

## Lecture 15

### Fermi-Dirac Distribution

#### Today:

1. Fermi energy, and momentum, DOS.
2. Statistics of gases.
3. Fermi-Dirac distribution.

Questions you should be able to answer by the end of today's lecture:

1. What are the basic steps used to derive the Fermi-Dirac distribution?
2. Where did the Fermionic properties of the electrons enter in the derivation?
3. What is the physical significance of the Fermi energy and Fermi  $\mathbf{k}$ -vector?
4. How does the position of Fermi level with respect to band structure determine the materials electron transport properties?

We are now going to introduce  $N$  electrons into the system at  $T=0$  and are going to ask what states are these electrons going to occupy? If there are many electrons they will fill a circle in 2D or a sphere in 3D, the surface of this sphere represents the electrons, which have the maximum energy, and also separates filled from unfilled states and is called the Fermi surface.

**Filling the available states - Statistics of Fermi Gas.**

**How do electrons get distributed between the states are available to them?**

Lets consider a simple case of a 2-particle gas. Particles A and B are identical in a system which has 3 possible eigenstates  $\alpha_1, \alpha_2$  and  $\alpha_3$ .

**The Maxwell-Boltzman case:** A and B are classical and distinguishable.

	$\alpha_1$	$\alpha_2$	$\alpha_3$
1	AB		
2		AB	
3			AB
4	A	B	
5	A		B
6		A	B
7	B	A	
8	B		A
9		B	A

**The Bose Einstein case:** A and B are indistinguishable ( $A=B$ ) and are Bosons.

	$\alpha_1$	$\alpha_2$	$\alpha_3$
1	AA		
2		AA	
3			AA
4	A	A	
5	A		A
6		A	A

**The Fermi-Dirac case:** A and B are indistinguishable ( $A=B$ ) and are Fermions.

	$\alpha_1$	$\alpha_2$	$\alpha_3$
1	A	A	
2	A		A
3		A	A

The number of different possible states for the whole gas:

MB=9, BE=6, FD=3

We can define the following parameter which characterizes the tendency of the particles to “bunch”:

$$\xi = \frac{\text{probability of two particles in the same state}}{\text{probability of two particles in different states}}$$

$$\xi_{MB} = \frac{1}{2}, \quad \xi_{BE} = 1, \quad \xi_{FD} = 0$$

Compared to the classical case the bosons tend to bunch while fermions (electrons) remain apart.

Now, let’s consider  $N$  identical electrons in a volume  $V$  at temperature  $T$ .

**Using the following notation:**

$\alpha_s$  – Single electron eigenstate.

$\varepsilon_s$  - Single electron energy eigenvalue.

$n_s$  - Occupation number - the number of electrons in eigenstate  $\alpha_s$ .

$S$  – an eigenstate (sometimes called a microstate) of the entire electron gas for a particular configuration. For example the 3 states in the table above are “microstates” of the two-electron gas with three available states.

$E_S$  – The energy eigenvalue for an eigenstate (microstate)  $S$  of the entire gas.

Assume we have in our system 3 states  $s$ , and two electrons what are the possible “microstates”?

	$\alpha_1$	$\alpha_2$	$\alpha_3$
$S=1$	e-	e-	
$S=2$	e-		e-
$S=3$		e-	e-

What are the properties of this gas?

(1) Total energy of the gas in an eigenstate  $S$ :

$$E_S = n_1\varepsilon_1 + n_2\varepsilon_2 + \dots = \sum_s n_s \varepsilon_s$$

$$\sum_s n_s = N$$

(2) It can be shown that the probability of finding the system in a particular eigenstate  $S$  of energy  $E_S$  is given by:

$$P(S) = \frac{e^{-\frac{E_S}{k_B T}}}{\sum_{\text{all } S} e^{-\frac{E_S}{k_B T}}}$$

Where the denominator is a very useful function called the **partition function**:  $Z = \sum_{\text{all } S} e^{-\frac{E_S}{k_B T}}$

**All thermodynamic properties of the gas can be calculated from the knowledge of  $Z$ .**

The partition function  $Z$  is related to the Helmholtz free energy of the system through:

$$F = -k_B T \ln Z$$

The summation is over all distinct states of the gas –  $S$  (i.e. all possible values of  $\{n_1, n_2, \dots, n_N\}$ ) this expression holds for all types of particles. The difference lies in the number of different states  $S$ .

The chemical potential is defined as the change in free energy upon adding a particle to the system:

$$\mu \equiv F(N+1) - F(N) = \frac{\partial F}{\partial N}$$

### Fermi-Dirac Distribution

The range of allowable single-electron state occupation number:  $n_s = 0, 1$

Since the particles are indistinguishable it is enough to use the occupation vector  $\{n_1, n_2, \dots\}$  to completely define a state.

A very important quantity is the **mean number of particles in a particular single electron state  $\alpha_s$** , for electrons:

$$\bar{n}_s = \left( \begin{array}{l} \text{sum of the probabilities of} \\ \text{obtaining gas states } S \text{ where} \\ \text{single-electron state } \alpha_s, \text{ is occupied} \end{array} \right)$$

Using the partition function defined above one can show that:  $\bar{n}_s = \frac{1}{e^{\frac{(\epsilon_s - \mu)}{kT}} + 1}$

**This relation (for fermions) is called the Fermi-Dirac distribution it plays a key role in determining electronic properties.**

Generally Fermi-Dirac function is written as:  $f(\epsilon) = \frac{1}{e^{\frac{(\epsilon - \mu)}{kT}} + 1}$

An important observation regarding the FD distribution:  $f(\epsilon) \xrightarrow{\epsilon \rightarrow \infty} 0$   
 $f(\epsilon) \leq 1$

These properties are consequences of Pauli's exclusion principle.

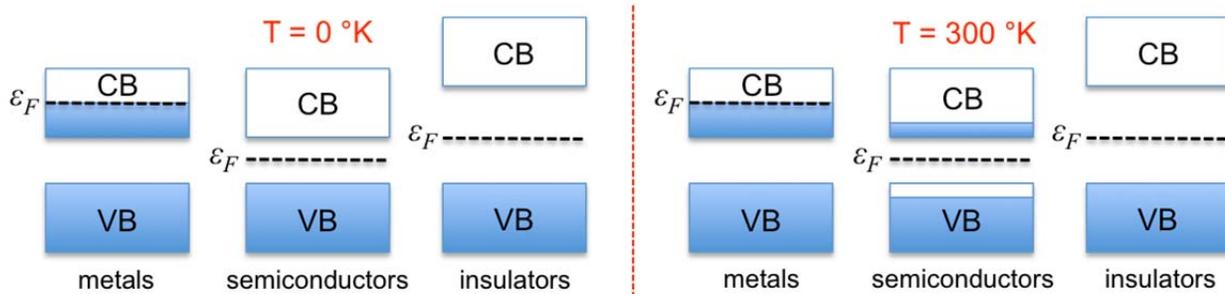
) U XUH UHP RYHG GXH VR FRS\UJ KWJHVMFVROV ) U V D E ) HLP L' LDF  
 DOG O D[ Z H00%ROV/P DQ' LVMEVROV 8QNRZ Q VRXUFH

For T=0K, we can show that:  $\lim_{T \rightarrow 0} f_{\vec{k},s} = \begin{cases} 1 & \varepsilon(\vec{k}) < \mu \\ 0 & \varepsilon(\vec{k}) > \mu \end{cases}$

As you can see electrons at 0K will occupy all the states with energies  $< \mu$  and will not occupy any states with energies  $> \mu$ .

As you can see **chemical potential**  $\mu$  is a very important intrinsic material property and it is often referred to as a **“Fermi level”**  $\mu = \varepsilon_F$ .

**The position of the Fermi level with respect to bands defines the nature of the material:**



**Definitions**

*Fermi sphere* – the surface in  $k$ -space that separates occupied from unoccupied levels.

*Fermi momentum* -  $\vec{p}_F = \hbar \vec{k}_F$

Fermi velocity -  $\frac{\vec{p}_F}{m}$  plays a role in metals similar to that of the thermal velocity in a classical gas.

Once we know Fermi energy we can find out the total number of “occupied states” using our D.O.S. function.

In 3D in metals:

$$N_{\text{electrons}} = 2 \frac{4\pi k_F^3}{3} \cdot \frac{1}{\left(\frac{2\pi}{L}\right)^3} = 2 \frac{4\pi k_F^3}{3} \frac{V}{(2\pi)^3} \rightarrow n = \frac{N}{V} = \frac{k_F^3}{3\pi^2}$$

All of these quantities depend on a single parameter the density of the free electrons

Typical values for the free electron densities in metals are:

$$Li = 4.7 \times 10^{22} \left[ \frac{\text{elec}}{\text{cm}^3} \right]$$

$$K = 1.3 \times 10^{22} \left[ \frac{\text{elec}}{\text{cm}^3} \right]$$

$$Ag = 5.86 \times 10^{22} \left[ \frac{\text{elec}}{\text{cm}^3} \right]$$

$$Fe = 17 \times 10^{22} \left[ \frac{\text{elec}}{\text{cm}^3} \right]$$

The corresponding de-Broglie wavelength is on the order on angstroms

The Fermi velocity is about 0.01c where c is the speed of light.

The Fermi energy is:  $\varepsilon_F = \frac{\hbar^2}{2m} k_F^2$ , typically in the range of 1.5-15eV.

To calculate the ground state energy E, of N electrons:  $E = 2 \sum_{k \leq k_F} \frac{\hbar^2}{2m} k^2$

Here all of the states are explicitly counted. Because of the small spacing in the k space it is also possible to transform to a continuous variable and integrate.

$$E = \int_{k < k_F} \underbrace{d^3k \frac{V}{8\pi^3}}_{\substack{\# \text{ of states in volume} \\ d^3k}} \frac{\hbar^2}{2m} k^2 = \frac{V}{\pi^2} \frac{\hbar^2 k_F^5}{10m}$$

The energy per electron in the ground state (using the expression for N/V from above):

$$\frac{E}{N} = \frac{V \hbar^5 k_F^5 / \pi^2 10m}{V k_F^3 / 3\pi^2} = \frac{3 \hbar^2 k_F^2}{5 2m} = \frac{3}{5} \epsilon_F$$

Compare this value with the average energy per particle in a classical Maxwell-Boltzmann gas:

$$E = \frac{3}{2} k_B T$$

If we define Fermi Temperature as:  $E_F = k_B T_F \Rightarrow T_F = \frac{E_F}{k_B}$

We would find that the classical gas would only reach the same energy per particle at temperature approaching  $T_F$  which is  $\sim 10^4$  K for metals.

### The heat capacity of the free electron gas

The heat capacity of an electron gas:

The equipartition theorem basically states that for each degree of freedom in the Hamiltonian there is a contribution of  $\frac{1}{2} k_B$  to the heat capacity. Therefore it is expected that the free electron gas will have a heat capacity of:

$$c_v = n \frac{3}{2} k_B$$

Yet in reality the contribution of the free electrons to the heat capacity in a metal was only 0.01 of that value? How come the electrons are mobile enough to participate in the conduction process but do not contribute to the heat capacity?

When we heat the sample from  $T=0$  K not every electron gains  $k_B T$  as expected from classical considerations. In fact only the electrons near the Fermi energy can absorb that extra kinetic energy by promoting themselves to higher energy orbitals. The rest of the electrons are trapped in their orbitals.

The fraction of electrons that can be excited is on the order of  $\sim \frac{T}{T_F}$

And the heat capacity then is:  $c_v = \frac{\pi^2}{2} \frac{k_B T}{\epsilon_F} n k_B$

MIT OpenCourseWare  
<http://ocw.mit.edu>

3.024 Electronic, Optical and Magnetic Properties of Materials  
Spring 2013

For information about citing these materials or our Terms of Use, visit: <http://ocw.mit.edu/terms>.