

Lecture #16

1. Understanding the properties of metals: the free electron model and the role of Pauli's exclusion principle.
2. Counting the states in the FE model.
3. Fermi energy, and momentum.
4. DOS
5. Fermi-Dirac distribution
6. Calculating thermodynamic properties of the electron gas
7. Heat capacity of the electron gas

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

1. Understand how to count the number of allowed eigenstates using the k-space graphic description.
2. What assumptions are used in the free electron model?
3. What is the physical significance of the Fermi energy and Fermi k vector?
4. Why is the Fermi temperature so high?
5. How do you calculate the DOS? What is its significance?
6. What are the basic steps used to derive the Fermi-Dirac distribution and where did the fermionic properties of the electrons enter in the derivation?
7. What electrons participate in determining the thermodynamic and transport properties of metals?

N independent electrons in a volume V (assuming periodic boundary conditions)

I] The system

N electrons in a box of side L such that $V = L^3$

II] Hamiltonian

$$\hat{H}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = -\sum_{i=1}^N \frac{\hbar^2}{2m} \nabla_i^2 = \sum_{i=1}^N \hat{H}_i$$

III] Eigenvalues and eigenfunctions,

$$\hat{H}_i u_k(x, y, z) = E_k u_k(x, y, z)$$

$$u_k(x, y, z) = u_k(\vec{r}) = \frac{1}{V^{1/2}} e^{i\vec{k} \cdot \vec{r}}$$

$$e_k = \frac{\hbar^2 (k_x^2 + k_y^2 + k_z^2)}{2m}$$

III] Boundary condition: Born Von-Karman

$$u_k(x + L, y, z) = u_k(x, y, z)$$

$$u_k(x, y, z + L) = u_k(x, y, z)$$

$$u_k(x, y + L, z) = u_k(x, y, z)$$

The k vector in this case is the momentum and the energy eigenfunctions are correspondingly momentum eigenfunctions.

$$\hat{P} u_k(\vec{r}) = \frac{\hbar}{i} \vec{\nabla} u_k(\vec{r}) = \hbar \vec{k} u_k(\vec{r})$$

we can also interpret the vector as a wave vector

$$|\vec{k}| = \frac{2\pi}{L}$$

where L is the de-Broglie wavelength.

The application of the boundary condition leads to the following identities,

$$e^{ik_x L} = e^{ik_y L} = e^{ik_z L} = 1$$

which in turn lead to quantization of the k vectors

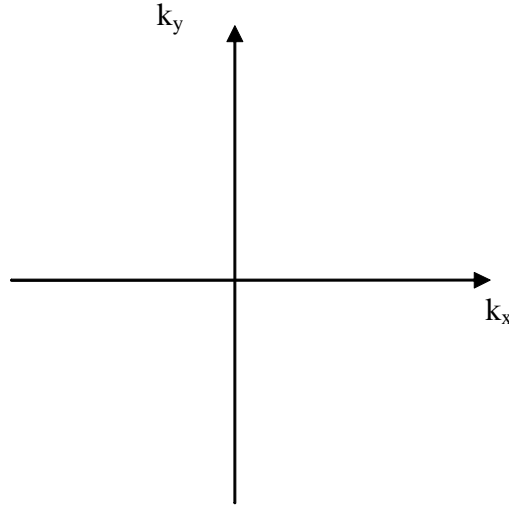
$$k_x = \frac{2\pi n_x}{L} \text{ (same for y and z)}$$

$$e_k = \frac{\hbar^2 (n_x^2 + n_y^2 + n_z^2)}{2mL^2}$$

Enumerating the states

(2D k_x - k_y plot introduction to k space – just an efficient way to display information)

The number of allowed points is just the volume of the k space divided by the volume occupied per point.



The region of k space of volume Ω will contain N allowed k points

$$N = \frac{\Omega}{\left(\frac{2p}{L}\right)^2}$$

the factor

$$\left(\frac{L}{2p}\right)^2$$

can be interpreted as the density of points in k space.

We now attempt to construct a many electron wavefunction of the free electron eigenstates using the symmetrization postulate

$$\mathcal{Y}(\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_{k_1}(\vec{r}_1) & \dots & u_{k_1}(\vec{r}_N) \\ u_{k_N}(\vec{r}_1) & & \end{vmatrix}$$

The process of identifying the combination of N , free electron eigenstates needed to produce the lowest possible energy configuration involves choosing the lowest energy k 's first and then choosing eigenfunctions associated with higher energies. The resulting volume occupied by the set of chosen k 's for a large number of electrons is approximately a sphere,

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.

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

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:

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

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

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

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

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

$$e_F = \frac{\hbar^2}{2m} k_F^2$$

typically in the range of 1.5-15eV

To calculate the ground state energy E, of N electrons,

$$E = 2 \sum_{k \leq k_F} \frac{\hbar^2}{2m} k^2$$

where 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),

$$\frac{E}{N} = \frac{3}{5} e_F \rightarrow T_F \approx 10^4 K$$

Density of Levels

A very useful number is the density of states (DOS) function it tells us how many states are located between energies $\epsilon \rightarrow \epsilon + d\epsilon$?

How is this number found?

First it is important to realize that $\epsilon(\vec{k}) = \epsilon$ represents a surface of constant energy.

Once we have a surface how do we calculate the volume enclosed between $\epsilon \rightarrow \epsilon + d\epsilon$?

For the free electron case

$$N = 2 \frac{4\pi k^3}{3} \cdot \frac{1}{\left(\frac{2\pi}{L}\right)^3} = \left(\frac{2m\epsilon}{\hbar^2}\right)^{3/2} \frac{V}{3\pi^2} = N(\epsilon)$$

The density of states function is defined as,

$$\frac{dN}{d\epsilon} = g(\epsilon) = \frac{m}{\hbar^2 \pi^2} \sqrt{2m\epsilon}$$

The number of one-electron levels in the energy range of $\epsilon \rightarrow \epsilon + d\epsilon$ per unit volume is:

$$g(\epsilon) d\epsilon$$

In general the density of states in a particular band is given by:

$$g_n(\epsilon) = \frac{1}{4\pi^3} \int_{S_n(\epsilon)} \frac{dS}{|\vec{\nabla}_k \epsilon(k)|}$$
$$g(\epsilon) = \sum_n g_n(\epsilon)$$

It used for calculating thermodynamic quantities:

$$U = \int d\epsilon g(\epsilon) f(\epsilon) \epsilon$$

The Fermi Dirac Distribution

Up till now we considered the properties of the free-electron gas at the ground state ($T=0$) what happens at elevated temperatures? One needs to calculate the properties of the excited states of the N electron system. The canonical ensemble formulation of statistical mechanics tell us that the properties of an N particle system which is in thermal equilibrium at temperature T should be calculated by averaging over all N particle eigenstates where each state of energy \mathbf{e} is weighted by

$$P(\mathbf{e}) = \frac{e^{-\mathbf{e}/k_B T}}{\sum_{\text{all states}} e^{-\mathbf{e}_i/k_B T}}$$

The denominator is called the partition function and is related to the Helmholtz free energy.

$$e^{-F/k_B T} = \sum_{\text{all states}} e^{-\mathbf{e}_i/k_B T}$$

The probability of having a particular 1 electron level with energy $-\mathbf{e}$ occupied by an electron is just,

$$f(\mathbf{e}) = \frac{1}{e^{(\mathbf{e}-\mathbf{m})/k_B T} + 1}$$

One can derive this probability by considering that it is nothing else but the sum of independent probabilities of having a particular energy level occupied

$$f(\mathbf{e}) = \sum_{\substack{\text{summation} \\ \text{over all states - } \mathbf{a} \\ \text{where there is} \\ \text{an electron in} \\ \text{level } \mathbf{E}}} P_{\mathbf{a}}(\mathbf{e})$$

It is also useful to note that the sum of all occupation numbers should equal the number of electrons in the system

$$N = \sum_{\text{all states}} f_i(\mathbf{e})$$

The chemical potential at temperature T is defined as the difference in free energies upon adding an additional particle to the system

$$\mathbf{m} = F_{N+1} - F_N$$

the chemical potential has a weak temperature dependence and is sometimes called the Fermi energy the energy is given by,

$$\mathbf{e}(\vec{k}) = \frac{\hbar^2}{2m} \vec{k}^2$$

Does this occupation probability function reproduce the ground state occupation?

$$f_{\vec{k},s} = \begin{cases} 1 & \mathbf{e}(\vec{k}) < \mathbf{e}_F \\ 0 & \mathbf{e}(\vec{k}) > \mathbf{e}_F \end{cases}$$

which is exactly what is recovered at the limit of T approaching 0 from the occupation function

$$\lim_{T \rightarrow 0} f_{\vec{k},s} = \begin{cases} 1 & \mathbf{e}(\vec{k}) < \mathbf{e}_F \\ 0 & \mathbf{e}(\vec{k}) > \mathbf{e}_F \end{cases}$$

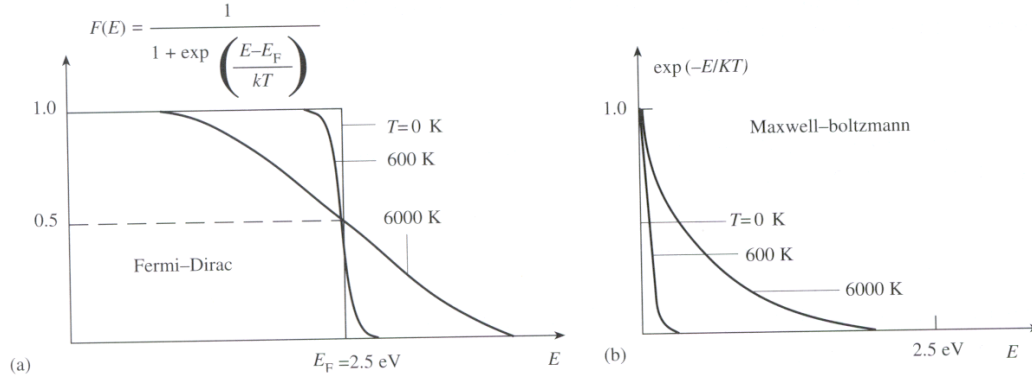


Fig. 6.1

(a) The Fermi-Dirac distribution function for a Fermi energy of 2.5 eV and for temperatures of 0 K, 600 K, and 6000 K.
(b) The classical Maxwell-Boltzmann distribution function of energies for the same temperatures.

We can use this function to evaluate different average quantities of the gas for example, The total energy of the system at temperature T ,

$$U = 2 \sum_{\substack{\text{all states} \\ \vec{k}}} \mathbf{e}(\vec{k}) f(\mathbf{e}(\vec{k}))$$

The energy density is given by,

$$u = \frac{U}{V} = \int d^3k \underbrace{\frac{1}{4\pi^3}}_{\substack{\text{\# of occupied} \\ \text{states in volume } d^3k}} f(\mathbf{e}(\vec{k})) \frac{\hbar^2}{2m} k^2$$

The density of states function is defined as,

$$g(\mathbf{e}) = \frac{m}{\hbar^2 \mathbf{p}^2} \sqrt{\frac{2m\mathbf{e}}{\hbar^2}}$$

and the number of one-electron levels in the energy range of $\mathbf{e} \rightarrow \mathbf{e} + d\mathbf{e}$ per unit volume is:

$$g(\mathbf{e}) d\mathbf{e}$$

$$u = \int_0^\infty d\mathbf{e} g(\mathbf{e}) f(\mathbf{e}) \mathbf{e}$$

$$n = \int_0^\infty d\mathbf{e} g(\mathbf{e}) f(\mathbf{e})$$

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 $1/2k$ 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 was only 0.01 of that value? The basic paradox was how were the electrons mobile enough to participate in the conduction process yet did not contribute to the heat capacity?

When we heat the sample from $T=0K$ 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 $\frac{T}{T_F}$

$$c_v = \frac{\mathbf{p}^2}{2} \frac{k_B T}{\mathbf{e}_F} n k_B$$