Mesoscopic systems are fabricated from various bulk materials, which are often, but not always, semiconductors. Some basic knowledge of their bulk properties is important and represents the major part of this chapter. Although this is in many respects just a polishing up of solid state physics at an introductory level, we introduce many specifics of the materials of interest along the way, in particular of Si and GaAs. Occasionally, conventional metals and carbon crystals are mentioned as well, although the reader is supposed to know their basics.

We begin by a brief recapitulation of the most relevant crystal structures in section 2.1, and proceed by looking at the corresponding electronic band structures of the materials in section 2.2. Here, it is of particular importance to model the valence and the conduction bands around their maximum and minimum, respectively. As always, we can approximate the energy dispersions near the band extremal points by parabolas, which leads to the concept of effective masses. We shall see that within this approximation, the crystal properties can be "put aside" in many cases. Instead, the charge carriers behave like free electrons with a modified mass. The properties of electrons and holes within the effective mass approximation are looked at in section 2.3. Also, the effective mass approximation allows us to work with envelope wave functions. With this approach, superpotentials like those frequently met in nanostructures, can be treated with a Schrödinger equation for just this superpotential. The crystal potential enters only via the effective masses as well as via its dielectric constant. This is a very elegant concept, which simplifies our life substantially in subsequent chapters. Developing this approximation is the topic of section 2.4.

Doping is the standard way to fill the bands of a semiconductor with a significant and temperature-independent carrier density. The important issues concerning doping are reviewed in section 2.5. In the subsequent section, we look at the transport properties of electron gases within the simplest version of the Boltzmann model. We will occasionally use these results when looking at diffusive samples later on. Furthermore, it is of help to know the approximations that enter this model, in order to appreciate the deviations we will look at in subsequent chapters. A non-vanishing resistance indicates that some sort of scattering mechanism must be present, which are the topic of section 2.7. Finally, we spend a few words on screening in section 2.8.

Readers who discover that parts of this chapter are white spots on their map of solid state physics knowledge are encouraged to consult one of several excellent introductory textbooks for further information, e.g., [Ashcroft1985, Ziman1995]. If everything sounds familiar, please consider this chapter as a warm-up exercise!
2.1 Crystal structures

Many elements and compounds crystallize in a face centered cubic (fcc) lattice. This is not surprising, since this crystal structure represents one of the two closed packings possible, which one might naively expect to occur when identical or very similar spheres are piled up. Both Si and GaAs have this lattice structure. The lattice constant $a$ is the length of one edge of a unit cell. Si is composed of two fcc lattices shifted relative to each other by $(a/4, a/4, a/4)$. GaAs also has a two-atom base, except that here, the one base atom is Ga, the other one As. This is the zincblend lattice. The lattice constants are 0.565 nm for Si and 0.543 nm for GaAs (both numbers hold for room temperature). Fig. 2.1 shows the Si and the GaAs structure.

The reciprocal lattice of an fcc lattice is a body-centered cubic (bcc) lattice. Since the crystal momentum is invariant under translations by reciprocal lattice vectors, we can represent the behavior of electrons and phonons within one elementary cell of the reciprocal lattice, which is always chosen as the first Brillouin zone. For an fcc lattice, this is a truncated octahedron, composed of 6 squares and 8 hexagons, see Fig. 2.1. The center of the first Brillouin zone is labelled the $\Gamma$-point, while the centers of the hexagons and squares are referred to as L- and X-points, respectively. Occasionally, one hits upon more exotic directions of lower symmetry, such as K, U, and W, which are located at the center of the edges and at the corners of the first Brillouin zone.

Germanium crystallize in a diamond structure like silicon. This is also the case for many compound semiconductors. Any binary combination of Al, Ga, or In with As, Sb or P (the so-
called III-V compounds) will result in a zincblend lattice. Combining these group III elements with nitrogen can lead to both an fcc lattice or a hexagonal lattice, depending on the crystallization process and the subsequent treatment. This is also the case for most II-VI compounds, such as CdSe or ZnS (which gave the zincblend structure its name, after all). Thus, when working with semiconductors, you will barely ever meet any further crystal structures. To finish this section, let us have a look at a particular simple lattice, namely a sheet of graphite, the second crystal structure carbon forms besides diamond. It consists of a hexagonal, lattice of $sp^2$-hybridized carbon atoms (Fig. 2.2).

![Figure 2.2: Structure of a graphite sheet. Left: The unit cell (gray) of this hexagonal lattice is spanned by the lattice vectors $|\vec{a}_1|$ and $|\vec{a}_2|$, with a lattice constant of $|\vec{a}_1| = |\vec{a}_2| = 0.246$ nm. It contains a basis of two carbon atoms (full circles) occupying non-equivalent sites. The distance of two neighboring atoms is 0.142 nm. Right: the first Brillouin zone of the graphite sheet with points of high symmetry.](image)

**Question 2.1:** Calculate the reciprocal lattice of the graphite sheet and construct its first Brillouin zone.

The reciprocal lattice is again hexagonal. The center of the first Brillouin zone is denoted by $\Gamma$, the corners by $K$, and the centers of the edges are labelled $L$, respectively (Fig. 2.2).
2.2 **Electronic energy bands**

An electronic energy band is an energy interval in which electronic states are allowed in the crystal. The bands are separated by *band gaps*. This energy structure is obtained by solving the Schrödinger equation for electrons in the crystal

\[
\left[-\frac{\hbar^2}{2m} \Delta + V_{\text{crystal}}(\vec{r})\right] \phi(\vec{k}, \vec{r}) = \epsilon(\vec{k}) \phi(\vec{k}, \vec{r}) \tag{2.1}
\]

Here, the electronic wave functions depend on both the wave vector \( \vec{k} \) and the spatial coordinates \( \vec{r} \). They are denoted by \( \phi(\vec{k}, \vec{r}) \), while \( V_{\text{crystal}}(\vec{r}) \) is the crystal potential. Elementary solid state physics tells us that the wave functions have to obey Bloch’s theorem, which states that they are of the form

\[
\phi(\vec{k}, \vec{r}) = u_{\vec{k}}(\vec{r}) e^{i\vec{k} \cdot \vec{r}} \tag{2.2}
\]

where \( u_{\vec{k}}(\vec{r}) \) has the periodicity of the crystal lattice. Such wave functions are *Bloch functions*. The task is to determine the eigenvalues \( \epsilon(\vec{k}) \) and eigenvectors, which is usually done by transforming the differential equation into an algebraic equation. An exact solution, though, is only possible for some special cases. Some reasonable approximation is therefore called for. How eq. (2.2) is then solved in detail depends on the model. The *nearly free electron model* starts from a free electron gas and treats a weak periodic crystal potential within perturbation theory. Here, the band gaps emerge from interferences of the electronic waves that get scattered at the crystal potential, which results in standing waves at the edges of the Brillouin zones. The reader is referred to the extensive literature on solid state physics for details. Here, we look at a different approach, which constructs the electronic eigenstates from those of the individual atoms that form the crystal. This approach is known as the *tight binding model*. Within this picture, the energy bands and the band gaps are remainders of the discrete energy spectrum of the atoms.

The tight-binding model is based on the assumption that the atomic orbitals \( \xi_j(\vec{r}) \) are a good starting point for constructing Bloch waves \( \xi_j(\vec{k}, \vec{r}) \). Let us assume there is only one atom per unit cell. We can obtain Bloch functions via

\[
\xi_j(\vec{k}, \vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}_n} e^{i\vec{k} \cdot \vec{R}_n} \xi_j(\vec{r} - \vec{R}_n) \tag{2.3}
\]

Here, the lattice vectors are denoted by \( \vec{R}_n \). The crystal wave functions can be expanded in these Bloch functions, such that

\[
\phi(\vec{k}, \vec{r}) = \sum_j d_j(\vec{k}) \xi_j(\vec{k}, \vec{r}) \tag{2.4}
\]

The Schrödinger equation for the Bloch functions is now multiplied by \( \xi_j^*(\vec{k}, \vec{r}) \) and integrated over space. The emerging algebraic equation has a nontrivial solution only for

\[
det[T_{ij}(\vec{k}) - \epsilon O_{ij}(\vec{k})] = 0 \tag{2.5}
\]
Here, $T_{ij}(\vec{k})$ and $O_{ij}(\vec{k})$ denote the "transfer matrix elements" and the "overlap matrix elements", respectively. They are defined as

$$T_{ij}(\vec{k}) = \langle \xi_i(\vec{k},\vec{r}) | H | \xi_j(\vec{k},\vec{r}) \rangle$$

and

$$O_{ij}(\vec{k}) = \langle \xi_i(\vec{k},\vec{r}) | \xi_j(\vec{k},\vec{r}) \rangle$$

These matrix elements are often approximated by inserting the known atomic orbitals, and choosing a suitable crystal potential, which can be used as a parameter to fit the experimentally determined properties of the crystal.

**Question 2.2:** Determine the energy dispersion for the simplest case, namely for a single band in one dimension, with a constant (and negative) transfer integral $\gamma$, and a vanishing overlap integral. Show that the energy dispersion in that case reads

$$E(\vec{k}) = E_0 + 2\gamma \cos(ka)!$$

As an example, we consider the graphite sheet, in which atomic $s$- and $p$- orbitals generate the bands of relevance, shown in Fig. 2.3. For the $p_z$ orbitals of the carbon atoms arranged in a honeycomb configuration, a bonding and an antibonding $\pi$ band results [Wallace1947]. To a first approximation, its tight-binding energy dispersion is

$$E_{\pi}(\vec{k}) = \pm T \sqrt{1 + 4 \cos \left( \frac{1}{2} \sqrt{3} k_x a \right) \cos \left( \frac{1}{2} k_y a \right) + 4 \cos^2 \left( \frac{1}{2} k_y a \right)} \quad (2.6)$$

Solids are usually classified as metals, semiconductors, and insulators. In a metal, at least one of the bands is partly occupied with electrons. These bands are called conduction bands in metals. In semiconductors and insulators, all bands are either full or empty at zero temperature. Here, the full band with the highest energy is the valence band, while the conduction band is the empty band with the lowest energy. In a semiconductor, a significant density of electrons can be transferred from the valence band into the conduction band by thermal excitation, which requires a band gap of less than 4 eV. Consequently, insulators have larger band gaps.

It turns out that the graphite sheet is a very special case in this classification scheme. The bonding $\pi$ band is in fact the valence band, while its antibonding counterpart is the conduction band. As can be seen from eq. (2.6), the valence band can be mapped onto the conduction band by a reflection at the planes defined by the $K$-points. The conduction band and the valence band of a graphite sheet, represented by bold lines in Fig. 2.3, touch each other at the $K$-points. It can thus be regarded as a semiconductor with zero band gap.\(^1\)

By adopting the tight-binding method appropriately, the band structure of other materials, like Si and GaAs, can be calculated. Naively, one might assume that due to the similar crystal structures, the band structures of the two semiconductors should be very similar as well. However, this is not the case, mainly because the Ga-As base is polar, while the Si base is\(^1\) in bulk graphite, the interaction between adjacent graphite sheets causes small energy shifts of both $\pi$- bands, such that they overlap somewhat around the $K$-points. It is therefore a metal with an extremely small carrier density.
covalent. Fig. 2.4 shows the structures of the valence and conduction bands of both crystals. The extremal points of the bands shown here dominate both the electronic and optical properties. The number of electrons in the conduction band, as well as that of one of the holes in the valence bands, is small compared to the number of available electronic states in all cases of relevance, and the few carriers will find themselves in close proximity to the band extremal points. Around these extremal points, we can expand the energy dispersion in a Taylor series up to second order:

\[
E(\vec{k}) = E_0 + \frac{1}{2} \vec{k} \cdot \left( \frac{\partial^2 E}{\partial k_i \partial k_j} \right) \cdot \vec{k}
\]

(2.7)

By comparing this expression with the energy dispersion of the free electron gas \( E(\vec{k}) = \hbar^2 \vec{k}^2 / 2m \), we see that the tensor of second derivatives of the energy can be identified with effective masses,

\[
\frac{1}{\hbar^2} \left( \frac{\partial^2 E}{\partial k_i \partial k_j} \right) = \left( \frac{1}{m^*} \right)_{ij}
\]

(2.8)

which is therefore also known as the effective mass tensor. It can be diagonalized, such that the extremal points of energy bands can be characterized by its three effective masses along the principal axes. Carriers in semiconductors therefore usually behave free-electron like, except that their masses have been changed by the crystal structure. Throughout the rest of the book, we will use effective masses to describe the behavior of carriers.
Question 2.3: What is the effective mass around the minimum of the energy band obtained in Question 2.2?

Let us have a somewhat closer look at these band structures. Si has a conduction band minimum at $0.85 \Gamma X$. Around this minimum, two different effective masses exist, a transverse mass in all directions perpendicular to the $\Gamma X$-direction, $m_{e,t} = 0.19 \, m$, and a longitudinal mass along the $\Gamma X$-direction, $m_{e,l} = 0.92 \, m$. Since there are 6 $X$-points, the conduction band minimum in Si shows a 6-fold degeneracy known as "valley degeneracy". In GaAs, the conduction band minimum is located at the $\Gamma$-point. Here, the 3 effective electron masses are identical: $m^*_{e,1}(GaAs) = m^*_{e,2}(GaAs) = m^*_{e,3}(GaAs) = 0.067 \, m$. In both materials,
there are two (nearly) degenerate valence bands at the $\Gamma$-point. As in most semiconductors of interest, the valence band emerges from atomic $p$-states, which have a threefold orbital degeneracy and a spin degeneracy of 2. Typically, the corresponding $\sigma$-band formed by the atomic $s$-orbitals has its maximum well below the maximum of the $p$-bands and do not have to be taken into account for transport considerations. In the crystal, the degeneracy of the $p$-orbitals is removed, and 3 different, spin degenerate bands are obtained. Two of them are shown in Fig. 2.4, while the third one is split off and shifted to lower energies. This splitting has its origin in the spin-orbit interaction. The spin-orbit Hamiltonian is given by

$$H_{so} = \frac{\hbar}{4m^2c^2} \vec{\sigma} \cdot \nabla V \times \vec{p}$$  \hspace{1cm} (2.9)$$

where $V$ is the electrostatic potential, and $\vec{\sigma}$ are the Pauli matrices. This is a relativistic term, which means we have to replace the Schrödinger equation by the Dirac equation, and the wave function becomes a two-component spinor. In a spherical symmetric potential, the spin-orbit Hamiltonian becomes proportional to the scalar product of the angular momentum and the spin $\vec{L} \cdot \vec{S}$. To get an idea what the spin-orbit Hamiltonian does to the energies, we assume that the interaction in the solid can be approximated by that one in the individual atoms. It is then clear from atomic physics that this term separates the four-fold degenerate $j = 3/2$ states from the twofold degenerate $j = 1/2$ states, where $j$ denotes the total angular momentum quantum number. The $j = 1/2$ state is lowered in energy, by an amount that essentially depends on the strength of the atomic Coulomb potential. The heavier the nucleus, the stronger is this spin-orbit splitting $\Delta_{so}$. This tendency can be seen experimentally: $\Delta_{so}$(graphite) $\approx 6\text{meV}$, $\Delta_{so}$(Si) $\approx 45\text{meV}$, and $\Delta_{so}$(GaAs) $\approx 340\text{meV}$.

The energy dispersions of the remaining four bands with $j = 3/2$ can be conveniently described within the $\vec{k} \cdot \vec{p}$ approximation, a method to model the dispersion around the extremal points of an energy band. We consider a semiconductor with a band maximum at $\vec{k} = 0$, as it is the case for the valence bands under study. Within the $\vec{k} \cdot \vec{p}$ model, the spatial derivatives in the Schrödinger equation of the crystal, eq. (2.2), are carried out only for the plane wave component of the Bloch function of the type (2.2). The equation

$$\left\{ \frac{p^2}{2m} + \frac{\hbar^2}{2m} \vec{k} \cdot \vec{p} + V(\vec{r}) \right\} u_{n,k}(\vec{r}) = E_{n,k} u_{n,k}(\vec{r})$$  \hspace{1cm} (2.10)$$

emerges. Here, $n$ denotes the band index. For $\vec{k} = 0$, it simplifies significantly, and we assume that an approximate solution can be found for all bands involved. A non-vanishing but small wave vector can then be treated as a perturbation.

First of all, the term $\propto \vec{k}^2$ produces an energy shift which depends on $\vec{k}$, but does not couple the bands. Technically, it can just be added to the crystal potential. The term containing $\vec{k} \cdot \vec{p}$, however, must be treated with degenerate perturbation theory. It turns out that the second-order term is the leading one, since the first-order term is linear in $\vec{k}$ and must thus vanish at a maximum. The matrix elements are given by

$$h_{ij}(\vec{k}) = \frac{\hbar^2}{m^2} \sum_{q=1, q \neq i,j}^{4} \frac{\langle n_{i,0} | \vec{k} \cdot \vec{p} | n_{q,0} \rangle \langle n_{q,0} | \vec{k} \cdot \vec{p} | n_{j,0} \rangle}{\epsilon_{n_{i,0}} - \epsilon_{n_{q,0}}}$$  \hspace{1cm} (2.11)$$
The bands are labelled by \( n_{i,j,q} \) here. This 4x4 matrix equation gives the energy eigenvalues of the type

\[
E_{lh, hh} = \frac{\hbar^2}{2m} \left[ \gamma_1 k^2 \pm \sqrt{4\gamma_2^2 k^4 + 12(\gamma_3^2 - \gamma_2^2)(k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_x^2)} \right] 
\]

(2.12)

The \( \gamma_i \) are the Luttinger parameters, which depend on the material. For GaAs, \( \gamma_1 = 6.95, \gamma_2 = 2.25, \) and \( \gamma_3 = 2.86 \). In Si, \( \gamma_1 = 4.29, \gamma_2 = 0.34, \) and \( \gamma_3 = 1.42 \). The “+” energy dispersion corresponds to a lighter effective mass for all directions in \( \mathbf{k} \)-space. The band is therefore referred to as the light hole (lh) band. Correspondingly, the “−” sign represents the energy dispersion for the heavy hole (hh) band. To get an idea of the shape of the hole bands, consider a surface of constant energy. The first term of the right hand side in eq. (2.12) describes a sphere, which is warped by the second term. The warping is \( \mathbf{k} \)-dependent and of opposite sign in the two bands for all directions. These surfaces are therefore known as warped spheres, see Fig. 2.5.

Note that both bands remain twofold degenerate in this treatment at \( \mathbf{k} = 0 \). This is known as the Kramers degeneracy. It is removed in polar crystals, such as GaAs or InP, due to the absence of an inversion center. The corresponding correction to the Hamiltonian is known as the Dresselhaus term. The resulting energy splitting, however, is small, i.e., in the range of \( \mu eV \), although it causes measurable effects occur at very low temperatures.

Per definition, hole masses are negative. A hole is thus a quasiparticle with negative effective mass and a negative charge of \( q = -e \). Since, as shown below, the ratio \( q/m^* \) enters in the conductivity, we can equivalently regard a hole as a particle with positive effective
mass and a charge $q = +e$. Due to the warped structure of the valence bands, the hole masses are averaged over all directions in the valence bands. Typical literature values are $m_{hh}^*(Si) = 0.54m$, $m_{lh}^*(Si) = 0.15m$, $m_{hh}^*(GaAs) = 0.51m$, and $m_{lh}^*(Si) = 0.08m$.

GaAs has a direct band gap, meaning that the minimum in the conduction band is at the same location in k-space as the maximum of the valence band. The band gap of Si is indirect. A large momentum transfer is necessary for exciting electrons from the valence band maximum into the conduction band minimum.

**Question 2.4:** Compare the momentum of a photon with the energy of the Si band gap with the momentum difference between the $\Gamma$-point and the conduction band minimum in Si!

Therefore, Si can absorb photons with an energy close to the band gap only if phonons are absorbed/emitted simultaneously. This is a rather unlikely process, which makes crystalline Si a poor material for optoelectronics.

Due to anharmonic contributions to the lattice vibrations, the crystals shrink as they get cooled down. As a consequence, the band gap increases with decreasing temperature. Empirically, one finds

$$E_{g, Si}(\Theta) = 1.17 \text{ eV} - \frac{4.73 \times 10^{-4} \Theta^2}{\Theta + 636 \text{ K}} \text{ eV}$$

$$E_{g, GaAs}(\Theta) = 1.52 \text{ eV} - \frac{5.4 \times 10^{-4} \Theta^2}{\Theta + 204 \text{ K}} \text{ eV}$$

For many applications, a fraction $x$ of the Ga atoms in GaAs is replaced by Al atoms, and the ternary $\text{Al}_x\text{Ga}_{1-x}\text{As}$ results. For $x \leq 0.38$, the band gap increases linearly with $x$, with a maximum at $E_g(\Gamma, x = 0.38) = 1.92 \text{ eV}$, and can be tailored for a specific application (see Fig. 2.6). For $x \geq 0.38$, however, the local minimum close to the X-point becomes the global minimum of the conduction band, and the material becomes an indirect semiconductor.

Pure AlAs as a band gap of $E_g = 2.16 \text{ eV}$. Note that the positions of the Al atoms are random,
which means that the ternary compound is not a crystal. Nevertheless, we can speak of band structures and effective masses, since such crystals can be treated within an averaging procedure known as “virtual crystal approximation” (see [Bastard1989]).

2.3 Occupation of energy bands

In this section, we study how the electrons occupy the valence and conduction bands. The electron density \( n \) in a band is obtained by integrating over the spectral electron density \( n(E) \), i.e. the density of electrons in the interval \([E, E + dE]\). The spectral electron density is given by the spectral density of electronic states \( D_d(E) \) available, multiplied by their occupation probability. Here, the index \( d \) denotes the dimensionality of the system. We will briefly discuss these two quantities.

2.3.1 The electronic density of states

The electronic density of states \( D_d(E) \) is the number of electronic states in \([E, E + dE]\) and per unit volume. It depends on the dimensionality \( d \) of the system and the energy dispersion \( E(\vec{k}) \) of the electronic band under consideration. The usual way to calculate \( D_d(E) \) is to determine the electronic mode density in \( k \)-space \( D_d(\vec{k}) \) of a cavity of size \( L^d \) and transform it into the energy space via \( E(\vec{k}) \). We carry out this calculation for a two-dimensional system with a parabolic energy dispersion, since this is what we will encounter most frequently in the following.

Consider a two-dimensional crystal cube with a base length \( L \), oriented along the \( x \)- and \( y \)-axes. We assume periodic boundary conditions, and use plane waves as base functions. \(^2\) An electronic state \( \Psi \) exists at wave vector \( \vec{k} \) if

\[
\Psi(\vec{r} + (L, L)) = \Psi(\vec{r}) \Rightarrow \vec{k} = \frac{2\pi}{L} (n_x, n_y)
\]

with \( n_i \) being an integer. The allowed wave vectors form a simple cubic lattice in \( k \)-space with a lattice constant of \( \frac{2\pi}{L} \). Each state is \( g \)-fold degenerate due to spin and valley degeneracies. Hence, there are \( g \) states in the volume \((\frac{2\pi}{L})^2\). States of equal \( |\vec{k}| \) are located at a circle. The number of states \( dN_2 \) in an annulus of radius \( \vec{k} \) and widths \( d\vec{k} \) is given by

\[
dN_2 = g \frac{2\pi k}{(2\pi/L)^2} dk
\]

with \( k = |\vec{k}| \). This gives a density of states in \( k \)-space of

\[
D_2(k) = \frac{1}{L^2} \frac{dN}{dk} = \frac{gk}{2\pi}
\]

\( D_2(E) \) is obtained from \( D_2(k) \) by a coordinate transformation

\[
D_2(E) = D_2(k) \frac{dk}{dE} = \frac{gm^*}{2\pi\hbar^2}
\]

\(^2\)It can be shown that the results do not depend on the boundary conditions.
Here, we have used the energy dispersion for electrons with an isotropic effective mass $m^*$,

$$E(\vec{k}) = \frac{\hbar^2 \vec{k}^2}{2m^*}$$

The density of states in 3, 2, and 1 dimensions are shown in Fig. 2.7.

**Question 2.5:** Calculate $D_3(E)$ and $D_1(E)$! Show that

$$D_3(E) = g \frac{(2m)^{3/2}}{4\pi^2 \hbar^3} \sqrt{E}$$

(2.14)

and

$$D_1(E) = g \frac{\sqrt{2m}}{2\pi \hbar} \frac{1}{\sqrt{E}}$$

(2.15)

How does the density of states look for a zero-dimensional system?

![Figure 2.7: The electronic density of states within the effective mass approximation as a function of energy, in one, two, and three dimensions.](image)

### 2.3.2 Occupation probability and chemical potential

In equilibrium, fermions occupy states of energy $E$ with a probability given by the Fermi-Dirac distribution function

$$f(E, \Theta) = \frac{1}{e^{(E - \mu)/k_B \Theta} + 1}$$

(2.16)

Here, $\mu$ denotes the chemical potential, i.e., the energy for which the density of occupied states with larger energies equals the density of empty states with lower energies. This definition, by the way, also holds if the occupation probability is not a Fermi-Dirac distribution. Furthermore, $\Theta$ is the temperature. The Fermi energy $E_F$ is the energy at which $f(E, \Theta = 0)$ jumps
2.3 Occupation of energy bands

from 1 to 0. Clearly, $\mu = E_F$ at $\Theta = 0$. For $\Theta > 0$, $\mu$ may differ from $E_F$, depending on the energy dependence of the density of states.

In a metal, at least one band is per definition partly occupied at $\Theta = 0$. Therefore, $E_F$ is located within an energy band. Semiconductors, on the other hand, are crystals where the conduction band is empty at $\Theta = 0$, and $E_F$ thus resides in the band gap. The same is of course true for insulators. The electron density in a band ranging from $E_{\text{bottom}}$ to $E_{\text{top}}$ is obtained from

$$n = \int_{E_{\text{bottom}}}^{E_{\text{top}}} n(E)dE = \int_{E_{\text{bottom}}}^{E_{\text{top}}} D_d(E)f(E,\Theta)dE$$  \hspace{1cm} (2.17)

Note that the dimensionality $d$ of $D_d(E)$ also determines the dimensionality of $n$. The Fermi function and the spectral electron density are sketched in Fig. 2.8.

![Figure 2.8](image_url)

**Figure 2.8:** Thermal smearing of the Fermi function (left), and the density of states ($d = 3$) as well as the spectral carrier density $n(E)$, right.

### 2.3.3 Intrinsic carrier concentration

The carrier concentration of a perfect, impurity-free crystal is called intrinsic. Here, the carriers are exclusively generated by thermal excitation of electrons from the valence band into the conduction band, which means that $n = p$ ($p$ denotes the hole density). Within the effective mass approximations and for a spin degenerate system ($g=2$), the carrier densities are given by

$$n = \frac{\sqrt{2m_e^*}}{\pi^2 \hbar^3} \int_{E_C}^{\infty} \sqrt{E - E_C}f(E,\Theta)dE;$$

$$p = \frac{\sqrt{2m_h^*}}{\pi^2 \hbar^3} \int_{-\infty}^{E_V} \sqrt{E_V - Ef(E,\Theta)}dE$$  \hspace{1cm} (2.18)
The chemical potential is close to the center of the band gap, slightly shifted towards the band with the lighter effective mass.\textsuperscript{3} Therefore, it is safe to assume that \(|E_{C,V} - \mu| \gg k_B\Theta\). This tells us that only the tails of the Fermi function, far away from the chemical potential, lie inside the bands, and can be well approximated by a Boltzmann distribution, i.e. \(f(E, \Theta) = \exp[-(E - \mu)/k_B\Theta]\). A brief calculation gives

\[ n = N_C e^{-(E_C - \mu)/k_B\Theta}; \quad p = P_V e^{(E_V - \mu)/k_B\Theta} \]  

\(N_C\) and \(P_V\) are known as “effective density of states”, given by

\[ N_C = \frac{1}{4} \left( \frac{2m^*_e k_B\Theta}{\pi \hbar^2} \right)^{3/2}; \quad P_V = \frac{1}{4} \left( \frac{2m^*_h k_B\Theta}{\pi \hbar^2} \right)^{3/2} \]

An immediate consequence is the “mass action law for charge carriers”

\[ n \cdot p = N_C P_V e^{-E_g/k_B\Theta} \Rightarrow n = p = \sqrt{N_C P_V e^{-E_g/2k_B\Theta}}\]

Inserting \(p\) in eq. (2.19) leads to

\[ \mu = E_V + \frac{1}{2} E_g + \frac{3}{4} k_B\Theta \ln m^*_h/m^*_e \]  

Fig. 2.9 summarizes the relations between density of states, Fermi function and intrinsic carrier densities in a semiconductor.

The exponential dependence of \(n\) and \(p\) on the temperature causes carrier freezeout as the temperature is reduced. At room temperature, we have an intrinsic electron density of \(n_{\text{Si}} = 1.45 \cdot 10^{16} \text{m}^{-3}\) for silicon and \(n_{\text{GaAs}} = 1.8 \cdot 10^{12} \text{m}^{-3}\) for GaAs, see exercise E 3.4.

At these typical, small carrier densities, the electron Fermi surface consists of six rotational ellipsoids in Si, and of a sphere in GaAs, as indicated in Fig. 2.4. In the valence band, the warped surfaces in the previous section represent Fermi spheres.

### 2.4 Envelope wave functions

So far, the materials have been homogeneous. The real crystal is certainly not perfect. Its translational symmetry can be perturbed, either by, e.g., unwanted lattice imperfections, or by intentionally built-in superpotentials. We will frequently see such superpotentials later on.

How do the wave functions and energy levels in such a perturbed crystal look like?

Consider a lattice imperfection with the perturbation potential \(V_p(\vec{r})\). For simplicity, we take only one electronic band into account. The Schrödinger equation for the imperfect crystal reads

\[ \left[ -\frac{\hbar^2}{2m} \Delta + V_{\text{lattice}}(\vec{r}) + V_p(\vec{r}) \right] \Phi(\vec{r}) = E \Phi(\vec{r}) \]  

\(\text{This is qualitatively clear as } \mu \text{ is given by the condition } n = p, \text{ and the density of states increases with increasing effective mass.}\)
The solution $\Phi(\vec{r})$ is no longer a Bloch function, but it can be expanded in the Bloch wave functions of the unperturbed band

$$\Phi(\vec{r}) = \sum_{\vec{k}'} c_{\vec{k}'} \xi(\vec{k}', \vec{r})$$  \hspace{1cm} (2.22)

Inserting this expansion into eq. (2.21), multiplying by $\xi^*(\vec{k}, \vec{r})$, integrating over the whole crystal gives

$$\epsilon(\vec{k}) c_{\vec{k}} + \sum_{\vec{k}'} c_{\vec{k}'} a(\vec{k}, \vec{k}') = E c_{\vec{k}}$$  \hspace{1cm} (2.23)

with the matrix elements

$$a(\vec{k}, \vec{k}') = \langle \xi(\vec{k}, \vec{r}) | V_p(\vec{r}) | \xi(\vec{k}', \vec{r}) \rangle$$  \hspace{1cm} (2.24)

We plan to rewrite eq. (2.23) in the form of a Schrödinger equation with a newly defined wave function, which will be the envelope function. This can be done by making two approximations, namely by (i) $V_p(\vec{r})$ varies "smoothly", meaning slowly on the scale of the lattice constant, and (ii) the effective mass approximation.
Our first task is finding an appropriate expression for $a(\vec{k}, \vec{k}')$. We have assumed that $V_p(\vec{r})$ varies slowly on the scale of individual unit cells. This means that we can keep $V_p(\vec{r})$ constant within each cell, which is referred to by the corresponding lattice vector $\vec{R}$. In order to use this in eq. (2.24), we split the integral, which runs over the whole crystal, into integrals running over unit cells, and sum them up:

$$a(\vec{k}, \vec{k}') = \sum_{\vec{R}} \int_{cell\vec{R}} \xi^*(\vec{k}, \vec{r}) V_p(\vec{r}) \xi(\vec{k}', \vec{r}) d\vec{r} = \sum_{\vec{R}} V_p(\vec{R}) \int_{cell\vec{R}} \xi^*(\vec{k}, \vec{r}) \xi(\vec{k}', \vec{r}) d\vec{r} \tag{2.25}$$

Since $\xi(\vec{k}, \vec{r})$ is of the form given by eq.(2.2), i.e. $\xi(\vec{k}, \vec{r}) = u_{\vec{k}}(\vec{r}) e^{i\vec{k} \cdot \vec{r}}$, the cell integral can be written as

$$\int_{cell\vec{R}} u_{\vec{k}}^*(\vec{R} + \vec{r}) u_{\vec{k}'}(\vec{R} + \vec{r}) e^{i(\vec{k}' - \vec{k}) \cdot \vec{r}} d\vec{r} \tag{2.26}$$

The function $u_{\vec{k}}^*(\vec{r}) u_{\vec{k}'}(\vec{r})$ has the periodicity of the lattice and can thus, according to the Fourier theorem, be expanded in harmonic functions with the same periodicity:

$$u_{\vec{k}}^*(\vec{r}) u_{\vec{k}'}(\vec{r}) = \sum_{\vec{G}} \alpha(\vec{G}) e^{i\vec{G} \cdot \vec{r}}; \quad \alpha(\vec{G}) = \frac{1}{V} \int_{V} u_{\vec{k}}^*(\vec{r}) u_{\vec{k}'}(\vec{r}) e^{-i\vec{G} \cdot \vec{r}} d\vec{r} \tag{2.27}$$

where $\vec{G}$ is a reciprocal lattice vector. With the Fourier expansion inserted in eq. (2.25), we obtain

$$a(\vec{k}, \vec{k}') = \sum_{\vec{G}, \vec{R}} \alpha(\vec{G}) V_p(\vec{R}) \int_{cell\vec{R}} e^{i(\vec{k}' - \vec{k}) \cdot \vec{r}} e^{i\vec{G} \cdot \vec{r}} d\vec{r} \tag{2.28}$$

which can be simplified considerably. First of all, $e^{i\vec{G} \cdot \vec{R}} = 1$, Second, since $V_p(\vec{r})$ varies smoothly, only Bloch waves within a narrow interval of $\vec{k}$ vectors will contribute to $a(\vec{k}, \vec{k}')$, and we can assume that $\vec{k}' - \vec{k}$ is small on the scale of the smallest reciprocal lattice vector. Therefore, it is justified to approximate $e^{i(\vec{k}' - \vec{k}) \cdot \vec{r}} \approx e^{i(\vec{k}' - \vec{k}) \cdot \vec{R}}$. After taking these considerations into account, eq. (2.28) reads

$$a(\vec{k}, \vec{k}') \approx \sum_{\vec{G}, \vec{R}} \alpha(\vec{G}) V_p(\vec{R}) e^{i(\vec{k}' - \vec{k}) \cdot \vec{R}} \int_{cell\vec{R}} e^{i\vec{G} \cdot \vec{r}} d\vec{r} \tag{2.29}$$

In addition, Green’s theorem for functions with the periodicity of the lattice [Ashcroft1985] tells us that

$$\int_{cell\vec{R}} e^{i\vec{G} \cdot \vec{r}} d\vec{r} = V_{cell} \delta_{\vec{G}, 0} \tag{2.29}$$

where $V_{cell}$ is the volume of the unit cell.
2.4 Envelope wave functions

**Question 2.6:** Prove eq. (2.29) for a one-dimensional crystal.

With eq. (2.29), we obtain

\[
a(\vec{k}, \vec{k}') = \alpha(0) \sum_{\vec{R}} V_p(\vec{R}) V_{\text{cell}} e^{i(\vec{R} - \vec{0})} \vec{R}
\]

Summing up the contributions of all cells can now be replaced by an integration over the whole crystal, such that

\[
a(\vec{k}, \vec{k}') = \alpha(0) \int_V V_p(\vec{r}) e^{i(\vec{k}' - \vec{k})} d\vec{r}
\]

It remains to determine \( \alpha(0) \), which we approximate by

\[
\alpha(0) = \frac{1}{V} \int_V u_\vec{k}^* \vec{r} u_{\vec{k}'}(\vec{r}) d\vec{r} \approx \frac{1}{V}
\]

This is justified since \( \vec{k}' \approx \vec{k} \), and the integral in the definition of \( \alpha(0) \) should give a value very close to 1 ( recall that the functions \( u_\vec{k} \) are normalized to 1). This finally leads to

\[
a(\vec{k}, \vec{k}') = \frac{1}{V} \int_V V_p(\vec{r}) e^{i(\vec{k}' - \vec{k})} d\vec{r}
\]

(2.30)

Inserting eq. (2.30) in eq. (2.23) and by using the effective mass approximation for the unperturbed crystal,

\[
\epsilon_\vec{k} = E_C + \frac{\hbar^2 \vec{k}^2}{2m^*}
\]

(2.31)

eq (2.23) changes to

\[
\frac{\hbar^2 \vec{k}^2}{2m^*} c_\vec{k} + [E_C - E] c_\vec{k} + \frac{1}{V} \sum_{\vec{k}'} c_{\vec{k}'} \int_V V_p(\vec{r}) e^{i(\vec{k}' - \vec{k})} d\vec{r} = 0
\]

(2.32)

We proceed by defining the envelope wave function as

\[
\psi(\vec{r}) = \frac{1}{\sqrt{V}} \sum_{\vec{k}'} c_{\vec{k}'} e^{i\vec{k}' \vec{r}}
\]

(2.33)

which we plan to insert the envelope wave function in eq. (2.32) by substituting \( c_{\vec{k}} \) and \( \vec{k}^2 c_{\vec{k}} \). This can be done via the relations

\[
c_{\vec{k}} = \sum_{\vec{k}'} c_{\vec{k}'} \delta(\vec{k} - \vec{k}') = \frac{1}{V} \int \sum_{\vec{k}'} c_{\vec{k}'} e^{i\vec{k}' \vec{r}} e^{-i\vec{k} \vec{r}} d\vec{r} = \frac{1}{\sqrt{V}} \int \psi(\vec{r}) e^{-i\vec{k} \vec{r}} d\vec{r}
\]
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\[ \vec{k}^2 c_G = \sum_{\vec{k}'} \vec{k}'^2 c_G \delta(\vec{k} - \vec{k'}) = \frac{1}{V} \int \sum_{\vec{k}'} \vec{k}'^2 c_G e^{i\vec{k}' \vec{r}} e^{-i\vec{k} \vec{r}} d\vec{r} = \]

\[ \frac{1}{\sqrt{V}} \int (-\Delta \psi(\vec{r})) e^{-i\vec{k} \vec{r}} d\vec{r} \]

The equation

\[ \int e^{-i\vec{k} \vec{r}} \left[ -\frac{\hbar^2 \Delta}{2m^*} + E_C - E + V_p(\vec{r}) \right] \psi(\vec{r}) d\vec{r} = 0 \]

is obtained, which is fulfilled for all \( \vec{k} \) only if

\[ \left[ -\frac{\hbar^2 \Delta}{2m^*} + V_p(\vec{r}) \right] \psi(\vec{r}) = \left[ E - E_C \right] \psi(\vec{r}) \]

(2.34)

This is the envelope wave equation. For perturbation potentials that vary slowly on the scale of the crystal unit cell, the energy eigenvalues of the \( V_p(\vec{r}) \) in the crystal correspond to the energy eigenvalues of \( V_p(\vec{r}) \) in a homogeneous medium with the dielectric constant of the crystal, and for particles which have the effective mass of the corresponding electronic band. The energy eigenvalues obtained from the envelope wave equation are relative to \( E_C \), the conduction band bottom, in our case. The envelope wave functions are thus just regular wave functions that solve eq. (2.34).

## 2.5 Doping

In many cases, it is desirable to have predominantly one type of mobile carrier, or to have a carrier density independent of temperature within a certain range. This can be achieved by implanting suitable impurities, also known as dopants, in the crystal. As an example, consider a Si atom replacing a Ga atom in a GaAs crystal (Fig. 2.10). Only three of the four valence electrons of Si can be placed in the covalent bonds with adjacent As atoms. The remaining electron will be bound to the attractive potential of the Si ion in the GaAs environment. This model will resemble a Coulomb potential in a medium with the dielectric constant of GaAs. It is straightforward to estimate the energy levels and the wave functions of this potential by using the effective mass approximation. The envelope wave equation for the electron in the donor potential reads

\[ \left[ -\frac{\hbar^2 \Delta}{2m_e} - \frac{e^2}{4\pi\epsilon_0 r} \right] \psi(\vec{r}) = \left[ E - E_C \right] \psi(\vec{r}) \]

(2.35)

The hydrogen-like energy levels of the doping atom are given with respect to the conduction band bottom. Compared to hydrogen, the energy spectrum is compressed by the factor \( \frac{1}{\epsilon^2} \frac{m_e^*}{m} \).

\[ E_D(n) = E_C + \frac{1}{\epsilon^2} \frac{m_e^*}{m} E_H = E_C - 13.6 \text{ eV} \cdot \frac{1}{\frac{3}{2}^2} \cdot \frac{1}{\frac{1}{2}^2} \frac{m_e^*}{m}. \]
2.5 Doping

Figure 2.10: Schematic example of a donor atom in a semiconductor.

Since for semiconductors, $\epsilon \approx 10$ and $m_e^* \approx 0.1 m$, the binding energy of a typical donor is reduced by a factor of $\approx 1000$ as compared to the hydrogen atom, and is just a few meV. The effective Bohr radius becomes very large. For the ground state of the dopant (j=1), it is found

$$a_B^* = \epsilon^2 \frac{m_e}{m_e^*} a_B \approx 5 \text{ nm},$$

which is much larger than the lattice constant. This in retrospect justifies our assumption that the doping electrons actually see the average dielectric constant of the host crystal.

Such weakly bound electrons can be easily thermally excited into the conduction band. Impurities that generate such levels are called donors. Simultaneously, states just above the valence band can be occupied by electrons from the valence band by thermal excitation (suppose the Si atom would replace an As atom). Impurities that generate this kind of state are called acceptors. Equivalently, we can rephrase this process and say “the acceptors donates a hole in the valence band”. In reality, the doping atoms usually do not replace the crystal atoms. Rather they are placed at interstitial sites, and it depends on the local potential whether the atom acts as a donor or as an acceptor. Typical n-dopants for Si are Sb and P, while B and Al are common p-dopants. In both cases, the binding energy of the electrons (holes) is in the range of 50 meV. Si and s are n-dopants for GaAs, with a binding energy of about 6 meV, while Be or Zn can be used for p-doping. Here, the hole binding energy is of the order of 30 meV. Some dopants, such as oxygen or chromium, have deep doping levels, which mean that they lie somewhere around the center of the band gap. This cannot be explained with the envelope function model, where only the parameters of the semiconductor host enter. It remains to mention that there are also excited dopant levels, which are of no further interest to us.

How do the carrier densities change due to the doping process? The mass action law still holds, but all doping atoms have to be included in the effective density of states. This, together with the charge neutrality condition, determines the carrier densities. We denote by $n_D$ and $p_A$...
the total density of donors/acceptors, by \( n_D^0 \) and \( p_A^0 \) the density of neutral donors/acceptors, and by \( n_D^+ \) and \( p_A^- \) the density of ionized donors/acceptors.

These quantities are related via \( n_D = n_D^0 + n_D^+ \) and \( p_A = p_A^0 + p_A^- \). In addition, charge neutrality requires \( n + p_A = p + n_D^+ \).

Let us take n-doping as an example and calculate \( n \). Now, the assumption made in the intrinsic case, \( k_B \Theta << E_C - \mu \) is no longer justified. The full solution of this problem is beyond our scope. Instead, we look at a simplifying approximation, which catches the main points.

Suppose that \( p_A = 0 \) and intrinsic carriers can be neglected. We further assume that \( E_C - \mu > k_B \Theta \), but \( E_D - \mu \approx k_B \Theta \). This means that the doping is so high that it pulls the chemical potential very close to the energy level of the dopant. It is important to note that for typical doping energies close to the valence or the conduction band, the occupation probability is no longer given by a Fermi-Dirac distribution. We discuss the origin qualitatively for a donor level. The derivation of eq. (2.16) is based on the assumption that each energy level can be occupied twice without an additional energy associated with the double occupancy. This is only true in the non-interacting case. In atoms, the Coulomb energy to be paid for sticking two electrons in the same orbital state typically exceeds the binding energy of the doping atom. If the donor ground state would be filled with two electrons, its energy increases above the conduction band edge, such that this state is unstable. Therefore, only three occupations have to be included in the quantum statistics leading to the probability distribution: the donor state is either empty, or occupied with an electron with spin up or spin down. The probability distribution

\[
f(E_D, \Theta) = \frac{1}{\frac{1}{2}e^{(E_D-\mu)/k_B \Theta} + 1}
\]

results. By a similar argument, it can be shown that for acceptor levels, the corresponding probability distribution reads

\[
f(E_A, \Theta) = \frac{1}{\frac{1}{2}e^{(\mu-E_A)/k_B \Theta} + 1}
\]

For a detailed discussion of this issue, see e.g. [Grosso2000]. Therefore, the density of occupied donor levels is given by

\[
n_D^0 = n_D (1 + \frac{1}{2} e^{(E_D-\mu)/k_B \Theta})^{-1}
\]

such that

\[
n = n_D^+ = n_D - n_D^0 = \frac{n_D}{1 + 2 e^{(\mu-E_D)/k_B \Theta}}
\]

(2.36)

Also, within our approximation, we can write \( n = N_C e^{-(E_C-\mu)/k_B T} \), similar to the intrinsic case. Inserting \( e^{\mu/k_B \Theta} = \frac{n}{N_C} e^{E_C/k_B \Theta} \) results in a quadratic equation for \( n \), the positive solution of which reads

\[
n = \frac{N_C}{4} e^{(E_D-E_C)/k_B \Theta} \left[ -1 + \sqrt{1 + \frac{8 n_D}{N_C} e^{(E_C-E_D)/k_B \Theta}} \right]
\]

(2.37)

Three regimes can be distinguished:
2.6 Diffusive transport and the Boltzmann equation

- \( k_B \Theta \ll E_C - E_D \) (freezeout regime). In this limit, eq. (2.37) gives
  \[
  n = \sqrt{\frac{N_C n_D}{2}} e^{-(E_C - E_D)/2k_B \Theta}
  \]
  By comparing this expression with the intrinsic case, one finds that the energy levels of the donors play the role of the valence band edge. In effect, the doping has reduced the band gap by three orders of magnitude. Due to the modified statistics, the effective donor density of states is half the doping density.

- \( k_B \Theta \gg E_C - E_D \), but \( k_B \Theta < E_g \) (saturation regime): expanding eq. (2.37) with respect to \((E_C - E_D)/k_B \Theta\) to first order gives \( n \approx N_D \). In this regime, the carrier density is constant, as long as intrinsic carriers can be neglected.

- \( k_B \Theta \approx E_g \) (intrinsic regime): This case is not included in eq. (2.37), but it is clear that now, the carrier concentration depends exponentially on the temperature, and the doping electrons can be neglected, since the doping density is per definition much lower than the density of crystal atoms. The three regimes are summarized in Fig. 2.11.

The chemical potential reacts accordingly to the temperature and can be easily calculated. For low temperatures, it resides close to the donor level, while at large temperatures, it approaches the middle of the band gap.

**Question 2.7:** Can you dope an insulator to make it conducting?

We have already mentioned that not all impurities generate shallow doping levels. Impurities with deep levels can be used for “undoping” samples. In some cases, it is desirable to have a semiconductor of extremely high resistivity at room temperature. Due to unavoidable, residual impurities which act as dopants, the resistivity of ultra-pure GaAs, for example, is not higher than about 1 \( \Omega \text{m} \). Chromium acts as an acceptor in GaAs with an energy level close to mid-gap. Hence, the residual doping electrons can be removed from the conduction band by a rather small density of Cr doping, which is, however, much higher than the residual n-doping (typical doping densities are of the order of \( n_{Cr} \approx 2 \cdot 10^{23} \text{ m}^{-3} \)). This way, the resistivities can be increased by more than three orders of magnitude. Therefore, such semiconductor materials are called semi-insulating. As a consequence, the Fermi level is typically fixed at the energy of the deep dopant, and one speaks of pinning of the Fermi level.

2.6 Diffusive transport and the Boltzmann equation

Before we discuss the basic components of diffusive transport theory, we briefly summarize some important results of solid state physics.

- Neither full nor empty bands carry current.
The resistance of a perfect crystal with at least one partially filled electronic band vanishes. The electrons obey the semiclassical equations of motion

$$\vec{v}(\vec{k}) = \frac{1}{\hbar} \vec{\nabla}_k E(\vec{k})$$

$$\frac{d\vec{k}}{dt} = -\frac{e}{\hbar} (\vec{E} + \vec{v}(\vec{k}) \times \vec{B})$$

Resistance is generated by deviations from the perfect lattice, such as phonons, impurities, lattice dislocations, but also by surfaces and interfaces.

Electron-electron scattering changes the total momentum of the electron gas only in exceptional cases, and does therefore, to a good approximation, not generate resistance.

For small electric fields applied, only a small fraction of the electrons around the Fermi energy contributes to the current.

In an introductory solid state physics course, transport usually means diffusive transport: a steady state is established between the external electromagnetic fields and the friction inside the solid, which on a microscopic scale is generated by various scattering events. The sample
size investigated is much larger than the mean free path, which is the distance an electron travels before it is scattered. This means we observe a homogeneous friction which stems from averaging over all microscopic scattering events.

The Boltzmann equation plays a central role in the theory of diffusive electronic transport. Even though electron-electron interactions and phase coherence are neglected already, the general version of the Boltzmann equation is a non-trivial integro-differential equation. Only after its linearization, the relaxation-time approximation and some further assumptions, the equation gives us a simple picture how an electric field acts on the carriers: essentially, within this approximation, the Fermi sphere is displaced in k-space without changing its shape. The relaxation time approximation introduces a phenomenological parameter known as “momentum relaxation time”, frequently also referred to as the “Drude scattering time”, $\tau$. All important scattering mechanisms are contained in this parameter. We can take it and use it in the Drude model, which is convenient to include magnetic field effects. We will make use of the Drude model on several occasions later on.

Anything that disturbs the perfect lattice will lead to scattering of electrons. Lattice imperfections, that we describe by a perturbation Hamiltonian $V_p$, will scatter electronic waves from the initial state $|\vec{k}\rangle$ in a final state $|\vec{k}'\rangle$. The scattering matrix elements $W_{\vec{k},\vec{k}'}$ have to be calculated from

$$W_{\vec{k},\vec{k}'} \propto |\langle\vec{k}'| V_p |\vec{k}\rangle|^2$$

(2.38)

A large subfield of transport theory is to calculate such matrix elements for all kinds of scatterers. We will mention some important scattering mechanisms below.

### 2.6.1 The Boltzmann equation

In general, both external fields as well as scattering will modify the Fermi distribution, which we write here as $f(\vec{k}) = [1 + e^{(E(\vec{k}) - \mu)/k_B T}]^{-1}$. The electron distribution function $\phi(\vec{k}, \vec{r}, t)$ is, in the most general case, not a Fermi function. It may depend on $\vec{r}$ and on the time $t$. Note that the points $\{\vec{k}, \vec{r}\}$ constitute the phase space. Therefore, $\frac{2}{(2\pi)^3}\phi(\vec{k}, \vec{r}, t)d\vec{k}d\vec{r}$ is the number of electrons in $d\vec{k}d\vec{r}$ for systems with a spin degeneracy of 2.

We consider the evolution of $\phi(\vec{k}, \vec{r}, t)$ in the time interval $dt$ after time $t$ due to an external, static electric field $\vec{E}$. We could add the effect of a magnetic field, which is dealt with in a similar way, although this is somewhat more elaborate [Seeger1997]. Within $dt$, an electron located at $(\vec{k}, \vec{r})$ in phase space at time $t$ moves to $(\vec{k} + \delta\vec{k}, \vec{r} + \delta\vec{r})$, which, according to the semiclassical equations of motion, equals $(\vec{k} - \frac{e}{\hbar}\vec{E}dt, \vec{r} + \vec{v}(\vec{k})dt)$. This only holds if the electron is not scattered into a different region of the phase space. Also, not all electrons in $(\vec{k} + \delta\vec{k}, \vec{r} + \delta\vec{r})$ at time $t + dt$ were at $(\vec{k}, \vec{r})$ at time $t$: they could have been scattered into this volume within $dt$. These scattering events may cause a change $\delta\phi$ in the electron density, which we write as $\delta\phi = \left[\frac{\partial\phi(\vec{k}, \vec{r}, t)}{\partial t}\right]_{\text{scatter}}d\vec{k}d\vec{r}dt$. This results in

$$\phi(\vec{k} - \frac{e}{\hbar}\vec{E}dt, \vec{r} + \vec{v}(\vec{k})dt, t + dt)d\vec{k}d\vec{r} = \phi(\vec{k}, \vec{r}, t)d\vec{k}d\vec{r} + \left[\frac{\partial\phi(\vec{k}, \vec{r}, t)}{\partial t}\right]_{\text{scatter}}dtd\vec{k}d\vec{r}$$

The size of the volume element $d\vec{k}d\vec{r}$ cannot change, which is the statement of Liouville’s theorem on the evolution of semiclassical systems in phase space. Now, the general Boltzmann
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equation is obtained by expanding the left hand side in a Taylor series in $dt$ up to first order:

$$\vec{v}(\vec{k}) \cdot \vec{\nabla} \phi(\vec{k}, \vec{r}, t) - \frac{e\vec{E}}{\hbar} \cdot \vec{\nabla}_k \phi(\vec{k}, \vec{r}, t) + \frac{\partial \phi(\vec{k}, \vec{r}, t)}{\partial t} = \left[ \frac{\partial \phi(\vec{k}, \vec{r}, t)}{\partial t} \right]_{\text{scatter}} \quad (2.39)$$

In principle, the scattering term can be calculated from the scattering matrix elements for all scattering mechanisms of relevance (like, e.g., electron-phonon scattering or impurity scattering, see [Seeger1997] for a detailed discussion), each weighted by the corresponding occupation probabilities of the initial states and the probabilities for finding the final state empty. These probabilities, however, are just the distribution functions $\phi(\vec{k}, \vec{r}, t)$ and $1 - \phi(\vec{k}, \vec{r}, t)$, respectively. Therefore, the general Boltzmann equation is in fact a complicated integro-differential equation, and models as well as approximations are needed to evaluate the scattering term.

A rather crude approximation consists of putting all these scattering mechanisms together and assume they generate an average "relaxation time" $\tau$, which we further assume to be independent of $\vec{k}$ and $\vec{r}$. It is based on the following picture. Let us further assume that the system is large enough to appear homogeneous in real space, such that we can drop the space coordinate. If we switch off the external field at time $t_0$, the distribution function will exponentially relax to $f(\vec{k})$ with a decay time $\tau$:

$$\phi(\vec{k}, t) = f(\vec{k}) + (\phi(\vec{k}, t_0) - f(\vec{k})) e^{-t/\tau}$$

This relaxation will take place exclusively via scattering, and hence

$$\frac{\partial \phi(\vec{k}, t)}{\partial t} = \left[ \frac{\partial \phi(\vec{k}, t)}{\partial t} \right]_{\text{scatter}} = -\frac{\phi(\vec{k}, t) - f(\vec{k})}{\tau}$$

which simplifies the general Boltzmann equation considerably. In a stationary state (no time dependence), it now reads

$$-\frac{e\vec{E}}{\hbar} \cdot \vec{\nabla}_k \phi(\vec{k}) = -\frac{\phi(\vec{k}) - f(\vec{k})}{\tau} \quad (2.40)$$

eq(2.40) can be further evaluated by considering small electric fields only. In this regime, the deviation of $\phi$ from the Fermi function should be roughly linear in $E$, and we can thus write $\vec{\nabla}_k \phi(\vec{k}) \approx \vec{\nabla}_k f(\vec{k})$. Now, eq. (2.32) represents a Taylor expansion of $\phi(\vec{k})$ in $(e\tau E/\hbar)$ up to first order:

$$\phi(\vec{k}) = f(\vec{k}) + \vec{\nabla}_k f(\vec{k}) \frac{e\tau E}{\hbar}$$

The right hand side is a good approximation for $f(\vec{k} + e\tau E/\hbar)$, provided that $e\tau E/\hbar \ll \vec{k}$. We thus finally find a simplified Boltzmann equation which states that under all the approximations made, small electric fields displace the Fermi surface in k-space by $e\tau E/\hbar$:

$$\phi(\vec{k}) = f(\vec{k} + \frac{e\tau E}{\hbar}) \quad (2.41)$$
2.6 Diffusive transport and the Boltzmann equation

Electrons get accelerated and scatter into empty states via elastic or inelastic processes, which emphasizes again the diffusive and dissipative character of the Boltzmann model. As a consequence, this displacement is quasi-static. In addition, we see that only electrons close to the edge of the Fermi sphere contribute to the current. For states deep inside the Fermi sphere, the partial current generated by an electron with momentum $\hbar \vec{k}$ is cancelled by the electron with momentum $-\hbar \vec{k}$.

2.6.2 The conductance predicted by the simplified Boltzmann equation

It remains to calculate the conductance $\sigma$ predicted by the assumptions leading to eq.(2.41). In general, $\sigma$ is a tensor defined by

$$ \vec{j} = \sigma \vec{E} $$

However, it makes sense to assume $\vec{j} \parallel \vec{E}$, such that $\sigma$ is actually a scalar. It is obtained from the current density via

$$ \vec{j} = \sigma \vec{E} \rightarrow \sigma = \frac{\vec{j} \vec{E}}{E^2} \quad (2.42) $$

In order to calculate $\vec{j}$, we have to integrate over the $\vec{k}$-space, weighing each state by its occupation probability. State $\vec{k}$ contributes a partial current of

$$ \vec{j}(\vec{k}) = -e\phi(\vec{k}) \vec{v}(\vec{k}) = -\frac{e \hbar}{m^*} \vec{k} \phi(\vec{k}) $$

Exponential relaxation is a consequence of Poisson processes, which are exemplified in chapter 8.
The total current density is obtained by summing up the contributions of all states. Since for a spin degeneracy of 2, each state occupies a volume of $4\pi^3/3$ in $\vec{k}$-space, this summation can be written as an integral
\[
\vec{j} = \int \vec{j}(\vec{k})d\vec{k} = -\frac{e\hbar}{4\pi^3m^*} \int \vec{k}f(\vec{k})d\vec{k} + \int \vec{k}\vec{\nabla}_k f(\vec{k})\frac{e\tau E}{\hbar}d\vec{k}
\]

Since
\[
\vec{\nabla}_k f(\vec{k}) = \frac{\partial f(\vec{k})}{\partial E} \vec{\nabla}_k E(\vec{k}) = \frac{\partial f(\vec{k})}{\partial E} \frac{h^2k}{m^*}
\]
the current density equals
\[
\vec{j} = -\frac{e^2\tau \hbar^2}{4\pi^3m^*} \int \vec{k}\frac{\partial f(\vec{k})}{\partial E}[\vec{k}\vec{E}]d\vec{k}
\]

With eq.(2.42), we can write
\[
\sigma = -\frac{e^2\tau \hbar^2}{4\pi^3m^*} \int \frac{(\vec{k}\vec{E})^2}{E^2} \frac{\partial f(\vec{k})}{\partial E} d\vec{k}
\]

For sufficiently low temperatures,
\[-\frac{\partial f(E)}{\partial E} = \delta(E - E_F) = \delta(k - k_F)\frac{m^*}{\hbar^2k}
\]
which results in the surface integral
\[
\sigma = \frac{e^2\tau}{4\pi^3m^*} \int \frac{(\vec{k}\vec{E})^2}{E^2} \delta(k - k_F) \frac{1}{k} d\vec{k} =
\]
\[
\frac{e^2\tau}{4\pi^3m^*} \int_{\theta=0}^{2\pi} \int_{\phi=0}^{\pi} \frac{k_F^2}{k} \cos^2(\phi) \sin(\phi) d\phi d\theta = \frac{e^2\tau k_F^3}{3\pi^2m^*}
\]

Since the electron density $n$ is given by $n = 3\pi^2k_F^3$, we find
\[
\sigma = \frac{ne^2\tau D}{m^*} = ne\mu
\]

Here, we have defined the electron mobility $\mu = e\tau D/m^*$. (2.43)

**Question 2.8:** Prove that $\sigma = ne\mu$ also holds in two dimensions.
2.6 Diffusive transport and the Boltzmann equation

Result (2.43) is at first sight quite strange: the conductivity is proportional to the total electron density, and it seems like all electrons would contribute equally to the current. However, we know that only the electrons at the Fermi surface carry current. The explanation is that a higher electron density increases the number of electrons and the electron velocity at the Fermi surface, which turns out to give a conductivity proportional to \( n \).

We can use eq. (2.43) to define a useful quantity, the drift velocity \( \vec{v}_d \) as

\[
\vec{v}_d = -\frac{\vec{j}}{en} = -\mu \vec{E} \tag{2.44}
\]

The drift velocity is thus an effective average velocity which leads to an equation for the current density that is formally identical to the Drude expression, which was derived by assuming that all electrons contribute equally to the current and move through the crystal with an average drift velocity.

Along similar lines, it can be shown that in the presence of additional magnetic fields, the current density can be written as

\[
\vec{j} = \sigma(\vec{E} + \vec{v}_d \times \vec{B}) \tag{2.45}
\]

This current density corresponds to the stationary solution of the classical equation of motion

\[
m^* \frac{d^2 \vec{r}}{dt^2} + \frac{m^*}{\tau} \vec{v}_d = -e(\vec{E} + \vec{v}_d \times \vec{B}) \tag{2.46}
\]

for electrons moving at velocity \( \vec{v}_d \) through the crystal, in the presence of electric and magnetic fields and with a Stokes-type friction term given by \( m^* \vec{v}_d / \tau \).

2.6.3 The magneto-resistivity tensor

We proceed by studying the electron transport according to eq. (2.46) in weak magnetic fields, with "weak" being specified by

\[
\omega_c = e |\vec{B}| / m_e^* \ll 1 / \tau \tag{2.47}
\]

This condition means that the distance the electrons travel before getting scattered (the mean free path \( \ell_c = v_F \tau \)) is small compared to the cyclotron radius \( r_c \). We will see in chapters 6 and 7 what happens when the electrons can complete the cyclotron orbits without getting scattered. Suppose a magnetic field is applied in z direction, \( \vec{B} = (0, 0, B) \). In such a case, we obtain

\[
j_x = \sigma E_x + \sigma v_y B = \sigma E_x + \frac{ne^2 \tau}{m_e^*} v_y B = \sigma E_x - j_y \omega_c \tau
\]

\[
j_y = \sigma E_y - \sigma v_x B = \sigma E_y - \frac{ne^2 \tau}{m_e^*} v_x B = \sigma E_y + j_x \omega_c \tau
\]

\[
j_z = \sigma E_z
\]
where \( v_j \) are the components of the drift velocity vector. Solving this system of equations for \( j \) gives 

\[
\mathbf{J} = \sigma \mathbf{E}
\]

with

\[
\sigma = \sigma_1 + \frac{\omega_c \tau}{1 + \omega_c^2 \tau^2}
\]

\( \sigma \) is known as the magneto-conductivity tensor. Its components can be experimentally determined by measuring four-probe resistances using “Hall bar”-shaped samples (Fig. 2.13). Voltage probes are attached to a rectangular thin film of the material, aligned parallel to the \( x \)- and \( y \)-direction, and perpendicular to the magnetic field direction. The transport in \( z \) direction remains unaffected by \( \mathbf{B} \) for us. We can determine the components \( \rho_{xx} \) and \( \rho_{xy} \) of the resistivity tensor by applying a current in \( x \)-direction and measuring the voltage drops \( V_x \) and \( V_y \). Since

\[
\begin{pmatrix}
V_x \\
V_y
\end{pmatrix}
= \begin{pmatrix}
\rho_{xx} & \rho_{xy} \\
-\rho_{xy} & \rho_{xx}
\end{pmatrix}
\begin{pmatrix}
I_x \\
I_y
\end{pmatrix}
\]

and

\[
\begin{pmatrix}
I_x \\
I_y
\end{pmatrix}
= \begin{pmatrix}
\sigma_{xx} & \sigma_{xy} \\
-\sigma_{xy} & \sigma_{xx}
\end{pmatrix}
\begin{pmatrix}
V_x \\
V_y
\end{pmatrix}
\]

we can establish the relation between the components of the resistivity and the conductivity tensors:

\[
\rho_{xx} = \frac{\sigma_{xx}}{\sigma_{xx}^2 + \sigma_{xy}^2}; \quad \rho_{xy} = -\frac{\sigma_{xy}}{\sigma_{xx}^2 + \sigma_{xy}^2}
\]  

(2.48)

We thus find that \( \rho_{xx} = 1/\sigma \) does not depend on \( \mathbf{B} \), and \( \rho_{xy} = -\omega_c \tau / \sigma = -B/en \). \( \rho_{xy} \) is the Hall resistivity, and \( R_H = -1/en \) is known as the Hall coefficient. Hall measurements are actually a standard tool to determine carrier densities. It may be counter-intuitive at first sight that for \( \rho_{xx} = 0 \), \( \sigma_{xx} \) becomes zero as well. Furthermore, the Onsager-Casimir symmetry relation should be mentioned, which states that the result of a measurement is exactly the same when all current- and voltage sources are exchanged, and the polarity of the magnetic field is reversed. One consequence is that two-probe measurements, i.e., for the voltage drop being measured at the source and drain contact, must be symmetric with respect to \( \mathbf{B} = 0 \).

### 2.7 Scattering mechanisms

As mentioned in Section 2.6, many scattering mechanisms contribute to the average momentum relaxation time \( \tau \). Each process has its characteristic matrix element \( W_{\mathbf{k}, \mathbf{k}'} \), eq. (2.38). The relevance of a particular kind of scattering varies greatly and depends on the carrier density as well as on the temperature. How in detail the matrix elements are calculated is treated in several excellent books, e.g., by [Seeger1997], and by [Ridley1999]. Each scattering mechanism can be characterized by its contribution to the carrier mobility \( \mu_i \), that sum up to the
2.7 Scattering mechanisms

Figure 2.13: Top: top view of a Hall geometry. The magnetic field is applied perpendicular to the sheet. Bottom: the components of the conductivity and the resistivity tensors are shown to the left and to the right, respectively.

total mobility according to the Matthiesen rule, \(1/\mu = \sum_i 1/\mu_i\). In pure crystals, the sole source of scattering are lattice vibrations. Electron-phonon scattering has several facets. In crystals with valley degeneracy, electrons may be scattered between valleys, which requires absorption or emission of a phonon. In polar and/or piezoelectric crystals, on the other hand, lattice vibrations go along with strong oscillating electric fields. In real crystals, charged impurities may dominate the scattering rates. We briefly present the most important scattering mechanisms below.

An impurity breaks the symmetry of the lattice and causes scattering. If the impurity is neutral, the scattering rates are usually negligible. Charged impurities, however, represent screened Coulomb scatterers, with peak potentials that can become comparable to the Fermi energy.\(^5\) Clearly, an electron with a larger kinetic energy will get deflected by a smaller angle as it gets scattered, and we can expect that the mobility increases as the temperature, and with is the average electron kinetic energy, increases. In fact, an evaluation of the corresponding matrix element shows that for weak Coulomb potentials and within the Born approximation, the resulting mobility is \(\propto \Theta^{3/2}\), multiplied by a logarithmic correction, i.e. a factor which depends logarithmically on \(\Theta\).

\(^5\)The screened Coulomb potential is studied in exercise 2.3.
Electron-phonon scattering can be divided into deformation potential scattering and scattering of electrons at the corresponding electric fields. By deformation potential scattering, we mean scattering at the lattice deformations caused by the phonons. Here, scattering at acoustic phonons is the most important mechanism. Since the energy transfers are small in electron-acoustic phonon scattering, it can be treated as quasi-elastic. A simple argument gives the correct temperature dependence. The density of acoustic phonons $n_{ac}$ is proportional to the Bose-Einstein distribution which, for large temperatures as compared to the phonon energy, varies as $1/\Theta$. Since the mobility is proportional to the $n_{ac}/\bar{v}$ ( $\bar{v}$ is the average electron velocity, which is $\propto \sqrt{\Theta}$), we expect that the mobility due electron-acoustic phonon scattering is $\propto \Theta^{-3/2}$. This is in fact observed experimentally.

Furthermore, both optical and acoustic phonons can assist the electron in scattering between the valleys in a crystal with valley degeneracy, such as Si. The corresponding momentum transfers are quite large, since the separation of the valley in reciprocal space is of the order of the size of the Brillouin zone.

This completes the list of the scattering mechanisms relevant in Si. In this material, ionized impurity dominates the mobility at low temperatures, while quasi-elastic acoustic phonon scattering is the most important mechanism at intermediate temperatures. For $\Theta > 200$ K, inter-valley scattering becomes significant as well. Consequently, the mobility in Si shows a
maximum as a function of temperature. Its position depends on both the impurity density and
and the carrier density. Electron mobilities up to \(1 \text{ m}^2/\text{Vs}\) have been achieved in Si.

GaAs is a polar material, and consequently, lattice vibrations are always accompanied
by oscillating electric fields. They are particularly strong for optical phonons. The resulting
scattering mechanism is called polar scattering. Optical phonons vanish for temperatures
below \(\approx 60 \text{ K}\), and consequently, polar scattering is relevant only above this temperature. In
the limit \(k_B \Theta \gg \hbar \omega_{\text{op}}\) (\(\omega_{\text{op}}\) denotes the optical phonon frequency, which for GaAs is of the
order of 5 meV, see Fig. 2.14), it can be shown that the resulting mobility varies as \(\Theta^{-1/2}\).
If the crystal is piezoelectric like GaAs, a crystal deformation generates a polarization field
as well, which is another source of scattering, which is called piezoelectric. As the polar
scattering, the mobility due to piezoelectric scattering is \(\propto \Theta^{-1/2}\), although this temperature
dependence holds for a larger range of temperatures.

Fig.2.15 summarizes the contributions of different scattering mechanisms to the electron
total mobility of GaAs. A comparison to measurements reveals that at low temperatures,
ionized impurity scattering dominates, while at larger temperatures, the mobility is entirely
determined by polar scattering. In a small temperature range around the emerging maximum
of the mobility, piezoelectric scattering is very significant. Furthermore, is is seen that acoustic
phonon scattering plays no role, in contrast to the scattering in Si.

2.8 Screening

The conduction electrons react to external perturbations. They collect in the potential valleys
and avoid the peaks. As a consequence, the external potential is reduced to an effective po-
tential in the crystal; the electrons “screen” the perturbation. The goal of this paragraph is to
present a qualitative picture how the electron density is modified by perturbations. For a more
detailed discussion of screening and electron-electron interactions, the reader is refered to
textbooks on solid state physics ([Ashcroft1985], [Grosso2000],[Ziman1995]).
By time dependent perturbation theory, it can be shown that the screening in a free electron
gas depends on the wave vector \(\vec{q}\) and the frequency \(\omega\) of the perturbation. It can be expressed
by a dielectric function \(\epsilon(\vec{q}, \omega)\) of the type

\[
\epsilon(\vec{q}, \omega) = 1 + \epsilon_{\text{lattice}} + \frac{\epsilon_0 q^2}{\epsilon_0 q^2} \sum \frac{f(k) - f(k + \vec{q})}{E(k + \vec{q}) - E(k) + i\alpha}.
\]

Here, \(\epsilon_{\text{lattice}}\) means the dielectric function of the lattice ([Ashcroft1985]), and \(\alpha \to 0\) is the
(small) convergence parameter that can be related to a scattering time (see the exercises).
The dielectric function describes how the Fourier components of the external potential energy
\(V_{\text{ext}}(\vec{q}, \omega)\) are screened and result in a effective potential energy \(V_{\text{eff}}(\vec{q}, \omega)\), namely

\[
V_{\text{eff}}(\vec{q}, \omega) = \frac{V_{\text{ext}}(\vec{q}, \omega)}{\epsilon(\vec{q}, \omega)}.
\]

In the static limit (\(\omega \to 0\)), within the effective mass approximation, and for low temperatures
\(k_B \Theta \ll E_F\), the sum in eq. (2.49) can be calculated analytically, and one finds

\[
\epsilon(\vec{q}) = 1 + \frac{k_F^2}{\epsilon_0 q^2} F^2\left(\frac{q^2}{2k_F}\right);
\]
Figure 2.15: Measured electron mobility in GaAs (circles) as function of temperature, including the theoretical contributions of relevant scattering mechanisms (full lines). The sample contained a donor density of $n_D = 4.8 \times 10^{19} \text{ m}^{-3}$ and an acceptor density of $n_A = 2.1 \times 10^{19} \text{ m}^{-3}$. After [Stillman1976].

$$F(s) = \frac{1}{2} + \frac{1-s^2}{4s} \ln \left| \frac{1+s}{1-s} \right|$$ (2.51)

Here, we have defined the Thomas-Fermi screening vector

$$k_{TF} = \epsilon \sqrt{\frac{D(E_F)}{\epsilon_0}}$$ (2.52)

The functions $F(s)$ and $\epsilon(\vec{q})$ are shown in Fig. 2.16. Most notably, $\epsilon(\vec{q})$ drops significantly as $\vec{q}$ increases. Above $2k_F$, it rapidly approaches 1. The reason is simply that for low temperatures, the wave vector of occupied states differs by no more than $2k_F$. The term $f(\vec{k}) - f(\vec{k} + \vec{q})$ means that only states contribute where the occupation of the two states characterized by $\vec{k}$ and $\vec{k} + \vec{q}$ is different. The number of contributing states thus increases as $0 \leq |\vec{q}| \leq 2k_F$, but remains constant for $|\vec{q}| > 2k_F$ in eq. (2.49), which means that $\epsilon(\vec{q})$ drops significantly at $|\vec{q}| = 2k_F$. This point in fact represents a logarithmic singularity, which has important consequences for the screening. As an example, consider the potential of a point charge with
2.8 Screening

Figure 2.16: The function $F(s)$, left, and the static dielectric function $\epsilon(\vec{q})$ for free electrons with typical experimental parameters in doped semiconductors ($k_F = 10^8$ m$^{-1}$).

an external potential energy given by

$$V_{\text{ext}}(r) = -Ze/r = -\frac{Ze^2}{(2\pi)^3} \int \frac{4\pi}{q^2} e^{i\vec{q}\cdot\vec{r}} d\vec{q}$$

Correspondingly, the effective potential energy can be written as

$$V_{\text{eff}}(r) = -Ze/r = -\frac{Ze^2}{(2\pi)^3} \int \frac{1}{\epsilon(q)} \frac{4\pi}{q^2} e^{i\vec{q}\cdot\vec{r}} d\vec{q}$$

The induced charge density $\rho_{\text{ind}}(\vec{r})$ is then given by the Poisson equation $\Delta V_{\text{ind}}(\vec{r}) = \Delta [V_{\text{eff}}(\vec{r}) - V_{\text{ext}}(\vec{r})] = -e\rho_{\text{ind}}(\vec{r})/\epsilon_0$, such that

$$\rho_{\text{ind}}(\vec{r}) = \frac{Ze}{(2\pi)^3} \int \frac{1}{\epsilon(q)} e^{i\vec{q}\cdot\vec{r}} d\vec{q}$$

Evaluating this integral shows that only terms with the argument $|\vec{q}| \approx 2k_F$ contribute significantly, and that for large $r$,

$$\rho_{\text{ind}}(\vec{r}) = \frac{Ze}{(2\pi)^3} \frac{k_F^2}{k_F^2 + (2k_F)^2} \cos(2k_F r) \frac{r^3}{r^3}$$

The charge density thus develops a periodic component, with a period of half the Fermi wavelength. This can be understood in terms of a standing wave due to a superposition of the incoming waves and the waves reflected at the perturbation potential. These oscillations are known as Friedel oscillations. ⁶

⁶Friedel oscillations are not a special property of screened Coulomb potentials. It can be shown [Gruner1977] that for large distances from the perturbing potential, $\rho_{\text{ind}}(\vec{r}) = A \frac{\cos(2k_F r + \phi)}{r^3}$, where the phase $\phi$ and the constant $A$ depend on the potential.
Papers and Exercises

E 2.1: A microchip factory processes "3-inch wafers", i.e., mono-crystalline, cylindrically shaped semiconductor disks, with a diameter of 3 inches and a height of 0.5 mm. Unfortunately, the silicon wafer badge and the GaAs wafer badge have not been labelled. Someone suggests to determine the material by weighing the wafers. Is this realistic?

Si has an atomic mass of 28.09 amu and crystallizes with a lattice constant of 0.543 nm. For Ga and As, the atomic mass is 69.72 amu, and 74.92 amu, respectively.; GaAs has a lattice constant of 0.565 nm. Calculate the weight of the two wafer types!

E 2.2: Suppose certain macromolecules form two-dimensional crystals. For each unit cell, $2\pi/3$ electrons are available for electronic bands. The unit cell is defined by the lattice vectors $\vec{a}_1 = (4 \text{ nm}, 0)$ and $\vec{a}_2 = (1 \text{ nm}, 3 \text{ nm})$.

(a) Calculate the reciprocal lattice vectors $\vec{b}_1, \vec{b}_2$. Draw the reciprocal lattice and construct the first and the second Brillouin zone.

(b) Suppose the energy dispersion can be approximated by that one of free electrons. What is the radius of the Fermi sphere? Draw the Fermi surface in the reciprocal lattice!

(c) Which period(s) would you expect in a de Haas -van Alphen experiment? The magnetic field is applied perpendicular to the crystal plane.

E 2.3: Study the dielectric function in the limit $|\vec{q}| \ll 2k_F$. Show that the potential of a screened point charge can be written as

$$V_{\text{eff}}(\vec{r}) = -\frac{Ze^2}{r} e^{-k_F r}$$

Screening in this limit is known as Thomas-Fermi screening.

E 2.4: Consider a periodic potential composed of $\delta$-functions

$$V(x) = -V_0 \sum_{n=-\infty}^{\infty} \delta(x + na)$$

with $V_0 > 0$ and $n$ integer.

(a) Determine the eigenvalue $E_0$ and the eigenfunction $\Phi_0(x)$ of a single $\delta$-function, $V_{\text{single}}(x) = -V_0 \delta(x)$.

(b) Show that the tight-binding wave functions of the crystal

$$\Psi_k(x) = \sum_{j=-\infty}^{\infty} \Phi_0(x - ja) \cdot e^{ikja}$$

satisfy Bloch’s theorem.
(c) Use the wave function and show by the method sketched in the text, that the dispersion relation takes the form

\[ E(k) = E_0 + \frac{\beta + \sum_{n=1}^{\infty} \gamma_n \cos(ka)}{1 + \sum_{n=1}^{\infty} \alpha_n \cos(ka)} \]

Note that life gets easier if the term with \( n = 0 \) is treated separately.

(d) What is the effective mass around \( k = 0 \)?

E 2.5: Use the band gap energies and the effective masses given in the text to calculate the effective densities of states \( N_c \) and \( P_v \), as well as the intrinsic carrier concentrations, for Si and GaAs at room temperature! What happens to the carrier concentrations as the materials are cooled to liquid nitrogen temperature?

**Further Reading**

There are several excellent books on solid state physics available, e.g., [Ashcroft1985],[Ziman1995], or [Grosso2000]. For particular properties of semiconductors, see [Seeger1997], [Yu1999]. The material parameters of the important semiconductors, are listed in a condensed, yet informative way in [Grahn1999].