$ trying to keep each electron bound to one atom. As atoms move closer together, their potentials start to overlap. In the limit that the potentials overlap a lot, the sum of the potentials can be very weakly position dependent:

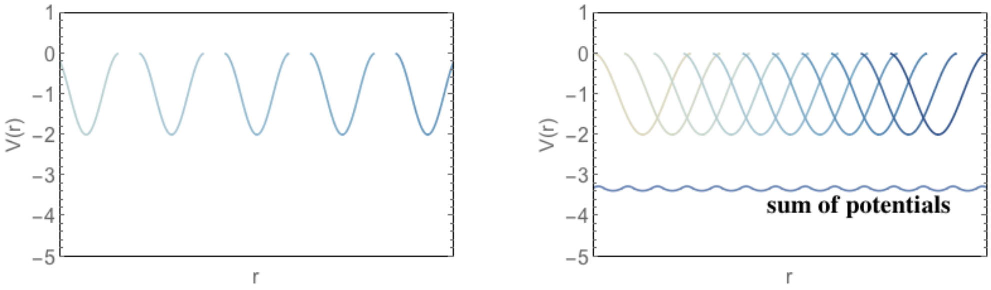
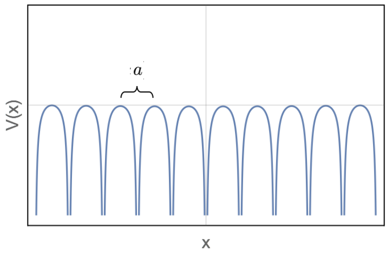


Figure 2. When atoms are far apart (left), the atomic potentials do not overlap. When atoms become close (right), potentials overlap with the net result of a nearly free potential: the sum of the potentials is nearly flat.

Most metals have a very regular lattice strcture. More precisely, these potentials are periodic, meaning that there exists a vector $\vec{a}$ such that $V(\vec{x}+\vec{a})=V(\vec{x})$. It is interesting therefore to consider a weak periodic potential as a model of the atomic system. This is known as the **nearly free electron model**. It is hard to calculate properties of periodic potentials in three dimensions exactly, but in one dimension we can actually find some exact solutions that are qualitatively similar to 3D systems and to real metals.

In one dimension, we are interested in finding the energies of a system with a periodic potential. By periodic potential, we mean that the full potential is the sum over potentials $V_1(x)$ representing atoms, shifted by the lattice spacing a. That is, the potential has the form

$$V(x)=\sum_{n=-\infty}^{\infty} V_1(x-na)= \tag{50}$$



Summing n from $-\infty$ to ∞ is an approximation, but allows us to find a nice simple form for the result.

Infinite periodic potentials have been studied in great detail and a lot of general results are known about them. A general result known as **Bloch's theorem** is that energy eigenstates can be written as

$$\psi_k(x)=e^{ika}u_k(x) \tag{51}$$

where a is the lattice spacing, k is the wavenumber and $u_k(x)$ is a function with the periodicity of the lattice, i.e. $u_k(x+a)=u_k(x)$ in this case. These solutions are known as **Bloch waves**. Bloch waves are like smooth plane waves e^{ikx} at scales $x\gtrsim a$ but have a bumpier structure, given by the Fourier transform of $u_k(x)$ at length scales less than a. Bloch's theorem holds in any number of dimensions.

Plugging Eq. (51) into the Schrodinger equation ($\frac{\hbar^2}{2m}\vec{\nabla}^2\psi+V(x)\psi=\varepsilon\psi$), you can show that for a given wavenumber k (the phase in Eq. (51)), the energies ε satisfy

$$\frac{\cos\left(\sqrt{\frac{2m_e\varepsilon}{\hbar^2}}\,a+\delta_k\right)}{|t_k|}=\cos\left(ka\right) \tag{52}$$

This is an implicit formula for the dispersion relation $\varepsilon(k)$ of the system. The quantities $|t_k|$ and δ_k are the magnitude and phase of the transmission coefficient $t_k=|t_k|e^{i\delta_k}$, which can also be calcualted from $V(x)$ (t_k is the transmission coefficient for scattering a wave with wavenumber k past $V_1(x)$). The appearance of t can be understood because the waves at a given k have to scatter past each individual potential in a regular way to become energy-eigenstate standing waves. We're not going to derive Eq. (52), but the derivation can be found in many solid-state physics books (e.g. Hook and Hall Chapter 4 or Ashcroft and Mermin Chapter 8).

To be concrete, consider a special case where the potentials are square wells. This case is known as the **Kronig-Penney** model and an exact solution is known. The solution is particularly simple in the limit where the width of the wells goes to zero and the strength of the wells to infinity so that each potential is a δ-function, i.e. $V_1(x) = \lambda\delta(x)$. In this case, the magnitude and phase of the transmission coefficient are given by

$$|t_k| = \cos\delta_k = \frac{1}{\sqrt{1 + \frac{m_e^2\lambda^2}{\hbar^4 k^2}}} \tag{53}$$

You can find the derivation of the Kronig-Penney model in many places, including Wikipedia. We're not going to derive it here.

Let's look at the the energies of the Kronig-Penney model as a function of k. We do this by finding solutions to Eq. (52) using the expressions in Eq. (53) for $|t_k|$ and δ_k. As usual, we begin by finding the solutions numerically. The result looks like this:

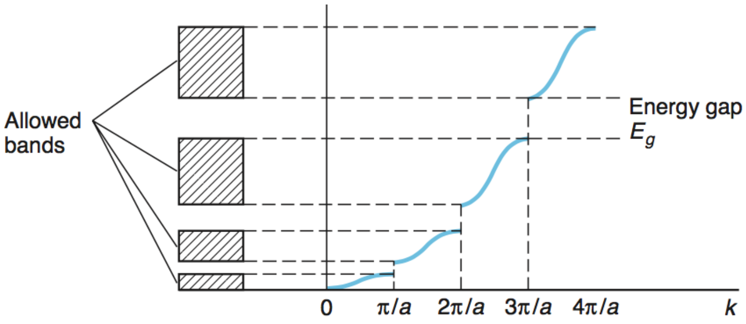


Figure 3. Allowed and forbidden region in the Kronig-Penney model. Only have the bands, for $k > 0$ are shown. There are mirror image bands for $k < 0$.

In this figure, you can see that the energies break up into a series of **bands**. The energy difference between the top of one band and bottom of the next is known as the **bandwidth**. As k is increased, there are certain energies that never appear. These are energies in the **band gap**. The Kronig-Penney model is the simplest exactly solvable model where the band structure appears. Bands are critical to understanding properties of metals and semiconductors.

We can see fairly easily from the general result in Eq. (52) why there are bands, i.e. why there are not solutions for every ε. Because t is a trasmission coefficient, $|t| < 1$ and thus the cosine on the left is bigger than the one on the right. So when the left cosine is bigger than $|t|$ then there can be no solution. This happens around the regions where $k = \frac{\pi}{a}, \frac{2\pi}{a}, \frac{3\pi}{a}, \cdots$ The band gaps are centered around these regions. The wavenumbers $k = \frac{\pi}{a}$ correspond to periodic eigenfunctions. If $\lambda = 0$ (no potential), these are just the normal particle-in-a-box modes. If $\lambda < 0$ the energy of these modes is lowered. If $\lambda > 0$ the energy is raised. Either way, there is no longer an energy corresponding to these modes with period of the lattice, hence the band gap.

As the potential is removed, $V \to 0$, we should recover the free-particle solutions. You can actually see this from the figure: as the gaps are removed, the bands merge into a parabola. The parabola is none other than the dispersion relation for the free electron gas, Eq (6): $\varepsilon = \frac{\hbar^2 k^2}{2m_e}$. To see this analytically, note that with the potential removed, the transmission coefficient is $t = 1$. From Eq. (52) we can see that when $|t| = 1$ and $\delta = 0$ then $\sqrt{\frac{2m_e E}{\hbar^2}} = k$, agreeing with the dispersion relation for the free electron gas.

Although this model was only one-dimensional, periodic potentials predict bands also in three dimensions, and bands are observed experimentally in metals. What is critically important in determining properties of the solid is whether the Fermi level is in the middle of a band or in the band gap. For example, suppose each potential corresponds to one atom and each atom donates one electron to the nearly-free electron gas. In this case, there are N electrons and the maximum k allowed (in 1D) is $k = N\frac{\pi}{L}$ with L the size of the system. Using $L = Na$ we see $k \leqslant \frac{\pi}{a}$, which, matching onto Figure 3 would be the highest occupied electron level right at the edge of the band. Remember though that electrons have two spin states, so each level is actually two-fold degenerate. This means that if each atom donates one electron, the lowest band will actually be only half filled. With a half-filled band the electrons can easily be excited, gaining energy and momentum. If you put an electric field on such a system, the electrons can adjust, picking up momentum in one direction:

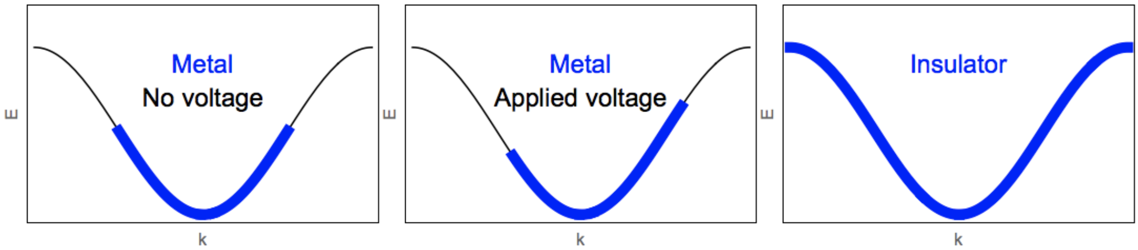


Figure 4. The thin curve in these plots shows the band: how the energy levels E depend on wavenumber k. The thick curve are the levels that are occupied. For metals in which atoms donate one electron each half the band is filled. With a half-filled band, an applied electric field can easily make the energy levels adjust, showing that such materials are conductors. Insulators have a completely filled band and cannot easily adjust to an applied field.

Thus mono-valent (one electron donated per atom) materials (most metals) are **conductors**. That metals conduct is closely related to their shininess: the conduction electrons move freely, so they easily absorb and re-emit radiation.

If each atom donates two electrons into the band, the band would be completely filled. In that case, a tiny amount of energy cannot excite the electron and the material does not conduct electricity well. Such materials are known as insulators or more precisely **band insulators**.

In three dimensions, the relationship $\varepsilon(\vec{k}) = \varepsilon_F$ defines a surface instead of two points. This surface is called the **Fermi surface**. The Fermi surface is an abstract surface in momentum space, not the real surface of a metal in position space. It describes the boundary between occupied and unoccupied energy levels at $T = 0$. For the free-electron gas where $\varepsilon = \frac{\hbar^2\vec{k}^2}{2m_e}$ this is the surface of constant $|\vec{k}|$ namely a sphere. In metals such as sodium which have very weakly bound valence electrons, so the free-electron gas model is an excellent approximation, the Fermi surface is indeed spherical. For other metals, the Fermi surface can have a different shape. Here are the Fermi surfaces for sodium, copper and graphene

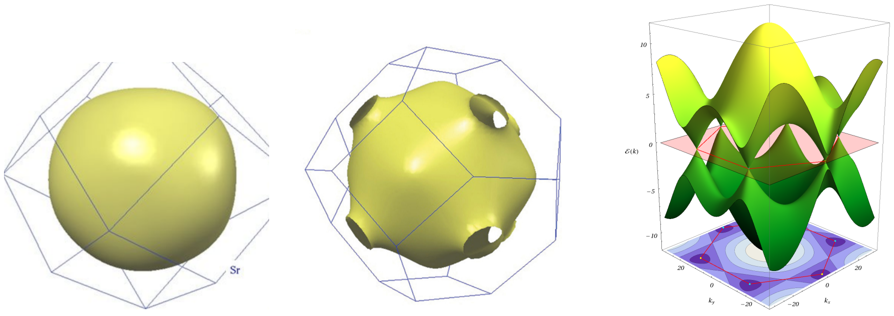


Figure 5. Fermi surfaces for sodium (left), copper (middle) and graphene (right).

In copper the things that look like holes in the Fermi surface are not really holes but rather the regions where $\frac{d\varepsilon}{dk}$ blows up. This is the 3D analog of a the 1D bandgap region in the Kronig-Penney model: when you go from one band to the next, ε jumps as k changes by a little bit, so $\frac{d\varepsilon}{dk}$ is large.

Graphene is a 2D sheet of carbon. So the values of $\vec{k}$ with $\varepsilon(\vec{k}) = \varepsilon_F$ are not a set of points, as in 1D, or a surface, as in 3D, but a curve. The curve is given by an intersection of a plane (the energy plane) with the surface. In the figure, the Fermi energy is indicated by the red plane. We see that as $\varepsilon \to \varepsilon_F$ the allowed k go to points along the surface of a cone. These cones are called **Dirac cones**. In an ultrarelativistic electron gas, the dispersion relation is $\varepsilon(\vec{k}) = c|\vec{k}|$. Because of the absolute value, the ultrarelativistic dispersion relation has the same cuspy behavior and Dirac cone structure we can see in the graphene Fermi surface. Thus electrons in graphene near the cusp act like ultrarelativistic particles, even though their energies can be $\varepsilon \lesssim \varepsilon_F \ll m_e c^2$. These effectively massless Fermion excitations give graphene some of its most interesting properties: it is the world's most conductive material. Normal metals have to move massive electrons around, but graphene can move around effectively massless ones. Graphene is also 200 times stronger than steel. By the way, graphene was discovered in 2004 by Geim and Novoselov by peeling scotch tape off a block of graphite (you make graphene every time you write with a pencil). Geim and Novoselov won the Nobel Prize for their discovery in 2010.

5 Summary

In this lecture we studied the statistical mechanics of fermions. A key concept in thermal Fermi systems is the Fermi level, defined as the energy below with all the states would be occupied and above which none of the states are occupied, at zero temperature. It is equal to the chemical potential at zero temperature.

The basic tool we use for studying fermionic systems is the free electron gas. This is a gas of non-interacting fermions quantized as non-relativistic particles-in-a-box. The density of states is $g(\varepsilon) = \frac{V}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2}\sqrt{\varepsilon}$. The free-electron gas predicts the bulk modulus andspeed of sound of metals in agreement with data. It also predicts the heat capacity of metals, and in particular that this heat capacity is linear in T at low temperature. This is in contrast to the heat capacity of phonons which scales like T^3 at low temperature (see Lecture 11). We computed the low-temperature limit of the heat capacity two ways. First, we applied a set of subtle mathematical tricks developed by Sommerfeld to expand for $T \ll T_F$. Second, we treated the free electron gas as a gas of electrons and holes (absence of electrons) with a symmetric spectrum around the Fermi level. This second method is much faster and motivates the broad use of holes as a theoretical tool. We'll come back to holes in Lecture 14.

A step beyond the free electron gas is the nearly free electron gas. Our treatment of the nearly-free gas was somewhat heuristic; the required calculations are not hard, and covered in any solid-state physics book, but they are beyond what we can do in one lecture. The important qualitative results we found were that

- The addition of periodic potentials generates bands, that is groups of energy levels separated by gaps.
- The band structure can explain insulators, when the Fermi level is in the middle of a band, and conductors, when the Fermi level is in a gap between bands.

Unfortunately, it is very difficult to connect the nearly free electron gas to actual metals. That is, we cannot determine which materials will conduct and which will insulate. To understand real materials, a more flexible method is the **tight-binding model** (Lecture 14), where the bands emerge from energy levels of atomic orbitals ($4s, 3d$, etc).