Section 7: Free electron model

A free electron model is the simplest way to represent the electronic structure of metals. Although the free electron model is a great oversimplification of the reality, surprisingly in many cases it works pretty well, so that it is able to describe many important properties of metals.

According to this model, the valence electrons of the constituent atoms of the crystal become conduction electrons and travel freely throughout the crystal. Therefore, within this model we neglect the interaction of conduction electrons with ions of the lattice and the interaction between the conduction electrons. In this sense we are talking about a *free electron gas*. However, there is a principle difference between the free electron gas and ordinary gas of molecules.

First, electrons are charged particles. Therefore, in order to maintain the *charge neutrality* of the whole crystal, we need to include positive ions. This is done within the *jelly model*, according to which the positive charge of ions is smeared out uniformly throughout the crystal. This positive background maintains the charge neutrality but does not exert any field on the electrons. Ions form a uniform jelly into which electrons move.

Second important property of the free electron gas is that it should meet the Pauli exclusion principle, which leads to important consequences.

One dimension

We consider first a free electron gas in one dimension. We assume that an electron of mass m is confined to a length L by infinite potential barriers. The wavefunction $\psi_n(x)$ of the electron is a solution of the Schrödinger equation $H\psi_n(x) = E_n\psi_n(x)$, where E_n is the energy of electron orbital. Since w can assume that the potential lies at zero, the Hamiltonian H includes only the kinetic energy so that

$$H\psi_n(x) = \frac{p^2}{2m}\psi_n(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_n(x) = E_n\psi_n(x).$$

(7.1)

Note that this is a one-electron equation, which means that we neglect the electron-electron interactions. We use the term *orbital* to describe the solution of this equation.

Since the $\psi_n(x)$ is a continuous function and is equal to zero beyond the length L, the boundary conditions for the wave function are $\psi_n(0) = \psi_n(L) = 0$. The solution of Eq.(7.1) is therefore

$$\psi_n(x) = A\sin\left(\frac{\pi n}{L}x\right),$$

(7.2)

where A is a constant and n is an integer. Substituting (7.2) into (7.1) we obtain for the eigenvalues

$$E_n = \frac{\hbar^2}{2m}\left(\frac{\pi n}{L}\right)^2.$$

(7.3)

These solutions correspond to standing waves with a different number of nodes within the potential well as is shown in Fig.1.
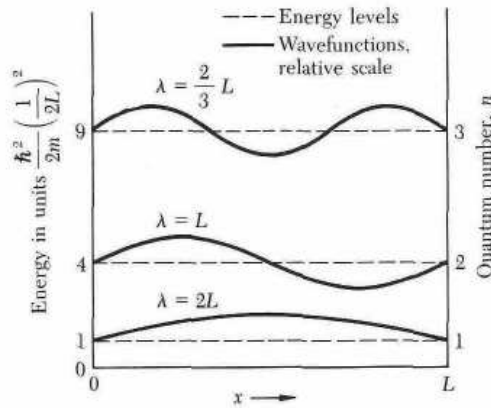
Fig.1 First three energy levels and wave-functions of a free electron of mass m confined to a line of length L. The energy levels are labeled according to the quantum number n which gives the number of half-wavelengths in the wavefunction. The wavelengths are indicated on the wavefunctions.

Now we need to accommodate N valence electrons in these quantum states. According to the Pauli exclusion principle no two electrons can have their quantum number identical. That is, each electronic quantum state can be occupied by at most one electron. The electronic state in a 1D solid is characterized by two quantum numbers that are n and m_s, where n describes the orbital $\psi_n(x)$, and m_s describes the projection of the spin momentum on a quantization axis. Electron spin is equal to S=1/2, so that there (2S+1)=2 possible spin states with $m_s = \pm\frac{1}{2}$. Therefore, each orbital labeled by the quantum number n can accommodate two electrons, one with spin up and one with spin down orientation.

Let n_F denote the highest filled energy level, where we start filling the levels from the bottom *(n = 1)* and continue filling higher levels with electrons until all N electrons are accommodated. It is convenient to suppose that N is an even number. The condition $2n_F = N$ determines n_F, the value of n for the uppermost filled level.

The energy of the highest occupied level is called the *Fermi energy E_F*. For the one-dimensional system of N electrons we find, using Eq. (7.3),

$$E_F = \frac{\hbar^2}{2m}\left(\frac{\pi N}{2L}\right)^2. \tag{7.4}$$

In metals the value of the Fermi energy is of the order of 5 eV.

The ground state of the N electron system is illustrated in Fig.2a: All the electronic levels are filled upto the Fermi energy. All the levels above are empty.

The Fermi distribution

This is the ground state of the N electron system at absolute zero. What happens if the temperature is increased? The kinetic energy of the electron gas increases with temperature. Therefore, some energy levels become occupied which were vacant at zero temperature, and some levels become vacant which were occupied at absolute zero. The distribution of electrons among the levels is

usually described by the *distribution function, f(E)*, which is defined as the probability that the level E is occupied by an electron. Thus if the level is certainly empty, then, $f(E) = 0$, while if it is certainly full, then $f(E) = 1$. In general, $f(E)$ has a value between zero and unity.
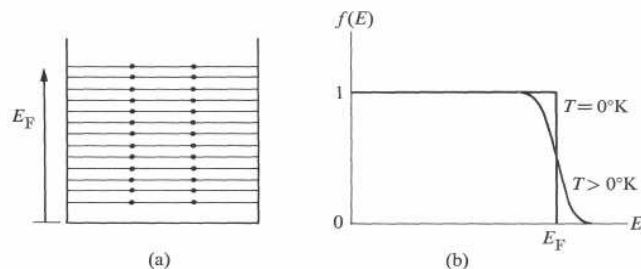

Fig. 2 (a) Occupation of energy levels according to the Pauli exclusion principle, (b) The distribution function $f(E)$, at $T = 0°K$ and $T > 0°K$.

It follows from the preceding discussion that the distribution function for electrons at $T = 0°K$ has the form

$$f(E) = \begin{cases} 1, & E < E_F \\ 0, & E > E_F \end{cases}.$$

(7.5)

That is, all levels below E_F are completely filled, and all those above E_F are completely empty. This function is plotted in Fig. 2(b), which shows the discontinuity at the Fermi energy.

When the system is heated ($T>0°K$), thermal energy excites the electrons. However, all the electrons do not share this energy equally, as would be the case in the classical treatment, because the electrons lying well below the Fermi level E_F cannot absorb energy. If they did so, they would move to a higher level, which would be already occupied, and hence the exclusion principle would be violated.

Recall in this context that the energy which an electron may absorb thermally is of the order k_BT (= 0.025 eV at room temperature), which is much smaller than E_F, this being of the order of 5 eV. Therefore only those electrons close to the Fermi level can be excited, because the levels above E_F are empty, and hence when those electrons move to a higher level there is no violation of the exclusion principle. Thus only these electrons - which are a small fraction of the total number - are capable of being thermally excited.

The distribution function at non-zero temperature is given by the *Fermi distribution function*. The derivation is presented in the appendix D of the textbook. The Fermi distribution function determines the probability that an orbital of energy E is occupied at thermal equilibrium

$$f(E) = \frac{1}{e^{(E-\mu)/k_BT} + 1}.$$

(7.6)

This function is also plotted in Fig. 2(b), which shows that it is substantially the same as the distribution at $T = 0°K$, except very close to the Fermi level, where some of the electrons are excited from below E_F to above it.

The quantity μ is called the chemical potential. The chemical potential can be determined in a way

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that the total number of electrons in the system is equal to *N*. At absolute zero $\mu = E_F$.

Three dimensions

The Schrödinger equation in the three dimensions takes the form

$$H\psi(\mathbf{r}) = \frac{p^2}{2m}\psi(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi(\mathbf{r}) = E\psi(\mathbf{r}). \tag{7.7}$$

If the electrons are confined to a cube of edge *L*, the solution is the standing wave

$$\psi(\mathbf{r}) = A\sin\left(\frac{\pi n_x}{L}x\right)\sin\left(\frac{\pi n_y}{L}y\right)\sin\left(\frac{\pi n_z}{L}z\right), \tag{7.8}$$

where n_x, n_y, and n_z are positive integers.

In many cases, however, it convenient to introduce periodic boundary conditions, as we did for lattice vibrations. The advantage of this description is that we assume that our crystal is infinite and disregard the influence of the outer boundaries of the crystal on the solution. We require then that our wavefunction is periodic in *x*, *y*, and *z* directions with period *L*, so that

$$\psi(x+L, y, z) = \psi(x, y, z), \tag{7.9}$$

and similarly for the *y* and *z* coordinates. The solution of the Schrödinger equation (7.7) which satisfies these boundary conditions has the form of the traveling plane wave:

$$\psi_{\mathbf{k}}(\mathbf{r}) = A\exp(i\mathbf{k}\cdot\mathbf{r}), \tag{7.10}$$

provided that the component of the wavevector **k** are determined from

$$k_x = \frac{2\pi n_x}{L}; \quad k_y = \frac{2\pi n_y}{L}; \quad k_z = \frac{2\pi n_z}{L}, \tag{7.11}$$

where n_x, n_y, and n_z are positive or negative integers.

If we now substitute this solution to Eq.(7.7) we obtain for the energies of the orbital with the wavevector **k**

$$E_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right). \tag{7.12}$$

The wavefunctions (7.10) are the eigenfunctions of the momentum $\mathbf{p} = -i\hbar\nabla$, which can be easily seen by differentiating (7.10) :

$$\mathbf{p}\psi_{\mathbf{k}}(\mathbf{r}) = -i\hbar\nabla\psi_{\mathbf{k}}(\mathbf{r}) = \hbar\mathbf{k}\psi_{\mathbf{k}}(\mathbf{r}). \tag{7.13}$$

The eigenvalue of the momentum is $\hbar\mathbf{k}$. The velocity of the electron is defined by $\mathbf{v} = \mathbf{p}/m = \hbar\mathbf{k}/m$.

In the ground state a system of *N* electrons occupies states with lowest possible energies. Therefore all the occupied states lie inside the sphere of radius k_F. The energy at the surface of this sphere is

the Fermi energy E_F. The magnitude of the wavevector k_F and the Fermi energy are related by the following equation:

$$E_F = \frac{\hbar^2 k_F^2}{2m}. \tag{7.14}$$

The Fermi energy and the Fermi wavevector (momentum) are determined by the number of valence electrons in the system. In order to find the relationship between N and k_F, we need to count the total number of orbitals in a sphere of radius k_F which should be equal to N. There are two available spin states for a given set of k_x, k_y, and k_z. The volume in the **k** space which is occupies by this state is equal to $(2\pi/L)^3$. Thus in the sphere of $(4\pi k_F^3/3)$ the total number of states is

$$2\frac{4\pi k_F^3/3}{(2\pi/L)^3} = \frac{V}{3\pi^2}k_F^3 = N, \tag{7.15}$$

where the factor 2 comes from the spin degeneracy. Then

$$k_F = \left(\frac{3\pi^2 N}{V}\right)^{1/3}, \tag{7.16}$$

which depends only of the electron concentration. We obtain then for the Fermi energy:

$$E_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}. \tag{7.17}$$

and the Fermi velocity

$$v_F = \frac{\hbar}{m}\left(\frac{3\pi^2 N}{V}\right)^{1/3}. \tag{7.18}$$

A few estimates for Na: Na has bcc structure with cubic lattice parameter a=4.2Å and one valence electron per atom. Since there are 2 atoms in a unit cell, the electron concentration is N/V = $2/(4.2\text{Å}^3)$ = $3\cdot10^{22}$cm^{-3}. Then, the Fermi momentum is $k_F \approx (3\cdot10\cdot3\cdot10^{22}\,cm^{-3})^{1/3} \approx 10^8\,cm^{-1} = 1\text{Å}^{-1}$. The Fermi energy is given by $E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2ma_0^2}k_F^2 a_0^2 \approx 13.6eV \cdot 0.25 \approx 3.5eV$. The Fermi temperature is defined $T_F = E_F/k_B \approx 40000K$ (1eV corresponds to $1.16\cdot10^4$K). The Fermi velocity can be found from $\frac{v_F}{c} = \frac{\hbar}{mca_0}k_F a_0 = \frac{\hbar}{mc}\frac{me^2}{\hbar^2}k_F a_0 = \frac{e^2}{\hbar c}k_F a_0 \approx \frac{1}{137}0.5 \approx 4\cdot10^{-3}$, which results in $v_F \approx 10^8\frac{cm}{s}$. We see that the velocity of electrons is relatively large.

An important quantity which characterizes electronic properties of a solid is the *density of states*, which is the *number of electronic states per unit energy range*. To find it we use Eq.(7.17) and write the total number of orbitals of energy $< E$:

$$N(E) = \frac{V}{3\pi^2}\left(\frac{2mE}{\hbar^2}\right)^{3/2}.$$ (7.19)

The density of states is then

$$D(E) = \frac{dN}{dE} = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2},$$ (7.20)

or equivalently

$$D(E) = \frac{3N}{2E}.$$ (7.21)

So within a factor of the order of unity, the number of states per unit energy interval at the Fermi energy, $D(E_F)$, is the total number of conduction electrons divided by the Fermi energy, just we would expect.

The density of states normalized in such a way that the integral

$$N = \int_0^{E_F} D(E)dE,$$ (7.22)

gives the total number of electrons in the system. At non-zero temperature we should take into account the Fermi distribution function so that

$$N = \int_0^\infty D(E)f(E)dE,$$ (7.23)

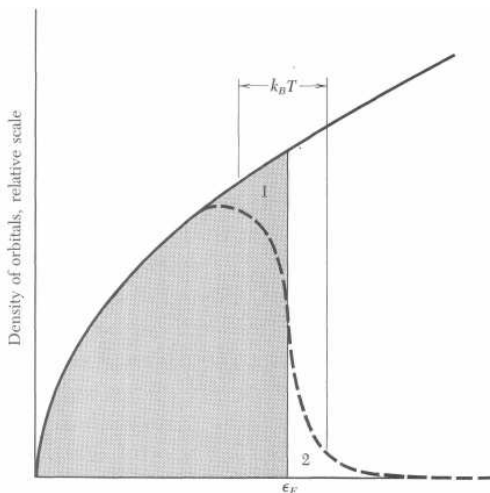This expression also determines the chemical potential.

Fig.3 Density of single-particle states as a function of energy, for a free electron gas in three dimensions. The dashed curve represents the density $f(E,T)D(E)$ of filled orbitals at a finite temperature, but such that kT is small in comparison with E_F. The shaded area represents the filled orbitals at absolute zero. The average energy is increased when the temperature is increased from 0 to T, for electrons are thermally excited from region 1 to region 2.

Heat capacity

The question that caused the greatest difficulty in the early development of the electron theory of metals concerns the heat capacity of the conduction electrons. Classical statistical mechanics predicts that a free particle should have a heat capacity of $3/2k_B$, where k_B is the Boltzmann constant. If N atoms each give one valence electron to the electron gas, and the electrons are freely mobile, then the electronic contribution to the heat capacity should be $3/2Nk_B$, just as for the atoms of a monatomic gas. But the observed electronic contribution at room temperature is usually less than 0.01 of this value.

This discrepancy was resolved only upon the discovery of the Pauli exclusion principle and the Fermi distribution function. When we heat the specimen from absolute zero not every electron gains an energy $\sim k_B T$ as expected classically, but only those electrons, which have the energy within an energy range $k_B T$ of the Fermi level, can be excited thermally. These electrons gain an energy, which is itself of the order of $k_B T$, as in Fig. 3. This gives a qualitative solution to the problem of the heat capacity of the conduction electron gas. If N is the total number of electrons, only a fraction of the order of $k_B T/E_F$ can be excited thermally at temperature T, because only these lie within an energy range of the order of $k_B T$ of the top of the energy distribution.

Each of these $Nk_B T/E_F$ electrons has a thermal energy of the order of $k_B T$. The total electronic thermal kinetic energy U is of the order of $U \approx (Nk_B T/E_F)k_B T$. The electronic heat capacity is $C_{el} = dU/dT \approx Nk_B(k_B T/E_F)$ and is directly proportional to T, in agreement with the experimental results discussed in the following section. At room temperature C is smaller than the classical value $\approx Nk_B$ by a factor 0.01 or less.

We now derive a quantitative expression for the electronic heat capacity valid at low temperatures $k_B T \ll E_F$. The total energy of a system of N electrons at temperature T is

$$U = \int_0^\infty E D(E) f(E,T) dE ,\qquad\qquad(7.24)$$

where $f(E,T)$ is the Fermi distribution function and $D(E)$ is the density of states. The heat capacity can be found by differentiating this equation with respect to temperature. Since only the distribution function depends on temperature we obtain:

$$C_{el} = \frac{dU}{dT} = \int_0^\infty E D(E) \frac{df(E,T)}{dT} dE .\qquad\qquad(7.25)$$

It is more convenient to represent this result in a different form:

$$C_{el} = \int_0^\infty (E - E_F) D(E) \frac{df(E,T)}{dT} dE .\qquad\qquad(7.26)$$

Eq. (7.27) is equivalent to Eq. (7.25) due to the fact which follows from Eq. (7.22):

$$0 = E_F \frac{dN}{dT} = E_F \int_0^\infty D(E) \frac{df(E,T)}{dT} dE .\qquad\qquad(7.27)$$

Since we are interested only temperatures for which $k_BT \ll E_F$ the derivative df/dT is large only at the energies which lie very close to the Fermi energy. Therefore, we can ignore the variation of $D(E)$ under the integral and take it outside the integrand at the Fermi energy, so that

$$C_{el} = D(E_F)\int_0^\infty (E - E_F)\frac{df(E,T)}{dT}dE \ . \tag{7.28}$$

We also ignore the variation of the chemical potential with temperature and assume that $\mu = E_F$, which is good approximation at room temperature and below. Then

$$\frac{df(E,T)}{dT} = \frac{E - E_F}{k_BT^2}\frac{e^{(E-E_F)/k_BT}}{\left[e^{(E-E_F)/k_BT}+1\right]^2} \ . \tag{7.29}$$

Eq.(7.28) can, then, be rewritten as

$$C_{el} = D(E_F)\int_0^\infty \frac{(E-E_F)^2}{k_BT^2}\frac{e^{(E-E_F)/k_BT}}{\left[e^{(E-E_F)/k_BT}+1\right]^2}dE = D(E_F)\int_{-E_F/k_BT}^\infty \frac{x^2\left(k_BT\right)^3}{k_BT^2}\frac{e^x}{\left(e^x+1\right)^2}dx \ . \tag{7.30}$$

Taking into account that $E_F \gg k_BT$, we can put the low integration limit to minus infinity and obtain

$$C_{el} = D(E_F)k_B^2T\int_{-\infty}^\infty \frac{x^2 e^x}{\left(e^x+1\right)^2}dx = \frac{\pi^2}{3}D(E_F)k_B^2T \ . \tag{7.31}$$

For a free electron gas we should use Eq.(7.21) for the density of states to finally obtain

$$C_{el} = \frac{\pi^2}{2}Nk_B\frac{T}{T_F} \ , \tag{7.32}$$

where we defined the Fermi temperature $T_F = E_F/k_B$. This is similar to what we expected to obtain according to the qualitative arguments given in the beginning of this section.

Experimentally the heat capacity at temperatures much below both the Debye temperature and the Fermi temperature can be represented in the form:

$$C = C_{el} + C_{ph} = \alpha T + \beta T^3 \ . \tag{7.33}$$

The electronic term is dominant at sufficiently low temperatures. The constants α and β can be obtained by fitting the experimental data.