

Lecture 3: Electron statistics in a solid

Contents

1	Density of states	1
1.1	DOS in a 3D uniform solid	3
1.2	DOS for a 2D solid	4
1.3	DOS for a 1D solid	5
2	Electron occupation probability	6
2.1	Fermi-Dirac statistics	7
3	Density of states in silver	9
4	Fermi function vs. Boltzmann function	10

1 Density of states

In the band theory of the solid, developed earlier, N atoms with N atomic orbitals formed N molecular orbitals. Each MO can take 2 electrons (opposite spin) so that there are a total of $2N$ energy states. These are discrete states but for large values of N the spacing between them are so small that they can be considered to be continuous, forming an *energy band*.

Density of states (DOS) is **defined as the number of available energy states per unit energy per unit volume**. The units are $J^{-1}m^{-3}$ or $eV^{-1}cm^{-3}$ and it provides information on how the energy states are distributed in a given solid. It is typically denoted as $g(E)$. The experimental density of states of a material can be measured by photo electron spectroscopy or Scanning Tunneling Microscopy (STM) or Electron Energy Loss spectroscopy (EELS). These techniques probe the density of empty or filled states around the Fermi energy, called Local DOS (LDOS). Density functional calculations can also be used to calculate the density of states. These

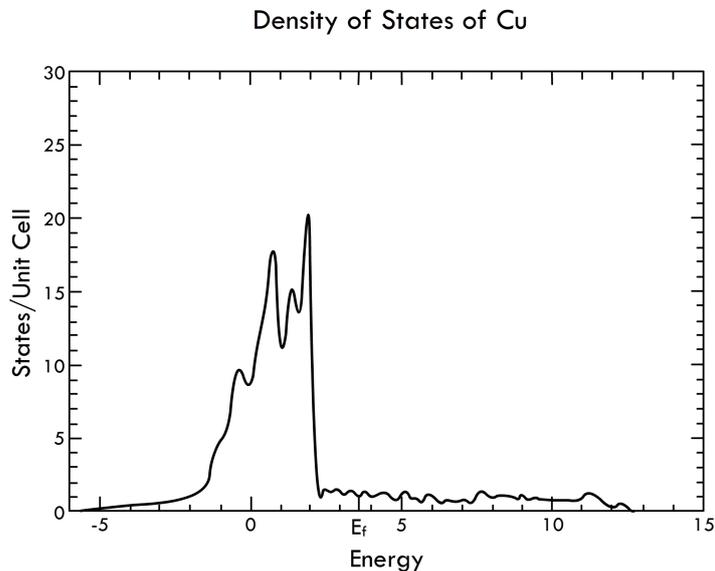


Figure 1: Calculated DOS of Cu around the Fermi level. The filled states lie below E_F while the empty states lie above E_F . The broad peak below E_F corresponds to the filled $3d$ states. Adapted from <http://www.personal.psu.edu/ams751/VASP-Cu/>

model the electron density distribution in a solid and also model the atomic potential within the solid. Figure 1 shows the calculated DOS for Cu around the Fermi energy.

The density of states can be used to calculate the total number of electron in a band. If $g(E)$ is the DOS, then the total number of electrons in a band, $S(E)$ is given by

$$S(E) = \int_E g(E)dE \quad (1)$$

where the integration is performed over the entire energy band. This equation assumes that the probability of occupation of the state is 1. This is not always true when we look at the conduction band of a semiconductor, where the occupation probability is defined by a Fermi function. An energy expression for the density of states, $g(E)$, will be useful for evaluation of the integral in equation 1.

1.1 DOS in a 3D uniform solid

To simplify the calculation for $g(E)$ consider a 3D solid with uniform potential. This is a simplification of a real solid but is a good approximation of the valence band of metals where the electrons are loosely bound to the atom and are delocalized. We will also use this approximation for electrons and holes near the edge of the band. For simplicity the uniform potential can be taken to be zero. For this solid the electron is defined by 3 quantum numbers (n_1, n_2, n_3) and its energy is given by

$$E = \frac{h^2}{8m_e L^2} (n_1^2 + n_2^2 + n_3^2) \quad (2)$$

Equation 2 is for a cubic solid of length L with the 3 quantum numbers for the 3 axes. m_e is the free electron mass. We can replace the 3 quantum numbers by a single value n so that equation 2 is modified into

$$E = \frac{h^2 n^2}{8m_e L^2} \quad (3)$$

For small values of n these energy levels are quantized, but for large values of n the spacing between them are close so that the energy levels can be considered to be continuous. So n represents the radius of a sphere, where the total number of states within the sphere is given by its volume. This is shown schematically in figure 2. Since the quantum numbers can only be positive (the quantum numbers represent the electron wavefunction and it can be shown that to avoid exponential increasing functions the quantum numbers have to be non-zero positive integers) we can only take the first quadrant of the sphere.

Hence the total number of ‘orbitals’ (energy states), $S_{orb}(n)$, is given by the volume of the sphere in the first quadrant

$$S_{orb}(n) = \frac{1}{8} \left(\frac{4}{3} \pi n^3 \right) = \frac{1}{6} \pi n^3 \quad (4)$$

Since each orbital can take two electrons of opposite spin, the total number of energy states (including spin), $S(n)$, is given by

$$S(n) = 2S_{orb}(n) = \frac{1}{3} \pi n^3 \quad (5)$$

We can relate n (quantum number of the electron in the solid) to the energy E using equation 2 to write the total number of states in terms of energy, $S(E)$. This is given by

$$S(E) = \frac{1}{3} \pi (8m_e E)^{\frac{3}{2}} \frac{L^3}{h^3} \quad (6)$$

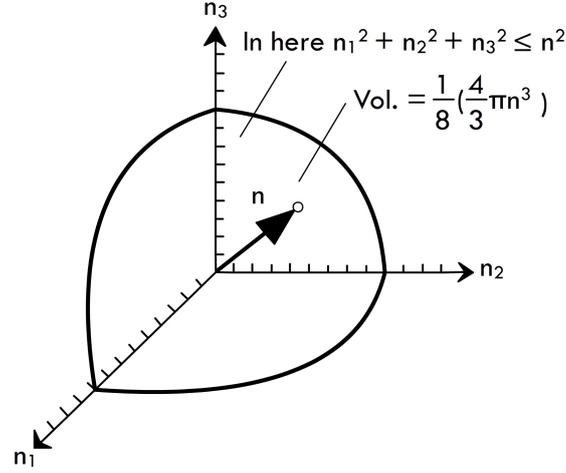


Figure 2: Energy states in a solid with uniform potential. The portion of the sphere corresponds to the constant energy surface. Only the first quadrant is to be considered since the quantum numbers are non-zero positive integers. Adapted from *Principles of Electronic Materials* - S.O. Kasap.

Dividing by the volume of the cube will give total number of states per unit volume, $S_v(E)$. The density of states is the differential of the total number of states, so that $g(E)$ is given by

$$g(E) = 8\pi\sqrt{2} \left(\frac{m_e}{h^2} \right)^{\frac{3}{2}} \sqrt{E} \quad (7)$$

Equation 7 gives the DOS in a solid with a uniform potential. At the bottom of the band, which is normally chosen as the reference so energy is set to 0, DOS is zero. As the energy increases $g(E)$ also increases. The functional form is shown schematically in figure 3. $g(E)$ represents the density of available states. It does not provide information whether those states are occupied or not. The occupation is given by the Fermi function and is usually a function of temperature.

1.2 DOS for a 2D solid

The density of states function will change upon changing the dimensionality of the solid. Consider the case of a 2D solid with a uniform potential. There are 2 quantum numbers, n_1 and n_2 , which are related to the energy, similar

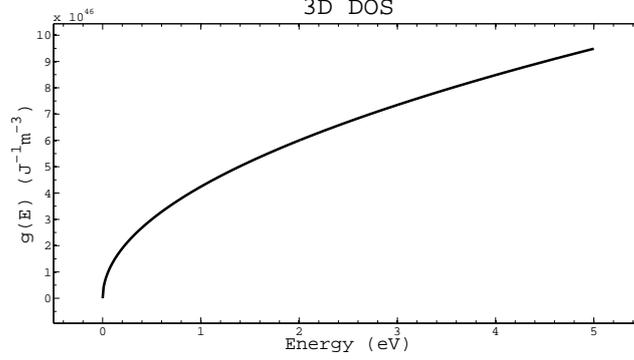


Figure 3: Plot of DOS vs. E for a 3D solid using free electron mass. This is a plot of equation 7 using MATLAB.

to equation 2.

$$E = \frac{h^2}{8m_e L^2} (n_1^2 + n_2^2) = \frac{h^2 n^2}{8m_e L^2} \quad (8)$$

For a 2D case, n , represents the radius of a circle, shown in figure 4, and only the first quadrant can be considered since the quantum numbers should be positive. It is possible to calculate the density of states per unit area, $S_{area}(n)$, including spin

$$S_{area}(n) = \frac{\pi n^2}{2} \quad (9)$$

Using equation 8 it is possible to calculate the DOS in terms of energy, $S_{area}(E)$

$$S_{area}(E) = \frac{4\pi m_e}{h^2} E \quad (10)$$

Differentiating equation 10 gives the density of states in two dimensions

$$g(E) = \frac{4\pi m_e}{h^2} \quad (11)$$

The density of states function is independent of energy, unlike 3D where $g(E)$ increases with energy. It is represented as a step function at different energy values.

1.3 DOS for a 1D solid

The calculation for a 1D solid is similar to the earlier calculations except that there is only one quantum number and spatially it is represented on a

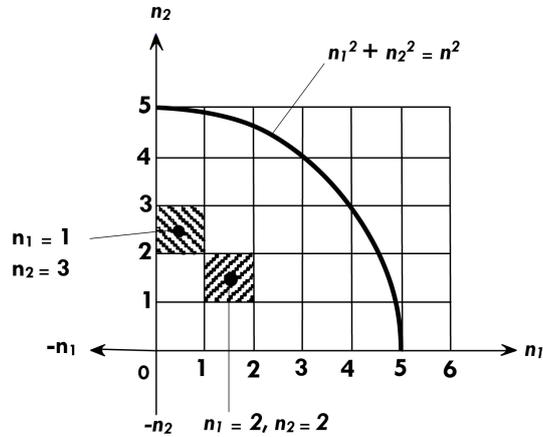


Figure 4: Energy states in a 2D solid with uniform potential. Instead of a sphere states of constant energy form a circle and only the first quadrant is relevant. Adapted from *Principles of Electronic Materials - S.O. Kasap*.

line (instead of circle in 2D and sphere in 3D). The total number of states, per unit length, $S(n)$, is just $2n$ and this is related to energy by equation 12.

$$n = \sqrt{\frac{8m_e}{h^2} E} \quad (12)$$

The density of states is given by

$$g(E) = \sqrt{\frac{8m_e}{h^2}} \frac{1}{\sqrt{E}} \quad (13)$$

In a 1D solid the density of states decreases with energy. For a zero dimensional solid, energy states are only discrete. Solids with two, one, and zero dimensionality can be obtained by reducing the length in one or more dimensions. A thin film is an example of a two dimensional solid (or a single or bi layer of graphene), while a quantum wire is a one dimensional solid. A quantum dot is a zero dimensional solid. The density of states and hence the electronic properties of these materials are different from a bulk solid. The DOS for solids of different dimensionalities are shown in figure 5.

2 Electron occupation probability

Density of states gives the number of available states for electrons to occupy. At absolute zero, electrons occupy the lowest energy state. Above $0 K$, there

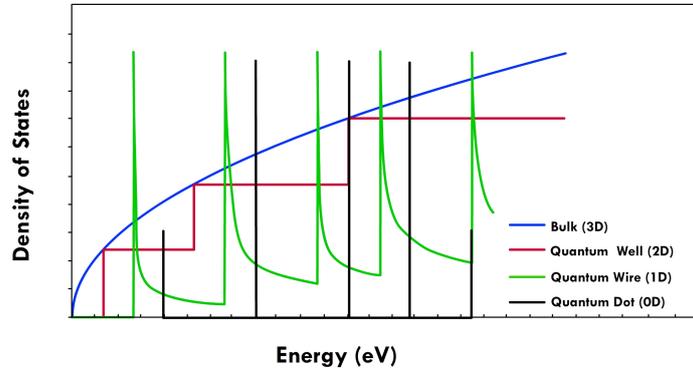


Figure 5: DOS for bulk, 2D, 1D, and 0D solids. The y-axis is a qualitative representation for the different dimensions. Adapted from <http://britneyspears.ac/physics/dos/dos.htm>

is always some thermal energy for the electrons to occupy the unoccupied energy states. There are different statistics to describe the occupation of energy levels. The simplest statistics is the **Boltzmann statistics** which gives the probability of occupation, $p(E)$, of a given energy state, E ,

$$p(E) = A \exp\left(-\frac{E}{k_B T}\right) \quad (14)$$

A is a constant. At 0 K all the particles have energy 0 and at any given T , $p(E)$ gives the probability of occupation. For a given temperature, $p(E)$ reduces as E increases, as shown in figure 6.

Boltzmann statistics works for a system of non-interacting particles but electrons have a strong repulsive interaction. By *Pauli's exclusion principle* only 2 electrons can occupy a given energy state (of opposite spin). So all electrons cannot occupy the same energy state, even at absolute zero. The statistics obeyed by electrons is given by the *Fermi-Dirac statistics*.

2.1 Fermi-Dirac statistics

In Fermi-Dirac statistics, the probability of electron occupation of a given energy state is represented by $f(E)$ and given by

$$f(E) = \frac{1}{1 + A \exp\left(\frac{E}{k_B T}\right)} \quad (15)$$

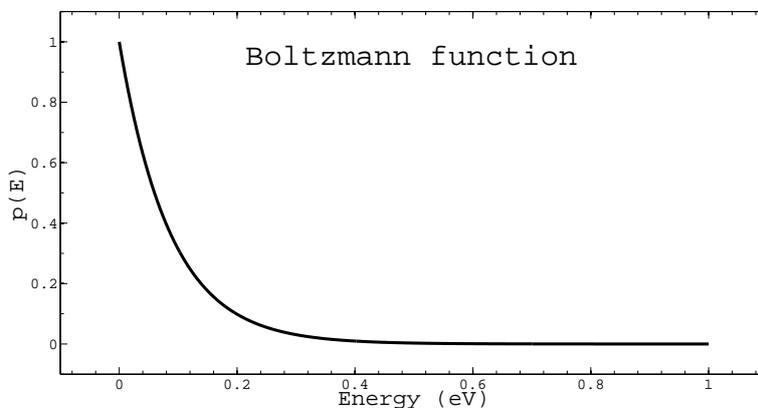


Figure 6: Boltzmann probability distribution vs. energy at 1000 K. The probability drops steeply as energy increases due to the exponential nature of the function. The plot was generated in MATLAB.

A is a constant. $f(E)$ is called the **Fermi function**. For solids A is related to the Fermi energy (E_F) so that $f(E)$ is given by

$$f(E) = \frac{1}{1 + \exp\left[\frac{(E - E_F)}{k_B T}\right]} \quad (16)$$

At absolute zero all energy levels below the Fermi level are occupied so that the occupation probability is 1. Above E_F the levels are empty so that $f(E)$ is 0. Also, at any temperature $f(E)$ at the Fermi level is 0.5. Figure 7 plots the Fermi function as a function of energy. When the energy difference ($E - E_F$) is much larger than $k_B T$ the Fermi function simplifies to the Boltzmann form shown in equation 14.

If $g(E)$ is the density of states and $f(E)$ gives the probability of occupation of those states at a given temperature, the number of occupied states, $n(E)$, is given by

$$n(E) = \int g(E)f(E)dE \quad (17)$$

If the number of occupied states in an energy band needs to be calculated the integration needs to be performed over the entire band. This will be a function of temperature, since the Fermi function is temperature dependent. Equation 17 can be used to calculate the concentration of electron and holes in semiconductors, which decides their conductivity.

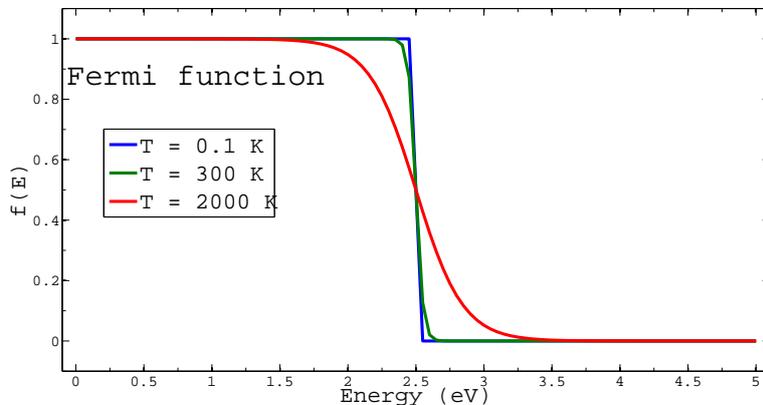


Figure 7: Fermi function vs. energy at three different temperatures. The probability drops steeply as energy is increased from the Fermi function. To increase the probability the temperature has to be increased. The plot was generated using MATLAB using $E_F = 2.5 \text{ eV}$. $T = 0.1 \text{ K}$ was used to simulate the 0 K distribution.

3 Density of states in silver

Consider an example to calculate the density of states in a metal, silver (Ag). Ag is a free electron metal, electrons in the outer shell are delocalized and are free to move in the material. Hence, valence electrons in Ag can be treated as electrons in an uniform potential. The atomic weight of Ag is 107.9 gmol^{-1} and the density (ρ) is 10.5 gcm^{-3} . Hence the number of atoms per unit volume (n_V) can be calculated

$$n_V = \frac{\rho N_A}{\text{At.wt}} \quad (18)$$

where N_A is Avogadro's number. This gives n_V to be $5.85 \times 10^{22} \text{ atoms cm}^{-3}$. The Fermi energy (E_F) of Ag is at 5.5 eV . This is with reference to the bottom of the valence band (taken as zero). So the density of states, at the Fermi energy, for Ag can be calculated using equation 7 is given by

$$g(E) = 8\pi\sqrt{2} \left(\frac{m_e}{h^2}\right)^{\frac{3}{2}} \sqrt{E_F} \quad (19)$$

where E_F is 5.5 eV . This gives a number $9.95 \times 10^{46} \text{ m}^{-3} \text{ J}^{-1}$ or converting the units $1.59 \times 10^{22} \text{ cm}^{-3} \text{ eV}^{-1}$. This is of the same order of magnitude as the number of atoms per unit volume. Close to the bottom of the band the density of states is still a substantial quantity. Consider an energy $k_B T$ above

the bottom of the band. At room temperature this energy is approximately 25 meV. Using equation 7 the density of states is $1.09 \times 10^{21} \text{ cm}^{-3} \text{ eV}^{-1}$ which is still a substantial fraction of the number of atoms.

In order to calculate the total number of electrons in the band equation 17 can be integrated from the bottom of the band to E_F . The occupation probability, $f(E)$, is 1.

$$n(E) = \int_0^{E_F} g(E)dE \quad (20)$$

The integral is

$$n(E) = 8\pi\sqrt{2} \left(\frac{m_e}{h^2}\right)^{\frac{3}{2}} \frac{2}{3} E_F \sqrt{E_F} \quad (21)$$

The calculated value of $n(E)$ is $5.08 \times 10^{22} \text{ cm}^{-3}$ which is very close to the number of atoms per cm^{-3} . Since each atom contributes one electron in Ag this is also the number of electrons and they fill all the states below E_F . Thus, a simple model of a solid with a uniform potential matches closely with reality. In silver, E_F is in the middle of the band so that there are empty available states for the electrons to occupy. When an electric field electrons travel opposite to this field and they can occupy these empty states. This makes Ag a very good conductor of electricity.

4 Fermi function vs. Boltzmann function

We can compare the occupation probability using Fermi function and the Boltzmann function. Consider the case when $(E - E_F)$ is equal to $k_B T$. $f(E)$, equation 16, is equal to 0.26, while Boltzmann function, equation 14, is 0.367. Consider when $(E - E_F)$ is equal to $2k_B T$. $f(E)$ is equal to 0.12, while Boltzmann function is 0.135. If $(E - E_F)$ is equal to $10k_B T$, $f(E)$ is 4.5×10^{-5} while the Boltzmann function is 4.54×10^{-5} . Thus, as $(E - E_F)$ becomes higher compared to $k_B T$, the Fermi function can be approximated by the Boltzmann distribution. This can be seen in figure 8, which compares the Boltzmann and Fermi function for energies above the Fermi energy (E_F). As seen from figure 8 when $(E - E_F)$ is around $2k_B T$ both functions start converge so that the Boltzmann approximation is valid for the Fermi function. At room temperature $10k_B T$ is 250 meV or 0.25 eV. This number is smaller than the band gap of most semiconductors (Si has band gap of 1.1 eV). So for calculating electron occupation in semiconductors the Boltzmann function is a good approximation for the Fermi function.

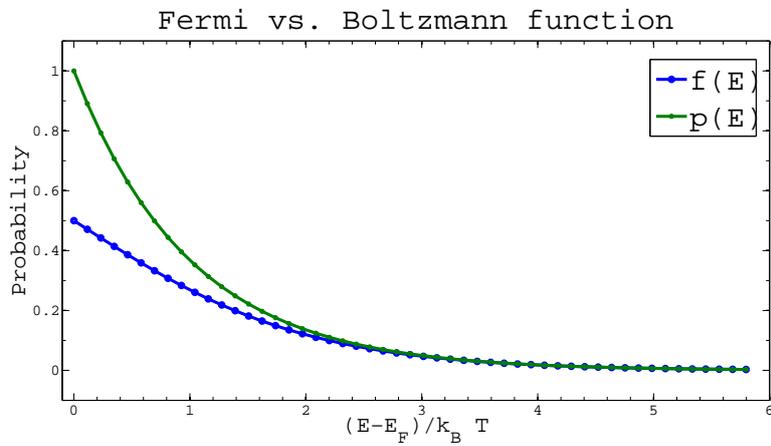


Figure 8: Comparison of the Fermi and Boltzmann probability distribution vs. normalized energy at constant temperature. Energy is plotted with reference to E_F and normalized by temperature. At low $(E - E_F)$ Fermi function is accurate while at higher values Boltzmann function is a good approximation. The plot was generated in MATLAB.