**§5.6 Transport phenomena.**

**§ 5.6.1 Classic approach.**

The classical equation for density of current is:

$$j = q \cdot n \cdot v = \sigma E \quad \text{or in matrix form} \quad j_\alpha = \sigma_{\alpha,\beta} E_\beta \qquad (1)$$

Here q-charge of the carrier of current , n-concentration of carriers, v-mobility of carriers, σ-conductivity tensor of a material. Resistance can be calculated using the well-known equation:

$$R = \rho \frac{l}{S}, \text{here } \rho = 1/\sigma - \text{resistivity} \qquad (2)$$

From the point of view of classical physics, resistance is associated with the collision of free electrons with atoms of the crystal lattice moreover, this effect takes place at any temperature include zero temperature. The elementary consideration gives the classical formula for conductivity:

$$\sigma = \frac{q^2 \tau n}{m}, \quad \text{and} \quad \rho = \frac{m}{q^2 \tau n} \qquad (3)$$

here τ- average time between two successive collisions of electron with atoms.
Only two parameters can be temperature dependent **n** and **τ**. Concentration of conduction electrons **n** practically is constant in metals. The parameter **τ**, associated with collisions of electrons with atoms, has such a dependence due to an increase in the amplitude of thermal vibrations of atoms with increasing temperature. This time can be calculated as the ratio of the minimum distance between atoms and mean thermal velocity of atoms to the.

$$\tau = \frac{a}{\sqrt{\langle v^2 \rangle}} \qquad (4)$$



Figure 26
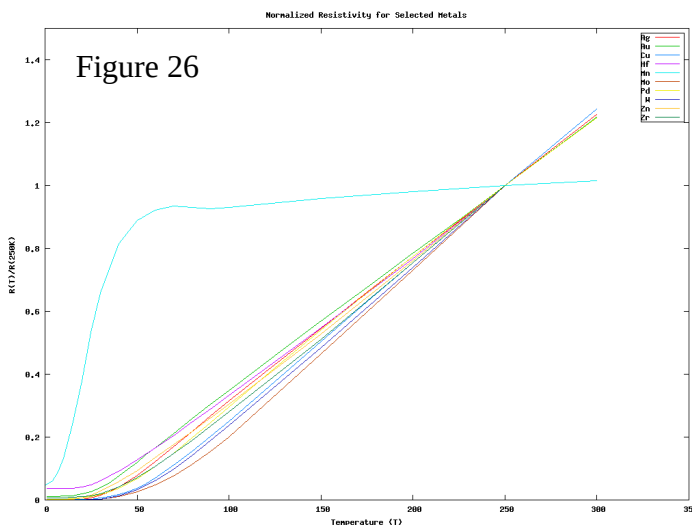
$\sqrt{\langle v^2 \rangle}$ root mean square velocity which proportional to $\sqrt{T}$ . The mean free path in the classical approach should be equal to the period of the crystal lattice (the minimum distance between atoms). This give the following dependence of resistivity on temperature:

$$\rho \propto \sqrt{T} \quad . \qquad (5)$$

But experiment show the linear dependence for a relatively high temperature (above 100k) see Figure 26. Horizontal section for temperatures below 50K related to scattering on defects of crystal lattice. This means that classical physics do not have a satisfactory explanation of this phenomena. Moreover, the resistance of semiconductors has an inverse relationship between resistance and temperature.

### § 5.6.2.1 Quantum mechanics approach for metals.

The more sequential approach is looks like so. Use the distribution function for electric current carriers. The physical meaning of it is a number of particles inside of volume $dV = d^3 r = dx\,dy\,dz$

$$dN = f(\vec{r},\vec{r},t)d^3 v\,d^3 r \tag{6}$$

and having the velocities in the range

$$[v_x, v_x + dv_x][v_y, v_y + dv_y][v_z, v_z + dv_z] \tag{7}$$

The distribution function can be represented as the sum of the equilibrium $\mathbf{f_0}$ and non-equilibrium $\mathbf{f_1}$ terms. The second term arises due to external influence. In the general case, the equilibrium part of the distribution function depends on the total energy of the system (a time-independent parameter), while the non-equilibrium part depends separately on coordinates, velocity, and time.

$$f(\vec{r},\vec{v},t) = f_0(E) + f_1(\vec{r},\vec{v},t) \tag{8}$$

Distribution function can be used to calculate density of current by this way:

$$j_x = \int_{-\infty}^{+\infty} v_x f(\vec{r},\vec{v},t)d^3 v \tag{9}$$

It is clear that current density associated to nonequilibrium part of distribution function:

$$j_x = \int_{-\infty}^{+\infty} v_x f(\vec{r},\vec{v},t)d^3 v = \int_{-\infty}^{+\infty} v_x f_0(\vec{r},\vec{v},t)d^3 v + \int_{-\infty}^{+\infty} v_x f_1(\vec{r},\vec{v},t)d^3 v \tag{10}$$

Due to the fact that equilibrium distribution function is even the first integral should be erual to zero. It means that to calculate the current density we must find the nonequilibrium part of distribution function.

For stationary states the number of particles incoming and outcoming from the some volume is equal. It is means that the corresponding derivative of distribution function on time must be equal to zero. The total derivative on time can be calculated by this way:

$$\frac{df}{dt} = \frac{df}{dx}\frac{dx}{dt} + \frac{df}{dv}\frac{dv}{dt} + \frac{\partial f}{\partial t} = \vec{v}\nabla_r f + \frac{\vec{F}}{m}\nabla_v f + \frac{\partial f}{\partial t} = 0 \quad \text{or} \quad \vec{v}\nabla_r f + \frac{\vec{F}}{m}\nabla_v f = -\frac{\partial f}{\partial t} \tag{11}$$

This is a so called Boltzmann kinetic equation to find the distribution function. The left side of equation contains the field terms and right side associated with scattering processes on obstacles and can be represented as follows:

$$\left(\frac{\partial f}{\partial t}\right)_v = \int_v \{f(v')w(v',v) - f(v)w(v,v')\}d^3 v' \tag{12}$$

here w(v,v')- is probability to change the velocity of electron from v to v' due to scattering on any obstacles. Finally the kinetic equation is follows:

$$\vec{v}\hat{\nabla}_r f + \frac{1}{m}\vec{F}\,\hat{\nabla}_v f = \int \{f(v',r,t)W(v',v) - f(v,r,t)W(v,v')\}\,d^3v' \tag{13}$$

To determine the function **f**, it is necessary to know the external force **F** and the scattering probability **W(v,v')**.

Let's start from metals. Metals is a good conductor due to large number of free electrons. For example in sodium this number id around $10^{21}cm^{-3}$. But do not forget that for room temperature, the real number of active free electrons is about 1% of their total number.

Electric current arises in metals under the influence of an external electric field, this means that this is a non-equilibrium phenomenon. An external electric field redistributes electrons in energy, change the distribution function. In the general case, for the equilibrium state, the electron distribution function (for high temperature) has the following form:

$$f_0(E) \sim e^{\frac{\mu - E}{kT}}, \text{ here } E = \frac{mv^2}{2} + U_{pot} \text{ - total energy and } \mu \text{ -chemical potential} \tag{14}$$

Substitution of equilibrium distribution function to (13) and after a little simplification: $\vec{v}\hat{\nabla}_r f(E) = \frac{1}{kT}(\vec{v}\vec{F})$

and $\frac{1}{m}\vec{F}\hat{\nabla}_v f = -\frac{1}{kT}(\vec{v}\vec{F})$ we get:

$$f_0 \int \{W(v',v) - W(v,v')\}\,d^3v' = 0 \tag{15}$$

But it is possible only if $W(v',v) = W(v,v')$ it means that direct and inverse processes of scattering have the same probability (the principle of microbalance). The derivative for collision term (10) for the elastic collision approximation is looks like this [3]:

$$\left(\frac{df}{dt}\right)_{scatt} = -f_1 \int W(\theta)(1 - \cos(\theta))\,d\Omega \tag{16}$$

here $f_1$ non-equilibrium part of the distribution function (13), θ - angle of collision, dΩ - solid angle (Figure 1a ). The unit of the integral is the inverse second, which means that a new parameter can be defined as relaxation time:

$$\frac{1}{\tau} = \int W(\theta)(1 - \cos(\theta))\,d\Omega \tag{17}$$

The relaxation time multiplied by the average electron velocity gives the well-known parameter - the mean free path length. After substitution (17) to (16) we have :

$$\left(\frac{df}{dt}\right)_{coll} = -\frac{f_1}{\tau} = -\frac{f - f_0}{\tau} \tag{18}$$

If we assume that external force F=0 so:

$$\frac{df}{dt} = -\frac{f - f_0}{\tau} \tag{19}$$

after integration we have:

$$(f - f_0) = (f - f_0)_{t=0}\,e^{-t/\tau} \tag{20}$$

This expression shows that after switching off the disturbing external force (external electric field for example), the system tends exponentially to the equilibrium state and during the relaxation time these disturbances decrease by a factor of e.

For practical appreciated cases $f_0 \gg f_1$ (weak external influence) this means that sometimes we can exchange $f \to f_0$. If on electrons acting only electric field along x axis ($F_x$=qE and in (97) $U_{pot}$=0) from (11) , (16) and (6) we gets:

$$f_1 = -qE \frac{f_0}{kT} \tau v_x \tag{21}$$

and density of current can be calculated by using formula (9).

$$j_x = \left( \frac{q^2}{kT} \int \tau(v,T) v_x e^{\frac{(\mu - mv^2/2)}{kT}} dv^3 \right) E = \sigma E \tag{22}$$

here $\sigma = \frac{q^2}{kT} \int \tau(v,T) v_x e^{\frac{(\mu - mv^2/2)}{kT}} dv^3$ can be interpreted as conductivity of material. More general expression for conductivity tensor looks like following [see 3]:

$$\sigma_{\alpha,\beta} = -\frac{q^2 m^3}{4\pi^3 \hbar^3} \int \tau(v) \frac{df_0}{dE} v_\alpha v_\beta d^3 v \quad \text{and Ohm law} \quad j_{\alpha,\beta} = \sum_\beta \sigma_{\alpha,\beta} E_\beta \tag{23}$$

As you can see the conductive properties depends on mechanism of carriers scattering determined by relaxation time τ(v,T). From the point of view of classical physics, for an ideal crystal at zero temperature is possible to electrons scattering by stationary atoms located at lattice sites.

But from the point of view of quantum mechanics, the situation is different. If we have a defect-free (ideal, periodic and infinity) lattice at zero temperature, scattering of electrons is possible only by immobile atoms. For this ideal periodic lattice the electron wave function should be represented in Bloch function form:

$$\varphi(\vec{r}) = u(\vec{r}) e^{i\vec{k}\vec{r}} \tag{24}$$

here, $u(\vec{r}) = u(\vec{r} + \vec{R}_n)$ - periodic part of wave function. It is important to emphasize that in this case the crystal does not resist the movement of electrons. The resistance of such a material is zero, and it exhibits the property of superconductivity. Any destruction of this periodicity (lattice defects, vibrations of an atom, crystal surface) leads to the impossibility of representing the wave function of an electron in the Bloch form and to appearance of electric resistance. In an ideal crystal, the electron as if in resonance with the lattice.

Let's try to calculate the relaxation time (14) in some simple cases. There is different mechanisms of electrons scattering (scattering on impurities, on disorders of lattice, on phonons and on surface), and the relaxation time for each case should be calculated separately and can be summated by Matthiessen rule:
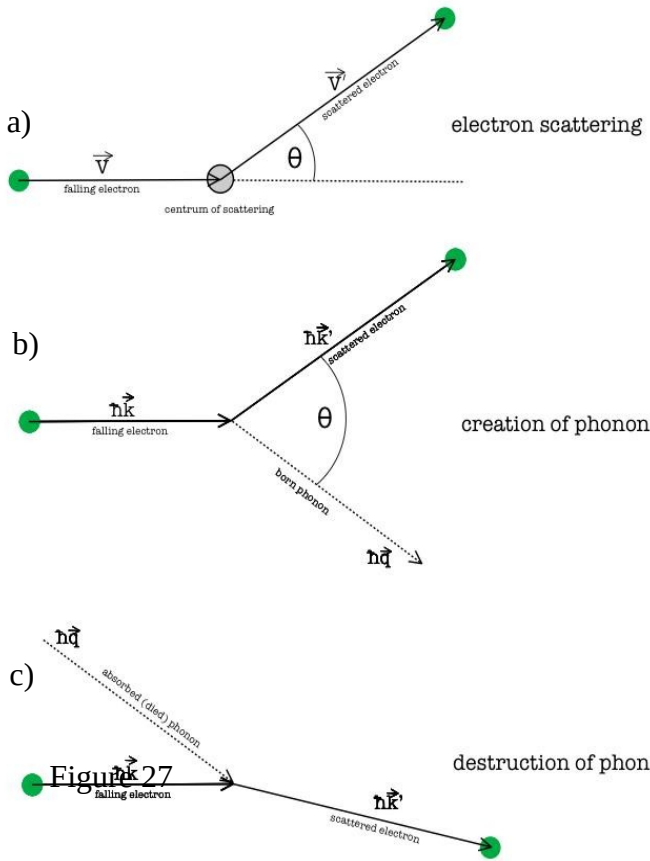
$$\frac{1}{\tau} = \frac{1}{\tau_{impurity}} + \frac{1}{\tau_{disorder}} + \frac{1}{\tau_{vibrations}} + \dots \tag{25}$$

We consider only the interactions of electrons with **phonons**. The scattering electron by an atom leads to the appearance of crystal vibrations or phonons with momentum $\hbar\vec{q}$ and energy $\hbar\omega$ . Remember that each phonon is associated with a corresponding harmonic wave in the crystal or (it is the same) with a corresponding harmonic oscillator. The collision of an electron with an atom creates a phonon or, in other words, excites a harmonic wave (harmonic oscillator) propagating along the crystal (see Figure 27b). The energy of corresponding harmonic oscillator in quantum mechanics calculating by the next formula:

$$E = \frac{\hbar\omega}{2}(2n+1), \text{here } n \in N \quad \text{can be interpreted as a number of created phonons.} \tag{26}$$

The quantum mechanical calculation for probability the scattering of electron on phonon-**W** see formula (11) gives (see [3]):

$$W^+ = w(q) N_q \cdot \delta(E_{k+q} - E_k - \hbar\omega_q)$$
$$W^- = w(q)(N_q + 1) \cdot \delta(E_{k-q} - E_k - \hbar\omega_q), \text{here } w(q) = \frac{4\pi}{9N} \frac{Cq^2}{M\omega_q} \tag{27}$$

a)



electron scattering

b)



creation of phonon

c)



destruction of phonon

Figure 27



Figure 27d

**N**-number of atoms, $N_q$ - number of phonons with wave vector **q**, $\omega_q$ - frequency of this phonon, **k,k'**-wave vector of electron before and after scattering. Here considered two process: first ($W^+$) — creation of phonon due to collision of electron with atom and second-($W^-$) absorption of phonon by electron (Figure 27b,27c).

But for phonons everything is not so simple. We needs to consider the acoustic and optical phonons separately.

For metals, we only have acoustic phonons (oscillations). The number of corresponding phonons can be calculated using the Bose-Einstein distribution function:

$$N_q(T) = \frac{1}{e^{\frac{hv}{kT}} - 1} \qquad (28)$$

The dependence of the frequency of acoustic phonons on the wave vector **q** looks like L3/Figure 3. The maximal characteristic frequency for metals is around 1THz. The corresponding dependence (25) from temperature is presented on Figure 27d. In high-temperature region this dependence is linear and have good agreement with experimental data.

It is clear that the basis contribution to the temperature dependence of materials gives low frequency phonons, $q \approx 0$ region on L3/Figure 3.
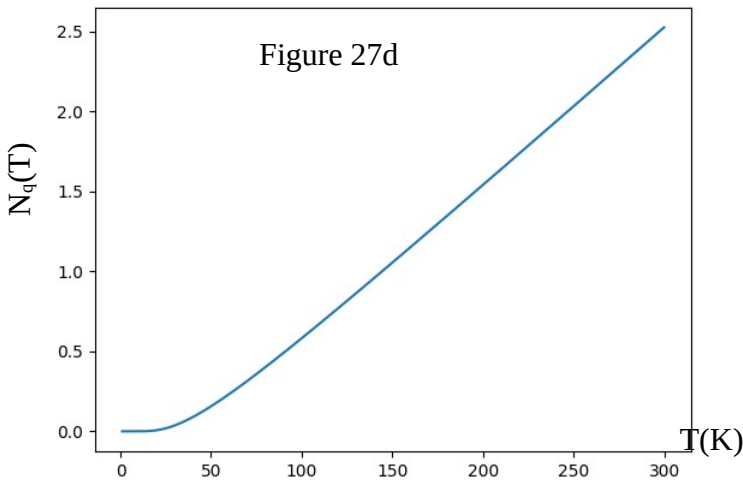
### §5.6.2.2 Some explanations about the electron distribution function.

**1.** For free electrons at low temperature the corresponding distribution function is (so called Fermi-Dirac function):

$$f(E,T)=\frac{1}{e^{\frac{E-\mu}{kT}}+1} \tag{29}$$

For electron concentration we have:

$$n=2\int G(E)f(E,T)dE \tag{30}$$

Here G(E) - density of state function **L 5.1.** This equation can be used to calculate chemical potential and after some simplifications :

$$\mu=E_F\left(1-\frac{\pi^2}{12}\left(\frac{kT}{E_F}\right)^2\right) \tag{31}$$

Important to emphasize that chemical potential in this case is practically equal to Fermi energy and at zero temperature we need to take into account quantum properties of electrons (Pauli excluding principles).

## 2. Classical approach

Fermi energy is proportional to concentration of free electrons $\sim n^{2/3}$. At a low concentration of free carriers (it applies to semiconductors), the $E_F$ should shift to the region of low energies. For high temperature $T>>T_F$, (this option is applicable in this case due to small Fermi energy in compare with energy of free electrons in semiconductors) function (29) can be simplified by using this facts. The unit can be neglected then:

$$f(E,T)=e^{\frac{\mu}{kT}}e^{-\frac{E}{kT}}=Ae^{-\frac{E}{kT}} \text{ here } A=e^{\frac{\mu}{kT}}-\text{normalizing parameter.} \tag{32}$$

The parameters A and μ could be found from formulas (30). The corresponding integral can be calculated analytically:

$$n=\int_o^{+\infty} G(E)A\,e^{-\frac{E}{kT}}dE=\frac{\left(2\pi m^*kT\right)^{\frac{3}{2}}}{4\pi^3\hbar^3}A \tag{33}$$

and

$$\mu(T)=kT\ln\left(\frac{4\pi^3\hbar^3 n}{\left(2\pi m^*kT\right)^{\frac{3}{2}}}\right) \tag{34}$$

The strong dependence of the chemical potential on temperature is related to the strong temperature dependence of the concentration of free electrons. The distribution function in this approximation is:

$$f(E,T)=\left(\frac{4\pi^3\hbar^3 n}{\left(2\pi m^*kT\right)^{\frac{3}{2}}}\right)e^{-\frac{E}{kT}} \tag{35}$$

This function is a classical Boltzmann distribution function for atoms of gases. This function is the classical Boltzmann distribution function for atoms of classical gases. This function does not include quantum effects and is applicable to classical particles. From the point of view of physics, this result is natural because for low concentration and high temperature electrons practically not interacting.

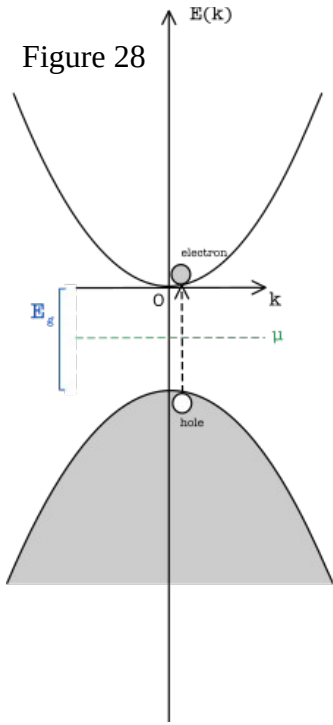### §5.6.2.3 Quantum mechanics approach for semiconductors.



Figure 28

The difference between metals and semiconductors lies in the distribution of electrons over the band structure. Unlike metals, semiconductors have at least two energy bands. The lower (valence) band is completely filled, and the upper (conducting) band is not filled at zero temperature; a band gap is located between these bands (Figure 28). The energy of electron in conduction zone and hole in valence zone is:

$$E_e = \frac{\hbar^2 k^2}{2 m_e}, E_p = -E_g - \frac{\hbar^2 k^2}{2 m_p} \tag{36}$$

Zero energy is at the minimum of the conductive zone. The distribution function for electrons is a standard Fermi-Dirac function.

$$f_e = \frac{1}{e^{\frac{E_e - \mu}{kT}} + 1} \tag{37}$$

For holes the analogical function can be calculated as following:

$$f_p = 1 - f_e = \frac{1}{e^{\frac{\mu - E_p}{kT}} + 1} = \frac{1}{e^{\frac{\mu + E_g + \frac{\hbar^2 k^2}{2 m_p}}{kT}} + 1} = \frac{1}{e^{\frac{\hbar^2 k^2}{2 m_e} - \mu} + 1} \tag{38}$$

The chemical potential can be calculated from condition of electrical neutrality of intrinsic semi-conductor. Number of electrons in conducting zone and holes in valence zone must be the same.

$$\int_{\text{over conducting zone}} 2g(e) f_e(E_e, T) dE = \int_{\text{over valence zone}} 2g(e) f_p(E_p, T) dE \tag{39}$$

The calculation of chemical potential gives:

$$\mu = -\frac{E_g}{2} + \frac{3}{4} kT \ln(m_p^* / m_e^*) \tag{40}$$

I want to remind once more time that Fermi level and chemical potential do not coincided for semiconductors. Fermi level located on the most upper occupied level of valence zone at zero temperature. Instead of real mass we need to use effective masses of electron and hole. If $m_e^* = m_p^*$ the chemical potential in intrinsic semiconductor (the concentrations of electrons and holes are equal) is located in the center of the band gap $\mu = E_g/2$. On Figure 29 you can see the distribution function for different temperatures. The concentration of electrons in conduction zone and holes in valence zone (for intrinsic semiconductor of course) are equal and in classical limit (high temperature and low concentration of carriers):

$$n = \frac{(2 \pi \sqrt{m_p m_e} kT)^{3/2}}{4 \pi^3 \hbar^3} e^{-\frac{E_g}{2kT}} = n_0 e^{-\frac{E_g}{2kT}} \tag{41}$$
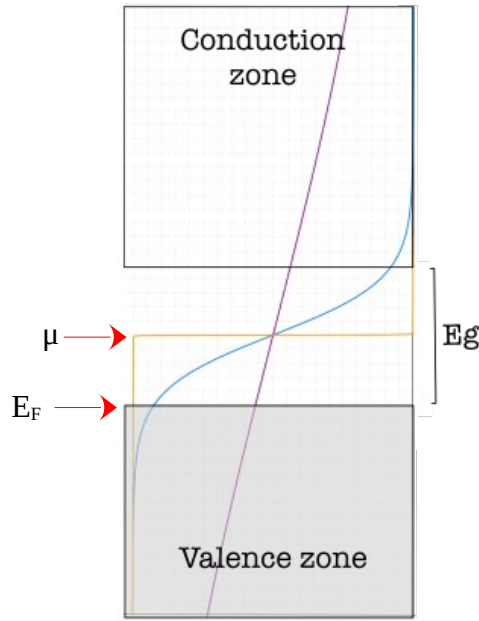
Figure 29

To explain the dependence of the resistivity of a semi-conductor on temperature, one can use the classical expression :

$$\rho(T)=\frac{m}{e^2 \tau(T)n(T)} \qquad (42)$$

The relaxation time τ (T) depends on temperature due to the same scattering processes as in metals and gives a linear dependence of resistivity on temperature. But for semiconductors there is one more phenomenon that gives an additional dependence on temperature - this is the concentration of carriers. The τ(T) decreases and n (T) increases exponentially with temperature. On Figure 30 represented the dependence of Si resistivity on temperature. The linear (metal like)dependence can be neglected so for semiconductor we have the next expressions:

$$\rho(T)=\rho_0 e^{\frac{E_g}{2kT}} \quad \text{or} \quad \ln(\rho(x))=\ln\rho_0+\frac{E_g}{2k}x, \text{here x=1/T} \qquad (43)$$

Calculation Eg using (123) and results taken from Figure 30 gives 1.14eV
(experimental data 1.1 eV ).
NB! *The effects associated with scattering (and the linear dependence of resistivity on temperature) can be neglected because the exponential function changes faster than any linear function.*


Figure 30