§5.1 Free electrons approximation.

Now is make sense use the simple models to describe the properties of electron subsystem. The most simplest is a model of free electrons. In the first approximation, the electron-electron repulsion can be neglected due to compensation by the Coulomb attraction between negative electrons and positive atomic nuclei. Despite the simplicity, this approximation can be applied to describe the properties of electrons in metals and as a start point for more accurate DFT (Density Functional Theory) approximation. We take into account the fact that electrons are Fermi particles but do not take into account spin-spin interactions. This approximation can be applied to describe the properties of electrons in metals.

The Schrodinger equation for free electron is:

$$\hat{H}\,\varphi = E\,\varphi, \quad \hat{T}_e \cdot \varphi = E \cdot \varphi \quad, \quad \hat{T}_e = -\frac{\hbar^2}{2m}\hat{\Delta} = -\frac{\hbar^2}{2m}\left(\frac{d^2}{dy^2} + \frac{d^2}{dx^2} + \frac{d^2}{dz^2}\right) - kenetic\,energy\,operator$$

$$-\frac{\hbar^2}{2m}\hat{\Delta}\cdot\varphi = E\cdot\varphi \quad \text{and finally} \quad -\frac{\hbar^2}{2m}\left(\frac{d^2}{dy^2} + \frac{d^2}{dx^2} + \frac{d^2}{dz^2}\right)\varphi = E\,\varphi \quad .$$

$$(1)$$

The wave function φ (x, y, z) depends on three coordinates x, y and z. Due to the equivalence of the coordinate axes, the total wave function can be represented as the product of a functions depending on the corresponding coordinate x, y or z.

$$\varphi(x,y,z) = \varphi_x(x)\varphi_y(y)\varphi_z(z)$$

$$(2)$$

This makes it possible to consider the motion of an electron separately along each axis. Coordinates can be separated. The Schrodinger equation for x-axis is:

$$-\frac{\hbar^2}{2m}\frac{d^2\varphi_x}{dx^2} = E\,\varphi_x \quad \text{or} \quad \frac{d^2\varphi_x}{dx^2} + \frac{2mE}{\hbar^2}\varphi_x = 0 \quad .$$

$$(3)$$

The solution is looks like so:

$$\varphi_x = A_x e^{ik_x x} \text{ and correspondingly } \varphi_y = A_y e^{ik_y y} \text{ and } \varphi_z = A_z e^{ik_z z}$$

$$(4)$$

and total function:

$$\varphi(x,y,z) = A_x A_y A_z e^{i\vec{k}\vec{r}}$$

$$(5)$$

here $\vec{k}$ - wave vector for electron. The values for wave vector can be defined from periodical boundary conditions. If the length of lattice in directions x,y, and z is correspondingly L_x, L_y and L_z so:

$$\varphi_x(x) = \varphi_x(x+m_x L_x), \; \varphi_y(y) = \varphi_y(y+m_y L_y), \; \varphi_z(z) = \varphi_z(z+m_z L_z)$$

$$(6)$$

here m_x, m_y and m_z are integer numbers. After substitution (4) to (6) we have:

$$\varphi_x(x) = \varphi_x(x+L_x) = A_x e^{ik_x x} = A_x e^{ik_x(x+L_x)}$$

$$(7)$$

and after simplification we have:

$$1 = e^{ik_x \cdot L_x}$$

$$(8)$$

It is possible only if $k_x \cdot L_x = 2\pi n_x$, here $n_x \in Z$, now we have an equation for calculating wave vector

$$k_x = \frac{2\pi}{L_x} n_x \quad \text{and analogically} \quad k_y = \frac{2\pi}{L_y} n_y \quad , \quad k_z = \frac{2\pi}{L_z} n_z \qquad (9)$$

It is important to understand that the wave vector and energy are discrete quantities. Not all possible energy, wave vector and momentum values are allowed, but only those that satisfy to the condition for the existence of standing waves (9), in our case of standing wave function. The standing wave arises from the self-interference of the wave function which arise due to periodical bounder conditions.

The combination of (9,4 and 3) gives the energy of free electron for different directions:

$$E_x = \frac{\hbar^2 k_x^2}{2m} \quad , \quad E_y = \frac{\hbar^2 k_y^2}{2m} \quad , \quad E_z = \frac{\hbar^2 k_z^2}{2m} \quad . \qquad (10)$$

and the total energy can be calculated as follows:

$$E = \frac{\hbar^2 (k_x^2 + k_y^2 + k_z^2)}{2m} = \frac{\hbar^2 k^2}{2m} = \frac{p^2}{2m}, \text{ here } k^2 = (k_x^2 + k_y^2 + k_z^2) \text{ and momentum } \vec{p} = \hbar \vec{k}. \qquad (11)$$

According to (5) the wave function is:

$$\varphi(x,y,z) = A_x A_y A_z e^{i\vec{k}\vec{r}} = A_x A_y A_z e^{i(k_x x + k_y y + k_z z)} \qquad (12)$$

The unknown constants A_x, A_y, A_z can calculated from normalizing condition for wave function:

$$\int\limits_0^\infty \varphi_x(x) dx = \int\limits_0^{L_x} \varphi_x(x) dx = 1 \qquad (13)$$

Using (7) give $A_x = 1/\sqrt{L_x}$, the rest of the constants can be calculated in the same way $A_y = 1/\sqrt{L_y}$, $A_z = 1/\sqrt{L_z}$. After substituting this result into (12), we have:

$$\varphi(x,y,z) = \frac{1}{\sqrt{(L_x L_y L_z)}} e^{i\vec{k}\vec{r}} = \frac{1}{\sqrt{V}} e^{i\vec{k}\vec{r}}, \qquad (14)$$

here V is a total volume occupied by gas of free electrons.

The summary for obtained results of solution of Schrodinger equation:

Wave function (Eigen function) $\quad \varphi(x,y,z) = \frac{1}{\sqrt{V}} e^{i(k_x \cdot x + k_y \cdot y + k_z \cdot z)}$,

Energy (Eigenvalues) $\quad\quad\quad\quad E = \frac{\hbar^2 (k_x^2 + k_y^2 + k_z^2)}{2m}$ $\qquad (15)$

Wave vectors $\quad\quad\quad\quad\quad\quad\quad k_\alpha = \frac{2\pi}{L_\alpha} n_\alpha, \text{here } \alpha \equiv x,y,z$

It is important to emphasize that the projections of wave vectors play the role of quantum numbers and can be used to number various quantum states. Hence, it makes sense to rewrite the previous expressions in the form:

Wave function (Eigen function) $\varphi_{k_x,k_y,k_z}(x,y,z)=\dfrac{1}{\sqrt{V}}e^{i(k_x \cdot x + k_y \cdot y + k_z \cdot z)},$

Energy (Eigenvalues) $E_{k_x,k_y,k_z}=\dfrac{\hbar^2(k_x^2+k_y^2+k_z^2)}{2m}=\dfrac{\hbar^2 k^2}{2m}$ (16)

Wave vectors $k_\alpha=\dfrac{2\pi}{L_\alpha}n_\alpha,$ here $\alpha\equiv x,y,z$

The energy of free electron depend on modulus of wave vector and this dependance is looks like this (for simplicity, we assume that $L_x=L_y=L_z=L$):
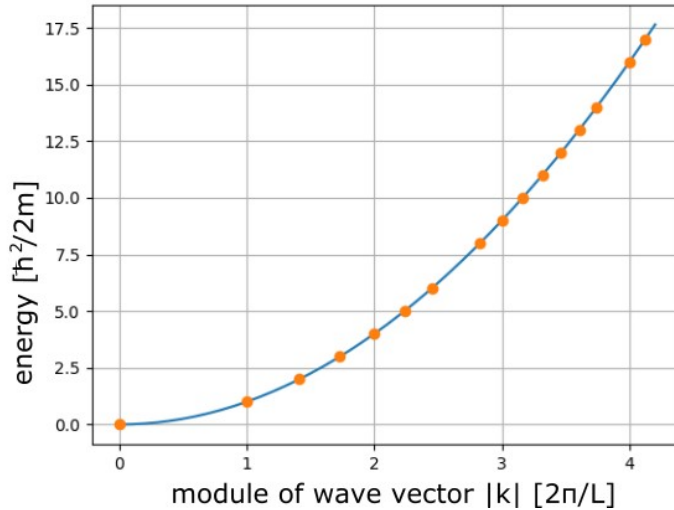

Figure 1

Point on the Figure 1 are the allowed values of energy. It is clear that allowed energy levels are degenerated. For example the ground state is degenerate 6 times. It is means that the same energy have the states with next possible combinations of quantum numbers $[k_x\,k_y\,k_z]$: $2\pi/L\cdot$ ([1 0 0] [0 1 0] [0 0 1] [-1 0 0] [0 -1 0] [0 0 -1]).

The number of electrons is very large but finite. Each quantum state, defined by their individual set of quantum numbers, is occupied by two electrons (due to Pauli principles).

At zero temperature, electrons occupy all states from zero energy to the highest occupied state. This highest occupied level is called the **Fermi level** and the corresponding energy is called the **Fermi energy**. All states over the Fermi level are non occupied.
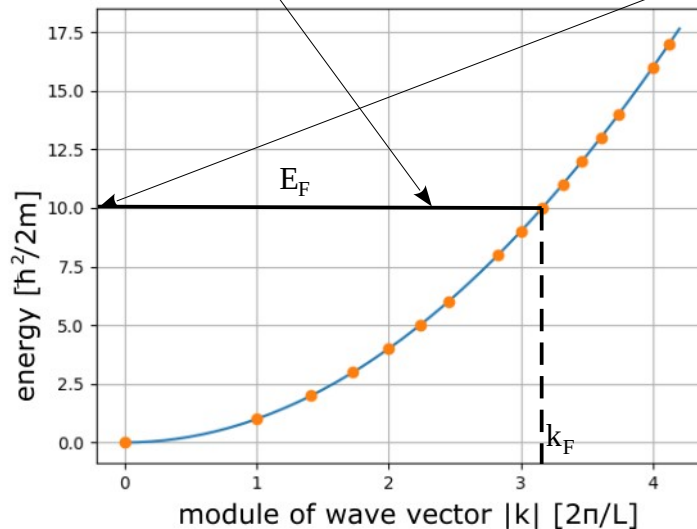

Figure 2

Here k_F is the wave vector corresponding to the Fermi energy. For gas of free electrons (16) these parameters are related as follows:

$$E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{P_F^2}{2m}, \text{here } p_F = \hbar k_F \tag{17}$$

To compute k_F, consider the space of k-vectors. This space is three-dimensional (since k-vectors are three-dimensional). According to (9), the admissible values of wave vectors fill a square grid with steps $\frac{2\pi}{L_x}$, $\frac{2\pi}{L_y}$ and $\frac{2\pi}{L_z}$, respectively (see Figure 3). This means that each valid k-vector occupies a cube with the same sides lengths. The volume of this cube is equal $\frac{(2\pi)^3}{V} = \frac{(2\pi)^3}{L_x L_y L_z}$. Electrons occupies all states with wave vectors from 0 to k_F, this means that all this wave vectors located inside of sphere with radius k_F.

The total number of occupied states N_{states} can be calculated as the ratio of the total volume of a sphere with radius k_F and the volume of a cube pertaining to one state.
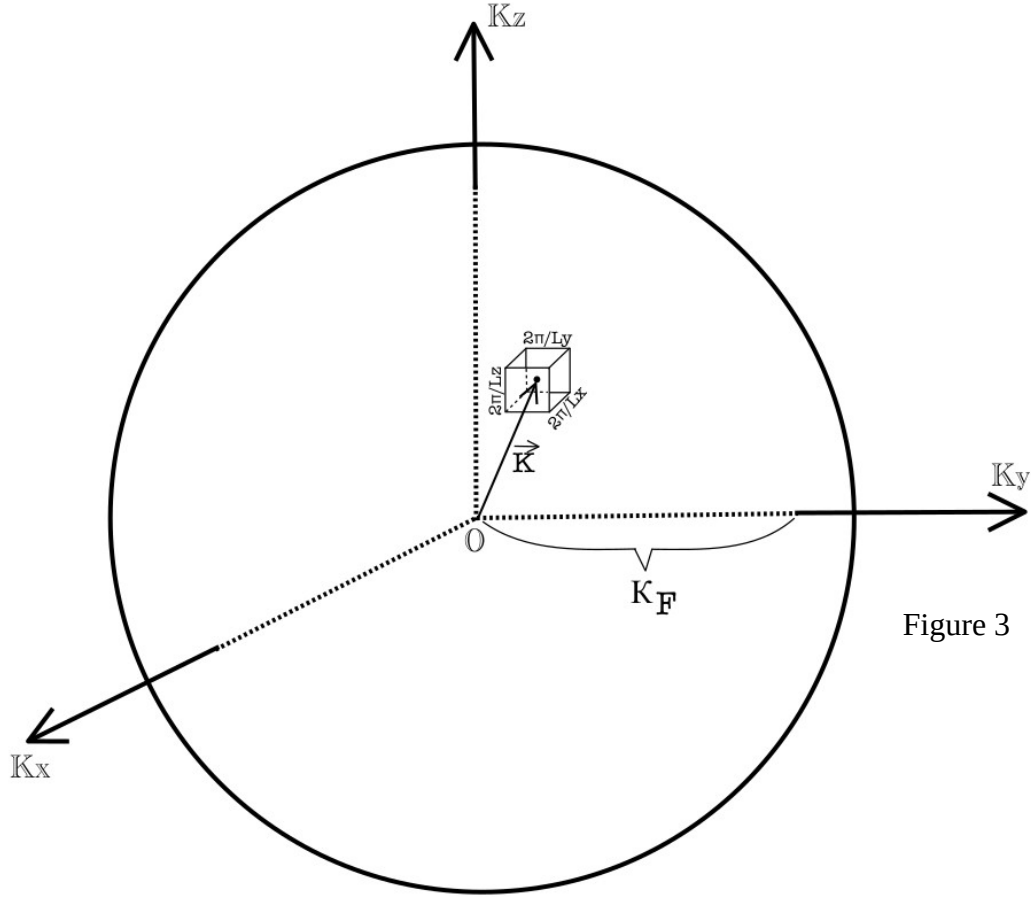

Figure 3

$$N_{states} = \frac{\frac{4\pi k_F^3}{3}}{\frac{(2\pi)^3}{V}} = \frac{k_F^3 V}{6\pi^2}, \text{so } k_F = \left(\frac{6\pi^2 N_{states}}{V}\right)^{\frac{1}{3}} \tag{18}$$

If total number of electrons is N then $N = 2 N_{states}$ and after substitution we have:
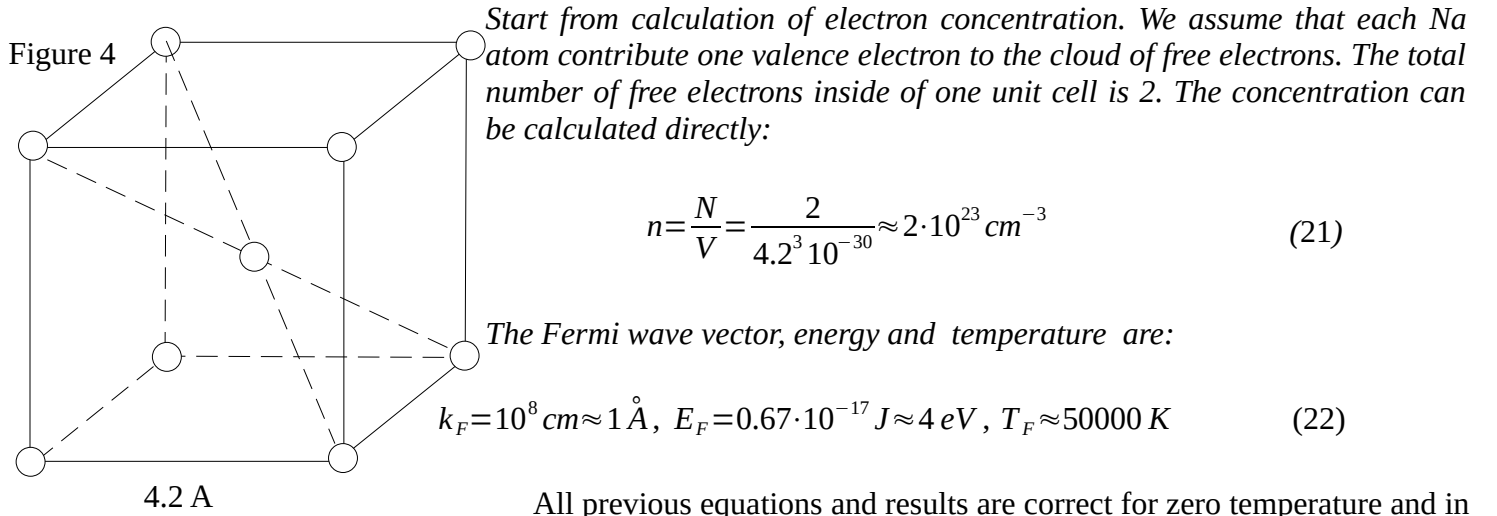
$$k_F = \left(\frac{3\pi^2 N}{V}\right)^{\frac{1}{3}} = (3\pi^2 n)^{\frac{1}{3}}, \text{ here } n = \frac{N}{V} \text{ - concentration of electrons} \tag{19}$$

The **Fermi energy** can be calculated directly:

$$E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2 (3\pi^2 n)^{\frac{2}{3}}}{2m} = \frac{(3\pi^2 \hbar^3)^{\frac{2}{3}}}{2m} n^{\frac{2}{3}} \tag{20}$$

The Fermi temperature $T_F = \dfrac{E_F}{k_B}$ can also be defined formally, the physical meaning is that this is the temperature that is required to excite all electrons not only located near Fermi level.

Example: *Let's calculate all these parameters for a sodium crystal (Na). The cubic unit cell of Na is looks like follows (Figure 4).*

Figure 4

Start from calculation of electron concentration. We assume that each Na atom contribute one valence electron to the cloud of free electrons. The total number of free electrons inside of one unit cell is 2. The concentration can be calculated directly:

$$n = \frac{N}{V} = \frac{2}{4.2^3 \, 10^{-30}} \approx 2 \cdot 10^{23} \, cm^{-3} \tag{21}$$

The Fermi wave vector, energy and temperature are:

$$k_F = 10^8 \, cm \approx 1 \, \mathring{A}, \ E_F = 0.67 \cdot 10^{-17} \, J \approx 4 \, eV, \ T_F \approx 50000 \, K \tag{22}$$

4.2 A

All previous equations and results are correct for zero temperature and in this case electrons occupied energy levels in the range $[0...E_F]$. But what happened if temperature of crystal is greater than zero. It is clear that in this case free electrons occupied all possible energy levels from 0 to ∞.

The probability of filling energy levels can be calculated from Fermi-Dirac distribution function:

$$f(E_{k_x,k_y,k_z},T) = \frac{1}{e^{\frac{E_{k_x,k_y,k_z} - \mu}{k_B T}} + 1} \tag{23}$$

Here μ – chemical potential (the chemical potential of a substance is the energy that can be absorbed or released due to a change in the number of particles of a given substance, for example, in a chemical reaction or phase transition. It is the energy of adding or removing one particle to a system without doing work) and $\{k_x, k_y, k_z\}$- a set of three quantum numbers numbering different states (16). To visualize this function is make sense to use dimensionless energy E/E_F and temperature T/T_F. The visualization result for different temperatures is shown in Figure 5.

Total number of electrons can be calculated by this way. The summation is carried out over all possible states.

$$\sum_{k_x,k_y,k_z} f(E_{k_x,k_y,k_z},T) = N_{state} \tag{24}$$

This equation determine the chemical potential **μ** as function of electrons concentration and temperature.

Let's define the useful function - density of states as ratio of the number of allowed states in range of energies from E to dE:

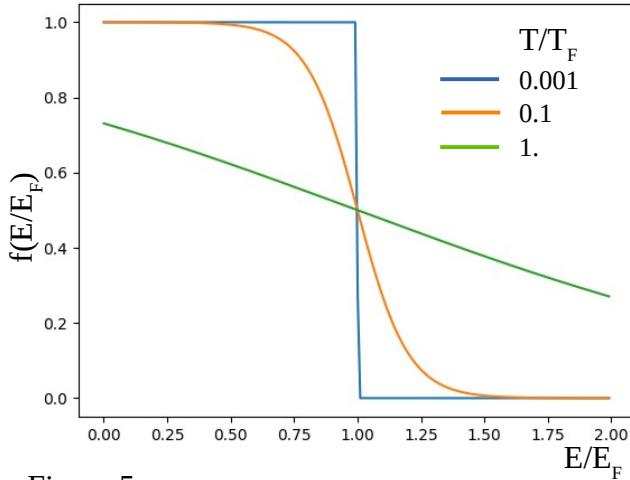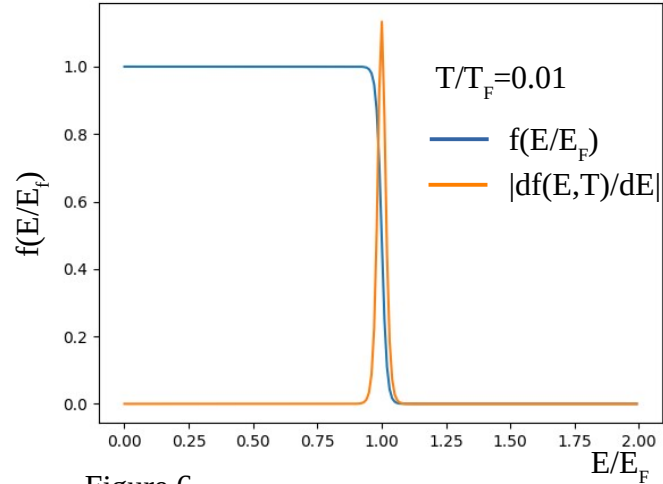$$g(E) = \frac{dN_{states}}{dE} \tag{25}$$

Figure 5

Figure 6

Using (20) and taken into account Pauli principle we have:

$$g(E) = \frac{\sqrt{2}}{2\pi^2} \frac{m^{3/2}}{\hbar^3} V \sqrt{E} = G(E) \cdot V \tag{26}$$

Thus the number of electrons for zero temperature can be calculated so:

$$n = 2 \cdot \int_o^{E_F} G(E) dE \quad \text{and total energy} \quad E_{tot} = 2 \int_0^{E_F} E \cdot G(E) dE = \frac{3h^2}{40m} \left(\frac{3}{\pi}\right)^{\frac{2}{3}} n^{\frac{5}{3}} \quad \text{or} \quad E_{tot} = C_{kin} n^{\frac{5}{3}} \tag{27}$$

And for non zero temperature we need to take into the account the distribution of electrons over all states (energy levels) from 0 to ∞ :

$$n = 2 \cdot \int_o^{\infty} G(E) f(E,T) dE \tag{28}$$

This integral can be calculated by parts and to simplify the calculation let's apply the next substitution $G(E) = \frac{\sqrt{2}}{2\pi^2} \frac{m^{3/2}}{\hbar^3} \sqrt{E} = \alpha \sqrt{(E)}$:

$$\alpha \int_0^{\infty} f(E,T) E^{\frac{1}{2}} dE = \frac{2\alpha}{3} E^{3/2} f(E,T) \big|_0^{\infty} - \frac{2\alpha}{3} \int_0^{\infty} E^{3/2} \frac{df(E,T)}{dE} dE \tag{29}$$

The first member is equal to zero. This give the next expression to calculate concentration:

$$n = 2 \int_0^\infty f(E,T) G(E) dE = \frac{4\alpha}{3} \int_0^\infty E^{3/2} \frac{df(E,T)}{dE} dE \tag{30}$$

The behavior of the derivative of the Fermi-Dirac function on temperature is shown in Fig. 6. For low temperatures, it looks like a delta function $\delta(E-\mu)$. If we take this into account and substitute the electron concentration in (26), then we get:

$$n = \frac{(2m)^{\frac{3}{2}}}{2\pi^2 \hbar^3} \mu^{3/2} \quad \text{and chemical potential is} \quad \mu = \frac{(2\pi\hbar)^2}{2m} \left(\frac{3n}{8\pi}\right)^{2/3} \tag{31}$$

If compare the last expression with (20) we see that are equal. It means that for low temperature we can use the next approximation $\mu = E_F$. But actually the chemical potential depend on temperature. This dependence is very weak and for relatively low temperature is looks like this:

$$\mu(T) = E_F \left[1 - \frac{\pi^2}{12} \cdot \left(\frac{T}{T_F}\right)^2\right] \tag{32}$$

For real metals (material with large number of free electrons) T_F is several tens of thousands degrees. This means that the approximation $\mu = E_F$ works well for the room temperature in free electron model.

Interesting question about the heat capacity of metals. As we know a metals consist from two subsystems, very light electrons and heavy nuclei. From point of view of classical physics the average heat kinetic energy of free electrons is equal to his total energy and can be calculated by this way $E_{tot} = E_{kin} = \frac{3}{2}kT$. The potential energy can be neglected (free electrons are non-interacting particles). For one heavy nuclei by the same way $\bar{E}_{tot} = \bar{E}_{kin} + \bar{E}_{pot} = \frac{3}{2}kT + \frac{3}{2}kT = 3kT$ due to average kinetic and potential energies are equal. If we assume that number of nuclei and free electrons are equal N the total internal energy of metals is: $E_{tot} = 4.5 kT N$. The heat-capacity for constant volume of crystal can be calculated so: $C_v = \frac{d\bar{E}}{dT} = 4.5 k_B N$. For one mole of matter N=N$_A$ then $C_v = \frac{d\bar{E}}{dT} = 4.5 k_B N_A = 4.5 R$ but experiment gives $C_v = 3R$. Why? It seems that the electrons for some reason do not contribute to the total energy of the crystal.

Let's calculate the heat capacity of free electrons to explain this paradox. This approximation working well for good metals. Let's start from calculation of total energy of free electrons. For non zero temperature it can be done so:

$$E = 2 \int_0^\infty E \cdot G(E) \cdot f(E,T) dE \tag{33}$$

This expression can be a little bit modified, actually we need to calculate the next integral:

$$E = 2 \int_0^\infty (E - E_F) \cdot G(E) \cdot f(E,T) dE \tag{34}$$

This substitution can be done because:

$$\int_0^\infty (E-E_F)\cdot G(E)\cdot f(E,T)dE=\int_0^\infty E\cdot G(E)\cdot f(E,T)dE-E_F\int_0^\infty G(E)\cdot f(E,T)dE=\int_0^\infty E\cdot G(E)\cdot f(E,T)dE-E_F n$$

If $C_v=\dfrac{d\bar{E}}{dT}$ then last member do not give contribution to C_V due to derivative with respect to T is equal to zero:

$$C_V=2\int_0^\infty (E-E_f)G(E)\frac{df(E,T)}{dT}dE \tag{35}$$

Here $\dfrac{df(E,T)}{dE}=\dfrac{(E-E_f)}{kT^2}\cdot\dfrac{e^{\frac{E-E_F}{kT}}}{\left(e^{\frac{E-E_F}{kT}}+1\right)^2}$. After replacement we will have:

$$C_V=\int_0^\infty G(E)\frac{(E-E_F)^2}{kT^2}\cdot\frac{e^{\frac{E-E_F}{kT}}}{\left(e^{\frac{E-E_F}{kT}}+1\right)^2}dE,$$ and substitution $x=\dfrac{E-E_F}{kT}$ gives $C_v=k\displaystyle\int_{-\frac{E_F}{kT}}^\infty G(E)\frac{x^2 e^x}{(e^x+1)^2}dx$. For

T<<T_F the derivative $\dfrac{df(E,T)}{dT}\approx\delta(E-E_F)$ and the down limit of integral $\dfrac{E_F}{kT}=\dfrac{T_F}{T}\approx+\infty$. So finally

$$C_v=k\,G(E_F)\int_{-\infty}^\infty \frac{x^2 e^x}{(e^x+1)^2}dx=\frac{\pi^3}{2}kN\frac{T}{T_F}$$ for one mole $N=N_A$ and then $C_V=\dfrac{\pi^3}{2}R\dfrac{T}{T_F}$.

For real metals T << T_F, this means that in fact, the contribution of free electrons to the total metal heat capacity can be neglected. The physical explanation of this paradox is simple. The Fermi temperature indicates to what temperature the metal must be heated in order to disturb all electrons with energies from 0 to E_F. This temperature is quite high and above the melting point of any metal. This means that at room temperature we can change the energy of electrons near the Fermi level. This is only few percentage from total number of free electrons. All other electrons are inactive, their energy cannot be changed. They do not affect the total heat capacity, since they just cannot absorb thermal energy.

Some conclusions from obtained results:

1. The free electron gas approach is working well for system with large number of free electrons for example for metals.
2. The number of "active" electrons (which can change their energy and thereby contribute to the heat capacity and to the creation of electric current) is a little. Not more than a few percentage from the total number of free electrons.
3. For real metals, the low-temperature approach is applicable, since the Fermi temperature is much higher than the melting point of most metals.
4. Important emphasize that Fermi energy and chemical potential is not the same parameter although sometime they are can be equal.