Solid state physics : electrons and phonons

Master Nanosciences (M1) UGA

Lecture notes 2020 by Xavier Blase

1 Chapter 1 : classical electrons and Drude model

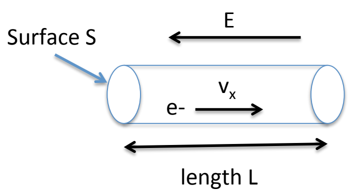
In this first introductory Chapter, we briefly go through Drude theory for the conduction of electricity in metals. This theory was performed in 1900, namely before the ”invention” of quantum mechanics, so that Drude attempted to treat electrons as classical particles. His theory proved to be eventually wrong, since electrons must be treated quantum mechanically, but many concepts and ideas are still being used today. It is further interesting to see how quantum mechanics differs from classical mechanics.

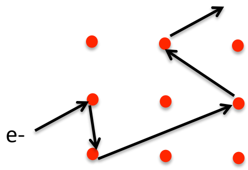
Bibliography. Ashcroft and Mermin, Solid State Physics, Chapter 1 (The Drude Theory of Metals), paragraphs ”Basic Assumptions, Collision and relaxation rates, DC electrical conductivity.”

1.1 Conductivity and the relaxation or scattering time

Assume a piece of material of length L and section S submitted to an external uniform electric field along $\hat{x}$ direction :

The current density j_x along $\hat{x}$, namely the charge crossing a unit surface per unit time, reads: $j_x = n(-e)v_x$ where n is the electronic density (the number of electrons per unit volume) and v_x the average electron velocity along the $\hat{x}$ direction.





Drude model of
electrons bumping
on ions

Drude model (year 1900): the electrons "bumps" into the ions; after each collision, electrons are scattered in every direction randomly so that the net average velocity in the absence of electric field is zero. There cannot be any net current in the absence of electric field.

When $E \neq 0$, the electrons accelerate between 2 collisions in the direction of the field. This is the drift velocity v_d which is not random and can contribute to a net current. Drude used the classical equation of motion for electrons (Newton's law : mass x acceleration = force) since quantum mechanics was not yet invented in 1900, yielding :

$$v_d(t) = v_d(0) - eEt/m_e \quad \text{with } m_e \text{ the mass of the electron}$$

with $(-eE)$ the force acting from the field on the electrons (dropping the $\hat{x}$ direction index). We can now take $v_d(t = 0) = 0$ on average taking the zero of time just after a collision where velocity are randomized. We call τ the scattering time that is the average time between 2 collisions. Then the average drift velocity is:

$$\langle v_d \rangle = -eE\tau/m_e \implies j = n(-e)\langle v_d \rangle = n(-e)(-e)E\tau/m_e$$

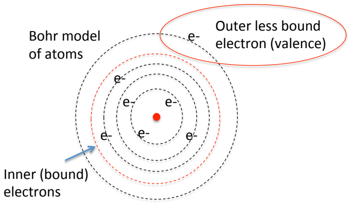
that is : $j = \sigma E$ with $\sigma = ne^2\tau/m_e$ the conductivity (Siemens/meter). The resistivity is $\rho = 1/\sigma$ (Ohm·meter). The (macroscopic) resistance is $R = \rho L/S$ in Ohm.

1.2 Electronic densities of conduction electrons

To calculate the conductivity, we first need the electronic density, more precisely the density of conducting electrons. It is rather easy to get an estimate of the atomic density, namely the number of atoms per unit volume. We can roughly estimate for example the number of atoms per unit volume in a solid where atoms are separated by a bond length of 2 $\mathring{A}$:

$$n_{atoms} = \frac{1}{(2 \times 10^{-10})^3} m^{-3} \quad \text{that is} \qquad n_{atoms} \simeq 10^{29} m^{-3} \simeq 10^{23} cm^{-3}$$

YES, but how many conduction electrons per atom ?? We must make the distinction between core and outer (or conduction or valence) electrons !! We very quatitatively adopt Bohr's model of atoms with shells of electrons



Cupper [Cu] = [Ar] $3d^{10}4s^1$ Only the $4s^1$ electron is itinerant (weakly bound).
Iron [Fe] = [Ar] $3d^7 4s^2$ The two $4s^2$ electrons are itinerant (weakly bound)

Conduction electrons density : • $n_{Cu} = 8.47 \times 10^{22} cm^{-3}$ and • $n_{Fe} = 17 \times 10^{22} cm^{-3}$

orbiting around their nucleus. Electrons in "inner shells" close to the nucleus are strongly bound and cannot travel away from the nucleus, while electrons in 'outer" shells are less bound and can be taken away by an electric field : only these outer electrons can participate to the current. They are called itinerant, conduction or valence electrons. Considering the shell structures of two metals, Copper (Cu) and Iron (Fe), one can see that Fe has twice as many conduction electrons as Cu. This is an information that can only rely on the knowledge of the electronic properties of the atoms in the periodic Table and the structuration in shells.

1.3 Typical resistivities and scattering times

Experimental measurements allow to access the resistivity of metals. At 273 K (see Tables distributed in class) one finds:

- $\rho_{Cu} = 1.56 \times 10^{-6}\ \Omega.cm = 1.56 \times 10^{-8} \Omega.m$
- $\rho_{Fe} = 8.9 \times 10^{-6}\ \Omega.cm = 8.9 \times 10^{-8} \Omega.m$

Taking now the relation $\sigma = 1/\rho = ne^2\tau/m_e$, one gets $\tau = m_e/ne^2\rho$ that is with the above values for the conduction electron density (n) and experimental resistivity ρ (and $e = 1.6 \times 10^{-19}$ C and $m_e = 9.11 \times 10^{-31}$ kg), one obtains:

- $\tau_{Cu} = 2.7 \times 10^{-14}$ seconds
- $\tau_{Fe} = 0.2 \times 10^{-14}$ seconds

Electrons are experiencing a collision every 10^{-14} seconds (roughly 10 femtoseconds).

1.4 Drude thermal velocity and the mean-free path

A important quantity is also the mean-free path l_{MFP} that is the average distance traveled between 2 collisions. Since we have the scattering time τ, the average time traveled between 2 collisions, we need a velocity. It is important to realize at that stage that the drift velocity induced by the electric field is actually small as compared to the random velocity acquired after a collision.[1] To get the magnitude of the velocity acquired on the average after a collision,

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[1] The drift velocity is small but not random in terms of direction !

Drude made an another classical approximation stemming from Boltzmann classical statistics known since the XIXth century, using the equipartition theorem of energy and the additional assumption that due to collisions, electrons thermalize with the ions. Since ions are at ambiant temperature, Drude considered that electrons travel between 2 collisions with the thermal velocity v_T (plus the small but ordered drift velocity). Equipartition theorem (Boltzmann), with an average energy $k_B T/2$ per classical degree of freedom (Boltzmann constant $k_B = 1.38 \times 10^{-23} m^2.kg.s^{-2}.K^{-1}$) gives :

$$\frac{1}{2} m_e v_T^2 \simeq \frac{3}{2} k_B T \quad \text{namely} \quad v_T = 1.11 \times 10^5 \quad \text{m/s (273 K)} .$$

We can then get Drude mean-free path $l_{MFP}^{Drude} = v_T \times \tau$, that is :

- (Cu at 273 K) $\quad l_{MFP}^{Drude} = (1.11 \times 10^5) \times (2.7 \times 10^{-14}) = 3 \times 10^{-9}$ m.
- (Fe at 273 K) $\quad l_{MFP}^{Drude} = (1.11 \times 10^5) \times (0.2 \times 10^{-14}) = 0.2 \times 10^{-9}$ m.

In Drude classical model of electrons, the mean-free path l_{MFP}^{Drude} is of the order of one to a few interatomic distances ! Drude was very happy since this result self-validated his model of electrons bumping on ions !!!

These results are however wrong. Modern quantum mechanical treatments and experiments show that actually the mean-free path is several order of magnitude larger, with for example:

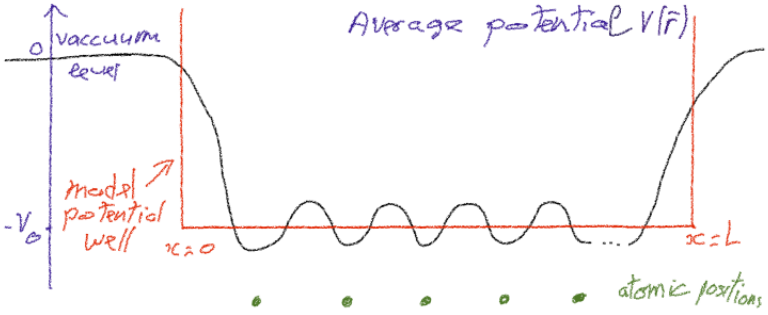
$$(Cu) \quad l_{MFP} \simeq 300 \mathring{A} \quad \text{at 300 K and} \quad l_{MFP} \simeq 3300 \mathring{A} \quad \text{at 77 K (liquid nitrogen)}$$

As a matter of fact, the actual velocity of electrons has nothing to do with the thermal velocity : the velocity of conduction electrons is purely quantum and is related in particular to Pauli exclusion principle. At room temperature, the true quantum velocity (or Fermi velocity) is one order of magnitude larger than the thermal velocity. We will see that in the next lecture. Further, as can be seen by looking at the mean-free path at 77 K, the scattering of electrons is not related to "bumping on ions" (one cannot imagine that ions get a hundred times farther way at low temperature !) As a matter of fact, electrons bumps on "phonons", namely collective vibrational modes of atoms that become less and less numerous at low temperature. We will study phonons at the end of this class.

2 Chapter 2 : Free but quantum electrons in a box

Bibliography. Ashcroft and Mermin, Solid State Physics, Chapter 2 (Sommerfeld theory of metals), paragraph "Ground-state properties of the electron gas"; Kittel, Introduction to Solid State Physics, Chapter 6 (Free electron Fermi gas), paragraphs Energy levels in one dimension, Free electron gas in three dimensions, Heat capacity of the electron gas (introductory qualitative demonstration). Warning: in these books, boundary conditions are treated using "periodic boundary conditions," not the simplest fixed boundary conditions used in class (see note below).

We now tackle the problem of the quantum treatment of electrons in solids using a simple but informative models of electrons confined in a box of the size of the solid (let's say a cube of length L where L is macroscopic). Experiments and accurate quantum calculations show that electrons in a solid are submitted to a periodic potential $V(\mathbf{r})$. This is the black potential in the picture below that represents a one-dimensional (1D) solid with atoms in green periodically repeated over a length L. $V(\mathbf{r})$ represents the action of the (attractive) ions and (repulsive) electrons, shows minima at the position of the ions and goes to zero (the vacuum potential level) outside the crystal. Overall, the potential in the crystal is attractive for electrons (the electrons do not flow out spontaneously outside the crystal !)



In the free electrons in a box model, one replaces the actual potential $V(\mathbf{r})$ by a potential well (in red in the figure above) that is constant in the solid, with an average $-V_0$ value, and infinite outside the box. An infinite value of the potential outside the box means that the electrons just cannot go outside the box. In what follows, we define the box (the solid) as a 3-dimensional (3D) cube such that $(0 < x, y, z < L)$. We put N electrons in the box (density $n = N/V$ with $V = L^3$). These electrons are said "free" since they do not interact with each other neither with the ions. As a matter of fact, all these interactions are inside the potential $V(\mathbf{r})$ that has been replaced by a constant potential $-V_0$.

2.1 Schrödinger equation, eigenstates and electronic energy levels

As a brief reminder of quantum mechanics, we recall that electrons are described by wavefunctions $\phi_n(\mathbf{r})$ such that $|\phi_n(\mathbf{r})|^2$ gives the probability that an electron “in the n-th quantum state” associated with ϕ_n can be found in $\mathbf{r}$. The integer (n) indexes formally all possible wavefunctions that can describe an electron in our system of interest. These wavefunctions $\phi_n(\mathbf{r})$ are solutions of the (static) Schrödinger equation, or eigenvalue equation, namely

$$\hat{H}\phi_n(\mathbf{r}) = \varepsilon_n\phi_n(\mathbf{r}) \quad \text{that is} \quad \Big(-\frac{\hbar^2\nabla^2}{2m_e} + V(\mathbf{r})\Big)\phi_n(\mathbf{r}) = \varepsilon_n\phi_n(\mathbf{r})$$

where $\hat{H}$ is the Hamiltonian operator, ε_n the energy of an electron in state (n), $\hbar^2\nabla^2/2m_e$ the kinetic energy operator (m_e mass of the electron), and $V(\mathbf{r})$ the potential. ∇ is the gradient operator with $\nabla^2 = d^2/dx^2 + d^2/dy^2 + d^2/dz^2$ in 3 dimensions (3D). The wavefunctions $\phi_n(\mathbf{r})$ solutions of the Schrödinger, or eigenvalue equations, are called the **eigenstates** of the system. An electron in a system of interest can only be described by eigenstates of the Hamiltonian of the system. If the spatial distribution of an electron corresponds to some eigenstates ϕ_n, its energy is then the corresponding energy ε_n (called sometimes eigenvalue). The electron is said to be in the n-th quantum state, namely the quantum state associated with the wavefunction $\phi_n(\mathbf{r})$ and energy ε_n.

In the box, we have $V(\mathbf{r}) = -V_0$ for $0 < x, y, z < L$, while $V(\mathbf{r}) = +\infty$ on the walls and outside the box. This means that the eigenstates $\phi_n(\mathbf{r})$ are strictly zero on the walls and outside the box: there is zero probability to find an electron outside the box. One can easily show that wavefunctions of the form:

$$\phi_n(\mathbf{r}) = A\sin(k_x x)\sin(k_y y)\sin(k_z z) \qquad \text{with } \mathbf{r} = (x, y, z)$$

are proper solutions of the eigenvalue equation, namely eigenstates of the Hamiltonian, and satisfy further the proper ”boundary conditions”, namely that $\phi_n(\mathbf{r})$ is zero for x or y or z equal to zero as required. A is a normalization constant such that the integral of $|\phi_n(\mathbf{r})|^2$ inside the box is equal to unity. The constants (k_x, k_y, k_z) form a **wavevector** $\vec{k}$. Using the relation e.g. $d^2\sin(k_x x)/dx^2 = -k_x^2\sin(k_x x)$, one have indeed straightforwardly:

$$\Big(-\frac{\hbar^2\nabla^2}{2m_e} - V_0\Big)\phi_n(\mathbf{r}) = \Big(\frac{\hbar^2(k_x^2 + k_y^2 + k_z^2)}{2m_e} - V_0\Big)\phi_n(\mathbf{r}) = \varepsilon_n\phi_n(\mathbf{r})$$

that is an energy :

$$\varepsilon_n = \frac{\hbar^2 k^2}{2m_e} - V_0 \quad \text{with} \quad \frac{\hbar^2 k^2}{2m_e} \quad \text{the kinetic energy.}$$

In the following we replace the index (n) by the wavevector $\vec{k}$ since the eigenstates and energies depend on $\vec{k}$, namely $\varepsilon_n \to \varepsilon_{\vec{k}}$ or $\varepsilon(\vec{k})$.

Exercise: show that A = $(8/L^3)^{1/2}$.

Periodic boundary conditions. In a few books, eigensolutions are taken to be propagating planewaves $\phi_{\vec{k}}(\mathbf{r}) = Ae^{i\vec{k}\cdot\vec{r}}$ with ”periodic boundary conditions”, namely e.g. $\phi_{\vec{k}}(x+L,y,z) = \phi_{\vec{k}}(x,y,z)$, rather than imposing strictly that the wavefunction cancel on the walls of the box, e.g. $\phi_{\vec{k}}(L,y,z) = 0$. We will use periodic boundary conditions for phonons in a few lectures but for the present purpose, it is just more complicated for the same results.

2.2 Boundary conditions and quantization of $\vec{k}$

This is a crucial step : let's now cancel the eigenstates $\phi_{\vec{k}}(\mathbf{r})$ on the remaining walls, namely (x=L) or (y=L) or (z=L). For the wavefunction to cancel on (x=L) for every (y,z), one need that :

$$\sin(k_x L) = 0 \quad \text{that is} \quad k_x L = n\pi \quad \text{with n an integer, that is} \quad k_x = n\pi/L$$

Note that (n) cannot be zero since the wavefunction would be zero everywhere. We further only keep n positive since $|\sin(n\pi x/L)|^2$ does not depend on the sign of n so that states associated with $\pm n$ represent the same electronic distribution, namely the same electronic state. Similarly, $k_y = m\pi/L$ and $k_z = l\pi/L$ with (m,l) non-zero positive integers. In short $\boxed{\vec{k} = (n,m,l)\pi/L}$ with (n,m,l) positive integers. Boundary conditions have imposed a quantization, or discretization, of the possible wavevectors $\vec{k}$ associated with free electrons in a box. As a result the electrons in the box have quantized energies :

$$\varepsilon(\vec{k}) \text{ or } \varepsilon(n,m,l) = \frac{\hbar^2 k^2}{2m_e} - V_0 = \frac{\hbar^2\pi^2}{2m_e L^2}(n^2+m^2+l^2) - V_0$$

with minimum kinetic energy $K_0 = 3\hbar^2\pi^2/2m_e L^2$ for (n=m=l=1) and minimum energy $\varepsilon(n=m=l=1) = K_0 - V_0$. By increasing (n,m,l) one obtains all the possible increasing values of energy $\varepsilon(\vec{k})$ that an electron can have in the box. We represent all these possible energies by increasing values under the form of little horizontal bars that are called "energy levels" (see figure below). For example, the next level just above the minimum energy level is obtained for (n=2, m=l=1) or (m=2, n=l=1) or (l=2, n=m=1). It is said that this level is "3-fold degenerate" since 3 different quantum states (with different wavevectors) can have the same energy.

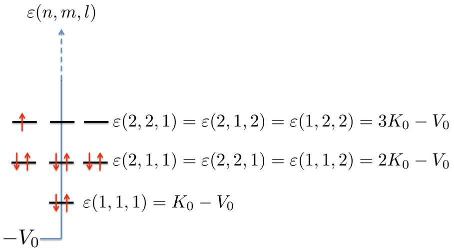


Fig. Diagram of the lowest "electronic energy levels" for free electrons in a 3D box, namely representation of the energies $\varepsilon(n,m,l)$ that free quantum electrons can have in the box. We represented in red a few electrons with their spin (up or down) on the lowest energy levels (see text).

2.3 Largest kinetic energy for electrons and Fermi level

An important property in a metal is that only a few electrons with maximum kinetic energy can participate to conducting the electricity, the heat, etc. These are the analogs of the "outer" conduction electrons in our simple atomic Bohr's model. We will justify this qualitatively in the next paragraphs. The question we want to answer therefore is what is the maximum kinetic energy for an electron belonging to a collection of N electrons in a box of volume L^3 ? We know that each of these N electrons should have an energy given by the $\varepsilon(n, m, l)$ energies defined above (solutions of the Schrödinger equation), but these energy levels with increasing (n,m,l) are present in an infinite number ! So which one do we select for our N electrons ? For answering this question we invoke (a) the stability principle and (b) the purely quantum Pauli exclusion principle.

RULES: In their most stable state at zero Kelvin, electrons are associated with the lowest possible energy levels with the limitation that only two electrons (fermions) with opposite spin can occupy the same $\varepsilon(n, m, l)$ energy level. The second rule applies to fermions in general : there can only be one Fermion in a given quantum state completely defined by its corresponding wavefunction $\phi_{\vec{k}}(\mathbf{r})$ and its spin (spin up or down).

As shown in the diagram above, we thus start by putting 2 electrons with opposite spin in the lowest $\varepsilon(1, 1, 1)$ level, then 2x3=6 electrons in the 3-fold level just above, etc. and we continue by filling up levels with increasing (n,m,l) numbers until we have placed our N electrons. We have thus a well defined scheme to know the energy of our electrons, and, in principle, to know the energy of the highest occupied level. In a metal this highest occupied level with maximum kinetic energy is called the Fermi level. But since typically in a metal there are 10^{23} electrons/cm^3, one cannot really count levels one by one until we have placed all our electrons !

End of first lecture.

2.4 Reciprocal space (or k-space) and Fermi sphere

As a result, in an elementary tiny "volume" $(\pi/L)^3$ in reciprocal space (a "volume" homogeneous to the inverse of a length cubed), there can only be one possible allowed **k**-vector ! Note that since the allowed k-vectors can only have positive (k_x, k_y, k_z) components, we consider only (1/8) of the **k**-space.

Let's call KE_F the Fermi kinetic energy, namely the maximum kinetic energy for an electron in the box. In our model, the Fermi energy is thus $E_F = KE_F - V_0$ putting in the constant potential inside the box.[2] The maximum

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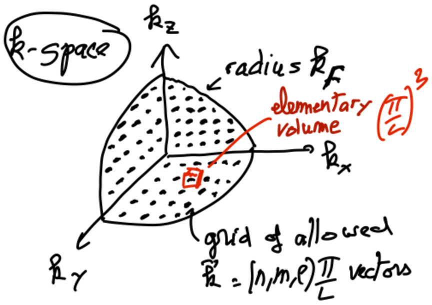
[2] In most books, V_0 is set to zero for conveniency since it is a rigid shift of all energies.



An elegant "trick" consists in going to the reciprocal space, or the space of the wavevectors **k** (or **k**-vectors in short). Each allowed $\mathbf{k} = (n, m, l)\pi/L$ vector (see above) is represented by a point in **k**-space forming a regular grid of points separated by a distance (π/L) in each direction.

kinetic energy $KE_F = \hbar^2 k_F^2/2m_e$ defines the Fermi wavevector k_F magnitude. The sphere in **k**-space of radius k_F is called the Fermi sphere.

All allowed **k**-vectors inside the Fermi sphere will define a quantum state associated with an energy level occupied by 2 electrons (since its energy is lower than the Fermi energy). Since each allowed **k**-vector is alone in a tiny $(\pi/L)^3$ volume, there are exactly

$$\frac{1}{8}\frac{\frac{4}{3}\pi k_F^3}{(\pi/L)^3} \quad \text{allowed } \mathbf{k}\text{-vectors inside } (1/8) \text{ of the Fermi sphere of radius } k_F$$

where the (1/8) factor insures that only positive (k_x, k_y, k_z) component are considered. Saying now that the total number N of electrons must be equal to the number of electrons that we can put in the quantum states associated with these allowed **k**-vectors smaller in magnitude than k_F, one obtains:

$$\boxed{N = 2 \times \frac{1}{8}\frac{\frac{4}{3}\pi k_F^3}{(\pi/L)^3} \Longrightarrow k_F^3 = 3\pi^2(N/L^3) = 3\pi^2 n}$$

where $(n = N/L^3)$ is the electronic density (not to be confused with the quantum number n ...) and where the factor 2 comes from the spin since each state characterized by a given **k**-vector can accommodate to electrons with opposite spin.

2.5 Fermi kinetic energy

The kinetic energy at the Fermi level is thus:

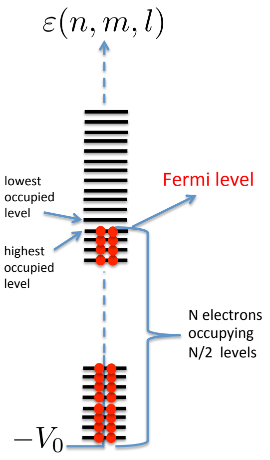
$$KE_F = \frac{\hbar^2 k_F^2}{2m_e} = \frac{\hbar^2}{2m_e}(3\pi^2 n)^{2/3} \quad \text{with n the electronic density.}$$

For Copper with $n = 8.5 \times 10^{28}$ conduction electrons/m^3, one obtains:

$$(Cu) \qquad KE_F \simeq 7eV \simeq 8.1 \times 10^4 K/k_B$$

Defining the Fermi velocity with $KE_F = \frac{1}{2}m_e v_F^2$ one finds $v_F \simeq 1.6 \times 10^6$ m/s.

The quantum Fermi kinetic energy is much much larger than the typical thermal energy. This is due to the Pauli principle that forces electrons to occupy high energy levels (only bosons could accumulate in low energy levels) ! The corresponding Fermi velocity is one order of magnitude larger than the thermal velocity at room temperature. Electrons cannot be treated classically !!!



Summary At zero Kelvin, the stability and Pauli repulsion principles for fermions dictate that the N electrons in the box occupy the (N/2) lowest

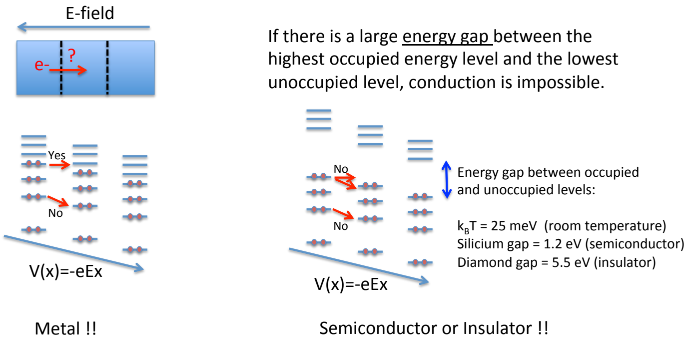
$$\varepsilon(n,m,l)=\frac{\hbar^2\pi^2}{2m_eL^2}(n^2+m^2+l^2)-V_0$$

energy levels (n,m,l positive integers) with 2-electrons with opposite spin possible per energy level. In a metal, the highest occupied energy levels defines the Fermi level. The typical kinetic energy for electrons at the Fermi level is of the order of a few eVs, much larger than the thermal temperature (k_BT=25 meV for room temperature). The difference in energy between the highest occupied and lowest unoccupied level is called the energy gap that goes to zero in a metal.

2.6 Only electrons close to the Fermi level can conduct electricity and heat

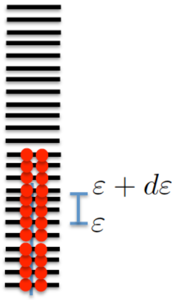
Let's discuss qualitatively the reason why only electrons close to the Fermi level (i.e. the highest occupied level in a metal) can participate to conducting electricity or heat. The idea again is that 2 electrons cannot occupy the same quantum state (as characterized by a wavefunction $\phi_{\vec{k}}$ and a spin). This is the principle of Pauli repulsion for fermions (see your Quantum Mechanics class). Let's consider now, as at the beginning of this lecture, a small rod of metal that we divide into little boxes (see Figure below). We can treat electrons in each of these boxes by the above model of free electrons in a box. Without an external electric field, or without any potential bias between each end of the conducting rod, all boxes are identical with the same energy levels and Fermi level. When we now add a bias, the energy levels are gradually shifted down along the conducting rod by the potential bias. The energy levels in a box are slightly lower in energy as compared to the box just "on the left".

An electron that conducts electricity or heat must jump from one box to another, leaving an occupied level to arrive into an unoccupied quantum level that has roughly the same energy (within k_BT). Looking at the Figure below, an electron well below the Fermi energy will only see occupied levels at the same energy in the box on the right : such an electron cannot move. Only electrons at the Fermi energy will see empty levels on the right and will be allowed to jump and participate to conduction. This is however only possible in a metal where the difference in energy between the highest occupied and lowest unoccupied levels is small (as compared e.g. to k_BT and the bias).



In a semiconductor or an insulator, there is a large energy gap between the highest occupied and lowest unoccupied levels. This energy gap is typically 1.2 eV in silicon (a semiconductor) and 5.5 eV in diamond (an insulator). In that case (see Figure above), the bias will never be large enough to bring the unoccupied energy levels at the energy of the occupied levels of the box just on the left. An electron coming from an occupied level can never find an empty level in the box just on the right. This is a qualitative explanation for the absence of current in semiconductor and insulators, and the fact that even in metals, only electrons close to the Fermi energy (largest kinetic energy) can participate to the electronic transport.

2.7 The density of states



An important question now is to know how many electrons have an energy close to the Fermi energy (for example within an energy k_BT of the Fermi energy, where k_BT is the room temperature thermal energy, typically 25 meV). To answer this question, we will more generally look for the number of quantum states (or energy levels) with a kinetic energy contained in an interval $[\varepsilon, \varepsilon + d\varepsilon]$ (see picture on the left). We will start by "counting" the number $\mathcal{N}(\varepsilon)$ of levels (or quantum states) with a kinetic energy lower than ε.

Taking the wavevector amplitude $k = \sqrt{2m_e\varepsilon/\hbar^2}$ corresponding to the kinetic energy ε, the number of quantum state with a kinetic energy lower than

ε, namely a wavevector lower in magnitude than $k = \sqrt{2m_e\varepsilon/\hbar^2}$ is given by:

$$\mathcal{N}(\varepsilon) = 2 \times \frac{1}{8} \times \frac{\frac{4}{3}\pi k^3}{(\pi/L)^3} = \frac{L^3}{3\pi^2}k^3 = \frac{L^3}{3\pi^2}(2m_e\varepsilon/\hbar^2)^{3/2}$$

This is exactly what we did before with the Fermi energy and Fermi wavevector but reproduced now for any (kinetic) energy and corresponding wavevector. The number of quantum states with a kinetic energy between $[\varepsilon, \varepsilon + d\varepsilon]$ is just

$$\mathcal{N}(\varepsilon + d\varepsilon) - \mathcal{N}(\varepsilon) = \frac{d\mathcal{N}(\varepsilon)}{d\varepsilon}d\varepsilon = \mathcal{D}(\varepsilon)d\varepsilon$$

The quantity $\mathcal{D}(\varepsilon)$ is called the density of states at the energy ε. By simple derivative of $\mathcal{N}(\varepsilon)$ one obtains:

$$\boxed{\mathcal{D}(\varepsilon) = \frac{V}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2}\sqrt{\varepsilon} \quad \text{density of states in 3D.}}$$

where V is the box volume. In a 3D box, the density of states increases as the square root of the energy. This means that with increasing energy, the energy levels gets denser and denser, or the number of levels (or quantum states) in a given energy window $d\varepsilon$ increases.

2.8 The total internal (kinetic) energy U

To illustrate the usefulness of the density of states $\mathcal{D}(\varepsilon)$ let's calculate the total kinetic energy of the N electrons in the system, namely the sum of the kinetic energy of each electron in the system (of the order of 10^{23} per cm^3). The formula is just

$$U = \int_0^{\varepsilon_F} d\varepsilon \mathcal{D}(\varepsilon)\varepsilon = \alpha\frac{\varepsilon_F^{5/2}}{5/2} \qquad \text{with} \qquad \alpha = \frac{V}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2}$$

In this formula, the number of electrons with an energy within $[\varepsilon, \varepsilon + d\varepsilon]$ is $d\varepsilon\mathcal{D}(\varepsilon)$ and they contribute to ε to the kinetic energy. The integrals stops at ε_F since there are no electrons with larger kinetic energy. This formula can be simplified by noticing that the total number of electrons should be

$$N = \int_0^{\varepsilon_F} d\varepsilon \mathcal{D}(\varepsilon) = \alpha\frac{\varepsilon_F^{3/2}}{3/2} \qquad \text{with} \qquad \alpha = \frac{V}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2}$$

so that very simply

$$\boxed{\frac{U}{N} = \frac{3}{5}\varepsilon_F}$$

The average kinetic energy per electron amounts to 3/5 of the maximum (Fermi) kinetic energy per electron.

But is all this an accurate description of metals ? A standard exercise (see Exercise 1 in your list of exercices) is to show that the so-called bulk modulus B (or incompressibility coefficient), that is given by the second-order derivative of the internal energy with respect to the volume: $B = V(\partial^2 U/\partial V^2)$, is calculated with this simple model to be within 1% of the experimental value for potassium. The agreement is not so good for all metals, mainly because the variation of the energy associated with “compressing the electron gas” is not always the main dominant term (ion-ion interactions may contribute when one reduces the volume). But the concept and ideas (energy levels, Fermi energy, density of states, energy gap between occupied and unoccupied levels, etc.) are central concepts in solid-state physics that are used to understand the properties of all solids.

2.9 Specific heat

Another interesting application of these ideas is the electronic specific heat, namely the energy due to heat that can be stored by electrons in a solid when the temperature is raised. We define the electronic specific heat per unit volume as $C = (1/V)(\partial \Delta U(T)/\partial T)$ where $\Delta U(T) = U(T) - U(T = 0)$ is the difference of internal energy at a finite temperature T as compared to the internal energy at T=0 K.

2.9.1 Classical specific heat

Following Drude classical model, classical equipartition theorem tells us that an electron can store $3k_BT/2$ heat energy. For N electrons, the T-derivative gives a classical electronic specific heat of $C = (N/V)3k_B/2$ that is temperature independent. This is a wrong result : experimentally, the specific heat is shown to behave as $C \simeq aT + bT^3$, where the linear coefficient in T comes from the electronic degrees of freedom, while the T^3 term comes from the energy stored in the vibrational modes of the ions (the “phonons” that we will discuss at the end of these lectures). This is indicated in the document reproduced below (from Kittel, chapter 6).

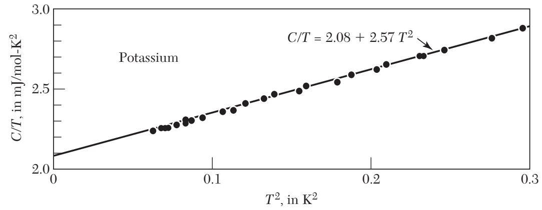
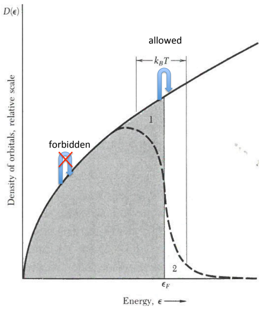


Figure 9 Experimental heat capacity values for potassium, plotted as C/T versus T^2. (After W. H. Lien and N. E. Phillips.)

2.9.2 Quantum specific heat

Again, to understand the proper T-dependence of the electronic specific heat, one must consider quantum electrons and the Pauli repulsion principle. In the classical model, it is assumed that all electrons can increase their energy by an average of $3k_BT/2$. In the quantum mechanical case, an electron that acquires an energy of the order of k_BT must find an empty energy levels located roughly at an energy of k_BT above the level it is occupying at T=0 K.

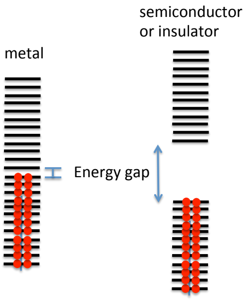


The graph on the left represents the density of states $\mathcal{D}(\varepsilon)$ calculated above. All levels with an energy smaller than the Fermi energy ε_F are occupied (shared area), all levels above the Fermi energy ε_F are empty. From this graph, it is clear that only electrons with an energy within k_BT of ε_F can increase their energy by k_BT and arrive in a empty level. Qualitatively, the number of electrons that have an energy within k_BT of the Fermi level is given by $\mathcal{D}(\varepsilon_F)k_BT$, where $\mathcal{D}(\varepsilon_F)$ is the density of states at the Fermi level.

These electrons can acquire k_BT in energy from the heat, so that in the quantum case: $\Delta U(T) \simeq \mathcal{D}(\varepsilon_F)k_BT \times k_BT$ and the electronic specific heat becomes: $C \simeq (2/V)\mathcal{D}(\varepsilon_F)k_B^2T$ with the correct linear behaviour in temperature. An exact calculation accounting for the proper population of levels at finite temperature (the so-called Fermi-Dirac population, see dashed line in the figure above and Kittel, "Free electron Fermi gas" chapter) would give:

$$C_{el}^{quantum} = \frac{\pi^2}{3V}\mathcal{D}(\varepsilon_F)k_B^2T$$

2.10 The free-electrons-in-a-box model cannot described macroscopic semiconductors or insulators



As discussed above, metals are characterized by a very small (on the scale of k_BT) energy difference (or energy gap or band gap) between the highest occupied and lowest unoccupied energy levels. On the contrary, in a semiconductor or insulator, this energy gap is very large, typically 1.2 eV in silicon and 5.5 eV in diamond. Let's show that the free-electron model discussed here above, cannot reproduce the energy gap of macroscopic semiconductors or insulators.

Let's remember that in 3D the electronic energy levels calculated above with the free-electrons-in-a-box model are quantized as follows:

$$\varepsilon(n,m,l) = \frac{\hbar^2}{2m_e}\left(\frac{\pi}{L}\right)^2(n^2+m^2+l^2) \quad \text{with} \quad (n,m,l) \quad \text{positive integers.}$$

As such, the typical spacing between energy levels is of the order of $\Delta\varepsilon(L) = \frac{\hbar^2}{2m_e}\left(\frac{\pi}{L}\right)^2$ that decreases with the square of the box length L. Using atomic units for which $\hbar = m_e = 1$ and where energies are in Hartree (1 Hartree = 2 Rydberg = 27.211 eV) and length in bohrs $a_0 = 0.529\mathring{A}$, one obtains:

$$\Delta\varepsilon(L) = \frac{1}{2}\left(\frac{\pi}{L/0.529}\right)^2 \times 27.211 \quad \text{eV} \quad \text{with L expressed in } \mathring{A}.$$

Plugging numbers for the length L of the box, we find:

$$\Delta\varepsilon(1\mathring{A}) \simeq 37.6 \text{ eV}; \quad \Delta\varepsilon(40\mathring{A}) \simeq 23.5 \text{ meV}; \quad \Delta\varepsilon(1\mu m) \simeq 4\times10^{-8} eV <<< k_B T$$

In conclusion, already for materials with micrometer size, the free-electrons-in-a-box model predicts an energy gap between energy levels that is much much smaller than room temperature (25 meV). This is obviously wrong for semiconductors and insulators such as silicon or diamond. As a matter of fact, this simple model just "counts" the number of electrons per volume (the density N/V). A metal and an insulator with the same density (n) will be exactly the same within this simple model. The free-electrons-in-a-box model has no information about the atomic structure (the 1s, 2s, 2p ... atomic energy levels) of the atoms composing the solid. Taking into account such informations will be the subject of the next lectures.