

Introduction to Statistical- and Solid-State Physics

Let us start this lecture with the overview of equilibrium distribution functions.

We have a system with different energy levels that can be occupied with different number of particles. The energies of the energy levels are E_i , and the number of particles on each level N_i .

The total energy E and the number of particles are fixed.

We are distinguishing between a macrostate and a microstate. The macrostate is the description of the state that relies on the macroscopic properties of the system. Macrostate is in general defined by the number of the particles on each energy state. These numbers are described by a distribution function.

The equilibrium distribution function describes the macrostate of the system if it is in the thermodynamic equilibrium. If the system is in equilibrium, we have a specific distribution of the particles across the energy levels. The equilibrium macrostate is stationary; it does not change with time if the system is isolated from its environment.

Microstate is defined by the states of each element of the system, this means by states of every particle. Many microstates can correspond to one macrostate. For instance, if the particles can be distinguished as we can distinguish colorful balls (every ball has different color), we can realize one distribution of the balls across the “energy” levels - i.e. one macrostate - in many different ways. For the derivation of the distribution function, the number of possible realization of one macrostate is of importance.

If we know the number of the realizations of one macrostate M , we can calculate the entropy of the system as $\ln(M)$. The macrostate with minimal entropy is the equilibrium macrostate, and the “distribution” function that defines the number of particles across E_i is in this case the equilibrium distribution function.

There are three equilibrium distribution functions of interest 1) Maxwell-Boltzmann- 2) Bose-Einstein- and 3) Fermi-Dirac-distribution function. These functions define the corresponding distributions of the particles across energy levels.

What is the difference between these distributions?

Maxwell-Boltzmann Distribution

In the case of Maxwell-Boltzmann-distribution, we assume that the particles can be distinguished between each other, as we can distinguish colorful balls (every ball has different color). This is shown in Fig 1.

Let us assume that every energy level has k states that can be occupied by the particles. In our picture k is equal two.

One macrostate is defined by a distribution function, or by the number of particles in every state. The state energy is E_i and the number of particles in one state is N_i . The total energy E and the number of particles N are constant.

We can calculate the number of realizations for one macrostate as follows: If we have N distinguishable particles, and if we sort out N_0 particles to “place” them on the lowest energy state, we can do this in m_0 different ways:

$$m_0 = \frac{N!}{(N - N_0)!N_0!}.$$

We used the formula for the combinations without repetition.

If we distribute these m_0 particles to k states of the lowest energy, this can be done in m_0' ways, where:

$$m_0' = k^{N_0} = 2^{N_0}.$$

(Every particle can be distributed in k ways.)

Further we would sort out N_1 particles from the remaining $N - N_0$, and so on, until we fill all the energy levels (in our example 0-3). The total number of the ways we can do such a particle distribution is the product of m_i' -s for all every levels:

$$M = m_0 = \frac{N!}{(N - N_0)!N_0!} k^{N_0} + \frac{(N - N_0)!}{(N - N_0 - N_1)!N_1!} k^{N_1} + \dots = N! \prod_{i=0}^3 \frac{k^{N_i}}{N_i!}. (\text{hey!!!}) \quad (1)$$

The entropy of the system is given by:

$$S = \ln(M).$$

Additionally, we have the boundary conditions:

$$\sum_{i=0}^3 E_i N_i = E, \quad \sum_{i=0}^3 N_i = N. \quad (2)$$

The equilibrium distribution function can be calculated from the minimum entropy condition

$$\delta S = 0, \quad (3)$$

under the consideration of the boundary conditions, given by Eq 2.

It can be obtained that Eq 3 holds for the following distribution:

$$N_i = N_0 \times e^{-E_i / kT}, \quad (4)$$

K is the Boltzmann constant and T the absolute temperature. Eq 4 is the Maxwell-Boltzmann distribution. Constant N_0 (equal to the number of particles in the ground energy level if $E_0 = 0$) and temperature T can be determined from the boundary conditions Eq 2.

Bose-Einstein Distribution

Bose-Einstein distribution can be calculated in similar way. This is illustrated in Fig 2.

We assume here that every state can be occupied by arbitrary number of particles. The particles are indistinguishable.

These are the properties of Bosons.

Since small items like balls can always be distinguished by some property, we will illustrate the Bose-Einstein particles occupying energy states as water in glasses. We can only say how many particles – i.e. how many water-atoms – are in one state (glass). We cannot distinguish the atoms.

We will repeat the same procedure as we had in the case of Maxwell-Boltzmann distribution, we will calculate the number of realization of one macrostate, which is defined by the number of particles N_i on each energy state E_i .

If we have N particles, or a glass with N water atoms, there is no more than one way to take N_0 atoms of water from it. If we now want to distribute N_0 atoms to k states (e.g. k states of the lowest energy), we could do this in m_0' ways:

$$m_0' = \frac{(N_0 + k - 1)!}{N_0! (k - 1)!}. \quad (5)$$

We used the following trick to obtain this formula: We imagined that the particles (water atoms) are lined above each other. Then we imagined that we have $k-1$ membranes (or similar things that can be “used” to separate the atoms into k groups) that are placed between the atoms. The atoms above one membrane are in one state, the atoms below in another state. We have in our system N_0+k-1 items – N_0 atoms and $k-1$ membranes. Eq 5 is the number of permutations of these N_0+k-1 items under the assumption that both the atoms and the membranes among themselves are indistinguishable.

The total number of the ways we can distribute the particles across all energy levels is the product of m_i' -s for all every levels:

$$M = \prod_{i=1}^3 \frac{(N_i + k - 1)!}{N_i! (k - 1)!}$$

As we proceeded above, the equilibrium distribution function can be calculated from the minimum entropy condition, under assumption of the boundary conditions for total number of particles and the total energy (Eq 2). As result, the Bose-Einstein distribution function is obtained:

$$N_i = \frac{1}{e^{(E_i - \mu)/kT} - 1} \cdot (6)$$

Temperature T and the potential energy μ (chemical potential) can be derived from the boundary conditions for total number of particles and the total energy (Eq 2). The difference $E_i - \mu$ must be positive.

Fermi-Dirac Distribution

For derivation of Fermi-Dirac distribution, we also assume that the particles are indistinguishable and that every energy level has k states.

We assume further that one state can be filled either with one particle or that it can be empty. It is not possible that more than one particle occupy one state. This is the way how Fermions behave.

We are calculating the number of microstates in the following way:

There is one way to take N_i particles (water atoms) out of glass of water.

Further, we want to distribute these N_i particles across k states. Due to the limitation – maximally one particle per state – we are not able to use the trick with the membranes and the atoms to derive the number of distribution-possibilities. However, the distribution-task equivalent to choosing of N_i states from a pool of k states. (Notice that $k \geq N_i$). We can do this in m_i' ways:

$$m_i' = \frac{k!}{(k - N_i)! N_i!} \cdot (7)$$

The last equation is the number of combinations without repetition.

The total number of the ways we can distribute the particles across all energy levels is the product of m_i' -s for all every levels:

$$M = \prod_{i=0}^3 \frac{k!}{(k - N_i)! N_i!}.$$

As we proceeded above, the equilibrium distribution function can be calculated from the minimum entropy condition, under assumption of the boundary conditions for total number of particles and the energy (Eq 2). As result the Fermi-Dirac distribution function is obtained:

$$N_i = \frac{1}{e^{(E_i - E_f)/kT} + 1} \cdot (8)$$

Temperature T and the potential energy E_f (Fermi energy) can be derived from the boundary conditions for total number of particles and the energy (Eq 2).

At T=0K, all energy levels $E_i \leq E_f$ are occupied by particles and all higher energy levels are empty.

Solid-State Physics (in part taken from Feynman's lectures on physics)

One could think that a low energy electron would have a great difficulty passing through a crystal. The atoms are large relative to their spacing and one would expect that the mean free path between collisions is of the order of Angstrom. However, if lattice is perfect the electrons are able to travel through the crystal smoothly and easily as if they were in vacuum [Feynman].

Imagine one dimensional system made of long line of atoms (ions). Every positive ion forms a potential well for electrons, though the Coulomb force. If the atoms are close enough, probability amplitude can leak from ion to ion, and the electrons can tunnel.

What are reasonable base states for electrons? Let us take as base states the states $|i\rangle$ with the corresponding wave functions that are confined in the area of every atom (ion) i . These states could correspond to the states of an electron in infinite potential wells, centered around ion i , and with energy E_0 . Clearly, such states are orthogonal (distinct), and they form a complete set of base states (?). Any state of electron $|\phi\rangle$ can be then described by giving all amplitudes:

$$c_i \equiv \langle i | \phi \rangle.$$

Therefore it holds:

$$|\phi\rangle = \sum_i |i\rangle c_i. \quad (1)$$

If electron is at one atom, there is a certain probability that it will jump to the atom on either side. $c_i(t)$ is the amplitude at a given moment t . The probability that we will find the electron if we looked at atom i at this time is given by $|c_i|^2$.

What will be the situation at some later time? We can calculate this starting from Schrödinger's equation:

$$i\hbar \frac{d}{dt} |\phi\rangle = \hat{H} |\phi\rangle. \quad (2)$$

If we substitute the representation Eq 1 into the Schrödinger's equation (Eq 2), and if we multiply the equation with $\langle n |$ we obtain:

$$i\hbar \frac{dc_n(t)}{dt} = \sum_i \langle n | \hat{H} | i \rangle c_i(t) \approx E_0 c_n(t) - A_0 c_{n+1}(t) - A_0 c_{n-1}(t), \quad (3)$$

with the real (?) coefficients:

$$A_0 = -\langle n | \hat{H} | n-1 \rangle = -\langle n | \hat{H} | n+1 \rangle = -\langle n-1 | \hat{H} | n \rangle = -\langle n+1 | \hat{H} | n \rangle.$$

E_0 is some discrete energy of the electron in a potential well around atom n . In this region, the Hamiltonian of the one dimensional crystal and the Hamiltonian of the potential well are similar. Therefore it holds: $\hat{H}|n\rangle \approx E_0|n\rangle$.

Since we are looking for stationary state $|\phi\rangle$ of defined energy E , the probabilities $|c_i|^2$ should be constant in time and the amplitudes have the form:

$$c_i(t) = a_i e^{(-\frac{iEt}{\hbar})}. \quad (4)$$

If we substitute Eq 4 into Eq 3, we obtain:

$$Ea_n = E_0a_n - A_0a_{n+1} - A_0a_{n-1}. \quad (5)$$

Let us define: $a_n \equiv a(x_n)$, where x_n is the position of atom n . The distance between atoms is b . Let us further try as the solution of Eq 5 the following function:

$$a_n \equiv a(x_n) = e^{(ikx_n)}. \quad (6)$$

It follows:

$$E = E_0 - 2A_0 \cos(kb). \quad (7)$$

We see that the energy is a continuous function of wave vector k . Since we assumed infinite number of base vectors, we obtain infinite number of states. The dispersion relation between the electron energy E and the wave vector k is shown in Fig 1. The energy can go from $E-2A$ to $E+2A$. We do not need to consider the wave vectors with the magnitude larger than π/b because they do not give new states, they just repeat the states we already have for smaller k -s. It holds: $a(k) = a(k + 2\pi/b)$.

We have taken as base states the states of the electrons in the potential wells, where the electron has energy E_0 . We can also take as base states the potential-well-states with a lower energy E_{-1} . Notice that the wave function that corresponds to the next energy level always has the opposite parity with respect to the one that corresponds to the previous level. As consequence of this, if $A_0 = -\langle n_0 + 1 | \hat{H} | n_0 \rangle$ that corresponds to energy level E_0 is positive, $A_{-1} = -\langle n_{-1} + 1 | \hat{H} | n_{-1} \rangle$ that corresponds to energy level E_{-1} will be negative. For the new set of base states that correspond to energy level E_{-1} , we will obtain the result similar to Eq 7:

$$E = E_{-1} - 2A_{-1} \cos(kb). \quad (8)$$

Depending on values E_0 , E_{-1} , A_0 and A_1 , we can have energy gap and energy bands. Further energy bands are also possible. The corresponding dispersion relations are shown in Fig 2.

Let us calculate now the number of available quantum states in the energy band around the base state energy E_0 . Let us assume that the one-dimensional crystal has a size L . The electron is localized within a space with dimension L . It can be shown that for every wave number k , the following condition should be fulfilled:

$$kL = 2\pi n .$$

n is integer. Therefore wave numbers k take only the discrete values:

$$k = 2\pi n / L .$$

The distance between these discrete values in k -space is:

$$\Delta k = 2\pi / L .$$

Hence the number of electron states within k -space line element dk is:

$$dk / \Delta k = \frac{dk}{2\pi / L} .$$

Since electrons are fermions, in each spatial state we can have no more than two electrons with different spins. The number of states (including spatial- and spin-states) in the energy band E_0 is therefore:

$$N = 2 \frac{\text{dim}(k - \text{space})}{\Delta k} = 2 \frac{2\pi / b}{2\pi / L} = 2N ,$$

with number of atoms N .

Suppose that in atoms when they are separated, the energy level E_0 was filled with only one electron. When we place the atoms close to each other, and form one-dimensional crystal, the energy band E_0 will be half filled. At $T=0K$ electrons will occupy the states with smallest energies. It is easy to notice (Fig 1) that the total energy of all electrons in the crystal will be smaller than it the sum of electron energies in the separated atoms, i.e. smaller than $N E_0$. We will therefore have a force that keeps the atoms together, since every system moves to the minimum energy configuration. We have chemical bonds. Note that in one-dimensional system, the band can be either half-filled re completely filled. In the second case there is no chemical bonding.

In the first case the one dimensional crystal would behave as metal (we will show later why), in the second case we would have a noble gas. Something like one-dimensional insulator is not possible.

What do we have in three-dimensional case? In one dimension, we can specify the spatial base-state of electron by giving the amplitudes that electron is at atom I and have the energy E_0 . In three-dimensional case we have degeneracy, electron is at atom I , have energy E_0 and some orientation in space – angular momentum. Only the electrons on the highest energy level are relevant for chemical bonding and electric current. The set of base states is therefore more complicated: $state = |L, L_z, i\rangle$, with L and L_z angular momentum intensity and its z -projection. The set of equations Eq 3, will be more complicated since there is the possibility that electron at atom I with momentum \mathbf{L} leaks into another momentum state.

The consequence of this is that one energy level in atom E_0 can be split in crystal into two energy bands with energy gap between them. The energies in one band are smaller than E_0 . The bonding states are within this band, they correspond to atomic orbitals that contribute to chemical bonding. If all bonding states are filled at $T=0K$, there is no electric conductivity (we will show later why). The filled band is called the valence band, the next band the conduction band. The crystal is in this case semiconductor or insulator, depending of the size of the energy gap between the valence- and the conduction band. If the lower energy band is half filled, the crystal is metal.

Another difference between one and three dimensional crystals is related to the crystal lattice geometry. If we have a cubical-, square-, structure (the next neighbors of one atom are in \mathbf{e}_x , \mathbf{e}_y and \mathbf{e}_z direction) the coefficients that have in general the form: $c_{\mathbf{L}}(i) = c_{\mathbf{L}}(\mathbf{R})$ are the product of the terms that depend only on x , y and z :

$$c_{\vec{L}}(\vec{R}) = c_{\vec{L}_x}(x)c_{\vec{L}_y}(y)c_{\vec{L}_z}(z).$$

The equation 3 will have separated derivatives with respect to x , y and z and the dispersion relation the form:

$$E = E_0 - 2A_{0\vec{L}_x} \cos(k_x b_x) + 2A_{0\vec{L}_y} \cos(k_y b_y) + 2A_{0\vec{L}_z} \cos(k_z b_z).$$

The state with the minimal and the maximal energy within a band gap has the wave vector \mathbf{k} equal to 0.

If the lattice is more complicated, for example has the diamond structure, the result is different. We can define the basis vectors, each atom can be reached by:

$$\vec{R} = l_1 a_1 \vec{e}_1 + l_2 a_2 \vec{e}_2 + l_3 a_3 \vec{e}_3.$$

However, the next neighbor atoms are not in directions \mathbf{e}_1 , \mathbf{e}_1 and \mathbf{e}_3 . As a consequence of this, the equation 3 will have mixed derivatives with respect to x , y and z and the dispersion relation will have more complicated form. For example for silicon, the function $E(\mathbf{k})$ is for conduction band not isotropic and the energy minimum is not for $\mathbf{k} = 0$.

In the previous sections we have found the states of definite energy. The probability to find the electron at one atom is the same for all atoms and does not change in time. We will now investigate the situation that could happen if a particle (photon) hits the semiconductor at some moment $t=0$, and generates a free electron that is in this moment localized at a certain position. There is electric field. The question is: how will the electron move?

We can describe an electron localized in space by making superposition of several electron states described by Eq 1, with the amplitudes of the base states:

$$c_i = e^{\left(-\frac{iEt}{\hbar}\right)} e^{(-ikx_i)}, \quad (9)$$

and slightly different values of the wave vector k and therefore slightly different energies E .

We will further take into account that the electron states are the solutions for the Hamiltonian that does not include the small electric field. The presence of field will cause spatial dependence of the energy E . (The energy E is nearly constant in any small region that spans over many wavelengths.) We can understand $E(k(x))$ as the kinetic energy of the electron. The electric field generates additional potential energy $U(x)$. It holds:

$$E(k(x)) + U(x) = E_{total} = const(x). \quad (10)$$

Since the coefficients (Eq 9) have the form of a wave, the superposition of of the electron states will lead to interference. If we make superposition of waves with the wave number slightly different from k , it can be shown (?) that the peak of the interference pattern will move in time with the group velocity:

$$v_{gr} = \frac{d\omega}{dk}; \quad \omega = E / \hbar$$

Therefore

$$v_{gr} = \frac{1}{\hbar} \frac{dE(k)}{dk}. \quad (11)$$

Since the wave packet moves in space, the derivation $dE(k(x))/dx$ will also slowly change, which will lead to a change of the group velocity - to acceleration of the wave packet.

Let us calculate this acceleration. It holds:

$$\frac{dv_{gr}}{dt} = \frac{dv_{gr}}{dk} \frac{dk}{dx} \frac{dx}{dt}.$$

X is the position of the wave packet, therefore:

$$\frac{dx}{dt} = v_{gr}, \Rightarrow \frac{dv_{gr}}{dt} = v_{gr} \frac{dv_{gr}}{dk} \frac{dk}{dx}. \quad (12)$$

The term dk/dx can be calculated by differentiation of the energy equation 10:

$$\frac{dU}{dx} + \frac{dE}{dk} \frac{dk}{dx} = 0.$$

Electric force F is equal to $-dU/dx$. Therefore:

$$\frac{dk}{dx} = \frac{F}{dE/dk}. \quad (13)$$

By substituting this result in Eq 12 we obtain:

$$\frac{dv_{gr}}{dt} = v_{gr} \frac{dv_{gr}}{dk} \frac{F}{dE/dk}. \quad (13)$$

If we substitute the formula for group velocity (Eq 11) into last equation we obtain:

$$\frac{dv_{gr}}{dt} = \frac{1}{\hbar} \frac{dv_{gr}}{dk} F.$$

Finally by substituting Eq 11 in the last equation again, we obtain:

$$\frac{dv_{gr}}{dt} = \frac{1}{\hbar^2} \frac{d^2 E}{dk^2} F.$$

Or:

$$F = m_e^* \frac{dv_{gr}}{dt}; \quad m_e^* \equiv \frac{\hbar^2}{\frac{d^2 E}{dk^2}}. \quad (14)$$

The wave packet is accelerating in electric field like a classical particle with mass m_e^* .

Let us take a look at the energy band that corresponds to base state energy E_0 in Fig 2. If electron has small k , due to positive curvature of $E(k)$, its effective mass is positive and its wave packet accelerates in the direction of force. However, if electron wave packet is formed from states from the top of the band, due to opposite curvature of $E(k)$, the effective mass is negative. The wave packet accelerates against the force.

Let us now try to estimate the current density through the crystal due to motion of all electrons in the band. Imagine that all the electrons are localized as wave packets at some moment $t=0$. Electric current will be the sum effect of motion of all wave packets.

$$J = \frac{e}{L} \int_k v_{gr}(k) g_k dk, \quad (15)$$

where we integrate over all k values, that correspond to the occupied energy states. Symbol g_k is the number of electron states (spatial- and spin-states) within k -space line element dk . As we showed above, it holds: $g_k = 2L/2\pi$ with L size of the crystal. Symbol e is the charge of an electron (negative number).

Let us check the formula for the case of no external force.

$$J = e \int_k v_{gr}(k) \frac{2}{2\pi} dk = e \int_k \frac{1}{\hbar} \frac{dE(k)}{dk} \frac{2}{2\pi} dk = \frac{2}{2\pi} \frac{e}{\hbar} (E|_{k_{\max}} - E|_{-k_{\max}}) = 0.$$

k_{\max} is the wave vector that corresponds to the highest occupied energy level. There is a balance of electron wave packets that move in both directions, the total current is 0.

Suppose now that we switch on the electric field ε . Let us calculate the change of the current density from this moment.

$$\frac{dJ}{dt} = e \int_k \frac{dv_{gr}(k)}{dt} \frac{2}{2\pi} dk = e \int_k \frac{1}{\hbar^2} \frac{d^2E}{dk^2} e\varepsilon \frac{2}{2\pi} dk = \frac{e^2 \varepsilon}{\hbar^2 \pi} \left(\left. \frac{dE}{dk} \right|_{k_{\max}} - \left. \frac{dE}{dk} \right|_{-k_{\max}} \right) = \frac{2e^2 \varepsilon}{\hbar^2 \pi} \frac{dE}{dk}.$$

For this derivation, we used the result Eq 14 and the fact that dE/dk is anti-symmetric function. The change of the current is proportional to the slope of the $E(k)$ curve at the highest occupied energy level. At the highest energy in a band, $dE(k)/dk$ is zero, therefore electrons in a full band cannot conduct current. Equal number of electrons accelerates in both directions. The derivative $dE(k)/dk$ is maximal in the middle of the energy band. Half-filled energy band leads to a largest conduction. This is the case of one-dimensional metal.

Suppose now that we have almost full energy band – only one electron (wave packet) is missing. The corresponding quantum states are close to the top of the band. Let us calculate the current in this case.

$$\frac{dJ}{dt} = e \sum_{j \neq i} \frac{dv_{gr}(k_j)}{dt} = e \sum_{all j} \frac{dv_{gr}(k_j)}{dt} - e \frac{dv_{gr}(k_i)}{dt} = 0 - e \frac{dv_{gr}(k_i)}{dt} = - \frac{e^2 \varepsilon}{\hbar^2} \left. \frac{d^2E}{dk^2} \right|_{k_i} = - \frac{e^2 \varepsilon}{m_e^*} \Big|_{k_i}.$$

Note that the effective mass m_e^* is negative at the highest energy level. Due to minus sign in front, the current change is in the direction of the electric field. The current has the same magnitude as in the case when only one particle with effective mass $|m_e^*|$ was moving in the field. The place where electron wave packet is missing is locally positive charged. Therefore we can chose for the charge of our imaginary particle to be positive. This is the concept of “holes”. It allows us to understand many effects more easily. For instance we can understand the promotion of an electron from valence to conducting band as generation of electron hole pair.

So far:

- 1) we have investigated the propagation of an electron in a crystal lattice
- 2) We have defined the state of electron by set of probability amplitudes that electron is localized at any particular atom
- 3) We have found the solutions for states of definite energy in the simple one dimensional case. The probability amplitudes have the form of waves, with quasi-continuous wave vector k . We have calculated the dispersion relation $E(k)$ and found out that allowed energies are grouped into energy bands
- 4) We have discussed the extension to three dimensional case, we came to conclusion that the states of definite energies are defined by similar wave like functions. Additional energy bands are possible and dispersion relations $E(k)$ are anisotropic.
- 5) We investigated the motion of localizes energy states in the force filed.

- 6) Electron wave packet with a wave vector $\sim k$ moves like a classical free particle with a

$$\text{mass: } m_e^* \equiv \hbar^2 / \frac{d^2 E}{dk^2}.$$

- 7) If one energy band is full there is no current conduction
 8) If one electron state close to the top of the band is empty, the electric current can be modelled by a positive hole with a positive effective mass
 9) If one band at $T=0K$ is completely full and the next band is completely empty, the crystal is insulator or semiconductor. The conduction is on $T=0K$ zero.

Until now we assumed $T=0K$, order in the system, so that electrons as fermions occupy the states beginning from some energy E_f . All states until this energy are full, the other states are empty. In the case of semiconductors, this mean that the valence band is full and the conduction band is empty.

Let us now assume $T>0K$. The question is: What is the macroscopic density of the electrons and holes? Due to thermal excitation electron can jump from the valence to the conduction band and leave the hole behind. For this process electron must receive the additional energy for the transition from band to band. This can happen through the interaction of the electron with vibration in the lattice (phonon) or through the interaction with photon. In this moment we don't need to consider the nature of the interaction. Our goal is not to describe the dynamics of the system. We are just interested for the conditions in the equilibrium. We would like to know: If our system is left alone for long time, so that nothing macroscopically can change any more, what is the probability that any electron quantum state with energy close to $E(k)$ is full. The statistical physics gives us the result. The probability is given by Fermi-Dirac distribution:

$$w = \frac{1}{e^{(E(k)-E_f)/kT} + 1}. \quad (16)$$

The derivation of this function has been described in the previous chapter.

The number of electrons in the conducting band divided by the crystal volume (conducting electron density) is:

$$n = \frac{1}{V} \int_{\text{all } \vec{k}} \frac{1}{e^{(E(k)-E_f)/kT} + 1} g_{\vec{k}} dk_x dk_y dk_z. \quad (17)$$

Notice that we consider a three-dimensional crystal. $g_{\vec{k}}$ is the number of electron states (spatial- and spin-states) within k -space volume element. V is the crystal volume. By generalizing the result for one dimension, we can obtain:

$$g_{\vec{k}} = \frac{2V}{(2\pi)^3}. \quad (18)$$

Similarly, the number of holes divided by the crystal volume (hole-density) is:

$$p = \frac{1}{V} \int_{\text{all } \vec{k}} \left[1 - \frac{1}{e^{(E(\vec{k})-E_f)/kT} + 1} \right] g_{\vec{k}} dk_x dk_y dk_z. \quad (19)$$

The hole is there where electron is missing therefore the probability that we have a hole is 1-w.

In order to calculate the integrals, we need E(k). The function E(k) can be quite complicated in three dimensional case. However, all the semiconductors behave quite similar. To understand this we will make an assumption. The Fermi energy E_f is inside the energy gap – it is far enough from the bottom of the conducting band, so that the exponential factor is much larger than one. The density of the conducting electrons becomes:

$$n = \frac{1}{V} \int_{\text{all } \vec{k}} e^{(E_f-E(\vec{k}))/kT} g_{\vec{k}} dk_x dk_y dk_z. \quad (20)$$

The density of holes is:

$$p = \frac{1}{V} \int_{\text{all } \vec{k}} e^{(E(\vec{k})-E_f)/kT} g_{\vec{k}} dk_x dk_y dk_z. \quad (21)$$

Since the exponential functions decrease rapidly, only the electron states close to the bottom of the conducting band and to the top of the valence band will contribute significantly to the conducting electron and hole densities.

We can therefore expand the equation E(k) in Taylor series close to the k value k₀ at the bottom of the conducting band. (We can do the same close to the top of the valence band.)

We will keep only the first and second derivative terms, as well as E(k₀) The first derivatives of E(k) are zero. If we assume that E(k) is symmetric with respect to k, using Eq 14 we obtain:

$$\frac{d^2 E}{dk_x^2} = \frac{d^2 E}{dk_y^2} = \frac{d^2 E}{dk_z^2} = \frac{\hbar^2}{m_e^*}.$$

The Taylor series for the bottom of the conducting band is then:

$$E_c(k) = E_c + \frac{\hbar^2}{2m_e^*} (\vec{k} - \vec{k}_0)^2. \quad (23)$$

E_c is the energy of the conducting band bottom.

Similar result can be obtained for the top of the valence band:

$$E_v(k) = E_v - \frac{\hbar^2}{2m_h^*} (\bar{k})^2. \quad (24)$$

These formulas are suitable for integrations in Eq 20 and Eq 21. Notice that the distributions in the integrals become Maxwell-Boltzmann distributions. The term m_e^* is the effective mass for electrons close to the bottom of the conducting band, m_h^* is effective mass for holes close to the top of valence band. The integrals can be analytically resolved by changing to spherical coordinates and extending the integration limit beyond the regular k-zone to infinity. We obtain:

$$n = 4\pi e^{(E_f - E_c)/kT} \int_0^\infty e^{-\frac{\hbar^2 k^2}{2m_e^* kT}} \frac{2}{(2\pi)^3} k^2 dk = 2 \left(\frac{2\pi m_e^* kT}{h^2} \right)^{3/2} e^{-\frac{E_c - E_f}{kT}} \equiv N_c e^{-\frac{E_c - E_f}{kT}}. \quad (25)$$

Where we used the result for the Maxwell-Boltzmann integral:

$$\int_0^\infty x^2 e^{-ax^2} dx = \frac{1}{4a} \sqrt{\frac{\pi}{a}}.$$

Similar result can be obtained for holes:

$$p = 2 \left(\frac{2\pi m_h^* kT}{h^2} \right)^{3/2} e^{-\frac{E_f - E_v}{kT}} \equiv N_v e^{-\frac{E_f - E_v}{kT}}. \quad (26)$$

E_c and E_v are the energy values at the bottom of the conduction- and top of the valence energy bands.

It is interesting to note that the product $n \times p$ does not depend of Fermi-energy:

$$np = N_c N_v e^{-\frac{E_c - E_v}{kT}} = N_c N_v e^{-\frac{E_g}{kT}} \equiv n_i^2. \quad (27)$$

E_g is the band gap energy. This formula holds in general case (intrinsic or doped semiconductor)

If we have intrinsic semiconductor – due to electro neutrality condition - the number of electrons in the conducting band must be equal to the number of holes. We obtain then:

$$n = p = n_i = \left(\frac{2\pi kT \sqrt{m_h^* m_e^*}}{h^2} \right)^{3/2} e^{-\frac{E_g}{2kT}} \quad (28)$$

This is the intrinsic concentration of charge carriers (“free” electrons in the conducting band and holes) in a semiconductor. The intrinsic concentration increases with T and it is larger when the energy gap E_g is smaller. As we have seen, the function $E(\mathbf{k})$ can have very complicate form in different crystal lattices, however the number of charge carriers depends only on the gap value and on the curvature of $E(\mathbf{k})$ line at the top of valence- and the bottom of conducting band.

Let us write a few numbers for silicon. The intrinsic charge carrier density at room temperature is: $1.45 \cdot 10^{10} \text{ cm}^{-3}$, the density of silicon atoms is $5 \cdot 10^{22} \text{ cm}^{-3}$. Therefore only every 10^{12} -th atom is ionized. Since the conduction is proportional to number of charge carriers, the conduction of intrinsic silicon is at room temperature $\sim 10^{12}$ times smaller than the conduction of e.g. copper. The other numbers are: energy gap $E_g = 1.12 \text{ eV}$.

In presence of electric potential V , the energy of electron can be written as:

$$E = E(k) + eV,$$

e is the negative electron charge. By taking this into account we can adjust the energies for the electrons near the edges of the conducting bands (Eqs 23 and 24) by adding the term eV . We obtain then the following carrier densities: For electrons:

$$n = N_c e^{-\frac{E_c - E_f}{kT}} e^{-\frac{eV}{kT}}. \quad (29)$$

For holes:

$$p = N_v e^{-\frac{E_f - E_v}{kT}} e^{+\frac{eV}{kT}}. \quad (30)$$

Notice that the densities depend on electrostatic energy like we had Maxwell-Boltzmann distributions for negatively charged electrons and positively charged holes.

It holds also:

$$np = n_i^2. \quad (31)$$

Note that in presence of electric field, we cannot assume electro-neutrality. Therefore

$$n \neq p.$$

The intrinsic carrier density is very small. Compared to it, the impurity concentration is usually much larger. We will now consider silicon with controlled addition of group V impurity, such as phosphorous. Group V atom can replace silicon atom (it has approximately correct size) and use up to four its valence electrons for covalent bonding with four silicon atoms. There will be a spare electron, with somewhat higher energy. This electron will be not so tightly bonded to its nucleus like the eight electrons that contribute to covalent bonding. Its binding energy is typically of the order of 10^{-2} eV – this is the energy that the electron needs to become available for conduction. To rephrase this in terms of band theory: The spare electron sits in the energy level which is $\sim 10^{-2}$ eV below the conducting band. If we have N_d impurity atoms in the crystal, there is N_d quantum places in the energy level. We assume here also that the concentration of impurities is so small so that the quantum states do not overlap – there is no splitting of impurity energy levels.

Since only small energy ($\sim 10^{-2}$ eV) is needed to excite the electrons from impurity levels into conduction band, we can expect at room temperature that almost all impurity electrons are excited to conduction band. Positive ions are left behind. Such impurities are called donors. If impurity density is much larger than n_i , which is almost always the case, we can assume:

$$n \approx N_d. \quad (32)$$

Note that the relation 27: $np = n_i^2$ is valid also for semiconductor with impurities. The concentration of holes in the presence of donors is therefore:

$$p \approx n_i^2 / N_d. \quad (33)$$

The Fermi-level will be a few tenths of eV (several kT) below the donor level. All this can be verified by calculating E_f from the condition of electro-neutrality:

$$n = p + N_d^+,$$

with N_d^+ number of ionized donors.

It holds:

$$N_d^+ = N_d \left(1 - \frac{1}{e^{(E_d - E_f)/kT} + 1} \right);$$

and the formulas Eq 25 and Eq 26 for n and p .

If we have a group III atom as impurity (for instance Boron), it will generate energy level $\sim 10^{-2}$ eV above the valence band. Since group III atoms can easily accept electrons from valence band and become negatively charged, they are called acceptors. We obtain equivalent formulas for the hole- and the free electron densities at room temperature:

$$p \approx N_a; \quad n \approx n_i^2 / N_a.$$

N_a is the density of acceptor atoms.

We should note that very small concentration of group III and group V impurities – e.g. one impurity atom in ten millions silicon atoms – can drastically increase the carrier concentration in silicon (10^5 times respecting to n_i). The key point in silicon technology is the preparation of extremely pure semiconductor and hence the possibility of controlling the impurities.

Non-Equilibrium State

What we did so far? We have investigated electrons in periodic potential (crystal lattice). We have then assumed equilibrium condition – the defined temperature and number of particles. We have used equilibrium distributions and calculated the free electron- and hole densities. As we already discussed in the previous chapter, the equilibrium distribution of particles across energy levels is simply the distribution with the greatest number of micro-realizations. It is the state our system will take if it is left alone for long time, so that nothing macroscopically can change any more.

Most systems of interest in engineering and science are not in equilibrium. One example is electric current in a semiconductor.

Statistical mechanics deals with non-equilibrium processes. We will define as first the non-equilibrium distribution function:

$$f(\vec{k}, \vec{r}, t). \quad (1)$$

Notice that this is a classical distribution function, because it simultaneously specifies both position r and momentum $\hbar k$ of the particles. The distribution function determines the number of electron wave packets in the macroscopic small volume $dr^3 dk^3$.

Every macroscopic value of interest such as current density j and particle density n can be calculated if we know the distribution function. Before we write the equations that describes the time evolution (change) of distribution function f , we will discuss the collision processes in the crystal. What are collisions?

Collisions, Recombination, Generation

We have seen that the electrons can move through a perfect crystal as in vacuum. An electron can, however, collide with phonon, photon, ionized impurity, lattice imperfection or other electron. If the energy transfer in the collision is large enough, electron can be knocked to another energy band. This leads to generation or recombination of electron-hole pairs. If only momentum of the incident electron is changed, but it stays in the same band, we are talking about scattering. The only difference between generation, recombination and scattering is the energy amount transferred to the electron.

In the thermodynamic equilibrium, the generation and recombination rates equal. The densities of electrons and holes are the result of the balance between recombination and generation.

We can distinguish between following recombination/generation processes:

- 1) Thermal recombination/generation
- 2) Radiative recombination/generation
- 3) Auger recombination/generation

Thermal generation occurs when one quanta of lattice vibration (phonon) is absorbed by valence electron. The electron then jumps to the conduction bands – electron hole pair is generated.

Similarly radiative generation occurs when a photon is absorbed by valence electron.

In the case of Auger generation, a high energy electron collides with an electron in the valence band promoting it to the conduction band.

Thermal, radiative and Auger recombination are inverse processes where one electron in the conduction band loses a part of its energy by creating a phonon, photon, or in a collision with another electron. The first electron then jumps into valence band and recombines with a hole.

Thermal Recombination and Generation

Let us here say a few more words about thermal recombination/generation. Crystal lattice can be imagined as a collection of mass centers (atoms) situated at definite positions and held together by the reaction of elastic restoring force. As consequence, the system will oscillate as a harmonic oscillator about its equilibrium. The oscillations of atoms in crystal will propagate like waves. Electron moving through crystal whose atoms are oscillating will experience a slightly different potential than if it is traversing a crystal whose atoms are completely frozen. This effect can be treated perturbatively. We know that when a disturbance perturbs a system

for a period of time it can induce a transition of an electron from an initial state into a different final state. The transition rate from one state into another is specified through Fermi's Golden Rule:

$$W = \frac{2\pi}{\hbar} |\langle f | V | i \rangle|^2 \delta(E_f - E_i) \quad (2)$$

State f is the final state of the whole system that includes vibrating atoms and electrons.

State "i" is the initial state. V is the small perturbative part of the Hamiltonian. V describes the additional interaction of vibrating atoms and electrons. The delta function implies that energy is conserved during the transition.

We can make one additional abstraction. We have a system of many harmonic oscillators –the atoms in the lattice. Such system can be also analyzed in terms of identical Bose-particles – “phonons”. If we have a standing wave Q in a crystal whose energy is $n\hbar\omega$ above the ground state, we can describe it in the following way: We can say that we have n phonons each of them with energy $\hbar\omega$ and momentum $\hbar Q$. The effect such a harmonic perturbation has on electron can be explained as interaction between the particles phonons and electrons. In this interaction a phonon is created or annihilated (absorbed). The sum of the crystal momentum of the electron $\hbar k$ and the phonon momentum $\hbar Q$ is conserved, as well as the total energy.

It can be calculated that the transition rate between initial electron state k_i and the final electron state k_f is: In the case of phonon absorption we have:

$$W = w(\vec{k}_i, \vec{k}_j) N(\vec{Q}) \delta(\vec{k}_f - \vec{k}_i - \vec{Q}) \delta(E_f - E_i - \hbar\omega) \quad (3)$$

In the case of phonon emission:

$$W = w(\vec{k}_i, \vec{k}_j) (N(\vec{Q}) + 1) \delta(\vec{k}_f - \vec{k}_i + \vec{Q}) \delta(E_f - E_i + \hbar\omega) . \quad (4)$$

$W(k_i, k_j)$ contains the overlap integral of two electron wave functions. $N(Q)$ is the number of phonons in state Q. Equal formula holds also in the case of photons.

As explained above, if the initial electron state is one band and the final in another band, the expressions Eq 3 and Eq 4 describe generation and recombination of electron-hole pairs. If the electron states are in the same energy band, we have electron-phonon scattering.

Since electrons are fermions, in a system with many electrons, a scattering event will occur only if the initial energy state is full and the final state is empty. Therefore the generation rate is:

$$S_g = (1 - f_p(\vec{k}_i))(1 - f_n(\vec{k}_f)) w(\vec{k}_i, \vec{k}_j) N(\vec{Q}) \delta(\vec{k}_f - \vec{k}_i - \vec{Q}) \delta(E_f - E_i - \hbar\omega) , \quad (5)$$

The functions $f_p(\vec{k}_i)$ and $f_n(\vec{k}_f)$ are probabilities that there is a hole in state \vec{k}_i in the valence band and an electron in state \vec{k}_f in the conduction band. The recombination rate is given by:

$$S_r = f_p(\vec{k}_i) f_n(\vec{k}_f) w(\vec{k}_i, \vec{k}_j) (N(\vec{Q}) + 1) \delta(\vec{k}_f - \vec{k}_i + \vec{Q}) \delta(E_f - E_i + \hbar\omega). \quad (6)$$

If we assume some phonon distribution, for example the equilibrium Bose-Einstein distribution:

$$N(\vec{Q}) = \frac{1}{e^{\hbar\omega/kT} - 1}, \quad (7)$$

(phonons are bosons), we can calculate the total generation and recombination rates:

$$S_g(\vec{k}_i|_{val_band}, \vec{k}_j|_{cond_band}) \quad (8)$$

$$S_r(\vec{k}_i|_{cond_band}, \vec{k}_j|_{val_band}) \quad (9)$$

by integrating over all phonon states Q . More general, any collision can be characterized by a total transition rate:

$$S(\vec{k}_i, \vec{k}_j) \quad (10).$$

If we assume Fermi-Dirac distributions for electrons and holes (equilibrium case):

$$f_n(\vec{k}) = \frac{1}{e^{(E_c(\vec{k}) - E_f)kT} + 1}; \quad f_p(\vec{k}) = 1 - \frac{1}{e^{(E_v(\vec{k}) - E_f)kT} + 1}; \quad (8)$$

it can be easily shown that the generation- and recombination rates (Eqs 8 and 9) are equal.

In the case of interaction with photons (electromagnetic field disturbs the lattice potential) results are almost identical. There is one difference: Since the photon velocity c is much larger than the phonon velocity (v_{sound}) phonon momentum is so small that we have $k_i \approx k_f$. Electron does not change its momentum in the interaction with photon. It does not scatter.

Time Evolution of Distribution Function

Let us now write the equation that describes the time evolution of the distribution function $f(\vec{k}, \vec{r}, t)$. If particles (electron wave packets) move only by action of external force (there is no

particle-particle scattering), their motion in (\mathbf{k}, \mathbf{r}) space will be similar to the motion of a fluid. The assumption is here that the external force is nearly constant in the region that occupies many wavelengths. Since probability is conserved, it must obey the continuity equation in (\mathbf{k}, \mathbf{r}) space.

$$\frac{\partial f}{\partial t} + (\nabla_{\mathbf{r}} f) \dot{\mathbf{r}} + (\nabla_{\mathbf{k}} f) \dot{\mathbf{k}} \equiv \frac{df}{dt} = 0. \quad (9)$$

It holds also:

$$\hbar \dot{\mathbf{k}} = \vec{F},$$

where F is the external force. Equation 9 can be rewritten:

$$\frac{\partial f}{\partial t} + (\nabla_{\mathbf{r}} f) \dot{\mathbf{r}} + (\nabla_{\mathbf{k}} f) \frac{\vec{F}}{\hbar} \equiv \frac{df}{dt} = 0. \quad (10)$$

The above equation is valid in the case that the momentum of the particles can be changed only by the action of external force and that no particles can be lost or generated. In crystal, we have collisions. After a collision a particle can jump into different place in \mathbf{k} -space, it can disappear (electron-hole recombination) or it can be generated. When all these effects are put together in one term, the equation for the time-change of the non-equilibrium free-electron-distribution f_n becomes:

$$\begin{aligned} \frac{df_n}{dt} = & - \int_{k_2} \left(S(\vec{k}_1, \vec{k}_2) f_n(\vec{k}_1) (1 - f_n(\vec{k}_2)) - S(\vec{k}_2, \vec{k}_1) f_n(\vec{k}_2) (1 - f_n(\vec{k}_1)) \right) dk_2 - \\ & - \int_{k_2} \left(S_r(\vec{k}_1, \vec{k}_2) f_n(\vec{k}_1) f_p(\vec{k}_2) - S_g(\vec{k}_2, \vec{k}_1) (1 - f_n(\vec{k}_1)) (1 - f_p(\vec{k}_2)) \right) dk_2. \end{aligned}$$

(11)

Equation 11 is the Boltzmann's equation. Function f_p is the distribution of holes. The first variable in all functions S (different transition rates) is always the initial momentum and the second variable the final momentum. The first integral (Boltzmann's integral) describes the scattering and the second integral the recombination and generation.

If we want only to find the quantities that represent the mean value of some observable, like for example the electron density given by:

$$n = \int_k f_n dk, \quad (12)$$

we can integrate the Boltzmann's equation 11 over all momenta k_1 .

If we want to find the the electron flux:

$$\vec{\Phi} = \int_k \vec{v} f_n dk \quad (13)$$

Or the current density:

$$\vec{j} = e \int_k \vec{v} f_n dk \quad (14)$$

We can multiply the Boltzmann's equation with velocity v and integrate it over all k_1 . In this way, we obtain 4 equations with 4 unknown functions $n(r, t)$ and $j_{x,y,z}(r, t)$. The integration of left hand side of Boltzmann's equation over k_1 gives:

$$\frac{\partial n}{\partial t} + (\nabla_r \vec{\Phi}).$$

The integration of the first Boltzmann's integral (scatterings) over k_1 must give zero. The electrons will not disappear or emerge from/at a certain space r due to scatterings. The integration of the second Boltzmann's integral which describes recombination and generation very approximately gives:

$$I_2 = knp - G. \quad (15)$$

The generation rate can be calculated if we recall that in the case of thermodynamic equilibrium recombination and generation are in balance. In equilibrium holds also: $np = n_i^2$. Therefore $G = k n_i^2$ and Eq 15 can be rewritten as:

$$I_2 = k(np - n_i^2). \quad (16)$$

Now we can write the complete result of the integration of Boltzmann's equation over k_1 :

$$\frac{\partial n}{\partial t} + (\nabla_r \vec{\Phi}) = -k(np - n_i^2). \quad (17)$$

This is the carrier continuity equation. The last equation is valid for the case of direct band to band recombination. If we assume additional recombination through the trap-levels (Shockley-Read-Hall-process), the following recombination term should be added:

$$R_T = \frac{(np - n_i^2)}{\tau_p (n + N_c e^{(E_t - E_c)/kT}) + \tau_n (p + N_v e^{(E_v - E_t)/kT})}, \quad (18)$$

Et is the trap energy. For a trap energy level located in the middle of the band gap – the recombination rate has its maximum.

Let us here say a few words about these trap levels. We have seen that the controlled addition of impurities of group III or V will produce energy levels inside the band gap close to the valence or conduction band. Similarly, any unwanted impurity or defect in crystal (caused e.g. by radiation) will also generate energy levels, which are usually near the middle of the band gap. These energy levels are localized to the place where impurity atom or the defect is. These energy levels behave as traps – capturing and reemitting electrons and holes. Electrons which are trapped generally recombine with holes in the valence band rather than to return to the conduction band. Even a very small amount of deep level traps can greatly alter the electron-hole recombination rate.

We have following definitions:

If one trap level is positive when electron state is empty and neutral when electron state is filled, it is donor like.

If one trap level is neutral when electron state is empty and negative when electron is there it is called to be acceptor like. Donors are donor-like levels that are very close to the conduction band.

To find the first velocity-moment of the Boltzmann equation (11), we will use the relaxation approximation: The Boltzmann integral is then approximated with:

$$I = -\frac{f - f_0}{\tau}. \quad (19)$$

Distribution f_0 is the equilibrium distribution. Equation 19 implies that the system will relax due to collisions to the equilibrium distribution after a characteristic time τ , which is called the relaxation time. Time τ characterizes the mean free time between collisions. The calculation of

the first velocity moment of the Boltzmann's equation under the relaxation time approximation leads to the following drift diffusion equations:

For electrons:

$$\vec{j}_n = -|e|\vec{\Phi} = -|e|\mu_n n \vec{F} + |e|D_n \nabla_x n, \quad (20)$$

And for holes:

$$\vec{j}_p = |e|\vec{\Phi} = |e|\mu_p p \vec{F} - |e|D_p \nabla_x p. \quad (21)$$

It holds for the diffusion constant:

$$D_{n/p} = \mu_{n/p} \frac{kT}{|e|}. \quad (22)$$

The mobility is given by:

$$\mu_{n/p} = \frac{|e|\tau}{m_{e/h}^*}.$$

These equations are derived under assumption that:

$$\langle E_k \rangle = \left\langle \frac{1}{2} m_{e/h}^* v_g^2 \right\rangle = \frac{3}{2} kT,$$

and a constant temperature T in space and time. The drift diffusion equations are valid if the relaxation time is much smaller than any relevant time constant in our system. The above drift diffusion equations are very important in semiconductor device analysis and are used to model the most of semiconductor devices.

What we have done:

We have considered the electrons in semiconductor (lattice) under equilibrium conditions – defined temperature, equilibrium distribution with greatest multiplicity (Fermi-Dirac distribution).

$$f = \frac{1}{e^{(E(k)-E_f)/kT} + 1}.$$

We have considered a real three dimensional semiconductor. We have approximated the Fermi-Dirac with Maxwell-Boltzmann distribution, expanded $E(k)$ in series, and integrated the density of states multiplied by the distribution over all wave vectors k to find the densities:

$$n = 2 \left(\frac{2\pi m_e^* kT}{h^2} \right)^{3/2} e^{-\frac{E_c - E_f}{kT}} \equiv N_c e^{-\frac{E_c - E_f}{kT}},$$

$$p = 2 \left(\frac{2\pi m_h^* kT}{h^2} \right)^{3/2} e^{-\frac{E_f - E_v}{kT}} \equiv N_v e^{-\frac{E_f - E_v}{kT}}.$$

It follows:

$$np = N_c N_v e^{-\frac{E_c - E_v}{kT}} = N_c N_v e^{-\frac{E_g}{kT}} \equiv n_i^2.$$

At room temperature the intrinsic density n_i is 10^{12} times smaller than the number of atoms. In presence of weak electric field it holds:

For electrons:

$$n = N_c e^{-\frac{E_c - E_f}{kT}} e^{-\frac{eV}{kT}}.$$

For holes:

$$p = N_v e^{-\frac{E_f - E_v}{kT}} e^{+\frac{eV}{kT}}.$$

Controlled addition of group V impurities (donors) leads to the following densities:

$$n \approx N_d; \quad p \approx n_i^2 / N_d,$$

N_d is donor density.

Controlled addition of group III impurities (acceptors) leads to the following densities:

$$p \approx N_a; \quad n \approx n_i^2 / N_a,$$

N_a is acceptor density.

Finally we have studied the non-equilibrium processes, such as current flow.

We have written the Boltzmann equation that describes the change of the non-equilibrium distribution function due to external force and due to particle collisions.

We have derived the continuity equation and the drift diffusion equations under assumption of a constant temperature and by using the relaxation time approximation.

Continuity equation for electrons is:

$$\frac{\partial n}{\partial t} + (\nabla_r \cdot \vec{\Phi}) = -k(np - n_i^2).$$

Drift-diffusion equation is:

$$\vec{j}_n = -|e|\vec{\Phi} = -|e|\mu_n n \vec{F} + |e|D_n \nabla_x n.$$

It holds:

$$D_{n/p} = \mu_{n/p} \frac{kT}{|e|},$$

And

$$\mu_{n/p} = \frac{|e|\tau}{m_{e/h}^*}.$$

If we substitute the equilibrium density into drift diffusion equation, we obtain:

$$\vec{j}_n = 0.$$

In equilibrium, drift- and diffusion currents are equal.