2 Description of Charge Transport in Amorphous Semiconductors

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2.1 Introduction

In this chapter and in Chapter 6 [1] we present basic ideas for description of charge carrier transport in disordered inorganic and organic materials. Charge transport in disordered...
materials via extended states analogous to that in crystalline semiconductors is discussed in detail in Chapter 1 of this book [2]. Here we will focus on the transport properties determined by the presence of localized electron states in disordered materials. Localized states can either play the role of traps terminating charge carrier transport via extended states or they can be used by charge carriers in the so-called hopping transport mode, in which the carriers move via direct tunneling between the localized states.

The development of the study of disordered materials is rather curious. The field was, to a great extent, stimulated by the discovery of the semiconducting glasses, such as amorphous selenium, a-Se, and other chalcogenide glasses, for example, a-As$_2$Se$_3$ [3]. These materials are usually obtained by quenching from the melts. Such glassy semiconductors first gave rise to the hope that in various device applications one would be able to replace rather expensive crystalline semiconductors by much cheaper and better manufacturable semiconductor glasses. In the 1960s and 1970s this caused a real burst in experimental and theoretical study of glassy semiconductors, reflected in several monographs. To the interested reader we can recommend the book by Mott and Davis [4]. At the same time much research interest was devoted to the problems of hopping transport in doped crystalline semiconductors, where localized states for charge carriers (electrons and holes) are created by donors and acceptors. The latter systems provide a really valuable test field for theoretical description of hopping transport, since the electronic structure of individual localized states in doped semiconductors is well known. For shallow impurities these states are simple hydrogen-like electron states with renormalized Bohr radius. Due to the screening of the core Coulomb potential of the impurity atom by the semiconductor matrix, the wavefunction of the valence electron or hole on shallow donors and acceptors has a much larger spatial extension than that in a hydrogen atom. Nevertheless the structure of the electron state is very similar to that in a hydrogen atom. This well-known electron structure of localized states allows one to develop theoretical description of hopping transport in detail. A perfect description of the theory can be found in the book by Shklovskii and Efros [5]. Unfortunately, chalcogenide semiconductor glasses appear extremely resistant against doping. This makes such systems unfavorable for device applications, in which doping effects play a decisive role as, for example, in transistors. Chalcogenide materials are now mostly used for rewritable optical memory storage devices, where the pronounced difference in optical and electrical properties between the amorphous and crystalline phases serves for data storage [6, 7]. These materials were, however, not able to replace expensive crystalline systems in routine semiconductor device applications.

A new era in the study of disordered materials for applications in semiconductor electronics began in the 1970s with another class of disordered systems: inorganic amorphous semiconductors, such as amorphous silicon a-Si, amorphous germanium, a-Ge, and their alloys. These materials are usually prepared as thin films by the deposition of atomic or molecular species. Particularly, hydrogenated amorphous silicon, a-Si:H, has been attracting much research attention, since incorporation of hydrogen essentially improves conducting properties favorable for device applications of amorphous semiconductors. In 1975 Spear and LeComber [8] showed that a-Si can be efficiently doped by donors and acceptors. This opened a possibility for using amorphous semiconductors in traditional semiconductor electronics. Many other disordered materials, such as hydrogenated amorphous carbon, a-C:H, and its alloys, polycrystalline and microcrystalline silicon, are rather close to a-Si:H with respect to their charge transport properties. These materials are used in various device applications as described in detail in Chapter 3 of this book [9] on the example of...
a-Si:H. Several good monographs are devoted to optoelectronic phenomena in amorphous semiconductors. Among others we can recommend the book by Overhof and Thomas [10] and that of Street [11].

In recent years much research has also been devoted to the study of various other disordered materials such as organic semiconductors and dye-sensitized amorphous semiconductors used in particular for photovoltaic applications. While the scientific community dealing with chalcogenide glasses, doped crystalline semiconductors and amorphous semiconductors usually followed the traditions of research based on the deep theoretical concepts developed by Mott, Anderson, Pollak, Shklovskii, Efros, Thomas, Overhof, Zvyagin and others, many researchers working with more modern systems, as for example, organic disordered materials and dye-sensitized solar cells, sometimes perform rather obscure theoretical treatments of the optodynamic phenomena in these materials, being unaware of the classical results, known for decades for treatment of the analogous phenomena in inorganic amorphous materials. It might therefore be instructive for researchers working in the widespread fields of disordered materials to learn more about the basic concepts developed for description of the charge transport effects in inorganic amorphous semiconductors, such as a-Si:H, where the theoretical concepts are already well established. In this chapter we present some of these basic concepts. In Chapter 6 of this book [1], we show how these concepts can be easily extended for description of charge transport in organic disordered materials, such as conjugated and molecularly doped polymers. We would like to emphasize that in various chemically very different organic and inorganic disordered materials the charge transport phenomena look very similar and can be described by similar theoretical concepts. Unfortunately, communities working with different materials are rather separated from each other. They organize scientific meetings and publish their research results, often being unaware of the achievements in parallel fields. Therefore the exchange of ideas between scientific communities dealing with similar charge transport phenomena in chemically different materials might be very useful. We claim that ideas presented below for the theoretical treatment of transport phenomena in inorganic amorphous materials may be of use for researchers working with other disordered materials.

2.2 GENERAL REMARKS ON CHARGE TRANSPORT IN DISORDERED MATERIALS

Although the literature on the transport phenomena in amorphous semiconductors is enormously rich, there are still many open questions in this field due to many problems specific to such materials. In contrast to ordered crystalline semiconductors with well-defined electronic energy structure consisting of energy bands and energy gaps, the electronic energy spectrum of disordered materials can be treated as quasi-continuous. Instead of bands and gaps, one can only distinguish in disordered materials between extended and localized states. In the former states, the charge carrier wavefunction is spread over the whole volume of a sample, while in the latter states the wavefunction of a charge carrier is localized in a spatially restricted region, and a charge carrier in such a state cannot spread as a plane wave, as in ordered materials. Localized electron states are known in ordered systems as well. In crystalline materials electrons and holes can be spatially localized, occupying donor and acceptor states or some other impurity states and structural defects. However, in the energy spectrum of such materials, the localized states
usually appear in the form of $\delta$-like discrete energy levels. In the essentially disordered semiconductors, on the contrary, the energy levels related to the spatially localized states usually fill the energy spectrum continuously. In disordered materials there exists some energy level that separates the extended states from the localized ones. This energy level is called the *mobility edge*, as described in detail in Chapter 1 of this book [2]. We will consider in the following mostly the energy states for electrons rather than for holes. Electron states above the mobility edge are extended and below the edge the states are localized. For holes the localized states lie energetically above the extended states. The energy region between the mobility edges for holes and electrons is called the *mobility gap*. The latter is analogous to the bandgap in ordered systems, albeit, contrary to the bandgap, the mobility gap contains energy states, namely the spatially localized states. Since the density of states (DOS) defined as the concentration of states per unit energy, per unit volume usually decreases when the energy moves away from the mobility edges towards the center of the mobility gap, the energy regions of localized states in the vicinity of the mobility edges are called *band tails*. We would like to emphasize that the charge transport properties depend essentially on the energy spectrum in the vicinity and below the mobility edge, i.e., in the band tails. Unfortunately the precise structure of the energy spectrum, even in the band tails, is not known for almost all disordered materials. The whole variety of optical and electrical investigation techniques have not yet proven able to determine this spectrum. Some of the experimental techniques directed to determining DOS are described in Chapter 3 [9]. Although these techniques provide some estimates for the DOS, the problem is still far from its solution. Since the information on the energy spectrum provided by experimental study is rather vague, it is difficult to develop a consistent theoretical description of charge transport from first principles. The absence of reliable information on the energy spectrum and on the structure of the wavefunctions in the vicinity and below the mobility edges can be considered as the main problem for researchers in their attempts to describe quantitatively the charge transport properties of disordered materials.

The general view of the energy spectrum in a disordered inorganic semiconductor is schematically shown in Figure 2.1. An analogous picture can be found in Chapter 3. The energy levels $\varepsilon_v$ and $\varepsilon_c$ denote the mobility edges for the valence and conduction bands, respectively. Electron states in the mobility gap between these energies are spatially localized. The states below $\varepsilon_v$ and above $\varepsilon_c$ can be occupied by delocalized holes and electrons. Some peaks in the DOS are shown in the mobility gap, which can be caused by some defects with particularly high concentration. These parts of the spectrum are discussed in more detail in Chapter 3. Although there is a consensus between researchers on the general view of the DOS in disordered materials, the particular structure of the energy spectrum is not known for most disordered systems. From the theoretical point of view the problem of calculating this spectrum is enormously difficult. There have been many lot of attempts to deduce the shape of the DOS in amorphous semiconductors by fitting various experimental data using some particular assumptions on the energy spectrum. We consider in the subsequent sections some of these attempts based on the study of thermally stimulated currents or on the study of the so-called dispersive transport. Several complimentary results can be found in Chapter 3. Here we first discuss some general transport properties of amorphous semiconductors established experimentally.

Particular attention of researchers is usually given to the temperature dependence of the electrical conductivity since this dependence can indicate the underlying transport mecha-
nism. In a rather broad temperature range, the direct current (DC) conductivity in disordered materials has the form

$$\sigma = \sigma_0 \exp \left[ - \left( \frac{\Delta}{kT} \right)^\beta \right]$$

(2.1)

where the preexponential factor $\sigma_0$ depends on the underlying system and the power exponent $\beta$ depends on the material and also sometimes on the temperature range in which the conductivity is studied; $\Delta$ is the activation energy and $k$ is the Boltzmann constant. In many inorganic disordered materials, such as vitreous and amorphous semiconductors, $\sigma_0$ is of the order of $10^2 - 10^4 \Omega^{-1} \text{cm}^{-1}$. In such materials the power exponent $\beta$ is close to unity at temperatures close to and higher than room temperature, while at lower temperatures, $\beta$ can be essentially smaller than unity. In organic disordered materials considered in Chapter 6, values of $\beta$ larger than unity also have been reported. For such systems the value $\beta \approx 2$ is usually considered appropriate [12].

Another important characteristic of the electrical properties of disordered materials is their alternate current (AC) conductivity measured under application of an external alternating electric field with frequency $\omega$. It has been established in numerous experimental studies that the real part of the AC conductivity in most disordered semiconductors depends on frequency according to the power law

$$\text{Re} \sigma(\omega) = C \omega^s$$

(2.2)

where $C$ is constant and the power $s$ is usually slightly smaller than unity. This power law has been observed in numerous materials at different temperatures in a wide frequency range. This frequency dependence differs drastically from that predicted by the standard kinetic theory developed for quasi-free charge carriers in crystalline systems. Equation (2.2) indicates the decisive role of electron transitions between localized states in disordered materials.
semiconductors. The corresponding theory is described in detail in Chapter 9 of this book [13]. We will consider in our chapter only the DC conductivity.

In order to develop a theoretical picture for transport properties of any material, the first questions one should answer are the question on the spectrum of the energy states for charge carriers and the question on the spatial structure of such states. Since these two central questions are not yet answered appropriately for noncrystalline materials, the theory of charge transport in disordered systems should be still considered as a phenomenological one. The DC conductivity can be generally represented in the form [14]

\[ \sigma = e \int \varepsilon d \mu (\varepsilon) n (\varepsilon) \]  

where \( e \) is the elementary charge, \( n (\varepsilon) d \varepsilon \) is the concentration of electrons in the states with energies between \( \varepsilon \) and \( \varepsilon + d \varepsilon \) and \( \mu (\varepsilon) \) is the mobility of these electrons. Integration in Equation (2.3) is carried out over all energies \( \varepsilon \). Under equilibrium conditions, the concentration of electrons \( n (\varepsilon) d \varepsilon \) is determined by the density of states \( g(\varepsilon) \) and the Fermi function \( f(\varepsilon) \) dependent on the position of the Fermi energy \( \varepsilon_F \) (or on a quasi-Fermi energy in the case of stationary excitation of electrons):

\[ n (\varepsilon) = g (\varepsilon) f (\varepsilon) \]  

where

\[ f (\varepsilon) = \frac{1}{1 + \exp \left( \frac{\varepsilon - \varepsilon_F}{kT} \right)} \]  

The Fermi level in almost all known inorganic disordered semiconductors in realistic conditions is situated in the mobility gap, i.e., in the energy range which corresponds to spatially localized electron states. The charge carrier mobility \( \mu (\varepsilon) \) in the localized states below the mobility edge is much smaller than that in the extended states above the mobility edge. Therefore at high temperatures, at which a considerable fraction of electrons can be found in the delocalized states above the mobility edge, these states dominate the electrical conductivity of the system. The corresponding transport mechanism under such conditions is similar to that in ordered crystalline semiconductors. Electrons in the states within the energy range of the width of the order \( kT \) above the mobility edge dominate the conductivity. In such a case the conductivity can be estimated as

\[ \sigma = e \mu c n (\varepsilon_c) kT \]  

where \( \mu_c \) is the electron mobility in the states above the mobility edge \( \varepsilon_c \), and \( n (\varepsilon_c) kT \) is their approximate concentration, where

\[ n (\varepsilon_c) = f (\varepsilon_c) g (\varepsilon_c) = \frac{g (\varepsilon_c)}{1 + \exp \left( \frac{\varepsilon_c - \varepsilon_F}{kT} \right)} \]
This equation is valid under the assumption that the typical energy scale of the DOS function $g(\varepsilon)$ above the mobility edge is larger than $kT$. The position of the Fermi level in disordered materials usually depends only slightly on temperature. Combining Equations (2.6) and (2.7), one obtains the temperature dependence of the DC conductivity described by Equation (2.1) with $\beta \approx 1$ observed in most inorganic disordered semiconductors at high temperatures.

In order to obtain the numerical value of the conductivity in this high-temperature regime, one needs to know the density of states in the vicinity of the mobility edge $g(\varepsilon_c)$ and also the magnitude of the electron mobility $\mu_c$ in the delocalized states above $\varepsilon_c$. While the magnitude of $g(\varepsilon_c)$ is usually believed to be close to the DOS value in the vicinity of the band edge in crystalline semiconductors, there is no consensus among researchers on the magnitude of $\mu_c$. Unfortunately, there are no reliable theoretical calculations for this quantity in most disordered materials. The only exception is provided by the so-called mixed crystals, as described in Chapter 1 of this book. In amorphous semiconductors $\mu_c$ is usually estimated to be in the range between $1 \text{cm}^2/\text{V} \cdot \text{s}$ and $10 \text{cm}^2/\text{V} \cdot \text{s}$ [4, 10].

At lower temperatures, at which fewer electrons occupy extended states above $\varepsilon_c$ and many more electrons are in localized states, hopping electron transitions between localized states can play an essential and even a decisive role in the charge transport. In the next section we consider the hopping transport mode in more detail. The hopping transport mechanism determines transport phenomena in inorganic semiconductors in the range of temperatures well below room temperature, while in organic disordered materials this mechanism is believed to dominate charge transport at all temperatures. The latter topic is addressed in Chapter 6. The next section on the general features of hopping transport can therefore also considered as an introduction to Chapter 6.

### 2.3 HOPPING CHARGE TRANSPORT IN DISORDERED MATERIALS VIA LOCALIZED STATES

Electron transport via delocalized states above the mobility edge dominates electrical conductivity of disordered materials only at high enough temperatures, at which an essential fraction of charge carriers fill these states. With decreasing temperature, the concentration of such electrons described by Equation (2.7) decreases exponentially and consequently their contribution to electrical conductivity diminishes. Under such circumstances, tunneling transitions of electrons between localized states in the band tails dominate charge transport in disordered semiconductors. This transport regime is called hopping conduction, since an incoherent sequence of tunneling transitions of charge carriers resembles a series of their hops between randomly distributed sites. Each site in this picture provides a spatially localized electron state with some energy $\varepsilon$. In the following we will assume that the localized states for electrons with concentration $N_0$ are randomly distributed in space and their energy distribution is described by the DOS function $g(\varepsilon)$:

$$g(\varepsilon) = \frac{N_0}{\varepsilon_0} G\left(\frac{\varepsilon}{\varepsilon_0}\right)$$

(2.8)

where $\varepsilon_0$ is the energy scale of the DOS distribution.
A tunneling transition probability of an electron from a localized state \( i \) to a lower in energy localized state \( j \) depends on the spatial separation \( r_{ij} \) between sites \( i \) and \( j \) as

\[
v_0 = v_0 \exp\left(-\frac{2r_{ij}}{\alpha}\right)
\]

where \( \alpha \) is the localization length which we assume equal for sites \( i \) and \( j \). This length determines the exponential decay of the electron wave function in the localized states as shown in Figure 2.2. The preexponential factor \( v_0 \) in Equation (2.9) depends on the electron interaction mechanism that causes the transition. Usually it is assumed that electron transitions contributing to charge transport in disordered materials are caused by interactions of electrons with phonons. Often the coefficient \( v_0 \) is simply assumed to be of the order of the phonon frequency \( \sim 10^{13} \text{s}^{-1} \), although a more rigorous consideration is in fact necessary to determine \( v_0 \). Such a consideration should take into account the particular structure of the electron localized states and also the details of the interaction mechanism [15, 16]. Often values of \( v_0 \) larger than \( 10^{13} \text{s}^{-1} \) are necessary to reach agreement between theoretical results and experimental data [17].

When an electron performs a transition upward in energy from a localized state \( i \) to a higher in energy localized state \( j \), the transition rate depends on the energy difference between the states. This difference should be compensated, for example, by absorption of a phonon with the corresponding energy [18]:

\[
v(r_{ij}, \epsilon_i, \epsilon_j) = v_0 \exp\left(-\frac{2r_{ij}}{\alpha}\right) \exp\left(-\frac{\epsilon_j - \epsilon_i + |\epsilon_j - \epsilon_i|}{2kT}\right)
\]

Equations (2.9) and (2.10) were written for the case in which electron occupies site \( i \) whereas site \( j \) is empty. If the system is in thermal equilibrium, the occupation probabilities of sites with different energies are determined by the Fermi statistics. This effect can be taken into account by modifying Equation (2.10) and adding the terms which account for the relative energy positions of sites \( i \) and \( j \) with respect to the Fermi energy, \( \epsilon_F \). Taking into account these occupation probabilities one should write the transition rate between sites \( i \) and \( j \) in the form [18]

![Figure 2.2](https://via.placeholder.com/150)

**Figure 2.2** Hopping transition between two localized states \( i \) and \( j \) with energies \( \epsilon_i \) and \( \epsilon_j \), respectively. The solid and dashed lines depict the carrier wavefunctions on sites \( i \) and \( j \), respectively; \( \alpha \) is the localization radius.
With the help of these formulas the problem of the theoretical description of hopping conduction can be easily formulated. One has to calculate the conductivity which is provided by transition events with the rates described by Equation (2.11) in the manifold of localized states with the DOS described by Equation (2.8).

### 2.3.1 Nearest-neighbor hopping

Before presenting the correct solution of the hopping problem we would like to emphasize the following. The style of the theory for electron transport via localized states in disordered materials essentially differs from that of the theories for electron transport in ordered crystalline materials. While in crystalline systems the description is usually based on various averaging procedures, in disordered materials the averaging procedures can in many cases lead to extremely erroneous results. We find it instructive to first analyze some of such approaches in order to illustrate the difference in the description of charge transport for ordered and disordered materials. Treating the scattering rates of electrons in ordered crystalline materials, one usually proceeds by averaging the scattering rates over the ensemble of scattering events. A similar procedure is often tried for disordered systems as well, although it is known from textbooks (see, for instance [5]) how erroneous such an approach can be in the case of disordered materials.

Let us consider the simplest example of hopping processes, namely, hopping of an electron through a system of isoeenergetic sites randomly distributed in space with some concentration $N_0$. It will be assumed that electron states are strongly localized and the strong inequality $N_0 \alpha^3 \ll 1$ is fulfilled. In such a case electrons prefer to hop between the spatially nearest sites and therefore this transport regime is often called the nearest-neighbor hopping (NNH). This type of hopping transport takes place in many real systems at high enough temperatures when the thermal energy $kT$ is larger than the energy scale $\varepsilon_0$ of the DOS. In such situation the energy-dependent terms in Equations (2.10) and (2.11) do not play any essential role and the hopping rates are determined solely by the spatial terms. The rate of the transition of an electron between two sites $i$ and $j$ is described in such a case by Equation (2.9). The average transition rate is easily obtained by weighting this expression with the probability to find the nearest neighbor at some particular distance $r_{ij}$ and by integrating over all possible distances:

$$\langle v \rangle = v_0 \int_0^\infty dr \exp \left( -\frac{2r}{\alpha} \right) 4\pi r^2 N_0 \exp \left( -\frac{4\pi}{3} r^3 N_0 \right) = \pi v_0 N_0 \alpha^4$$  \hspace{1cm} (2.12)

Assuming that this average hopping rate describes the mobility, diffusivity and conductivity of charge carriers, one apparently comes to the erroneous conclusion that these quantities are linearly proportional to the concentration of localized states $N_0$. However, experiments evidence an exponential dependence of transport coefficients on $N_0$ [5].

Let us look therefore at the correct solution of the problem. This solution is provided in the case considered, $N_0 \alpha^3 \ll 1$, by the percolation theory [5]. In order to find the transport path, one treats a pair of sites as connected if the relative separation between the sites is...
smaller than some given distance $R$ and checks whether there is a continuous path through the system via such connected sites. If such path is not possible the magnitude of $R$ is increased and the procedure is repeated. At some particular value $R = R_c$ a continuous path through the infinite system via sites with relative separations $R \leq R_c$ arises. Various mathematical considerations give for $R_c$ in three-dimensional space the relation $[5, 19, 20]$

$$\frac{4\pi}{3} N_0 R^3 = B_c$$

(2.13)

where $B_c = 2.7 \pm 0.1$ is the average number of neighboring sites available within the distance smaller than $R_c$. The corresponding value of $R_c$ should be inserted into Equation (2.9) in order to determine such kinetic coefficients as the mobility, diffusivity and conductivity [5]. The idea behind this procedure is the following. Due to the exponential dependence of the transition rates on the distances between the sites, the rates of electron transitions over distances $r < R_c$ are much larger than those over distances $R_c$. Such fast transitions do not play any essential role as a limiting factor for electron transport and hence they can be neglected in the calculations of the resistivity of the system. Transitions over distances $R_c$ are the slowest among those which are still necessary for the DC transport and hence such transitions determine the conductivity. The structure of the percolation cluster responsible for charge transport is shown schematically in Figure 2.3.

The transport path consists of the quasi-one-dimensional segments each containing a 'difficult' transition over the distance $- R_c$. Inserting $R_c$ determined by Equation (2.13) into Equation (2.9) one obtains the dependence of the conductivity on the concentration of localization sites proportional to $\exp(-2R_c/\alpha)$ in the form

\[ \frac{4\pi}{3} N_0 R^3 = B_c \]

Figure 2.3 A schematic typical transport path with the lowest resistance. Circles depict localized states. The arrow points out the most 'difficult' transition over the distance $R_c$. 

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Y2
\[
\sigma = \sigma_0 \exp\left(-\frac{\gamma}{\alpha N_0^{1/3}}\right)
\]  
(2.14)

where \(\sigma_0\) is the concentration-independent preexponential factor and \(\gamma = 1.73 \pm 0.03\). Such arguments do not allow one to determine the exponent in the kinetic coefficients with accuracy better than a number of the order of unity [5]. One should however note that the quantity in the exponent in Equation (2.14) is much larger than unity for a system with strongly localized states under validity of the inequality \(N_0 \alpha^3 << 1\). This inequality justifies the above derivation. In numerous experimental studies of the hopping conductivity via randomly placed impurity atoms in doped crystalline semiconductors the dependence described by Equation (2.14) has been confirmed [5]. The drastic difference between this correct result and the erroneous one based on Equation (2.12) is apparent. Unfortunately the belief of many researchers in the validity of the procedure based on the averaging of hopping rates is so strong that the agreement between Equation (2.14) and the experimental data is sometimes called occasional. We would like to emphasize once more that the ensemble averaging of hopping rates leads to erroneous results. The magnitude of the average rate in Equation (2.12) is dominated by rare configurations of very close pairs of sites with separations of the order of the localization length \(\alpha\). Of course, such pairs allow very fast electron transitions, but electrons cannot move over considerable distances by using only such close pairs. Therefore, the magnitude of the average transition rate is irrelevant for calculations of the hopping conductivity [5, 21, 22]. The correct concentration dependence of the conductivity in the NNH regime is given by Equation (2.14).

So far, Equation (2.14) was obtained under the assumption that only spatial factors determine transition rates of electrons via localized states. This assumption is valid only at rather high temperatures. If the temperature is not as high and the thermal energy \(kT\) is comparable to or smaller than the energy spread of the localized states involved into the charge transport process, the problem of calculating the hopping conductivity becomes much more complicated. In such a case, the interplay between the energy-dependent and the distance-dependent terms in Equations (2.10) and (2.11) determines the conductivity. The lower the temperature, the more important become the energy-dependent terms in the expressions for transition probabilities of electrons in Equations (2.10) and (2.11). If the spatially nearest-neighboring sites have very different energies as shown in Figure 2.4,

**Figure 2.4** Two alternative hopping transitions between occupied states (full circles) and unoccupied states. The dashed line depicts the position of the Fermi level. Transitions (1) and (2) correspond to the nearest-neighbor hopping and to the variable range hopping regimes, respectively.

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the probability of electron transition between these sites upward in energy can be so low that it would be more favorable for the electron to hop to a more distant site if this site has energy closer to the initial one than to the nearest neighbor. Hence the typical length of electron transitions increases with decreasing temperature. This transport regime was therefore named variable-range hopping. We describe this transport mode in the following section.

### 2.3.2 Variable-range hopping

The concept of variable-range hopping (VRH) was put forward by Mott [4] who considered electron transport via a system of randomly distributed localized states at low temperatures. We start by presenting Mott’s arguments. At low temperatures, the most efficient transitions for transport are electron transitions between states with energies in the vicinity of the Fermi level, since only in this energy range can filled and empty states with close energies be found. Consider the hopping conductivity resulting from energy levels within a narrow energy strap with the width $2\Delta \varepsilon$ symmetric with respect to the Fermi level as shown in Figure 2.5. The energy width of the efficient strap for electron transport can be estimated from the relation

$$g(\varepsilon_F) \Delta \varepsilon \varepsilon_F^3(\Delta \varepsilon) = 1$$

(2.15)

This criterion is similar to that used in Equation (2.13) for NNH, though we do not care here about numerical coefficients. Here we have to do with the percolation problem in four-dimensional space since, in addition to the spatial terms considered in Section 2.3.1, we

![Figure 2.5](image.png)

**Figure 2.5** Effective region in the vicinity of the Fermi level, where the charge transport takes place at low temperatures
have now to consider also the site energies. For the transition rates described by Equation (2.11) the corresponding percolation problem has not yet been solved precisely. In Equation (2.15) it is assumed that the energy width $2\Delta \varepsilon$ is rather small and the DOS function $g(\varepsilon)$ is nearly constant in the range $\varepsilon_F \pm \Delta \varepsilon$. One can obtain the typical hopping distance from Equation (2.15) as a function of the energy width $\Delta \varepsilon$ in the form

$$r(\Delta \varepsilon) = [g(\varepsilon_F) \Delta \varepsilon]^{-1/3}$$  \hspace{1cm} (2.16)

and substitute it into Equation (2.10) in order to express the typical hopping rate

$$v = v_0 \exp \left\{ - \frac{2}{[g(\varepsilon_F) \Delta \varepsilon]^{1/3}} - \frac{\Delta \varepsilon}{kT} \right\}$$  \hspace{1cm} (2.17)

The optimal energy width $\Delta \varepsilon$ that provides the maximum of the hopping rate can be determined from the condition $dv/d\Delta \varepsilon = 0$. The result reads

$$\Delta \varepsilon = \left[ \frac{2kT}{3g^{1/3}(\varepsilon_F)} \right]^{1/4}$$  \hspace{1cm} (2.18)

After substitution of Equation (2.18) into Equation (2.17) one obtains the famous Mott formula for the temperature-dependent conductivity in the VRH regime

$$\sigma = \sigma_0 \left[ -\left( \frac{T_0}{T} \right)^{1/4} \right]$$  \hspace{1cm} (2.19)

where $T_0$ is the characteristic temperature:

$$T_0 = \frac{\beta}{k g(\varepsilon_F) \alpha^3},$$  \hspace{1cm} (2.20)

Mott gave only a semi-quantitative derivation of Equation (2.19), from which the exact value of the numerical constant $\beta$ cannot be determined. Various theoretical studies in three-dimensional systems suggest for $\beta$ values in the range from 10.0 to 37.8 [23]. According to our computer simulations, the appropriate value is close to 17.6 [24].

The Mott law implies that the density of states in the vicinity of the Fermi level is independent of energy. However it is known that due to the long-range electron–electron interactions between localized electrons a gap (the so-called Coulomb gap) in the DOS arises in the vicinity of the Fermi energy [25, 26]. The gap is shown schematically in Figure 1.6. Using simple semi-quantitative arguments, Efros and Shklovskii [26] suggested a parabolic shape for the DOS function in the vicinity of the Fermi level

$$g(\varepsilon) = \frac{\eta \kappa^3}{e^\varepsilon}(\varepsilon - \varepsilon_F)^2$$  \hspace{1cm} (2.21)

where $\kappa$ is the dielectric constant, $e$ is the elementary charge and $\eta$ is a numerical coefficient. This result has been later confirmed by numerous computer simulations (see, for
example, [27]). At low temperatures, the density of states near the Fermi level has a parabolic shape, and it vanishes exactly at the Fermi energy. With rising temperature, the gap disappears (see, for example, [28]).

As we have seen above, localized states in the vicinity of the Fermi energy are the most efficient ones for transport at low temperatures. Therefore the Coulomb gap essentially modifies the temperature dependence of the hopping conductivity in the VRH regime at low temperatures as compared with Equation (2.19). The formal analysis of the \( T \)-dependence of the conductivity in the presence of the Coulomb gap is similar to that for Mott’s law discussed above. Using the parabolic energy dependence of the DOS function one comes to the result [5]

\[
\sigma = \sigma_0 \left[ -\left( \frac{T_0}{T} \right)^{1/2} \right]
\]

(2.22)

with \( T_0 = \beta e^2/\kappa \alpha k \), where \( \beta \) is a numerical coefficient.

Equations (2.19) and (2.22) are among the most famous theoretical results in the field of variable-range hopping conduction. However these formulas are usually of little help for researchers working with noncrystalline materials, such as amorphous, vitreous or organic semiconductors. The reason is the following. The above formulas were derived for the case of either constant DOS (Equation 2.19) or a parabolic DOS (Equation 2.22) in the energy range essential for hopping conduction. These conditions can be usually met in the impurity band of a lightly doped crystalline semiconductor. However, in noncrystalline materials, the energy distribution of localized states is described by the DOS function which has a much stronger energy dependence than the parabolic one. In amorphous, vitreous and microcrystalline semiconductors the energy dependence of the DOS function is believed

![Figure 2.6 Schematic view of the Coulomb gap](image)
to be exponential, while in organic materials it is usually assumed as Gaussian. In such cases, new concepts are necessary in order to describe the hopping conduction. In the next section we present such concepts and calculate the dependences of the conductivity on temperature and on the concentration of localized states in inorganic disordered materials.

2.4 DESCRIPTION OF CHARGE-CARRIER ENERGY RELAXATION AND HOPPING CONDUCTION IN INORGANIC NONCRYSTALLINE MATERIALS

In most inorganic noncrystalline materials, such as vitreous, amorphous and polycrystalline semiconductors the localized states for electrons are distributed in a rather broad energy range with the width of the order of an electron volt. The DOS function that describes this energy distribution in such systems is believed to have an exponential shape [9]

\[ g(\varepsilon) = \frac{N_0}{\varepsilon_0} \exp\left(\frac{-\varepsilon}{\varepsilon_0}\right) \]  

(2.23)

where energy \( \varepsilon \) is counted positive from the mobility edge towards the center of the mobility gap, \( N_0 \) is the total concentration of localized states in the band tail, and \( \varepsilon_0 \) determines the energy scale of the tail. We consider here electrons as charge carriers. The results for holes can be obtained in an analogous way. The magnitudes of \( \varepsilon_0 \) in inorganic noncrystalline materials are believed to vary between \(-0.025\) and \(-0.05\) eV, depending on the system under consideration [9].

It is worth noting, that the arguments in favor of the purely exponential shape of the DOS in the band tails of inorganic noncrystalline materials described by Equation (2.23) cannot be considered as well justified. They are usually based on rather ambiguous interpretation of experimental data. One of the strongest arguments in favor of Equation (2.23) is the experimental observation of the exponential decay of the light-absorption coefficient for photons with an energy deficit \( \varepsilon \) with respect to the energy width of the mobility gap (see, for example, [4, 9]). One should mention however that this argument is valid only under the assumption that the energy dependence of the absorption coefficient is determined solely by the energy dependence of the DOS. In many cases, in particular in doped semiconductors, the matrix element for the electron excitation by a photon does strongly depend on energy [5, 29, 30]. Hence the argument on the shape of the DOS based on the energy dependence of the light absorption coefficient should be taken cautiously.

Another argument in favor of Equation (2.23) comes from measurements of the dispersive transport in time-of-flight experiments. In order to interpret the observed time dependence of the mobility of charge carriers, it is convenient to assume the DOS for the band tail in the form of Equation (2.23) (see, for example, [31]). In the following section we analyze the dispersive transport and show how the conclusion on the exponential shape of the band tail DOS in the inorganic disordered materials has been derived in the study of this phenomenon.
2.4.1 Dispersive transport in disordered materials

Nonstationary processes in noncrystalline semiconductors differ sometimes, essentially from such processes in the crystalline counterparts. As an example, we consider the time-of-flight study of the charge-carrier mobility. In this technique electrons and holes are usually generated by a short pulse of well-absorbed light in the vicinity of a sample surface. The sample is affected by the external constant electric field that causes motion of charge carriers towards the opposite sample surface. Which carriers move—electrons or holes—depends on the field polarity. Assuming the density of charge carriers to be low, the initial spatial width of the carrier packet small, the sample macroscopically homogeneous, the recombination in the sample volume negligible, one can easily interpret experimental observations. The key quantity in the time-of-flight measurements is the electrical current density as a function of time. If the injection of charge carriers from the contacts can be neglected, the current is [32]

\[ I(t) = \frac{dP(t)}{dt} - \frac{dQ(t)}{dt}, \quad (2.24) \]

where \( P(t) \) is the dipole moment of the system due to moving carriers and \( Q(t) \) is the total charge of moving carriers. In crystalline semiconductors the curve \( I(t) \) has usually a pronounced plateau followed by a rapid fall of the current, as shown schematically in Figure 2.7. The typical time \( \tau_r \) of the carrier transit through the sample is called the transit time. Knowing the length of the sample \( L \) and the strength of the applied electric field \( F \), one can easily determine the carrier drift velocity \( v_d = L/\tau_r \) and the carrier mobility:

\[ \mu = \frac{L}{F\tau_r}, \quad (2.25) \]

In crystalline semiconductors with broad plateaus in the \( I(t) \) curve, the shape of the carrier packet can be described by a Gaussian curve with width \( w = \sqrt{D\tau_r} \) determined by the diffusion coefficient of carriers \( D \). Therefore this type of transit is called Gaussian and the transport regime with such transits typical for ordered crystalline semiconductors is called

![Figure 2.7](image)

**Figure 2.7** Electrical current as a function of the normalized time. Curve 2 corresponds to a longer transit time \( \tau_r \) than curve 1.
Gaussian transport. The decay time of the current in such regime is \( \tau_d = v_c^{-1} \sqrt{D \tau_u} \). The latter is determined by the charge carriers leaving the sample after their transits.

In the noncrystalline inorganic semiconductors, the shape of the current transits in the time-of-flight measurements drastically differs from that shown in Figure 2.7. In the disordered materials the plateau in the curves \( I(t) \) usually does not show up and the after-transit kink in the dependence \( I(t) \) seen in Figure 2.7 is replaced by a pronounced shapeless tail as shown in the insert in Figure 2.8. This behavior is caused by a very wide dispersion of transit times for charge carriers. Therefore this transport regime is called dispersive transport in contrast to the Gaussian transport with narrow distribution of transit times caused solely by diffusive broadening of the carrier packet. It is difficult to determine a single transit time \( \tau_u \) in the time-of-flight measurements for dispersive transport from the featureless curves \( I(t) \). However if one plots the \( I(t) \) curve on a double-logarithmical scale, as shown in Figure 1.8, it is usually possible to observe the time corresponding to the change in the slope of the current decay curves \( I(t) \). This time is identified as a transit time \( \tau_u \) for dispersive transport. Approximately, one can describe \( I(t) \) in the form

\[
I(t) / I(t_{tr}) = \frac{1}{\sqrt{2\pi}} e^{-t^2/(2\sigma^2)}
\]

Figure 2.8 Normalized electrical current as a function of the normalized time typical for dispersive transport regime (schematic illustration). Dashed lines illustrate asymptotic Equations (2.26) with \( \alpha_e = \alpha_c = 0.5 \). The value of \( t_{tr} \) corresponds to the kink in the double-logarithmic curve.
where $\alpha_i$ and $\alpha_f$ are smaller than unity and often $\alpha_i = \alpha_f$ [32].

The anomalous time dependence of the transient current can be understood if one assumes that the motion of the center of mass of the charge carrier packet $\bar{x}$ slows down in course of time so that

$$\bar{x}(t) \propto t^\alpha$$

and the spatial width of the carrier packet is described not by the macroscopic diffusion, but rather it is of the order $\bar{x}$ [32]

$$\omega(t) \sim \bar{x}(t).$$

Combining Equations (2.24), (2.27), and (2.28) one obtains Equation (2.26) [32]. Assuming that at low electric fields the shift of the center of mass of the carrier packet is linearly proportional to the field strength, $\bar{x} = F \bar{r}^a$, one obtains the field dependence of the transit time in the form $\tau_{tr} \sim (L/F)^{1/a}$, which agrees well with experimental observations [32].

A more sophisticated mathematical description of the dispersive transport in the framework of a continuous random walk model leading to time dependences described above was suggested by Scher and Montroll [33].

A microscopic transport mechanism behind this phenomenological treatment should be further clarified. Scher and Montroll [33] suggested that the continuous random walk of a charge carrier with the necessary properties can arise in a hopping regime, in which charge carriers move via isoenergetic localized states with transition rates exponentially dependent on separations between such states as described in Section 2.3. According to this picture a carrier will be confronted with successively more and more difficult transitions in course of its random hopping motion, which would slow down its motion continuously, as described phenomenologically by Equation (2.27). However, Pollak [34] showed that the distribution of local transition times in a random walk would lead to the time dependences necessary to explain the broad dispersion of transient times only if there are traps, which catch charge carriers within times much smaller than the times of the release of carriers out of these traps. Otherwise carriers would be captured at time scales comparable to the release times and no dispersion would arise [34]. Hopping via randomly distributed isoenergetic sites would not lead to the broad dispersion of transient times since carriers always can leave the traps at a time scale at which they are captured [34]. Pollak also showed that a system with a sufficiently broad energy distribution of traps can, on the contrary, provide the necessary dispersion of transit times since carriers can be trapped rapidly from the transport states into energetically deep traps where they spend a long time before they are released back into transport states. The energy distribution of traps would lead to the broad distribution of the release times due to the exponential dependence of the release time on the trap energy [34]. Below we consider this model of dispersive transport in more detail following the very transparent approach of Orenstein and Kastner [31].

If one assumes that carriers in the localized states below the mobility edge $\epsilon_c$ are immobile, one can easily describe the carrier transport and energy relaxation (also called thermalization) in the framework of the so-called multiple-trapping model. In this model
hopping transitions of electrons between localized states are neglected and charge carriers can move only via extended states above $e_c$. This assumption can be true if the cutoff of the mobility is sharp compared with energy dependence of the occupation numbers of states determined by temperature and described by the Fermi distribution. Let us consider the energy distribution of electrons generated by a short pulse in the extended states above $e_c$. Assuming a constant capture crosssection of carriers into localized band-tail states, the states below $e_c$ will be first uniformly populated and the distribution of carriers after the first trapping event is determined solely by the density of states (DOS) in the tail. As time goes on, carriers from shallow states will be released into conducting states above $e_c$, while the trapping process remains random. This will lead to the redistribution of trapped carriers from shallow states into deeper energy states in the band tail. A demarcation energy, $E_d(t)$, separates the deep states whose occupation remains uniform from shallow states which are in thermal equilibrium with $e_c$ [31]. This demarcation level corresponds to the energy at which the trap-release time, $\tau(\epsilon)$, is of the order of the delay time after the laser pulse, $t$.

Counting energies $\epsilon$ of localized states positive from the mobility edge $e_c$ towards the center of the mobility gap, one can express the release time as

$$\tau(\epsilon) = v_0^{-1} \exp \left( \frac{\epsilon}{kT} \right)$$

and obtain the demarcation energy, determined by the condition $\tau(\epsilon_d) = t$, in the form

$$\epsilon_d(t) = kT \ln (v_0 t),$$

where $v_0$ is the attempt-to-escape frequency, usually assumed equal to the frequency of phonons (lattice vibrations) of the order $10^{12}$–$10^{13}$ s$^{-1}$ [31]. Thus $E_d(t)$ moves with time downward in the band tail away from $e_c$ as depicted in Figure 2.9. The carriers will be distributed

**Figure 2.9** Density of states (a) in which electrons are rapidly trapped after excitation. The time evolution of the electron distribution after excitation (b) is shown for three different times: $t$, $10t$, and $100t$ (reproduced from [31] with permission from Elsevier)
in energy according to the product of the occupation probability and the density of states, \( g(\varepsilon) \). For cases where \( g(\varepsilon) \) decreases rapidly with energy away from \( \varepsilon_c \), most of photoexcited carriers reside near \( \varepsilon_d(t) \) as illustrated in Figure 2.9.

The time-dependent current, \( I(t) \), is proportional to the carrier density, \( n(t) \) in high-mobility states above \( \varepsilon_c \) at time \( t \). Due to the definition of the demarcation energy \( \varepsilon_d(t) \) there is a thermal equilibrium between the states in the vicinity of the mobility edge \( \varepsilon_c \) and the states in the vicinity of \( \varepsilon_d(t) \). Therefore one can easily estimate the concentration of electrons in the conducting states at \( \varepsilon_c \) as [31]

\[
\frac{n(t)}{N} \equiv \frac{g(\varepsilon_c)}{\varepsilon_d} \exp \left( \frac{\varepsilon_c - \varepsilon_d}{kT} \right) \tag{2.31}
\]

where \( N \) is the total concentration of photoexcited charge carriers. Keeping in mind that we count energies positive downward from the mobility edge \( \varepsilon_c \equiv 0 \) and using Equations (2.23) and (2.30), one obtains from Equation (2.31)

\[
\frac{n(t)}{N} \equiv \left( \frac{1}{v_0 t} \right)^{1-\alpha}, \tag{2.32}
\]

with \( \alpha = kT/\varepsilon_0 \). This analysis applies directly to the time-of-flight measurements where the current density, proportional to the density of mobile carriers \( n(t) \), decreases with time according to Equation (2.26). Moreover, the linear temperature dependence of the dispersion parameter \( \alpha \) derived above is often observed experimentally in inorganic noncrystalline semiconductors [32]. This agreement between experimental data on dispersive transport and the very transparent theoretical picture based on the energy dependence of the DOS, \( g(\varepsilon) \), described by Equation (2.23) is often used as a reason to assume the validity of such a DOS in inorganic noncrystalline semiconductors such as a-Si:H.

Before finishing the description of the dispersive transport we would like to emphasize one important feature of the energy relaxation of charge carriers in the exponential DOS described by Equation (2.23). The values of the energy scale \( \varepsilon_0 \) of the DOS function in almost all known inorganic noncrystalline materials lie above \(-0.025 \) eV, which means that, at temperatures below room temperature, thermal energy \( kT \) is smaller than \( \varepsilon_0 \). Under such conditions the demarcation energy in the above picture moves with time away from the mobility edge without a limit. However in real systems the concentration of localized states in the band tail is not infinite and the above picture loses its validity as soon as the total amount of photogenerated carriers \( N \) becomes comparable to the number of localized states in the band tail below the demarcation energy. Using the above equations one can estimate the corresponding time delay \( t_{\text{lim}} \) from the condition \( v_0 t_{\text{lim}} = (N_0/N)^{1/\alpha} \). At times \( t \) larger than \( t_{\text{lim}} \) carriers achieve thermal equilibrium and the transport is no longer dispersive, since the concentration of mobile carriers cannot decrease with time due to the energy relaxation described above. It usually makes not much sense to study the behavior of a single charge carrier and to calculate its mobility in a system with the exponential DOS described by Equation (2.23) since this carrier infinitely relaxes downward in energy and its mobility continuously decreases. The effect of the occupation of localized states in the band tail will be described in Section 2.8.
So far we have considered the trivial version of the multiple-trapping model for the energy relaxation of charge carriers in the exponential band tail allowing only transitions between localized and extended states and neglecting direct tunneling transitions between localized states in the band tail. In the next section we remove this restriction and consider the same problem of the energy relaxation of charge carriers in the exponential band tail, including tunneling hopping transitions between localized states. The conclusion from this study will be the following. Almost all statements of the simplified consideration above remain valid. One should simply replace the mobility edge $\varepsilon_c$ by some energy level in the band tail, called the transport energy.

### 2.4.2 The concept of the transport energy

In the following we continue to assume that the DOS in a band tail of a noncrystalline material has the energy dependence described by Equation (2.23). This simple function will allow us to introduce in the most transparent analytical form some valuable concepts developed so far for description of electrical conduction in noncrystalline semiconductors. We first present the concept of the so-called transport energy, which, in our view, provides the most transparent description of the charge transport and energy relaxation of electrons in such materials. The crucial role of a particular energy level in the hopping transport of electrons via localized band-tail states with the DOS described by Equation (2.23) was first recognized by Grünewald and Thomas [35] in their numerical analysis of equilibrium variable-range hopping conductivity. This problem was later considered by Shapiro and Adler [36], who came to the same conclusion as Grünewald and Thomas, namely, that the vicinity of some particular energy level dominates the hopping transport of electrons in the band tails. In addition, they achieved an analytical formula for this level and showed that its position does not depend on the Fermi energy.

Independently, a rather different problem of nonequilibrium energy relaxation of electrons by hopping through the band tail with the DOS described by Equation (2.23) was solved at the same time by Monroe [37]. He showed that an electron, starting from the mobility edge, most likely makes a series of hops downward in energy. This character of the relaxation process changes drastically at some particular energy $\varepsilon_t$, which Monroe called the transport energy (TE). The hopping process near and below TE resembles a multiple-trapping type of relaxation with the TE playing the role of the mobility edge. In the multiple-trapping relaxation process [31] only electron transitions between delocalized states above the mobility edge and the localized band-tail states are allowed, while hopping transitions between the localized tail states are neglected. Hence, every second transition brings electron to the mobility edge. The TE of Monroe [37] plays the role of this edge for the hopping relaxation. It coincides exactly with the energy level discovered by Grünewald and Thomas [35] and by Shapiro and Adler [36] for equilibrium hopping transport. Shklovskii et al. [38] have shown that the same energy level $\varepsilon_t$ also determines recombination and transport of electrons in the nonequilibrium steady state under continuous photogeneration in a system with the DOS described by Equation (2.23).

We see, therefore, that the TE determines both equilibrium and nonequilibrium and both transient and steady-state transport phenomena. The question then arises as to why this energy level is so universal that hopping of electrons in its vicinity dominates all transport phenomena. We give below a derivation of the TE based on consideration of a single
hopping event of an electron localized deep in the band tail. It is the transport energy that maximizes the hopping rate as a final electron energy in the hop, independently of its initial energy [39]. All derivations below are carried out for the case $kT < \varepsilon_0$.

Consider an electron in a tail state with energy $\varepsilon_i$. According to Equation (2.9), the typical rate of a downward hop of such an electron to a localized state somewhat deeper in the tail energy $\varepsilon_j \geq \varepsilon_i$ is

$$v_i(\varepsilon_i) = v_0 \exp \left[ -\frac{2r(\varepsilon_i)}{\alpha} \right]$$  \hspace{1cm} (2.33)

where

$$r(\varepsilon) = \left[ \frac{4\pi}{3} \int_{-\infty}^{\infty} dx \ g(x) \right]^{1/3}$$  \hspace{1cm} (2.34)

The typical rate of an upward hop of such an electron to a localized state shallower in the tail with energy $\varepsilon_j \leq \varepsilon_i$ is

$$v_j(\varepsilon_i, \delta) = v_0 \exp \left[ -\frac{2r(\varepsilon_i - \delta)}{\alpha} - \frac{\delta}{kT} \right]$$  \hspace{1cm} (2.35)

where $\delta = \varepsilon_i - \varepsilon_j \geq 0$. This expression is not exact. The average nearest-neighbor distance, $r(\varepsilon_i - \delta)$, is based on all states deeper than $\varepsilon_i - \delta$. For the exponential tail this is equivalent to considering a slice of energy with the width of the order $\varepsilon_0$. This works for a DOS that varies slowly compared with $kT$, but not in general. It is also assumed for simplicity that the localization length $\alpha$ does not depend on energy. The latter assumption can be easily released on the cost of a somewhat more complicated form of the equations. We will analyze the hopping rates at a given temperature $T$, and try to find the energy difference $\delta$ which provides the fastest typical hopping rate for an electron placed initially at energy $\varepsilon_i$. The corresponding energy difference $\delta$ is determined by the condition

$$\frac{dv_j(\varepsilon_i, \delta)}{d\delta} = 0.$$  \hspace{1cm} (2.36)

Using Equations (2.23), (2.34), and (2.35), we obtain that the hopping rate in Equation (2.35) has its maximum at

$$\delta = \varepsilon_i - 3\varepsilon_0 \ln \frac{3\varepsilon_0 (4\pi/3)^{1/3} N_0^{1/3} \alpha}{2kT}$$  \hspace{1cm} (2.37)

The second term in the right-hand side of Equation (2.37), but with the opposite sign, determines the energy level $\varepsilon_i$ called, after Monroe [37], the transport energy:

$$\varepsilon_i = 3\varepsilon_0 \ln \frac{3\varepsilon_0 (4\pi/3)^{1/3} N_0^{1/3} \alpha}{2kT}$$  \hspace{1cm} (2.38)
We see from Equation (2.37) that the fastest hop occurs to a state with energy in the vicinity of the TE, independently of the initial energy $\varepsilon_i$, provided $\varepsilon_i$ is deeper in the tail than $\varepsilon_t$, i.e., if $\delta \geq 0$. This result coincides with that of Monroe [37]. At low temperatures, the TE $\varepsilon_t$ is situated deep in the band tail, while with rising temperature it moves upward towards the mobility edge. At some temperature $T_c$, the TE merges with the mobility edge. At higher temperatures, $T > T_c$, the hopping exchange of electrons between localized band-tail states becomes inefficient and the dynamic behavior of electrons is well accounted for by the multiple-trapping model described in Section 2.4.1. At low temperatures, $T < T_c$, the TE replaces the mobility edge in the multiple-trapping process [37], as shown in Figure 2.10. The width $W$ of the maximum of the hopping rate is determined by the requirement that near $\varepsilon_t$ the hopping rate, $v(\varepsilon_i, \delta)$, differs by less than a factor of $e$ (the base of natural logarithms) from the value $v(\varepsilon_i, \varepsilon_i - \varepsilon_t)$. One finds [38]

$$W = \sqrt{6e_i kT} \quad (2.39)$$

For shallow states with $\varepsilon_i \leq \varepsilon_t$ the fastest hop, on the average, is a downward hop to a nearest spatially localized state in the band tail with the rate determined by Equations (2.33) and (2.34). We recall that the energies of electron states are counted positive downward from the mobility edge towards the center of the mobility gap. This means that electrons in the shallow states with $\varepsilon_i \leq \varepsilon_t$ normally hop into deeper states with $\varepsilon > \varepsilon_t$, whereas electrons in the deep states with $\varepsilon > \varepsilon_t$ usually hop upward into states with energies near $\varepsilon_t$ in the energy interval $W$, determined by Equation (2.39).

This shows that $\varepsilon_t$ must play a crucial role in those phenomena which are determined by hopping of electrons in the band tails. Let us consider here for illustration the hopping

**Figure 2.10** Hopping path via the transport energy. In the left frame, exponential DOS is shown schematically. The right frame depicts the transport path constructed from upward and downward hopes. The upward transitions bring a charge carrier to the sites with energies in the vicinity of the transport energy $\varepsilon_t$.
energy relaxation of electrons in a system with the DOS described by Equation (2.23). This problem was studied initially by Monroe [37].

Consider an electron in some shallow localized energy state with the energy close to the mobility edge. Let the temperature be low, \( T < T_c \), so that the \( \text{TE}(\varepsilon_t) \) lies well below the mobility edge, which we consider here as a reference energy \( \varepsilon_c = 0 \). The problem is to find the typical energy \( \varepsilon_d(t) \) of the electron as a function of time, \( t \). At early times, as long as \( \varepsilon_d(t) < \varepsilon_c \), the relaxation is governed by Equations (2.33) and (2.34). The depth \( \varepsilon_d(t) \) of an electron in the band tail is determined by the condition

\[
v_d[\varepsilon_d(t)]t = 1 \quad (2.40)
\]

This leads to the double logarithmic dependence \( \varepsilon_d \approx \varepsilon_0 \ln[\ln(v_d t)] + C \) with constant \( C \) dependent on \( \varepsilon_0, N_0, \) and \( \alpha \). Indeed, Equations (2.33) and (2.40) prescribe the logarithmic form for the time dependence of the hopping distance \( r(t) \) and Equations (2.23) and (2.34) lead to another logarithmic dependence \( \varepsilon_d[r(t)] \) [37]. At the time

\[
t_c = v_0^{-1} \exp\left(\frac{3\varepsilon_0}{kT}\right) \quad (2.41)
\]

the typical electron energy \( \varepsilon_d(t) \) approaches the \( \text{TE}(\varepsilon_t) \) and the style of the relaxation process changes. At \( t > t_c \), every second hop brings the electron into states in the vicinity of the \( \text{TE}(\varepsilon_t) \) from where it falls downward in energy to the nearest in space localized state. For the latter relaxation process the typical electron energy analogous to the demarcation energy in Equation (2.30) is determined by the condition [37]

\[
v_t[\varepsilon_d(t), \varepsilon_t]t = 1, \quad (2.42)
\]

where \( v_t[\varepsilon_d(t), \varepsilon_t] \) is the typical rate of electron hop upward from the demarcation energy towards the \( \text{TE} \) [37]. This condition leads to the typical energy position of the relaxing electron at time \( t \) determined as

\[
\varepsilon_d(t) = 3\varepsilon_0 \ln[\ln(v_t t)] - 8\varepsilon_0/(N_0\alpha^3) \quad (2.43)
\]

This is a very important result, showing that in a system with purely exponential energy dependence of the DOS, described by Equation (2.23), the typical energy of a set of independently relaxing electrons would continuously dive with time deeper and deeper into the mobility gap, as described in Section 2.4.1.

We would like to emphasize once more that one should be cautious with application of theoretical methods traditional for crystalline materials to the description of charge transport phenomena in disordered systems. For example, in some theoretical studies based on the Fokker–Planck equation, it has been claimed that the maximum of the energy distribution of electrons coincides with the \( \text{TE}(\varepsilon_t) \) and hence it is independent of time (see, for example [40]). Such statements are in contradiction to the above result with the maximum of the distribution at energy \( \varepsilon_d(t) \) given by Equation (2.43). One should realize that the Fokker–Planck approach presumes a diffusive style of charge carrier energy relaxation. Hence, it is invalid for description of the energy relaxation in the exponential tails, in which
electron can jump over the full energy range of the DOS (from a very deep energy state towards the TE) in a single hopping event [41].

2.5 EINSTEIN’S RELATIONSHIP FOR HOPPING ELECTRONS

2.5.1 Nonequilibrium charge carriers

In this section we would like to consider a very interesting problem related to the nonequilibrium energy relaxation of charge carriers in the band-tail states. It is well known that at low temperatures, $T \leq 50\,K$, the photoconductivity in various inorganic noncrystalline materials, such as amorphous and microcrystalline semiconductors, does not depend on temperature [42–44]. At low temperatures, the TE ($\varepsilon_n$) lies very deep in the band tail and most electrons hop downward in energy. Concomitantly, the photoconductivity is a temperature-independent quantity determined by the energy loss hopping of electrons via the band-tail states [45]. In such hopping relaxation, neither diffusion coefficient $D$, nor mobility of carriers $\mu$, depends on temperature and the conventional form of the Einstein relationship $\mu = eD/\kappa T$ cannot be valid. The question arises then as to what is the relation between $\mu$ and $D$ for the energy-loss hopping relaxation. We answer this question below.

Let us start considering a system of nonequilibrium electrons in the band-tail states at $T = 0$. The only process that can happen with an electron is its hop downward in energy (upward hops are not possible at $T = 0$) to a nearest localized state in the tail. The rate of such process is described by Equations (2.33), (2.34), and (2.23). If the spatial distribution of localized tail states is isotropic, the probability of finding the nearest neighbor is also isotropic in the absence of the external electric field. In such a case, the process of the hopping energy relaxation of electrons leads to the spatial movement of electrons that resembles the diffusion in space. However, the median length of a hop (the distance $r$ to the nearest neighbor available), as well as the median time $\tau = v_d(r)$ of a hop (see Equation 2.33) increases in the course of relaxation, since the hopping process brings electrons deeper into the tail. Nevertheless one can ascribe to such a process a diffusion coefficient [45]

$$D(r) = \frac{1}{6} v_d(r) r^2$$

Here $v_d(r)r^2$ replaces the product of the ‘mean free path’ $r$ and the ‘velocity’ $rv_d(r)$ and the coefficient 1/6 accounts for the spatial symmetry of the problem. According to Equations (2.33), (2.34), (2.23), and (2.44), this diffusion coefficient decreases exponentially with increasing $r$ and hence with the number of successive electron hops in the relaxation process.

In order to calculate the mobility of electrons in their energy-loss hopping relaxation under the influence of the electric field, one should take into account the spatial asymmetry of the hopping process due to the field [21, 45]. Let us consider an electron in a localized state at energy $\varepsilon$. If the external electric field with a strength $F$ is applied along direction $x$, the concentration of tail states available for a hop of this electron at $T = 0$ (i.e., those, which have energies deeper in the tail than $\varepsilon$) is [45]
\[ N(\varepsilon, x) = N(\varepsilon) \left( 1 + \frac{F x}{\varepsilon_0} \right) \]  \hspace{1cm} (2.45)

where

\[ N(\varepsilon) = \int_{\varepsilon}^{N} d\varepsilon \exp \left( -\frac{\varepsilon}{\varepsilon_0} \right) \] \hspace{1cm} (2.46)

The strong inequality \( e F x \ll \varepsilon_0 \) was assumed in the derivation of Equation (2.45).

Due to the exponential dependence of the hopping rate on the hopping length \( r \), the electron predominantly hops to the nearest tail state among available states if \( r \gg \alpha \), which we assume to be valid. Let us calculate the average projection \( \langle \hat{x} \rangle \) on the field direction of the vector \( r \) from the initial state at energy \( \varepsilon \) to the nearest available neighbor among sites with concentration \( N(\varepsilon, x) \) determined by Equation (2.45). Introducing spherical coordinates with the angle \( \theta \) between \( r \) and \( x \)-axis, we obtain [21]

\[
\langle x \rangle = \int_{0}^{\frac{2\pi}{\varepsilon}} d\phi \int_{\frac{\pi}{2}}^{\pi} d\theta \sin \theta \int_{0}^{\theta} d\rho \rho^3 \cos \theta N(\varepsilon, r, \cos \theta) \]

\[
\times \exp \left[ -\int_{0}^{\frac{2\pi}{\varepsilon}} d\phi \int_{\frac{\pi}{2}}^{\pi} d\theta \sin \theta \int_{0}^{\theta} d\rho \rho'^3 N(\varepsilon, r', \cos \theta) \right] \] \hspace{1cm} (2.47)

Substituting Equation (2.45) for \( N(\varepsilon, r', \cos \theta) \), calculating the integrals in Equation (2.47) and omitting the second-order terms

\[
\left( \frac{e N^{-1/3}(\varepsilon) F}{\varepsilon_0} \right)^2 \ll 1 \] \hspace{1cm} (2.48)

we obtain

\[
\langle x \rangle = \frac{e F N^{-2/3}(\varepsilon) \Gamma(5/3)}{3\varepsilon_0 (4\pi/3)^{2/3}} \] \hspace{1cm} (2.49)

where \( \Gamma(z) = \int_{0}^{\infty} dy \exp(-y) y^{z-1} \) is the gamma-function and \( N(\varepsilon) \) is determined by Equation (2.46). Equation (2.49) gives the average displacement in the field direction of an electron that hops downward from a state at energy \( \varepsilon \) to the nearest available neighbour in the band tail. The average length \( \langle \hat{r} \rangle \) of such a hop is

\[
\langle x \rangle = \int_{0}^{\infty} dr 4\pi N(\varepsilon) \exp \left( -\frac{4\pi}{3} N(\varepsilon) r^3 \right) = \Gamma(4/3) \left( \frac{4\pi N(\varepsilon)}{3} \right)^{-1/3} \] \hspace{1cm} (2.50)

One can ascribe to the hopping process the mobility

\[
\mu = \frac{v}{F} = \frac{\langle x \rangle v(\hat{r})}{F} = \frac{\Gamma(5/3) e N^{-2/3}(\varepsilon) v(\hat{r})}{3(4\pi/3)^{2/3} \varepsilon_0} \] \hspace{1cm} (2.51)

and the diffusion coefficient

\[ Y_2 \]
\[
D = \frac{1}{6} \langle r \rangle^2 v(\langle r \rangle) = \frac{1}{6} N^{-2/3}(\varepsilon) v(\langle r \rangle) \frac{\Gamma(2)}{(4\pi/3)^{2/3}}
\]

(2.52)

Expressions (2.51) and (2.52) lead to the relationship between \( \mu \) and \( D \) in the form

\[
\mu = \frac{2\Gamma(5/3)e}{\Gamma(4/3)\varepsilon_0} D = 2.3 \frac{e}{\varepsilon_0} D
\]

(2.53)

This formula replaces the Einstein relationship \( \mu = eD/kT \) in the case of the energy-loss hopping of electrons in the exponential band tail. One should realize that Equation (2.53) was derived in the linear regime with respect to the applied field under the assumption that \( eF \ll \varepsilon_0 \). According to Equation (2.49), the quantity \( \langle \psi \rangle \) is proportional to \( N^{-2/3}(\varepsilon) = N_0^{-2/3} \exp[2\varepsilon/(3\varepsilon_0)] \), i.e., it increases exponentially in the course of the relaxation towards larger localization energies \( \varepsilon \). This means that, for deep localized states in the band tail, the condition \( eF \ll \varepsilon_0 \) breaks down. The energy border for application of the linear theory depends on the strength of the electric field, \( F \). The smaller the value of \( F \), the deeper in the tail is this border. However, for any \( F \), there is always a border energy in the tail below which the condition \( eF \ll \varepsilon_0 \) can no longer be fulfilled and nonlinear effects play the decisive role for hopping conduction of charge carriers. In Section 2.9 we show how one can describe the nonlinear effects with respect to the applied electric field.

The diffusivity-to-mobility ratio for the nonequilibrium transport in amorphous semiconductors has been tested experimentally by Gu et al. [46]. It was claimed that the hole diffusion coefficient in the experimental study is not more than twice as large as predicted by the classical Einstein formula \( D = kT\mu/e \), if one uses the experimental value of the mobility \( \mu \). This result was considered as the upper bound for any true failure of the Einstein relation. It is worth noting, however, that the measurements of the drift mobility were carried out by Gu et al. for temperatures above 200 K, while Equation (2.53) has been derived for the limit of the infinitesimal temperature [21]. Computer simulations [47] show that, at such high temperatures, the relation between \( \mu \) and \( D \) differs very little from the classical Einstein formula. Therefore it is not surprising that no essential deviations from this formula were manifested in the experiments of Gu et al. [46]. In order to check any considerable deviation from the conventional Einstein formula caused by nonequilibrium conditions, one should perform experiments at much lower temperatures \( T < 50 \text{K} \), at which transport of charge carriers is dominated by the energy-loss hopping.

### 2.5.2 Equilibrium charge carriers

One should clearly realize that Equation (2.53) is valid for the nonequilibrium energy-loss relaxation, in which only downward in energy electron transitions between localized states can occur. This regime is valid at low temperatures, at which the transport energy \( \varepsilon_t \) is very deep in the band tail. With increasing temperature, the upward in energy hops become more and more efficient for electron relaxation. Under these circumstances, the relation between \( \mu \) and \( D \) evolves gradually with rising temperature from its temperature-independent form at \( T = 0 \) to the conventional Einstein relationship, \( \mu = eD/kT \) [47] at \( kT > \varepsilon_0 \).
It is, however, worth noting that, even in the case of thermal equilibrium, the Einstein formula in its classical form $\mu = eD/kT$ is valid only for nondegenerate systems, in which most carriers are distributed in the states with energies much higher than the Fermi level $\varepsilon_F$. In such a case, the Fermi distribution can be approximated by the Boltzmann function, for which one easily obtains the relation between the drift mobility and the diffusion constant in the classical form $\mu = eD/kT$ [48]. In the opposite case of the degenerate system, a generalized Einstein formula should be used [49, 50]

$$\mu = eD \frac{1}{n} \frac{\partial n}{\partial \varepsilon_F}$$  (2.54)

where $n$ is the total concentration of charge carriers that determines the position of the Fermi level $\varepsilon_F$.

Ritter et al. [51] were the first who applied Equation (2.54) to the degenerate system of charge carriers distributed in the exponential DOS, and obtained a remarkable result that the Einstein formula in such a systems reads as

$$\mu = \frac{e}{\varepsilon_0} D$$  (2.55)

We would like to emphasize that this formula is valid for the system of charge carriers in thermal equilibrium, while Equation (2.53) describes the relation between $\mu$ and $D$ for essentially nonequilibrium process of the energy-loss hopping.

Whether the equilibrium system of charge carriers in the exponential DOS should be considered as degenerate or a nondegenerate depends solely on the relation between the energy scale of the DOS function $\varepsilon_0$ and the thermal energy $kT$. Remarkably, it does not depend on the concentration of charge carriers $n$. Straightforward calculations [51, 52] and computer simulations [47] show that at $kT < \varepsilon_0$, the relation between $\mu$ and $D$ is described by Equation (2.55) and the system of equilibrium carriers should be considered as a degenerate one. In the case $kT > \varepsilon_0$, the equilibrium system of carriers is always nondegenerate and the relation between $\mu$ and $D$ is described by the classical Einstein formula $\mu = eD/kT$.

2.6 STEADY-STATE PHOTOCONDUCTIVITY

Specific photoconducting properties of amorphous semiconductors, in particular of a-Si:H, are responsible for device applications of amorphous materials in solar cells and in field transistors, and therefore these properties are most often studied [9]. The literature with experimental data on the photoconductivity (PC) of amorphous semiconductors is enormously rich. The phenomenon has been studied for more than 30 years. Nevertheless, the theoretical interpretation of the effect is still a subject of controversy. In Figure 2.11 a temperature dependence of the steady-state PC $\sigma_p(T)$ in a-Si:H is shown [43]. This shape of the $\sigma_p(T)$ curve has been well known for 20 years [42]. Moreover, almost all different amorphous materials, including a-BCx: H, a-B: H, a-Se, alloy glasses, a-Si, a-Ge, intrinsic a-Si:H as well as $p$-doped and $n$-doped a-Si:H demonstrate such a dependence, as shown in Figure 2.12 [42, 43, 53–55]. Being common for different amorphous materials, this
dependence $\sigma_s(T)$ needs a general theoretical interpretation. Experiments show that transport of photoexcited carriers at low temperatures is fundamentally different from that near and above room temperature. Below 50 K the PC becomes temperature independent and it is essentially independent of the doping level and of the concentration of defects [42, 53, 54] in contrast to the strong dependence on the material parameters and on temperature above ~100 K [9]. In Section 2.6.1 we describe a theory of the PC in a-Si : H at temperatures $T < 50$ K, at which the PC is temperature independent. In Section 2.6.2 we address the steep rise of the PC at higher temperatures.

### 2.6.1 Low-temperature photoconductivity

The relatively simple and universal behavior of the PC at low temperatures suggests that the conduction process is related to very general features of amorphous semiconductors.
Hoheisel et al. [42] suggested that the low-$T$ photoconductivity $\sigma_p(0)$ is due to photoexcited carriers passing through the extended states before they become trapped into localized band-tail states. With the mobility in the extended states about $10\,\text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$ and a capture time of free carriers $\tau \approx 10^{-13}\,\text{s}$ the authors found good agreement with their experimental value $\sigma_p/eG = 10^{-12}\,\text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$. Here the photoconductivity $\sigma_p$ is normalized by the electron charge and by the bulk generation rate $G$. It is difficult, however, to explain with this model the observation of Vanecek et al. [56] that $\sigma_p/eG$ is independent of the photon energy $\hbar\omega$ above the mobility gap energy and decreases only slowly when $\hbar\omega$ is decreased to values smaller than the gap. Moreover, $\sigma_p$ begins to rise with temperature at temperatures sufficiently low, that reexcitation of charge carriers from tail states into extended states cannot play an essential role. Furthermore, time-of-flight measurements of the carrier mobility indicate that, at low temperatures, the mobility is dominated by hopping processes between localized states in the band tails [57–60].

In order to understand electronic properties of a system under steady-state generation, one should first find the appropriate recombination mechanism that provides the balance to

---

**Figure 2.12** Temperature dependence of the normalized photoconductivity for several amorphous semiconductors, illustrating the universality of the shape of the $\sigma_p(T)$ curves. The alloy glass is sputtered film of the composition $\text{As}_{35}\text{Te}_{28}\text{S}_{21}\text{Ge}_{15}\text{S}_1$ (reproduced from [54] with permission from Elsevier)
the continuous photogeneration of charge carriers. Recombination between electrons and holes can be either radiative or nonradiative. Numerous studies of the PC and of the photoluminescence (PL) in a-Si:H with concentration of dangling bonds below \(10^{16} \text{ cm}^{-3}\) revealed that, at least at low temperatures, recombination is dominated by radiative processes [61–65]. Therefore we describe below the theory of the PC at low temperatures, taking into account the radiative recombination mechanism [38, 45, 66].

As first mentioned by Hoheisel et al. [42], electrons and holes that recombine geminately do not contribute to the steady-state PC. We recall that in geminate recombination, electron recombines with the hole created with this electron in the same generation event. Therefore, in order to calculate the steady-state PC, one should focus on the carriers recombining nongeminately. Nongeminate recombination arises when the electron–hole pair succeeds in separating to a distance \(-\frac{1}{2}n^{-4/3}\), where \(n\) is the steady-state concentration of electrons (or holes) under the chosen generation intensity \(G\). Hence the first step in the calculation of the PC is to determine \(n\) as a function of \(G\).

Let us consider a fate of a geminate electron–hole pair created by a photon with energy close to the width of the mobility gap. Electron and hole are quickly captured into localized states in the band tails. From these states they can either recombine with the rate

\[
v_e(R) = \tau_0^{i} \exp\left(-\frac{2R}{\alpha}\right)\tag{2.56}
\]

or make a jump into localized states with lower energies (upward hops are not possible at low temperatures). For simplicity we consider hopping of electrons only, assuming holes immobile. An electron makes a hop to a localized state at distance \(r\) with the rate

\[
v_i(r) = v_0 \exp\left(-\frac{2r}{\alpha}\right)\tag{2.57}
\]

In Equations (2.56) and (2.57) \(R\) is the electron–hole separation and \(\alpha\) is the localization length of the electron. The preexponential factor in Equation (2.56) is of the order of the typical dipole radiative rate \(\tau_0^{i} = 10^{9} \text{ s}^{-1}\), while the preexponential factor for nonradiative transition in Equation (2.57) is of the order of the phonon frequency \(v_0 = 10^{13} \text{ s}^{-1}\). As shown by Shklovskii et al. [38, 45, 66], the huge difference in the magnitudes between \(v_0\) and \(\tau_0^{i}\) introduces a characteristic length scale

\[
R_c = \frac{\alpha}{2} \ln (v_0 \tau_0)\tag{2.58}
\]

At electron–hole separations \(r\) smaller than \(R_c\), recombination is improbable since \(v_e(R) \ll v_i(r)\) due to the large difference in the preexponential factors. At separations \(r\) larger than \(R_c\), recombination can compete with hopping diffusion and the probability of an electron–hole pair avoiding radiative recombination up to separations \(r \gg R_c\) is determined by the universal function [38, 45, 66]

\[
\eta(r) = \xi \left(\frac{R_c}{r}\right)^\beta\tag{2.59}
\]

Y2
with $\xi = 3.0 \pm 0.1$ and the critical index $\beta = 1.16 \pm 0.01$ [38]. Below, we use the approximate value $\beta = 1$.

The steady-state concentration of electrons $n$ at low temperatures is determined by the equation

$$G\eta\left(\frac{n^{-1/3}}{2}\right) = \frac{n}{\tau_0} \exp\left(-\frac{n^{-1/3}}{\alpha}\right)$$

(2.60)

with the solution

$$n(G) = \left[\alpha L(G)\right]^3$$

(2.61)

where quantity $L(G)$ satisfies the equation

$$L = \ln\left[\left(\tau_0 G\alpha^3 L^3 \ln(\tau_0 v_0)\right)^{-1}\right]$$

(2.62)

The left-hand side of Equation (2.60) represents the generation rate of electrons, which survive through hopping to the distance $\frac{1}{3}n^{-1/3}$ and therefore avoid the geminate recombination. The right-hand side is the recombination rate of such electrons. Equations (2.61) and (2.62) determine the dependence of the steady-state concentration of electrons on the generation rate. This dependence is to be compared with the experimental one obtained by measurements of the light-induced electron spin resonance. The latter show the dependence $n(G) \propto G^d$ with $d \approx 0.2$ for generation rates in the range $10^{16} < G < 10^{21}$ cm$^{-3}$s$^{-1}$ [67]. This result is in good agreement with the result of Equations (2.61) and (2.62) for parameters $\alpha = 1\text{nm}$ and $v_0\tau_0 \approx 10^4$, usually assumed for a-Si : H [11].

These arguments provide the solution of the apparent contradiction between the geminate character of the photoluminescence and nongeminate character of the electron spin resonance signal at $G < 10^{16}$ cm$^{-3}$s$^{-1}$ [9]. As shown in [38, 45, 66] the photoluminescence is determined by the majority of generated electron–hole pairs recombining at distances of the order of $R_c$, determined by Equation (2.58). Only a small proportion of electron–hole pairs generated per second in a cm$^3$ survive to distances $n^{-1/3} \gg R_c$, and hence recombine nongeminate, as described by the survival probability $\eta(n^{-1/3})$ in Equation (2.59). However, the lifetime $\tau(n^{-1/3})$ of these nongeminate pairs is so large that they accumulate in the system and determine the electron spin resonance signal. In order to calculate the magnitude of the photocurrent density $j$, one should multiply the generation rate of electron–hole pairs which recombine nongeminate (the expression in the left-hand side of Equation 2.60) with the typical field-induced dipole moment along the field direction $d$ attained by a nongeminate pair before it recombines. The latter quantity depends on the strength of the applied electric field $F$ and on the energy scale of the DOS $\varepsilon_0$. Straightforward calculations [38, 45, 66] give

$$d(F) = n^{-1/3} \frac{e^2 F n^{-1/3}}{12\varepsilon_0}$$

(2.63)

leading to the expression for the photoconductivity $\sigma_p = j/F$ in the form
Using the solution of Equation (2.60) one obtains

\[ \sigma_p = G G \left( n \frac{1}{3} \right) \frac{e^2 F n^{-1/3}}{2 \epsilon_0} \]  

(2.64)

Since \( L \) depends logarithmically on the generation rate \( G \), we find from Equations (2.65) and (2.62)

\[ \sigma_p \propto G^\gamma \]  

(2.66)

with

\[ y = 1 - \frac{1}{L} \]  

(2.67)

Equations (2.65) and (2.67) give the values \( \sigma_p/eG = 4 \times 10^{-12} \text{cm}^2/\text{V} \) and \( \gamma = 0.93 \) at \( G = 10^{20} \text{cm}^3/\text{s}^{-1} \) for the reasonable choice of material parameters \( \alpha = 1 \text{nm}, v_0 \tau_0 = 10^4 \), and \( \epsilon_0 = 0.025 \text{eV} \) [38]. Experimentally one finds \( \sigma_p/eG = 4 \times 10^{-11} \text{cm}^2/\text{V} \) and \( \gamma = 0.95 \pm 0.02 \) [42, 68]. So far we have considered the low-temperature PC in an intrinsic amorphous semiconductor. The detailed theory of the low-temperature PC in doped amorphous semiconductors can be found in [69]. In the next section we discuss the temperature dependence of the PC.

### 2.6.2 Temperature dependence of the photoconductivity

Let us first estimate the temperature \( T \), at which photoconductivity in amorphous semiconductors becomes dependent on temperature, and above which the picture of the energy-loss hopping is no longer valid. This happens when the transport energy \( \epsilon_{\text{TE}}(T) \) (TE) crosses the low-temperature quasi-Fermi level \( \epsilon_{\text{F}}^0 \). The latter quantity can be also considered as the typical recombination energy of electrons in the energy-loss hopping, which for the exponential DOS can be determined as [38]

\[ \epsilon_{\text{F}}^0 = \epsilon_0 \ln \left( \frac{N_0}{n} \right) \]  

(2.68)

where \( n \) is the steady-state concentration of electrons. The energy-loss hopping described in Section 2.6.1 dominates the transport and recombination of carriers at such low temperatures that the TE is deeper in the tail than the quasi-Fermi level \( \epsilon_{\text{F}}^0 \). With rising temperature, the TE moves upward into more shallow states. Equating \( \epsilon_{\text{F}}^0 \) determined by Equation (2.68) to \( \epsilon_{\text{F}}(T) \) determined by Equation (2.38) one obtains
\[
\tilde{T} = \frac{3\varepsilon_0}{2k} \left(\frac{4\pi}{3} \alpha n^3\right)^{1/3}
\]  
(2.69)

Substituting Equation (2.61) into this expression one finds [38]

\[
\tilde{T} = \frac{3\varepsilon_0}{2k} \left(\frac{4\pi}{3} \alpha n^3\right)^{1/3} \frac{1}{L(G)}
\]  
(2.70)

Using the values of \( L \) from Section 2.6.1, one obtains \( \tilde{T} \approx 45 \text{K} \) for \( G \approx 10^{20} \text{cm}^{-3}\text{s}^{-1} \). This value of \( \tilde{T} \) agrees well with the experimental data that show the PC almost temperature independent at temperatures below approximately 50 K. Since \( L \) depends on the generation rate only logarithmically, the value of \( \tilde{T} \) is not very sensitive to the magnitude of the generation rate.

At temperatures higher than \( \tilde{T} \), the TE lies above the low-temperature recombination level \( \varepsilon_0 \), and the picture of the energy-loss hopping described in Section 2.6.1 is no longer valid for calculations of the PC. At such temperatures the upward-energy hops of charge carriers toward the vicinity of the TE determine both transport and recombination. The calculations of the PC at such elevated temperatures are described in detail in [38]. In these calculations one first derives the balance equation that determines the steady-state concentration of charge carriers \( n \) under continuous generation with excitation density \( G \), in which recombination is due to the thermally stimulated diffusion of electrons via states in the vicinity of the TE. Possessing the value of the concentration, one determines the temperature-dependent quasi Fermi level \( \varepsilon_F \) for the chosen DOS determined by Equation (2.23). Then it is easy to calculate the magnitude of the PC, \( \sigma_p(T, G) \), via Equations (2.3)–(2.5) using the value of the quasi-Fermi level for \( \varepsilon_F \) and the easily calculated value of the mobility via the localized states in the vicinity of the TE [38]. The results of such calculations describe the steep increase of the PC at temperatures above \( \tilde{T} \) seen in Figures 2.11 and 2.12. The interested reader can find all necessary details of the theory in [38]. Here we would like to discuss only one interesting phenomenon not considered in [38].

In Figure 2.11 it is clearly seen that the steep increase of the PC with temperature that begins at \( T \approx 50 \text{K} \) is followed by the decrease of the PC at \( T \approx 100 \text{K} \). This is a rather universal behavior for the PC in amorphous semiconductors, which can be easily interpreted in the following picture. Equations (2.69) and (2.70) show that the temperature \( \tilde{T} \), at which the slow energy-loss hopping is replaced by the much faster motion of charge carriers via the states in the vicinity of the TE, is proportional to the energy scale of the band tail \( \varepsilon_0 \). Since this scale for the valence band in a-Si:H is approximately twice as large as that for the conduction band [9], holes become mobile at temperature \( \tilde{T}_h \) approximately twice as large as the corresponding temperature \( \tilde{T}_e \) for electrons. Therefore the general picture of the temperature-dependent PC in amorphous semiconductors is as follows. At temperatures below \( \tilde{T}_e \approx 50 \text{K} \) the PC is almost temperature independent, being determined by the slow energy-loss hopping and recombination of charge carriers. At \( T > \tilde{T}_e \approx 50 \text{K} \), but with \( T < \tilde{T}_h \approx 100 \text{K} \), electrons become more mobile and their thermal activation towards localized states in the vicinity of the TE (for electrons) strongly enhances the PC due to the enormous increase of the electron mobility that overcompensates the decrease in their concentration due to the enhanced recombination compared with the low-temperature case.
At temperature $T \approx \tilde{T}_h = 100$ K, holes also become much more mobile compared with their mobilities in the energy-loss hopping regime at low temperatures. These mobile holes can drastically enhance the recombination efficiency, which leads to the drastic decrease of the steady-state carrier concentration at $T \geq \tilde{T}_h = 100$ K and concomitantly to the decrease of the PC. At higher temperatures the TE merges with the mobility edge and the description based on the transport energy concept is no longer valid. At $T \geq 200$ K the increase of the PC with temperature can be well described by analogy with the same behavior in crystalline semiconductors, since the PC at such high temperatures is determined by transport via delocalized conduction band states above the mobility edge. This general picture of the PC is valid for various amorphous semiconductors and it can be used for interpretation of numerous experimental data [42, 43, 53–55].

### 2.7 THERMALLY STIMULATED CURRENTS—A TOOL TO DETERMINE DOS?

Measurements of the thermally stimulated conductivity (TSC) belong to the routine methods to study the electronic properties of semiconductors. In these measurements a sample is cooled to a low temperature $T_0$, then photoexcited for a time period $t_e$ and, after a delay period $t_0$, the sample is heated the dark at a constant rate $\gamma$ while the thermostimulated current is measured. The TSC technique has attracted increasing attention in studies of disordered semiconductors, in the hope of obtaining important information on the energy distribution of the density of states (DOS) in the mobility gap. It is worth noting, however, that the information on the DOS extracted from the TSC measurements essentially depends on the interpretation of the TSC phenomenon.

The first theory of the TSC in a system with a continuous energy distribution of localized states below the band edge was suggested by Simmons et al. [70]. In this theory only carriers in the extended states above the mobility edge were considered as mobile, and it was assumed that the carriers thermally released from the traps are swept out of the sample before they can recombine. Such a theory might be valid, perhaps at very high electric fields, at which carriers are swept out very efficiently and also at high temperatures at which hopping via localized band-tail states can be neglected. However, measurements of the TSC are usually carried out at low fields and at low temperatures. In such conditions hopping and recombination processes cannot be neglected. The theory of the TSC taking at least recombination into account was suggested by Fritzsche and Ibaraki [71]. This theory is still widely used to interpret modern experiments. Fritzsche and Ibaraki assumed that after a long delay $t_0$ (about 1 h) the distribution of photoexcited carriers in the trapping states corresponds to the thermal equilibrium at temperature $T_0$. Only carriers in the extended states above the mobility edge were considered as contributing to the current. The TSC was assumed to arise from a balance between the thermal emission and recombination. As the sample is heated in the dark, the thermal emission occurs from progressively lower-lying traps, and the magnitude of the TSC $\sigma_{TSC}$ is therefore expected to be proportional to the product of the DOS $g(\epsilon)$ and the occupation probability $f_0(\epsilon, T_0)$ at the end of the delay time [71]

$$
\sigma_{TSC} \propto e \mu_0 \tau_0 g(\epsilon_m) f_0(\epsilon_m, T_0)
$$

(2.71)
where \( e \) is the electron charge, \( \mu \tau_0 \) is the free electron mobility–lifetime product and \( \varepsilon_{\text{tr}} \) is the time-dependent energy, from which the thermal emission is most efficient. This energy moves toward the middle of the mobility gap with time and temperature [72]. The crucial assumptions of this approach are the following: (i) the retrapping processes were not taken into account at all; (ii) the exact balance between the thermal emission and recombination was assumed.

Generally the TSC is determined by the interplay between the thermal emission of electrons from the traps into conducting states and their retrapping and recombination. The concentration of the conducting electrons \( n \) obeys the equation

\[
\frac{dn}{dt} = \frac{dn_+}{dt} - \frac{dn_-}{dt} - \frac{n}{\tau_0}
\]

where \( \frac{dn_+}{dt} \) and \( \frac{dn_-}{dt} \) are the rates of the increase of \( n \) due to thermal release of electrons from the traps and its decrease due to retrapping, respectively, and \( \tau_0 \) is the lifetime of the conducting electrons that depends on \( n \), \( T \) and also on the whole concentration of trapped carriers in the system. Fritzsche and Ibaraki [71] neglected the term \( \frac{dn_-}{dt} \) and they assumed the ‘steady state’ \( \frac{dn}{dt} = 0 \), to be valid, which automatically leads to Equation (2.71).

Predictions of this approach were verified experimentally. Zhou and Elliott [73] were the first to claim inconsistencies between this theory and experimental results at low temperatures. Analyzing the similarity between the temperature dependence of the TSC and that of the PC, Zhou and Elliott came to the conclusion that the TSC is controlled by recombination rather than by thermal emission of trapped electrons. Under such circumstances Equation (2.71) is not valid. Besides this inconsistency, it is not possible to justify the neglect of the retrapping processes in the TSC. Even at room temperature the retrapping time is by many orders of magnitude smaller than the recombination time [74]. At lower temperatures at which the TSC is usually measured the relation between these times in favor of the fast retrapping should be even more drastic. Therefore the retrapping processes must be undoubtedly taken into account in the theoretical interpretation of the TSC.

A theory of the TSC taking into account trapping, retrapping and recombination has been suggested by Gu et al. [75], but under the assumption that only delocalized carriers in the states above the mobility edge are mobile. This is correct at rather high temperatures while the TSC is usually studied at low temperatures, at which transport is via hopping of electrons in the band tails. A comprehensive theory of the TSC in the hopping regime taking into account trapping, retrapping and recombination was suggested [76]. This theory is based on the concept of the transport energy (TE) introduced in Section 2.4.2. We will not present this theory here in detail. Instead we draw below a qualitative picture of the TSC in the hopping regime.

Thermally stimulated conductivity \( \sigma_{\text{TSC}} \) is determined by the expression

\[
\sigma_{\text{TSC}} = \epsilon\mu(T)n(T)
\]

where \( n(T) \) is the concentration of mobile electrons in the states with energies in the vicinity of the TE and \( \mu(T) \) is their hopping mobility. The mobility of electrons in the vicinity of the TE sharply increases with \( T \), since the TE moves with rising temperature toward the energy states with higher DOS, making the tunneling of electrons between localized states
much more efficient. In the correct description, the low-temperature TSC is determined by the interplay between the hopping mobility $\mu(T)$ increasing with $T$ and the concentration of carriers in the vicinity of the TE, decreasing in the course of time due to recombination and also due to the higher energy distance between the Fermi level and the TE with rising temperature. There is no necessity to consider the steady-state condition $dn/dt = 0$.

In Figure 2.13 typical temperature dependences of the TSC are shown for different initial temperatures $T_0$, which were obtained at the heating rate $\gamma = 2$ K/min. For $T_0 < 65$ K a pronounced maximum at $T_m \approx 90$ K is observed, which is independent of $T_0$. Such curves can be found in numerous publications [73, 76, 77], albeit with different values of $T_m$, always independent of $T_0$. In order to get a better insight into the physics behind these results, let us compare the values of $\sigma_{TSC}$ at $T \approx 55$ K in Figure 2.13 for $T_0 = 20$ K and $T_0 = 50$ K. In the latter case $\sigma_{TSC}(55$ K) is much lower than in the former. The mobility determined just by the actual temperature ($T \approx 55$ K) is the same in both cases. Therefore, in accord with Equation (2.73), the only reason for the difference in the values of $\sigma_{TSC}(55$ K) can be the difference in the values of $n(T)$ in these two cases. As long as the light intensity $G$ and the excitation duration $t_0$ were the same [76], the total amount of generated carriers was also the same in these two cases. Hence the only reason why there are more carriers at $T = 55$ K in the case of $T_0 = 20$ K than in the case of $T_0 = 50$ K is that the recombination process at $T_0 = 50$ K is more efficient than at $T_0 = 20$ K. Therefore, after the delay period $t_0 = 30$ min, which was the same in both cases [76], there were many more electrons at the start of heating at $T_0 = 20$ K than at $T_0 = 50$ K. During the slow heating process the carriers continue to recombine and their number disappearing from the system per second is higher for higher total amount of carriers, i.e., recombination at $T = 55$ K is more intensive in the case of $T_0 = 20$ K than in the case of $T_0 = 50$ K. Therefore, the TSC curve increases more steeply at $T_0 = 50$ K than at $T_0 = 20$ K since the concentration of mobile carriers $n(T)$ decreases less at $T_0 = 50$ K than at $T_0 = 20$ K, while the mobility increase with temperature in both cases is the same. After the curve of $\sigma_{TSC}$ for $T_0 = 50$ K merges into that for $T_0 = 20$ K there is no longer any difference between these two curves. Curves for higher values of $T_0$ merge into

![Figure 2.13](image.png)  
**Figure 2.13** The TSC curves for a-Si:H with different starting temperatures $T_0$ in the range 20–100K (reproduced with permission from [76]; copyright 1997 by the American Physical Society)
the curve for $T_0 = 20\, \text{K}$ at higher temperatures, respectively. It is clearly seen in Figure 2.13 that there is some universal TSC curve (for given values of $G$, $t_e$, and $t_0$) and all data for different values $T_0$ merge into it. The higher is $T_0$ the lower is the starting concentration of carriers, because more of them recombine within the delay period $t_0$ at higher $T_0$. On the other hand, recombination is less efficient for lower concentration of carriers. The carrier mobility, depending only on $T$, does not depend on the starting temperature $T_0$. Therefore, the increase of $\sigma_{TSC}$ with $T$ is always steeper for higher $T_0$, in good agreement with experimental data (Figure 2.13). In the frequently used steady-state description of Fritzschke and Ibaraki [71] the tendency should be just the opposite: the initial rise of $\sigma_{TSC}$ with $T$ should be steeper for lower $T_0$, being determined by the function $f_0$ at $T = T_0$ in Equation (2.71). The maximum in the $\sigma_{TSC}$ dependence in our picture is determined by the interplay between the mobility of charge carriers rising with temperature and their concentration decreasing due to recombination in the course of time. In order to check this conclusion, measurements of the TSC were carried out at different heating rates $\gamma$. According to our picture, the maximum should shift toward higher temperatures, and it should increase in the amplitude at higher heating rates, since recombination is less pronounced at shorter times needed to achieve the given value of $T$ at larger $\gamma$. Experimental data presented in Figure 2.14 confirm the expected trend. They also clearly show that the temperature corresponding to the maximum of the TSC curve $\sigma_{TSC}$ and the amplitude of the maximum itself are determined by the experimental conditions (for example, by the heating rate $\gamma$) and they should not be interpreted as a direct indication of some particular structure of the DOS of localized states in the band tails of disordered semiconductors. Therefore, we conclude that the TSC measurements should be interpreted with much more caution than is sometimes the case in the scientific literature. The DOS function does play an essential role in the calculation of the TSC. However, in order to make any conclusions on this important function, one should use the appropriate theory and compare its results with experimental data instead of claiming the shape of the DOS directly from the experimental curve using unjustified expressions such as Equation (2.71).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{TSC_spectra.png}
\caption{The TSC spectra in a-Si:H for different heating rates $\gamma$ (reproduced with permission from [76]; copyright 1997 by the American Physical Society)}
\end{figure}
2.8 DARK CONDUCTIVITY IN AMORPHOUS SEMICONDUCTORS

As discussed in Section 2.2, the experimentally observed dark conductivity $\sigma_d(T)$ in amorphous semiconductors at temperatures around room temperature can be well described by the activated Arrhenius law (Equation 2.1 with $\beta = 1$). The interpretation of this dependence is similar to that in crystalline semiconductors. Charge carriers are activated from the Fermi energy to the delocalized states above the mobility edge, where they move as a quasi-free particles with some effective mass. The conductivity in such a case is well described by Equations (2.6) and (2.7). More interesting and complicated for description from the theoretical point of view is the behavior of the dark conductivity at lower temperatures, at which conduction is dominated by hopping transitions of charge carriers between the localized band-tail states. This transport process is a variable-range hopping (VRH) in the localized states with an exponential energy distribution. One way to calculate $\sigma_d(T)$ is to use the general Equation (2.3) and the concept of the transport energy (TE) described in Section 2.4.2. One can easily show that the integrand in Equation (2.3) with concentration of charge carriers $n(\varepsilon)$ described by Equations (2.4), (2.5), and (2.23), and the hopping mobility $\mu(\varepsilon)$ approximated by Equation (2.51), has a sharp maximum at the energy $\varepsilon$ equal to the TE determined by Equation (2.38). In such an approach one easily arrives at the expression for $\sigma_d(T)$ in the form [78]

$$\sigma_d = \frac{e^2 v_0 r_t^2}{kT} \exp\left(\frac{2r_t}{\alpha} \right) \int_{\varepsilon_0}^{\varepsilon} \frac{d\varepsilon g(\varepsilon)}{1 + \exp[(\varepsilon - \varepsilon_F)/kT]} \exp\left(\frac{\varepsilon - \varepsilon_F}{kT}\right)$$

$$+ \frac{C e^2 v_0}{\varepsilon_0} \int_{\varepsilon_0}^{r_0} \frac{d\varepsilon g(\varepsilon)}{1 + \exp[(\varepsilon - \varepsilon_F)/kT]} \exp\left(\frac{-2r(\varepsilon)}{\alpha}\right)$$

(2.74)

where $\varepsilon_F$ is the Fermi level and the typical hopping distance $r(\varepsilon)$ at energy $\varepsilon$ can be estimated as

$$r(\varepsilon) = \left[\left(\frac{4\pi}{3B_c}\right)\int_{\varepsilon_0}^{\varepsilon} g(\varepsilon) \, d\varepsilon\right]^{-1/3}$$

(2.75)

with $r_t = r(\varepsilon_t)$ being the hopping distance at the TE. The coefficient $C = 2.3$ in Equation (2.74) is due to the modified form of the Einstein relation for energy-loss hopping given by Equation (2.53). The coefficient $B_c = 2.7$ in Equation (2.75) takes into account the necessity to fulfil the percolation criterion given by Equation (2.13).

Although the above approach, based on the concept of the transport energy, is transparent, it is not the most accurate for calculations of $\sigma_d(T)$. There is a more accurate, though less transparent approach based on the percolation theory. The details of the percolation approach can be found, for example, in [5]. Its application to the variable-range hopping in exponential band tails was first studied by Grünewald and Thomas [35] and later the theory was developed by Vissenberg and Matters [79]. In the percolation approach one treats the transition rates between all pairs of sites $i$ and $j$, taking into account both the quantum mechanical transition probabilities and also the probabilities that one of the sites in a pair is filled by a charge carrier, while the other site is empty, as described by Equation (2.11). The hopping rate can be expressed as
\[ v_j = v_0 \exp\left(-\frac{2\eta_j}{\alpha}\right) \exp\left(-\frac{|\varepsilon_i - \varepsilon_j| + |\varepsilon_j - \varepsilon_x| + |\varepsilon_x - \varepsilon_i|}{2kT}\right) = v_0 \exp(-\xi_j) \] (2.76)

Connecting only sites with \( \xi_j < \xi \), and increasing \( \xi \), one determines the value \( \xi = \xi_c \), at which the infinite percolation cluster of interconnected sites first appears. This cluster is responsible for the hopping motion of charged carriers in the DC regime [5]. The critical value \( \xi_c \) determines the exponential temperature and concentration dependences of transport coefficients

\[ \sigma_d = \sigma_0 \exp(-\xi_c) \] (2.77)

where \( \sigma_0 \) is a prefactor not given by the percolation theory. The problem is to calculate the exponent \( \xi_c \). Vissenberg and Matters [79] calculated \( \sigma_d(T) \) using the classical percolation criterion that \( B_c \), determined as the number of valid bonds per site at the percolation threshold, is equal to 2.8.

For a given total concentration of electrons in the system \( n \) Vissenberg and Matters [79] obtained the following expression for \( \sigma_d(T) \)

\[ \sigma_d(n, T) = \sigma_0 \left[ \frac{\pi n (e_0/kT)^3}{(2\alpha)^3 B_c \Gamma(1-kT/e_0) \Gamma(1+kT/e_0)} \right]^{e_0/kT} \] (2.78)

where display \( \Gamma(z) = \int_0^\infty dy \exp(-y)y^{z-1} \).

It is worth noting that the temperature dependence of the dark conductivity provided by Equation (2.78) for the VRH in the exponential DOS has nothing to do with Mott’s law described by Equation (2.19). Unfortunately, the opposite is often claimed in the scientific literature [80, 81]. Mott’s law (Equation 2.19) is valid for the VRH process in the vicinity of the Fermi level in a system with energy-independent DOS. As we have seen in Section 2.3.2, even a slight energy dependence of the DOS, such as a parabolic one in the case of the Coulomb gap, drastically changes the temperature dependence of the VRH conductivity as compared with Mott’s formula. For the parabolic gap, \( \sigma_d(T) \) is described by Equation (2.22) instead of Equation (2.19). In the case of the exponential DOS described by Equation (2.23), the temperature dependence \( \sigma_d(T) \) has an Arrhenius character \( \sigma_d \propto \exp(-\Delta/kT) \), according to Equation (2.78) with an activation energy \( \Delta \) that is weakly (logarithmically) temperature dependent [79]. Only in the limit of extremely low and practically unachievable temperatures can Mott’s law be observed in systems with exponential DOS.

In order to verify the analytical percolation approach used by Vissenberg and Matters [79] and also in order to check the accuracy of the analytical approach based on the TE, we performed a series of straightforward computer simulations of the percolation problem for the dark hopping conductivity in the exponential DOS [78]. The simulation was based on a straightforward Monte Carlo algorithm directed to finding the percolation threshold in a system of randomly placed localization sites with energy distribution described by Equation (2.23). The sites were placed in a cube with a length chosen to provide a number of sites \( m \) for a given concentration \( N_0 \). No correlation between the spatial positions of sites and their energies was assumed. The hopping parameter \( \xi_j \) was calculated for each pair of sites according to Equation (2.76) and the percolation threshold \( \xi_c(m) \) was found, which provides a continuous path through the system via states with \( \xi_j < \xi_c(m) \). Five runs of the
algorithm were performed for each set of the system parameters with different random generator seed numbers and the results were averaged over these runs. The accuracy in determination of $\xi_c(m)$ for each run was $\xi_c(m) \pm 0.1$. The standard deviations of the $\xi_c(m)$ values for single runs never exceeded 0.2. Calculations for each set of parameters were performed for $m = 10^5, 2 \times 10^5,$ and $5 \times 10^5$ and the value of $\xi_c$ for the infinite system was determined via linear extrapolation of $\xi_c(m)$ as a function of $1/m$.

In Figure 2.15 the results of the computer simulation for $\xi_c$ as a function of temperature are shown (squares) in comparison with the results of the percolation analytical approach of Vissenberg and Matters [79] (dashed-dotted line) and with the results obtained by the TE approach according to Equation (2.74) (dashed line). The simulation parameters, such as $N_0$, $n$, $\alpha$, and $\epsilon_0$, were chosen equal to those given in [79]. Since the analytical approach based on the TE concept does not allow one to determine the preexponential factor $\sigma_0$ in Equation (2.77), we adjusted this factor in order to equate $\xi_c$ in the TE description to that obtained in the simulation for the lowest considered temperature $T = 55$ K. Hence only the slope in the temperature dependence of $\xi_c$ can be found in the framework of the TE approach. Furthermore, the TE approach for the chosen material parameters is self-consistent only at rather low temperatures $T < 70$ K, since for higher temperatures the assumptions used for the derivation of the TE are no longer valid. Comparison with the computer simulation in Figure 2.15 shows that, in the range of low temperatures, the TE approach gives a correct temperature dependence $\sigma_0(T)$. The same can be generally claimed for the analytical approach based on the percolation theory [79]. This theory is self-consistent in a much broader temperature range than the TE description. The analytical percolation approach is supposed to be accurate at $kT < \epsilon_0$ and $-\epsilon_F \gg \epsilon_0$ [79]. These conditions are fulfilled in a very broad temperature range. Some deviations between the results of the analytical percolation approach and those of computer simulations at temperatures above $\sim 100$ K seen in Figure 2.15 are not of high importance since at temperatures above $\sim 150$ K, conduction in amorphous semiconductors is dominated by charge carriers in delocalized

![Figure 2.15](c02.indd) Temperature dependence of the hopping conductivity for exponential density of states. The squares represent the results of the simulation, the dashed line is drawn according to Equation (2.74) for the TE theory, and the dash-dotted line represents the analytical percolation theory of Vissenberg and Matters [79] (reproduced from [78] with permission from Elsevier)
states above the mobility edges and hopping conduction via localized states in the band tails plays a secondary role.

2.9 NONLINEAR FIELD EFFECTS

Transport phenomena under the influence of high electric fields in inorganic noncrystalline materials, such as amorphous semiconductors, has been the object of intensive experimental and theoretical study for decades. This is implied by observations of strong nonlinearity in the field dependences of the dark conductivity [82, 83], of the photoconductivity [84] and of the charge carrier drift mobility [82, 85, 86] at high electric fields. This effect is most pronounced at low temperatures, when charge transport is determined by electron hopping via localized band-tail states (Figure 2.16).

Whereas the field-dependent hopping conductivity at low temperatures was always a challenge for theoretical description, the theories for the temperature dependence of the hopping conductivity at low electric fields were successfully developed for all transport
regimes discussed: for the dark conductivity [35, 79], for the drift mobility [37], and for the photoconductivity [38]. In all these theories, hopping transitions of electrons between localized states in the exponential band tails play a decisive role, as described above.

Shklovskii was the first who recognized that strong electric field plays, for hopping conduction, a role similar to that of temperature [87]. In order to obtain the field dependence of the conductivity $\sigma(F)$ at high fields, Shklovskii replaced the temperature $T$ in the well-known dependence $\sigma(T)$ for low fields by a function $T_{\text{eff}}(F)$ of the form [87]

$$T_{\text{eff}} = \frac{eF\alpha}{2k}$$

where $e$ is the elementary charge, $k$ is the Boltzmann constant, and $\alpha$ is the localization length of electrons in the band-tail states. A very similar result was obtained later by Grünewald and Movaghar in their study of the hopping energy relaxation of electrons through band tails at very low temperatures and high electric fields [88]. The same idea was also used by Shklovskii et al. [38], who suggested that, at $T = 0$, one can calculate the field dependence of the stationary photoconductivity in amorphous semiconductors by replacing the laboratory temperature $T$ in formulas for the low-field finite-temperature theory by an effective temperature $T_{\text{eff}}(F)$ given by Equation (2.79).

It is easy to understand why electric field plays a role similar to that of temperature for the energy relaxation of electrons. In the presence of the field, the number of sites available for charge transport at $T = 0$ is essentially enhanced in the direction prescribed by the field, as shown in Figure 2.17. Hence, electrons can relax faster at higher fields. From the figure it is seen that an electron can increase its energy with respect to the mobility edge by the amount $\varepsilon = eFx$ in a hopping event over a distance $x$ in the direction prescribed by the electric field. The process resembles thermal activation. The analogy becomes closer when we express the transition rate for the hop as

$$v = v_0 \exp \left( -\frac{2x}{\alpha} \right) = v_0 \exp \left( -\frac{2\varepsilon}{eF\alpha} \right) = v_0 \exp \left[ -\frac{\varepsilon}{kT_{\text{db}}(F)} \right]$$

where $T_{\text{db}}(F)$ is provided by Equation (2.79).

This effective activation induced by electric field produces at $T = 0$ a Boltzmann tail in the energy distribution function of electrons via localized states, as shown by numerical calculations [89, 90]. In Figure 2.16, a field-dependent photoconductivity in a-Si:H is shown for several temperatures [84]. If we compare the values of the photoconductivity at the lowest measured temperature, $T = 20\text{K}$ in Figure 2.16, with the values of the low-field photoconductivity at $T = T_{\text{db}} = eF\alpha/2k$ measured by Hoheisel et al. [42] and by Stradins and Fritzche [43], we come to the conclusion that the data agree quantitatively if one assumes the value for the localization length $\alpha = 1.05\text{nm}$ [38], which is very close to the value $\alpha = 1.0\text{nm}$ known for a-Si:H from independent estimates [11]. This comparison shows that the concept of the effective temperature based on Equation (2.79) provides a powerful tool to estimate the nonlinearity of transport coefficients with respect to the electric field using the low-field results for the temperature dependences of such coefficients.

However, experiments are usually carried out not at $T = 0$, but at finite temperatures, and the question arises on how to describe the transport phenomena in the presence of both
factors, finite $T$ and high $F$. By studying the steady-state energy distribution of electrons in numerical calculations and computer simulations [89, 90] and by straightforward computer simulations of the steady-state hopping conductivity and the transient energy relaxation of electrons [91] the following result has been found. The whole set of transport coefficients can be represented as a function of a single parameter $T_{\text{eff}}(F, T)$

$$T_{\text{eff}}(F, T) = \left[ T^\beta + \left( \frac{\gamma eF\alpha}{k} \right)^{\beta \gamma / \beta} \right]$$

(2.81)

with $\beta = 2$ and values of $\gamma$ in the range $0.5–0.9$, depending on which transport coefficient is considered [91]. We are aware of no analytical theory that can support this numerical result.

In the end of this section we would like to make the following remark. Very often in the scientific literature it is claimed that transport coefficients in the hopping regime should have a purely exponential dependence on the applied electric field (see, for instance, [86]). The idea behind such statements seems rather transparent. Electric field diminishes potential barriers between localized states by the amount $\Delta \varepsilon = eFx$, where $x$ is the projection of the hopping radius on the field direction. At a first glance, this should diminish the activation energies in Equations (2.10) and (2.11) by this amount $\Delta \varepsilon = eFx$, and lead to the term $\exp(eFx/kT)$ in the expressions for the charge carrier mobility, diffusivity and conductivity. One should, however, take into account that hopping transport in all real materials is the

Figure 2.17 Tunnelling transition of a charge carrier in the band tail affected by a strong electric field. Traveling the distance $x$, the carrier acquires energy $eFx$, where $F$ is the strength of the electric field, and $e$ is the elementary charge (reproduced with permission from [91]; copyright 1995 by the American Physical Society)
essentially variable-range hopping process. In such a process the interplay between spatial and energy-dependent terms in the exponents of the transition probabilities determines the conduction path, as discussed above. Therefore it is not enough to take into account the influence of the strong electric field only on the activation energies of single hopping transitions. One should consider the modification of the whole transport path due to the effect of the strong electric field. It is this VRH nature of hopping process that leads to a more complicated field dependence of the transport coefficients expressed by Equations (2.80), (2.81).

2.10 CONCLUDING REMARKS

In this chapter we have presented several basic concepts developed for the description of charge carrier transport in ionorganic disordered semiconductors, such as amorphous and microcrystalline materials. Although these concepts are based on the rather old ideas of the variable-range hopping conduction, they unfortunately have not yet become the working tool for many researchers dealing with amorphous materials. Furthermore, these concepts are even less known by researchers working with other kinds of disordered materials, such as for example organic materials or dye-sensitized structures, which are presently intensively studied for various device applications, particularly, in photovoltaics. We would like to emphasize that transport phenomena in chemically different disordered materials look rather similar, being determined by the presence of localized electron states. In such a case one can use the concepts described in this chapter for theoretical interpretation of the observed charge transport effects in chemically different materials. Here we have given a mathematical description, assuming that the density of localized states has the exponential shape described by Equation (2.23). Of course, the particular dependences of the kinetic charge transport coefficients on material parameters and temperature are specific for the particular shape of the DOS. However, the mathematical apparatus presented here is rather universal and it can be applied to the theoretical description of charge transport phenomena in materials with other shapes of the DOS than the exponential one. For example, in Chapter 6 of this book we show the application of the concepts described in the current chapter to organic disordered materials, in which the DOS is believed to be Gaussian.

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