physica **pss** status solidi **b**
www.pss-b.com
*basic solid state physics*

# Theoretical description of charge transport in disordered organic semiconductors

**Review Article**

**S. D. Baranovskii***

Faculty of Physics and Material Sciences Center, Philipps-Universität, 35032 Marburg, Germany

*e-mail baranovs@staff.uni-marburg.de, Phone: +49-6421-2825582, Fax: +49-6421-2824511

Twenty years ago Heinz Bässler published in this journal the seminal review article on charge transport in disordered organic semiconductors [Phys. Status Solidi B **175**, 15 (1993)], which has become one of the most popular references in this research field. Thanks to this paper, our understanding of charge transport in disordered organic materials has been essentially improved in the past two decades. New theoretical methods have been developed and new results on various phenomena related to charge transport in disordered organic materials have been obtained. The aim of the current review is to present these new theoretical methods and to highlight the most essential results obtained in their framework. While theoretical consideration in the article by Bässler was based on computer simulations, particular attention in the current review is given to the development of analytical theories. Dependences of charge carrier mobility and diffusivity on temperature, electric field, carrier concentration and on material and sample parameters are discussed in detail.
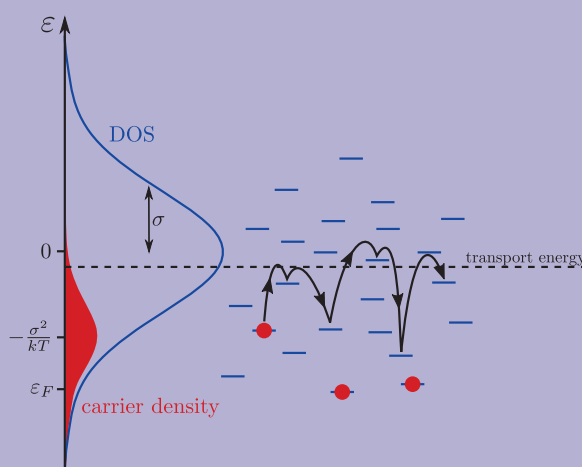
Schematic behaviour of charge carriers within the Gaussian density of states (DOS)

© 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

**1 Introduction** This article is written to meet the growing interest of researchers in charge transport properties of organic disordered semiconductors (ODSs), such as molecularly doped polymers [1–3], conjugated polymers [4, 5] and low-molecular-weight organic glasses [6, 7]. This interest is caused by successful applications of such materials in various devices and by their promises for future applications. Most of the realized organic electronic devices consist of thin amorphous or polycrystalline layers. Many of such materials can be processed in solution or dispersion and are printable. Manufacturability and low production costs of ODSs, along with their specific charge transport properties, make these materials favourable and in some cases unique for various applications, particularly for large-area devices,

where demands on the mobility of charge carriers are not very high. ODSs dominate already today the electrophotographic image recording on the industrial scale and are becoming more and more important for applications in light-emitting diodes (OLEDs) [8, 9], in field-effect transistors (OFETs) [10], as well as for photovoltaic applications in organic solar cells (OSCs) [11]. Charge transport properties of ODSs are decisive for all these applications. Therefore, study of charge transport has dominated research on organic materials in the recent years.

In 1993, Heinz Bässler published in this very Journal the seminal review article on charge transport in ODSs 'Charge Transport in Disordered Organic Photoconductors: A Monte Carlo Simulation Study' [1], which is currently the second

**Wiley Online Library**

most cited article published in Physica Status Solidi. Notably, the number of citations of this paper, henceforth called Paper I in the current report, has been almost continuously growing in the recent years (from 430 citations in years 2003–2007 to 588 citations in years 2008–2012 registered on the Web of Knowledge). This frequent referencing evidences not only the high value of Paper I, but also the increasing interest of researchers on the topic: Theoretical description of charge transport in ODSs.

As typical for a rapidly developing research field, views of researchers sometimes deviate from each other essentially. Nevertheless, it will be shown in the current contribution that in spite of those essential deviations, the basic ideas promoted by Bässler in Paper I [1] and in the older review paper [12] have proven to be correct. These basic ideas can be briefly formulated as follows: Charge transport in single-component and multicomponent ODSs is due to incoherent hopping of carriers via randomly distributed localized states with a Gaussian energy spectrum:

$$g(\varepsilon) = \frac{N}{\sigma\sqrt{2\pi}} \exp\left(-\frac{\varepsilon^2}{2\sigma^2}\right). \tag{1}$$

Here, $\sigma$ is the energy scale of the density of states (DOS) usually estimated in ODSs as $\sigma \approx 0.1\,\mathrm{eV}$ [1] and $N$ is the concentration of randomly distributed localized states (also called localization sites) that charge carriers can use for hopping transport. A typical estimate for the latter quantity is between $N \simeq 10^{20}\,\mathrm{cm^{-3}}$ and $N \simeq 10^{21}\,\mathrm{cm^{-3}}$ [13–20]. The rate for carrier transition from an occupied site $i$ to an empty site $j$, separated by distance $r_{ij}$, is usually assumed [1, 12] to be described by the Miller–Abrahams expression [21]

$$\nu_{ij} = \nu_0 \exp\left(-\frac{2r_{ij}}{\alpha} - \frac{\varepsilon_j - \varepsilon_i + |\varepsilon_i - \varepsilon_j|}{2kT}\right). \tag{2}$$

Here, $\alpha$ is the localization length of charge carriers in the localized states usually estimated by an order of $10^{-8}\,\mathrm{cm}$

**Prof. Dr. Sergei Baranovskii** received his Ph.D. (1981) in Theoretical Physics from Ioffe Physical-Technical Institute of the Russian Academy of Sciences in St. Petersburg, where he worked as a senior researcher till 1990. Since 1990, he has been working at the Philipps University Marburg, Germany, where he got Habilitation in Theoretical Physics (1995). His research interests are devoted to optical properties of semiconductor quantum structures and to charge transport and optical properties of amorphous organic and inorganic materials. He is the author and co-author of more than 200 publications in international journals, of 6 book chapters and the editor of two books.

[2, 22], $\varepsilon_i$, $\varepsilon_j$ are the carrier energies on sites $i$ and $j$, respectively, $k$ is the Boltzman constant, and $T$ is the temperature. The energy difference between states $i$ and $j$ should be compensated, for example by absorption or emission of phonons. The prefactor $\nu_0$, often called the attempt-to-escape frequency, depends on the interaction mechanism that causes transitions. In the case of interaction with phonons, its value is usually assumed close to the phonon frequency $\nu_0 \approx 10^{12}\,\mathrm{s^{-1}}$ [12, 23]. If spatial positions and energies of localized states can be considered independent from each other, this model is traditionally called the Gaussian Disorder Model (GDM). If site energies are correlated with their spatial positions the model is traditionally called the Correlated Disorder Model (CDM) [24, 25]. The energy spectrum in the latter case can also be Gaussian. Since site energies depend on the applied electric field, transport kinetic coefficients, such as the carrier mobility $\mu$ and diffusion coefficient $D$, can also depend on the magnitude of the applied electric field $F$. Furthermore, these kinetic coefficients should depend on the concentration of charge carriers $n$, on the concentration of localized states $N$, and on temperature $T$. The theoretical description of such dependences is the topic of the current report.

Since the main message of Paper I was repeated in numerous review articles, monographs and edited books on charge transport in ODSs [26–36], the question might arise on why to provide yet another review article on this topic. Several reasons should be highlighted here.

(i) Focusing on the effects of $T$, $N$ and $F$ on carrier mobility and diffusivity, Paper I did not address at all the dependence of transport coefficients on the concentration of carriers $n$. It happened probably because at that time most interest was focused on the data obtained by time-of-flight measurements at low carrier concentrations, $n \ll N$ and on properties of OLEDs, also at $n \ll N$. However, in the recent years much interest has been devoted to developing OFETs, operating at relatively high carrier concentrations [37–39], so that the dependences of the mobility $\mu$ and diffusivity $D$ on carrier concentration $n$ become important for ODSs.

Although the dependence of carrier mobility on $n$ in the hopping regime is a trivial effect, well known to the scientific community for decades, it appeared somehow remarkable for researchers working with ODSs [16, 38, 39]. Therefore, it is worth noting that the hopping rate has the form of Eq. (2) only in the case if the starting site $i$ is occupied by the carrier and the target site $j$ is empty. In the general case, the transition rate for a pair of sites $i$, $j$, i.e. the contribution of such a pair to charge transport, depends also on the position of the Fermi level $\varepsilon_F$ [21]:

$$\nu_{ij} = \nu_0 \exp\left(-\frac{2r_{ij}}{\alpha} - \frac{|\varepsilon_i - \varepsilon_j| + |\varepsilon_i - \varepsilon_F| + |\varepsilon_j - \varepsilon_F|}{2kT}\right). \tag{3}$$

Indeed, if both sites $i$ and $j$ have energies $\varepsilon_i$, $\varepsilon_j$ far above $\varepsilon_F$, these sites are mostly unoccupied, i.e. there is no charge carrier on this pair of sites to provide transport. Therefore, such a pair of sites cannot contribute to transport, regardless

Review

Article

Phys. Status Solidi B 251, No. 3 (2014)                                                                                     489

of how close in space and in energy they might be. In the opposite case, when both energies $\varepsilon_i$, $\varepsilon_j$ are far below $\varepsilon_F$, both sites are mostly occupied and there is no place for a carrier to hop into. Hence, the contribution of any pair of sites $i$ and $j$ to charge transport depends on the carrier concentration $n$ via the dependence of the Fermi energy on $n$ [21] and concomitantly the carrier mobility $\mu$ should depend on $n$.

Not the dependence of the mobility $\mu$ on carrier concentration $n$ is therefore remarkable, but the *independence* of $\mu$ on $n$ observed experimentally at low $n$ in most studied ODSs [38–42]. In Section 3, we show that this independence of $\mu$ on $n$ in numerous ODSs provides the decisive argument in favour of the Gaussian DOS, a new argument as compared to those given in Paper I.

(ii) This new and more solid argument in favour of the Gaussian DOS in ODSs based on the studies of the dependence $\mu(n)$ is of high importance for the whole field. Although the energy spectrum available for charge carriers is the key property of a system, as it determines all opto-electronic properties including charge transport, there is no consensus among researchers on the shape of the DOS in ODSs. Apparently, the arguments in favour of the Gaussian DOS promoted in Paper I and in the older review article [12] were not convincing enough: In 1998, Vissenberg and Matters [43] assumed a purely exponential DOS in ODSs of the form

$$g(\varepsilon) = \frac{N}{\varepsilon_0} \exp\left(\frac{\varepsilon}{\varepsilon_0}\right), \qquad (4)$$

where $\varepsilon_0$ is the energy scale of the DOS. They performed calculations in spirit of those by Grünewald and Thomas [44], concluding that they 'do not expect the results to be qualitatively different for a different choice of $g(\varepsilon)$, as long as $g(\varepsilon)$ increases strongly with $\varepsilon$'. Since then, numerous researchers used the exponential DOS for ODSs [15, 38, 39, 45–60]. Furthermore, some researchers claim that the exponential DOS is an accurate approximation of the Gaussian DOS in the energy range in which transistors operate [38, 39]. However, the same researchers demonstrate the independence of $\mu$ on $n$ at low carrier concentrations $n$, typical for OLEDs, a feature that is definitely not compatible with the exponential DOS [61]. It is shown in Section 3 that the results for Gaussian and exponential shapes of the DOS are qualitatively different, particularly for the dependences of carrier mobility $\mu$ on the concentration of carriers $n$ and on temperature $T$. It will be shown that the experimentally observed dependence $\mu(n)$ at least in widely studied ODSs, such as PPV and P3HT [38, 39] evidences the Gaussian shape of the DOS.

(iii) Theoretical research on charge transport in ODSs was and is still mainly based on numerical modelling not supported by solid theoretical concepts. For instance, simulated results for carrier mobility and diffusivity were fitted in Paper I by empirical analytical expressions, some of which can hardly be justified. This is particularly true for the field dependence of the carrier mobility $\mu(F)$, which is one of the most popular results from Paper I. This issue is discussed in

Section 7 of the current report. Some dependences of transport coefficients on material parameters were considered as universal simply because other parameters were not changed in course of simulations. Empirical fitting of numerical data not supported by solid theoretical concepts can be valid in some restricted range of parameters, but not in general.

Remarkably, the $n$-dependent carrier mobility in a Gaussian DOS, not yet considered in Paper I, is also often treated by empirical fitting of numerical results [16] providing analytical equations, which do not have a solid theoretical basis and cannot be valid in a broad range of parameters. This approach has been promoted as the Extended Gaussian Disorder Model (EGDM) [16, 62]. The EGDM is claimed [62] to be Bässler's GDM, but including the dependence of the mobility $\mu$ on the concentration of carriers $n$.

The dependence of $\mu$ on $n$ had been recognized as the inherent property of Bässler's GDM in numerous theoretical studies [14, 63–68] long before the EGDM was invented [16]. Furthermore, a comprehensive analysis of experimental data for $\mu(n)$ in the framework of the GDM has been performed [65, 66], demonstrating the ability of the GDM to account for the concentration-dependent mobility in ODSs.

The question should arise on how the fitting of numerical data obtained in the framework of the GDM, which 'should merely be considered as a description of the numerical data in a limited parameter range' [16], 'not providing fundamental understanding' for $\mu(T, n)$ [69] could become an 'extension' of the model. According to Refs. [16, 62], the empirical fitting of numerical data obtained in the framework of the GDM becomes an extended model (EGDM). This situation with the EGDM shows how strongly research on ODSs is focused on doing physics by empirical fitting of numerical results. Based on clear concepts developed for the concentration-dependent mobility in ODSs [14, 61, 63–68], the issue of $\mu(T, n)$ will be addressed in Section 6 of the current report.

(iv) The strong focus on doing theory by empirical fitting might be caused by the widely spread opinion that the Gaussian DOS is not suitable for analytical solutions [1, 27, 28, 70]. We show below that theoretical concepts well known for at least 40 years, which have successfully been applied to describe hopping transport in inorganic disordered materials, are well suitable to describe hopping transport in ODSs with the Gaussian DOS. Among such approaches one should highlight the percolation theory [22, 44, 63, 64, 71–73], the concept of the transport energy (TE) [22, 44, 63, 64, 74–78], and the concept of the effective temperature [79–83]. This theoretical development stayed out of the scope of researchers working with ODSs for a long time. The only analytical approach attempted in Paper I was based on the ensemble averaging of hopping rates. This method discussed in Section 4 of the current report is not perfectly suitable to describe hopping transport [71–73]. After the peak of theoretical developments for description of the Variable–Range–Hopping (VRH) in the early 1970s [71–73], most theoretical efforts were focused on studying the interplay between the energy and spatial factors in Eq. (3) and their effect on hopping transport [32, 84]. The

spatial factors are characterized by the spatial extent of the wave functions, $\alpha$, while the energy factors are characterized by the DOS, whose effect on hopping conduction has always been in the focus of the research. In particular, the effects of the parabolic DOS [84–86] and of the exponential DOS [44, 75, 76] on hopping conduction were studied in detail. In the field of ODSs, this development is not always known [87]. Empirical fitting of numerical results is so popular for theoretical research in ODSs that it is sometimes used even for the simplest case of transport through lattices with electron transitions only between the neighbouring sites [69, 88]. However, analytical solutions for hopping transport through lattices are possible based on the percolation theory [84, 89].

Furthermore, doing physics by numerical modelling provides results, which are not always reliable because of the restricted size of simulated arrays, as illustrated by the following example. It was shown by analytical theories that the field-dependent diffusion coefficient of carriers $D(F)$ in a Gaussian DOS is determined by the energy levels close to $\varepsilon_{\mathrm{dif}} = -2\sigma^2/kT$ [90–92]. The probability to find such a deep energy level in a simulated array with $M$ sites is about $\sim M \exp[-2(\sigma/kT)^2]$. Taking the values $\sigma = 0.1$ eV and $kT = 0.025$ eV, one concludes that in order to simulate the diffusion process appropriately, i.e. to have in the simulated array at least several sites with energies in the vicinity of $\varepsilon_{\mathrm{dif}} = -2\sigma^2/(kT)$, this array should contain more than $10^{14}$ sites. This number of sites can hardly be found in numerical simulations. We discuss the consequences of such finite-size effects in Sections 9 and 10.

In the current report, the emphasis is put on the theoretical concepts and not on the numerical modelling, although simulation results are frequently used in order to check the validity of the analytical approaches in the restricted parameter ranges. The report focuses solely on the description of charge transport. Such important topics as charge generation and recombination are out of our scope. The topic of charge generation, which is particularly important for applications of ODSs in solar cells, has been highlighted recently in several review papers [93–95]. With respect to recombination, claims in the current literature on recombination processes for charge carriers in ODSs look so contradictory that making final conclusions seems not yet possible. Our report can be considered as complimentary to the recent review paper by Tessler et al. [35], who focused mainly on the applications of general concepts to organic thin-film devices, while the current report mainly describes the basic theoretical methods to account for charge transport properties in disordered organic materials.

We will start by describing the model for charge transport in ODSs. Particular attention will be given to the principal difference between systems with a Gaussian DOS and those with an exponential DOS. Arguments will be provided in favour of the Gaussian DOS in ODSs complementary to those already given in Paper I. Various aspects of the charge transport will be discussed paying most attention to the analytical theoretical concepts.

**2 Model for charge transport in ODSs** Traditionally, two classes of organic disordered materials are distinguished: amorphous polymers and materials containing small molecules. Also polycrystalline polymers often demonstrate properties similar to those of amorphous systems. Although the variety of such materials is very rich, the basic charge transport mechanism in most of them is common: incoherent tunnelling (hopping) of carriers between localized states. The canonical examples of disordered organic materials with the hopping transport mechanism are the binary systems based on doped polymer matrices. Examples include polyvinylcarbazole (PVK) or bispolycarbonate (Lexan) doped with either strong electron acceptors such as, for example trinitrofluorenone acting as an electron transporting agent, or strong electron donors such as, for example derivatives of triphenylamine or triphenylmethane for hole transport. The hopping transport mechanism discussed in this report is widely believed to be inherent also to single component ODSs [12]. The latter are organic materials, in which only one sort of molecules is present, except for unavoidable chemical impurities. Charge carriers in ODSs are believed to be highly localized [1]. Localization centres are molecules or molecular subunits, henceforth called sites. These sites are located in statistically different environments. As a consequence, the site energies determined by the short-range environment and by electronic polarization, fluctuate from site to site [96]. The fluctuations are typically of the order of 0.1 eV [1, 96], which is about 1 order of magnitude larger than the corresponding transfer integrals [96]. Therefore, carrier wave functions can be considered strongly localized [2, 96–98]. The decay length of the carrier wave function, $\alpha$, on single sites has been evaluated in numerous studies of the concentration-dependent drift mobility. For example for trinitrofluorenone in PVK the estimates $\alpha \simeq 1.1 \times 10^{-8}$ cm and $\alpha \simeq 1.8 \times 10^{-8}$ cm were obtained for holes and electrons, respectively [2]. For dispersions of N-isopropylcarbazole in polycarbonate the estimate $\alpha \simeq 0.62 \times 10^{-8}$ cm for holes has been obtained [98]. Numerical fitting of the mobility data in NRS-PPV and in OC$_1$C$_{10}$-PPV points at the values $\alpha \simeq 1.8 \times 10^{-8}$ cm and $\alpha \simeq 1.6 \times 10^{-8}$ cm, respectively [16]. These small values of the wave function decay length confirm the strong localization of charge carriers. In most previous studies, this decay length was considered independent of the site energy. We will also use this assumption in our consideration below because it essentially simplifies theoretical considerations. This assumption, specifically for disordered organic solids, seems plausible due to the strong localization of carriers in such systems.

In order to understand the charge transport mechanism in ODSs, let us briefly recall some experimental observations that are decisive for formulating the transport model. Among those are the dependences of the carrier drift mobility, diffusivity and conductivity on temperature $T$, on the concentration of carriers $n$, and on such an important material parameter as the spatial concentration of localized states $N$.

Review
Article

Phys. Status Solidi B 251, No. 3 (2014)                                    491

**2.1 Dependence of transport coefficients on the concentration of sites $N$: hopping transport** Already at the beginning of research on molecularly doped polymers, it was established that the dependences of the carrier kinetic coefficients on the concentration of localized states $N$ in several ODSs at low $N$ are essentially nonlinear [2, 98–102]. These dependences were often fitted by the expression [2, 98–101]

$$\mu \propto r^2 \exp\left(-\frac{2r}{\alpha}\right), \qquad (5)$$

which presumes that a typical hopping rate for charge transport depends on $r = N^{-1/3}$ in accord with Eqs. (2) and (3) characteristic for tunnelling (hopping) of charge carriers between sites with separation $r_{ij} \approx r$. Along with the low mobility value in ODSs and with the temperature dependence of $\mu$ discussed in Section 2.2, this $\mu(N)$ dependence is one of the decisive arguments in favour of the hopping transport mode in ODSs. In Paper I, the dependence $\mu(N)$ was interpreted either via the diluted lattice model, or via the lattice site percolation [1]. In the latter case, it was searched for a percolation threshold $N_C$ in the sense that there is no transport at $N < N_C$ while there is transport at $N > N_C$. Herewith the percolation approach to a random site distribution, which is widely used to describe hopping transport in inorganic semiconductors [84], has been somehow underestimated. We address this issue in more detail in Section 4.2.

**2.2 DOS in organic disordered semiconductors** The structure of the DOS in ODSs is probably the most controversial issue in research on these materials. Although the energy spectrum in ODSs is decisive for optoelectronic properties, as is the case for any system, there is no agreement among researchers working with ODSs on the structure of the DOS in such systems. The discussion is mostly focused on whether the DOS is Gaussian as described by Eq. (1), or exponential in the form given by Eq. (4). Furthermore, it is often claimed that the shape of the DOS, Gaussian or exponential, is not decisive for transport properties in ODSs, since physics should be similar for both forms of the DOS [38, 43, 103–106]. Remarkably the latter statement can be found already in some older papers [107, 108] where it was claimed that while the Gaussian DOS looks physically more feasible, the exponential DOS accounts for the studied optoelectronic properties in all respects. We will show in Section 3 that the Gaussian DOS and the exponential DOS yield qualitatively different results in many respects and that experimental observations on the most studied ODSs favour the Gaussian shape of the DOS.

A Gaussian shape of the DOS was suggested for ODSs by Gutmann and Lyons [109]. Silinsh [110] argued that the energy scale $\sigma$ of the Gaussian DOS points at the polarization of the matrix as the main cause of disorder in ODSs and hence of the distribution of potentials. However, the central-limit theorem often used to support the Gaussian distribution of polarization potentials [1, 12, 110] does not necessarily lead to the Gaussian distribution of energies. If quantum effects

contribute to site energies, the distribution of energies does not follow the distribution of potentials. If quantum effects are essential, a Gaussian distribution of potentials can lead to a much weaker energy dependent DOS [111].

First-principles theories for calculating energy spectra in ODSs are highly desirable. Studies based on molecular-dynamical simulations have been already performed for Alq$_3$ (tris(8-hydroxyquinoline)aluminium) [112–114] indicating a Gaussian DOS for molecular energies in this material. However, the main theoretical tool for determining DOS in ODSs is still based on a comparison between the results of computer simulations carried out for a given DOS with experimental data. On the basis of such a comparison, it is sometimes claimed that a single Gaussian tail cannot fit experimental data, for instance those on the recombination kinetics in ODSs, at least in two-phase systems [47]. The latter issue is addressed in Section 9 in more detail.

Experimental methods to determine the DOS are also often limited. For instance, measurements of thermally stimulated currents (TSC), often attempted in order to determine the DOS [1, 12], do not provide reliable information on the energy spectrum because of the multiple trapping (MT) and retrapping effects [115]. The Gaussian shape of the optical absorption [1] also cannot be indicative for the DOS since the transition matrix element in disordered systems cannot be assumed energy-independent [116, 117], while such an assumption is necessary in order to mimic the energy dependence of the absorption coefficient by the shape of the DOS. The results of space-charge-limited currents (SCLC) are not sensitive to the differences between the Gaussian and the exponential DOS [107] Hence, the only strong argument in favour of the Gaussian DOS from those given in previous reviews [1, 26–36] is based on the temperature dependence of the carrier zero-field mobility $\mu(T)$, measured in time-of-flight experiments at low carrier concentrations. Besides the indication of the shape of the DOS, the observed strong increase of the carrier mobility with temperature indicates the hopping transport mechanism in ODSs [1, 12].

Experimental data for carrier mobility in ODSs at low carrier concentrations demonstrate typically the temperature dependence in the form [1, 98, 118–120]

$$\mu(T) \simeq \mu_0 \exp\left[-\left(\frac{T_0}{T}\right)^2\right], \qquad (6)$$

with properly adjusted parameters $T_0$ and $\mu_0$. At high carrier concentrations, particularly in OFETs, the dependence $\mu(T)$ often has the Arrhenius form [121]

$$\mu(T) \simeq \mu' \exp\left[-\frac{\Delta}{kT}\right], \qquad (7)$$

well known also for inorganic disordered semiconductors, such as chalcogenide glasses and amorphous silicon. While both regimes described by Eqs. (6) and (7) appear in systems with a Gaussian DOS (depending on the concentration of charge carriers [32, 63]), in systems with exponential

DOS only the Arrhenius law is to be expected. This issue is discussed in detail in Section 3. With respect to the case of low carrier concentrations, at which the dependence given by Eq. (6) is expected, it is sometimes argued that because the measurements of $\mu(T)$ are usually carried out in a restricted temperature range, it is difficult to distinguish between dependences (6) and (7) [15, 106] when choosing appropriate adjustable parameters $\mu'$ and $\Delta$. However, as discussed in Paper I [1], extrapolation of experimental data to $T \to \infty$ via Eq. (7) typically gives values $\mu' \approx 10\,\mathrm{cm}^2$ $\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ or larger, which is unrealistically high for a non-crystalline molecular solid, while extrapolation to $T \to \infty$ via Eq. (6) typically yields values $\mu_0$ of the order $10^{-2}$ to $10^{-1}\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ as expected for hopping transport [1].

The dependence $\mu(T)$ as described by Eq. (6) has been reproduced in analytical theories [122–125] and in computer simulations [126] based on the Gaussian shape of the DOS, supporting the DOS expressed by Eq. (1). Computer simulations evidence the temperature dependence of the drift mobility in the form

$$\mu(T) = \mu_0 \exp\left[-\left(C\frac{\sigma}{kT}\right)^2\right] \qquad (8)$$

at long times corresponding to a nondispersive transport regime [1, 26–28]. The value $C = 2/3$ has become a conventional estimate for the coefficient $C$ in Eq. (8) [1, 26–28]. In fact, computer simulations [126] yield the value $C \simeq 0.69$, while rather sophisticated analytical calculations [127, 128] predict a close value $C \simeq 0.64$. Eq. (8) with $C = 2/3$ is widely believed to be universal, and it is sometimes used to determine the energy scale $\sigma$ of the DOS from the experimental measurements by plotting $\ln(\mu)$ versus $T^{-2}$ [129].

Although the agreement between the experimental $\mu(T)$ given by Eq. (6) with reasonable values for $\mu_0$ and the theoretical $\mu(T)$ given by Eq. (8) for a Gaussian DOS could be considered as an argument in favour of the Gaussian DOS, there is still no consensus among researchers on the shape of the DOS in ODSs probably because the assumption of an exponential DOS often allows one to fit experimental data [103–108] with an accuracy comparable to the case of a Gaussian DOS. Moreover, if one plots these two DOS functions in a limited energy range with appropriate parameters, $\sigma$ in Eq. (1) and $\varepsilon_0$ in Eq. (4), one can recognize clear similarities between the corresponding curves in the low-energy range decisive for charge transport in ODSs [38, 110]. This, however, does not necessarily mean that physics in both cases is similar. In the following section, we show in which respects physics in a Gaussian DOS differs drastically from that in an exponential DOS and what experimental observations can help to distinguish between these two shapes of the DOS. The results will favour the Gaussian DOS in ODSs.

**3 Further arguments in favour of a Gaussian DOS: Exponential DOS against Gaussian DOS** Let us compare the features of energy distributions of carriers in
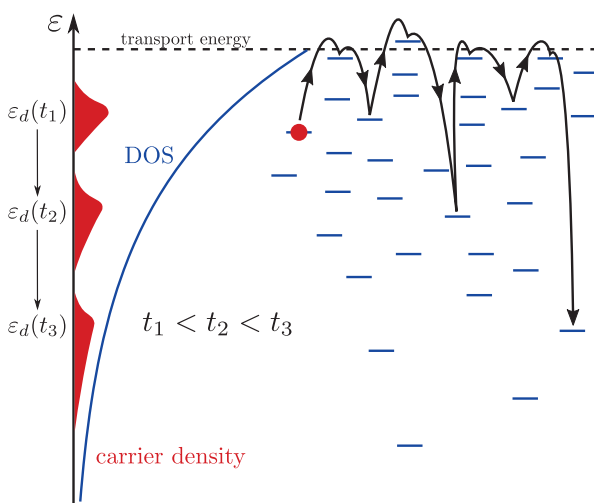


**Figure 1** Schematic picture of the time evolution of carrier distribution through activation to the transport energy.

two classes of DOS functions:

(i) exponential DOS with $\varepsilon_0 > kT$, or DOS with a weaker than exponential energy dependence;

(ii) DOS with steeper than exponential energy dependence.

As shown below, the principal difference between these two classes of DOS functions is prescribed by the exponential shape of the Fermi distribution

$$f(\varepsilon) = \left[1 + \exp\frac{(\varepsilon - \varepsilon_\mathrm{F})}{kT}\right]^{-1}. \qquad (9)$$

For the sake of clarity, we compare the features of an exponential DOS ($\varepsilon_0 > kT$), with those of a Gaussian DOS, since these two DOS functions are most often assumed for ODSs.

**3.1 Exponential DOS** The most essential results for the behaviour of carriers in a system of sites with an exponential DOS are the following.

(i) Activation of carriers from deep energy states to the vicinity of a particular energy level $\varepsilon_\mathrm{t}$, called the *transport energy* (TE), as shown in Fig. 1, plays the decisive role for all equilibrium and non-equilibrium transport phenomena [44, 75, 76, 130]. In Section 4.3, we address the TE in detail.

(ii) In diluted systems with low carrier concentration $n$ (which is usually the case in time-of-flight experiments), the carrier mobility $\mu$ is time-dependent and therefore not well defined. This is the essence of the so-called dispersive transport regime [131]. As illustrated in Fig. 1, in an empty system charge carriers dive in energy unlimitedly at $kT < \varepsilon_0$. In course of the energy diving, most carriers are distributed around the time- and temperature-dependent demarcation energy $\varepsilon_\mathrm{d}(t)$ determined by the condition [75]

$$\nu\left[\varepsilon_\mathrm{d}(t) \to \varepsilon_\mathrm{t}\right] t \approx 1. \qquad (10)$$

**Review**

**Article**

Phys. Status Solidi B 251, No. 3 (2014)                                                                      493

This condition means that within the time $t$, activation to the TE $\varepsilon_t$ is possible from states with energies above $\varepsilon_d(t)$ and improbable from states below $\varepsilon_d(t)$. Hence, the states above $\varepsilon_d(t)$ can be considered in thermal equilibrium, while states below $\varepsilon_d(t)$ are not able to get rid of carriers within the time $t$ and, therefore, they should be occupied in accord with the DOS. Since the equilibrium distribution decays upwards above $\varepsilon_d(t)$ within the scale $kT$ and since the DOS decays downwards within the scale $\varepsilon_0$, the maximum of the carrier distribution corresponds to the vicinity of $\varepsilon_d(t)$ as illustrated in Fig. 1. Using Eq. (2) with $\varepsilon_i = \varepsilon_d(t)$, $\varepsilon_j = \varepsilon_t$ and $r_{ij} = r(\varepsilon_t)$, where

$$r(\varepsilon) = \left[ \frac{4\pi}{3} \int_{-\infty}^{\varepsilon} g(\varepsilon')d\varepsilon' \right]^{-1/3}, \tag{11}$$

one obtains

$$\varepsilon_d(t) \approx \varepsilon_t - kT \ln(\nu_0 t) + \frac{kT 2r(\varepsilon_t)}{\alpha}. \tag{12}$$

If $\varepsilon_t$ coincides with the mobility edge at $\varepsilon = 0$, i.e. in the framework of the classical MT model without tunnelling transitions ($r \to 0$), Eq. (12) reads [131]

$$\varepsilon_d(t) = -kT \ln(\nu_0 t). \tag{13}$$

In course of time, the demarcation level $\varepsilon_d(t)$ moves downwards in energy, and activation to the vicinity of the TE becomes more and more difficult for diving carriers. Therefore, the speed of spatial carrier motion slows down, so that transport coefficients appear time-dependent. The more time carriers spend in the system, the lower values of the mobility are measured. Hence, measured mobility values depend on the thickness of the sample and on the applied electric field even in the Ohmic regime, since these parameters determine the time of transients. Therefore, measured mobility values are not characteristic for a given material at a given temperature, or, in other words, mobility in the exponential DOS is not defined for diluted systems. Sometimes, it is claimed that unlimited energy diving of carriers in the empty system is a unique property of the exponential DOS [60]. In fact, this is the property of any DOS that depends on energy weaker than exponentially, since this feature is the consequence of the exponential shape of the Fermi/Boltzmann distribution behaving more steeply than the DOS.

(iii) In a system with finite concentration of carriers $n$ in the exponential DOS, mobility in the equilibrium conditions always depends on $n$, since the diving in energy described above stops only when the demarcation energy $\varepsilon_d(t)$ arrives at the vicinity of the $n$-dependent Fermi level $\varepsilon_F(n)$. In the exponential DOS, assuming thermal equilibrium and $kT < \varepsilon_0$, most carriers occupy energies in the vicinity of $\varepsilon_F$: the carrier distribution decays exponentially within the scale $kT$ above $\varepsilon_F$ due to the Fermi function and it decays within the scale $\varepsilon_0$ below $\varepsilon_F$ following the DOS. Therefore, as illustrated in Fig. 2, there are two important energies for transport of
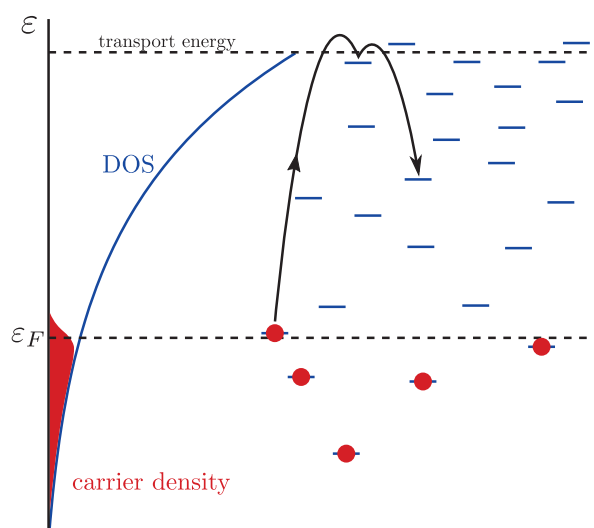


**Figure 2** Schematic equilibrium energy distribution of carriers in an exponential DOS.

charge carriers in the exponential DOS: the TE $\varepsilon_t$ and Fermi level $\varepsilon_F$. Whereas most carriers in the exponential DOS in thermal equilibrium occupy energies close to the Fermi level $\varepsilon_F$, this is *not* the case at small $n$ in a Gaussian DOS, as discussed in the following Section 3.2.

**3.2 Gaussian DOS** The most essential results for the behaviour of carriers in a system of sites with Gaussian DOS described by Eq. (1) are the following.

(i) Similarly to the case of an exponential DOS, a particular energy level $\varepsilon_t$ called the transport energy is responsible for charge transport and for energy relaxation of carriers in the Gaussian DOS [63, 77, 132].

(ii) In contrast to the case of the exponential DOS, in a Gaussian DOS at low carrier concentration $n$, most carriers in thermal equilibrium are distributed not around the Fermi level. Instead carriers are situated around the so-called equilibration energy $\varepsilon_\infty$. This equilibration energy is usually identified with the average energy determined as [1, 133]

$$\varepsilon_\infty = \frac{\int_{-\infty}^{\infty} \varepsilon g(\varepsilon) \exp(-\varepsilon/kT)d\varepsilon}{\int_{-\infty}^{\infty} g(\varepsilon) \exp(-\varepsilon/kT)d\varepsilon} = -\frac{\sigma^2}{kT}. \tag{14}$$

In fact, a better definition of the equilibration energy $\varepsilon_\infty$ would be to identify it with the energy corresponding to the maximum of the product $g(\varepsilon)f(\varepsilon)$. However, we will follow the traditional definition of $\varepsilon_\infty$ via Eq. (14) suggested in Paper I [1], since for the Gaussian DOS given by Eq. (1) valid in ODSs, the maximum of the product $g(\varepsilon)f(\varepsilon)$ corresponds to $\varepsilon_\infty$ given by Eq. (14). If the concentration of carriers $n$ is small, so that the Fermi level $\varepsilon_F$ is far below this equilibration energy, $\varepsilon_\infty - \varepsilon_F \gg kT$, most carriers occupy energy levels in the vicinity of $\varepsilon_\infty$ and not in the vicinity of the Fermi energy $\varepsilon_F$. It might look counterintuitive that most carriers are gathered in the states with very low filing probability,
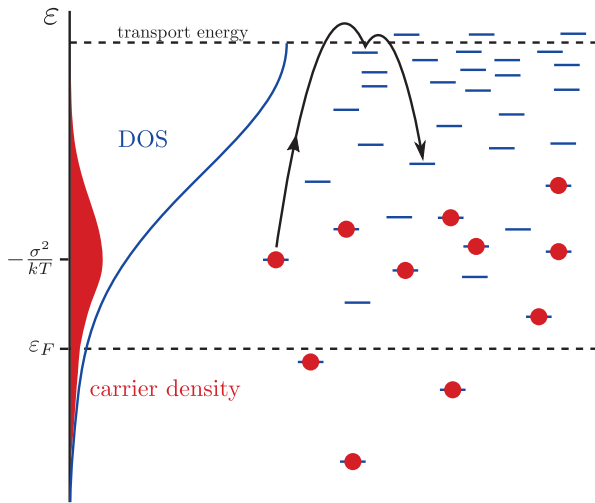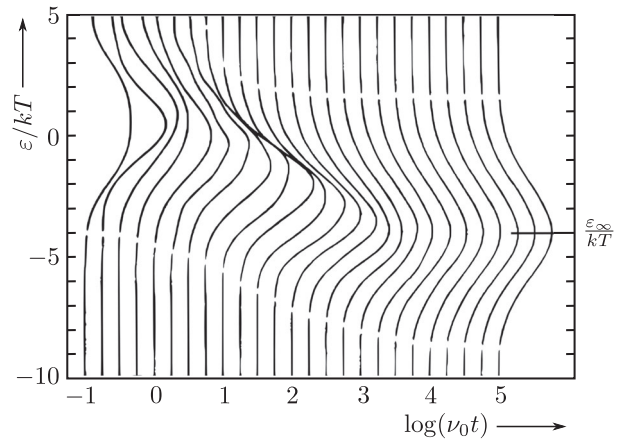
**Figure 3** Schematic equilibrium energy distribution of carriers in a Gaussian DOS.



**Figure 4** Temporal evolution of the distribution of carrier energies in a Gaussian DOS of width $\sigma = 2kT$. $\varepsilon_\infty$ denotes the theoretical mean energy in the long-time limit (reproduced with permission from [1]; Copyright 1993 by Wiley).

much lower than that for states in the vicinity of the Fermi level. The filling probability for states at $\varepsilon_\infty$ is lower than that for states around the Fermi level by the factor

$$\frac{f(\varepsilon_\infty)}{f(\varepsilon_F)} \sim \exp\left(-\left[\frac{(\varepsilon_\infty - \varepsilon_F)}{kT}\right]\right). \tag{15}$$

This ratio is much less than unity for $(\varepsilon_\infty - \varepsilon_F) \gg kT$. However, the Gaussian DOS decreases downwards in energy below $\varepsilon_\infty$ so steeply that the increase of the filling factor for deep energy levels, though exponential in accord with Eq. (9), cannot compensate the decreasing Gaussian DOS. The equilibrium carrier distribution in a Gaussian DOS is shown schematically in Fig. 3. This is in drastic contrast to the distribution of carriers in the exponential DOS, where at $kT < \varepsilon_0$ most carriers occupy energy levels in the vicinity of the Fermi energy, as shown in Fig. 2.

(iii) In contrast to the case of the exponential DOS, in an empty system with Gaussian DOS mobility is a well-defined quantity that has a clear physical meaning even for a single carrier present in the system [22, 78]. This is true because after relaxing from higher energy levels towards the equilibration energy $\varepsilon_\infty$ during some relaxation time $\tau_{rel}$, the carriers stop diving further, even if states with energies below $\varepsilon_\infty$ are unoccupied. Within time of the order $\tau_{rel}$ transport is dispersive with the time-dependent mobility $\mu(t)$, similar to the case of the exponential DOS described in Section 3.1. At $t < \tau_{rel}$, the energy distribution of carriers has the maximum in the vicinity of the time-dependent energy $\varepsilon_d(t)$ described by Eq. (12), while at longer times, $t > \tau_{rel}$ mobility acquires a time-independent well-defined value [22, 78]. Numerically simulated temporal evolution of the energy distribution of noninteracting carriers relaxing in a Gaussian DOS is schematically shown in Fig. 4 reproduced from Paper I [1]. In the simulation, the initial energy distribution of carriers was taken random, i.e. coinciding with the shape of the DOS [1]. In course of time, the carrier energy distribution

moves downwards until its maximum arrives at the energy $\varepsilon_\infty$ determined by Eq. (14) and stays stable afterwards [1].

(iv) While in the exponential DOS all essential physical processes take place in the energy range between only two important energy levels, the TE $\varepsilon_t$ and the concentration-dependent Fermi level $\varepsilon_F(n)$, so that equilibrium mobility always depends on the concentration of carriers $n$, the situation in the Gaussian DOS is more complicated. As shown in Fig. 3, there are three important energies: $\varepsilon_t$, $\varepsilon_F(n)$, and $\varepsilon_\infty = -\sigma^2/kT$. Moreover, the relation between energy levels $\varepsilon_F(n)$ and $\varepsilon_\infty$ depends on the carrier concentration $n$ since the Fermi level depends on $n$ via the relation

$$\int_{-\infty}^{\infty} g(\varepsilon) f(\varepsilon, \varepsilon_F) d\varepsilon = n, \tag{16}$$

The levels $\varepsilon_F(n)$ and $\varepsilon_\infty$ coincide at a carrier concentration $n_c$ determined by the equation [63, 65, 68]

$$\varepsilon_F(n_c) = \varepsilon_\infty. \tag{17}$$

In Fig. 5, the crossing between $\varepsilon_F(n)$ and $\varepsilon_\infty$ with varying $n$ is illustrated [132].

At $n \ll n_c$ the concentration-dependent Fermi level is situated far below the equilibration energy $\varepsilon_\infty$, around which most electrons are distributed. Because of the deep position of $\varepsilon_F$, the filling of energy levels around $\varepsilon_\infty$ is very low and hence carriers behave independently from each other. At such low $n$, all essential physical processes take place in the energy range between $\varepsilon_\infty$ and $\varepsilon_t$, and the *carrier mobility $\mu$ does not depend on the concentration of carriers $n$*. This is drastically different to the case of the exponential DOS, where mobility is always concentration-dependent. With increasing $n$, the Fermi level $\varepsilon_F(n)$ shifts upwards in energy and arrives at the vicinity of the equilibration energy $\varepsilon_\infty$ at $n \approx n_c$ determined by Eq. (17). For $n > n_c$, the Fermi level is above $\varepsilon_\infty$ and essential physical processes take place in the energy range between $\varepsilon_t$ and $\varepsilon_F(n)$. In this regime, the carrier mobility in

**Review**

**Article**

Phys. Status Solidi B 251, No. 3 (2014) 495
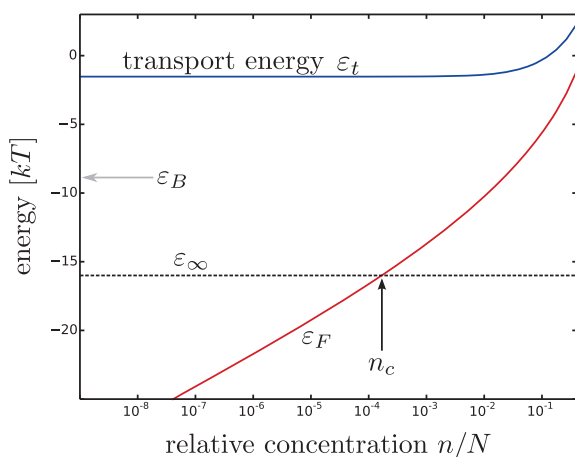
**Figure 5** Positions of the concentration-dependent Fermi energy $\varepsilon_F(n)$ given by Eq. (16) and of the equilibration energy $\varepsilon_\infty$ given by Eq. (14) at $\sigma/kT = 4$. Positions of the TE $\varepsilon_t$ and of $\varepsilon_B$ (determined in Section 4.3) are also shown (reproduced with permission from [132]; Copyright 2010 by the American Institute of Physics).



**Figure 6** Schematic dependences of the Fermi energy and of the carrier mobility on concentration of carriers $n$ in a Gaussian DOS. Concentration $n_c$ corresponds to the condition given by Eq. (17).
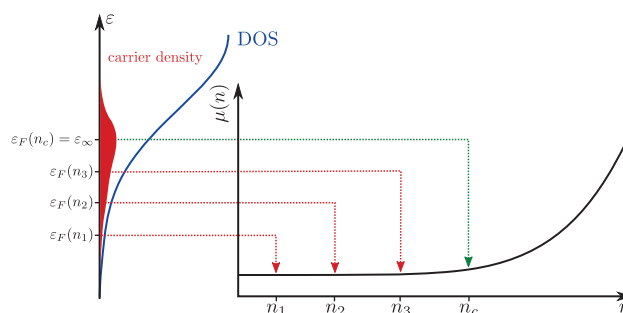
a Gaussian DOS becomes *dependent* on the carrier concentration $n$ [61, 63–65, 68] in full analogy to the case of the exponential DOS described above.

The interplay between the two energies $\varepsilon_\infty$ and $\varepsilon_F$ can be also considered as a function of temperature $T$ at constant carrier concentration $n$. In fact, it was initially suggested in this very form [63]:

$$\varepsilon_F(T_c, n) = \varepsilon_\infty(T_c), \qquad (18)$$

and only later has been reformulated in the form of Eq. (17) [61, 65, 68]. At $T < T_c$, or $n > n_c$, the Fermi level is situated above $\varepsilon_\infty$, and the charge carrier mobility is expected to exhibit a simple activated behavior $\ln(\mu/\mu') \propto -(\Delta/kT)$ given by Eq. (7) with $\Delta = \varepsilon_t - \varepsilon_F$ [32, 63]. At $T > T_c$, or $n < n_c$, the Fermi level is situated below $\varepsilon_\infty$, not affecting the charge transport as described above. In the latter case, the temperature dependence of the mobility has the form $\ln(\mu/\mu_0) \propto -(\sigma/kT)^2$ given by Eq. (6) [32, 63, 78]. Often the dependence $\ln(\mu/\mu_0) \propto T^{-2}$ is considered as evidence for a Gaussian DOS, while the Arrhenius temperature dependence $\ln(\mu/\mu') \propto T^{-1}$ is claimed to indicate a purely exponential DOS. The important conclusion from the above consideration is the possibility to account for both kinds of temperature dependences of hopping conductivity described by Eqs. (6) and (7) in the framework of the universal theoretical model based on the Gaussian DOS. *The temperature dependence of the conductivity and mobility is sensitive to the concentration of charge carriers $n$* [32, 63].

(v) Having a carrier mobility independent of carrier concentration $n$ at $n < n_c$ and dependent on $n$ at $n > n_c$, one comes to the dependence $\mu(n)$ in the Gaussian DOS shown schematically in Fig. 6. Remarkably, literally this shape of the dependence $\mu(n)$ has been observed experimentally for widely studied ODSs, PPV and P3HT [38]. The data from Ref. [38] are reproduced in Fig. 7.

The plateau at $n < n_c$ clearly rules out the possibility of an exponential DOS in these materials. The independence of the mobility on carrier concentration up to rather high concentrations $n \simeq 10^{18}\,\mathrm{cm}^{-3}$ has been evidenced experimentally for PPV also in Ref. [134]. Furthermore, such a concentration-independent mobility at low $n$ has been established experimentally not only for PPV and P3HT, but also for three derivatives of quinquethiophenes, called 5T [40, 41], definitely ruling out an exponential DOS also for these ODSs. The arguments from [63, 65] given above, though published prior to most experimental studies, were apparently overseen by experimentalists [38, 58–60, 103–106], who focused on the range of concentrations $n > n_c$ with the concentration-dependent mobility, claiming correctly that this regime can be described by a Gaussian DOS as well as by an exponential DOS. A theory for the dependence of the mobility $\mu$ on carrier concentration $n$ will be provided in Section 6 of the current report. It is worth emphasizing once more that not the trivial regime with concentration-dependent mobility is indicative for the DOS, but the regime at $n < n_c$, in which the measured data cannot be described by an exponential DOS, while the data fit perfectly into the transport picture with a Gaussian DOS [32, 61, 63, 65, 68, 132].
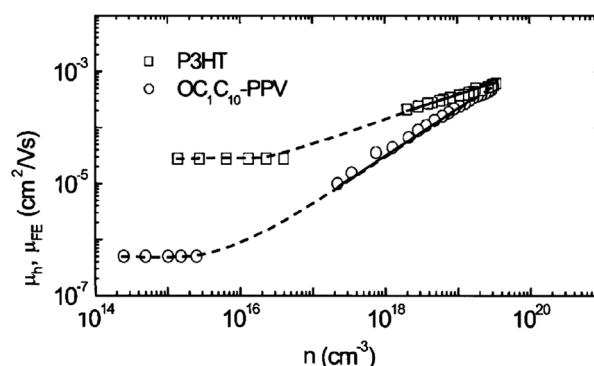


**Figure 7** Experimentally measured hole mobility as a function of carrier density $n$ in a diode and field-effect transistor for P3HT and OC$_1$C$_{10}$-PPV. The dashed line is a guide to the eye (data reproduced with permission from [38]; Copyright 2003 by the American Physical Society).

In fact, in any DOS decaying steeper than the exponential one the equilibration energy similar to $\varepsilon_\infty$ would exist, leading to the relation described by Eq. (17) and concomitantly to the plateau in the dependence $\mu(n)$ at $n < n_c$, where $n_c$ is given by Eq. (17) for the corresponding choice of the DOS. As shown by the detailed study [61], the critical concentration $n_c$ determined by Eq. (17) depends drastically on the shape of the DOS and a comparison with experimental data for PPV and P3HT from Ref. [38] evidences that the energy spectrum in these widely studied materials is very close to the Gaussian one [61]. Note that the result for the DOS based on the criterion (17) [61] seems universal with respect to systems with and without space-energy correlations, i.e. for GDM and CDM.

The theoretical approaches described above rely on the assumption that the DOS (at least the portion of energy spectra participating in transport) can be sufficiently well described by functions with a single energy scale ($\sigma$ in Eq. (1) or $\varepsilon_0$ in Eq. (4)). This might be well justified as long as there is no superposition of inhomogeneously broadened, electronically inequivalent molecular states that may give rise to several humps in the DOS. A DOS structure with several peaks in its upper energy part has been reported for several organic semiconductors on the basis of experimental studies using the Scanning Kelvin Probe force Microscopy (SKPM) and the gate-modulated activation energy spectroscopy [105, 135–140]. Remarkably, in most of these studies an exponential low-energy tail in the DOS has been reported.

It might be worth to check the data obtained by SKPM, which report exponential low-energy tails of the DOS, using the method suggested in Ref. [61]. The idea is to measure the concentration dependence of the carrier mobility at low carrier concentrations, at which the low-energy tail of the DOS dominates charge transport. If this tail is exponential, as declared in several experimental studies based on the SKPM technique, carrier mobility should depend on the concentration of carriers $n$ even at very low $n$ values. If a concentration-independent mobility is observed even at very low carrier concentrations (which is the case in P3HT, $OC_1C_{10}$-PPV and 5T [38–41]) one should check the validity of the experimental methods used for measuring DOS and revise them appropriately.

The emphasis in the current review is put on the theoretical description of hopping charge transport in the GDM. In the following Section 4, the most powerful theoretical methods to describe this transport mode will be highlighted. In the subsequent sections, particular problems related to the dependences of transport coefficients on temperature, on the concentration of sites, on external electric field, on the concentration of carriers and on some material parameters will be addressed.

**4 Theoretical study of hopping transport** The best type of theory for hopping charge transport in ODSs would be, of course, a first-principles theory that starts from the particular chemical and geometrical structure of the system and calculates the mobility of charge carriers from the first principles taking into account the dependence of hopping rates on electronic coupling elements, on reorganization energies, and on dynamically changing positions and orientations of the molecules. Such a program has recently been attempted addressing charge transport particularly in $Alq_3$ (tris(8-hydroxyquinoline)aluminium) [141]. Although the exact evaluation of all contributions essential for charge transport in a molecular assembly is currently considered as computationally prohibitive [142], the future probably belongs to this kind of theory. However, the current state of theoretical research on charge transport in ODSs is yet far behind this desired level.

The great achievement of Paper I [1] was the formulation of a simple phenomenological model – the GDM – that, in spite of its simplicity, picks up the most essential features of charge transport in ODSs, namely the dependences of carrier mobility on temperature, on the concentration of charge carriers, on electric field, on the concentration of localized states, etc. However, the mainstream level of theoretical research based on the GDM does not yet correspond to the level of theoretical research on hopping transport achieved for decades in the parallel field of hopping transport in inorganic disordered systems reflected, for instance, in the monograph by Shklovskii and Efros [84].

The main theoretical tool to study charge transport used in Paper I was a phenomenological fitting of numerical results obtained by Monte Carlo simulations. In such an approach, one simulates or calculates numerically the dependences of kinetic coefficients on essential parameters, such as temperature and electric field, and afterwards searches for analytical formulas, which could fit the obtained dependences with a help of several fitting coefficients [1]. Such a phenomenological fitting is still popular among researchers working with ODSs, who simply add the concentration of carriers $n$ [16] to the fittings performed in Paper I at low $n$ [1]. Although user-friendly, this approach can hardly be considered as a consequent theory, since it is based on parameterizations, which usually do not have a fundamental background. Dependences of carrier mobility on physical parameters, like temperature $T$, are often considered universal, simply because other parameters, for instance the concentration of sites $N$, do not change in the course of the simulations [1]. Theoretical description of charge transport in ODSs given in Paper I apparently needs an extension based on more developed theoretical tools. Such tools have been successfully used for decades for the description of charge transport in inorganic amorphous and doped semiconductors, though they have not yet become popular in the field of ODSs. It is the main goal of the current report to highlight these theoretical approaches in application to ODSs. Before addressing the particular approaches in more detail, we point out in the following section some theoretical highlights, which seem essential for analytical description of charge transport in ODSs.

**4.1 Highlights in the theory of hopping transport relevant to ODSs** The following results seem

Phys. Status Solidi B 251, No. 3 (2014)

Review

Article

497

essential for developing the analytical theory of hopping transport in ODSs.

(i) 1969: *Breakthrough in the description of hopping transport via spatially and energetically distributed localized states: VRH* [143]. The essence of the theory is the interplay between spatial- and energy-dependent factors leading to the idea of the VRH: the lower the temperature $T$, the more distant are carrier hops essential for transport [143]. Since 1969, theoretical research in hopping transport has been mainly focused on the interplay between the spatial extension of localized states and the DOS function. For a DOS that weakly depends on energy in the vicinity of $\varepsilon_F$, the temperature dependence of hopping conductivity $\sigma_{dc}$ at low $T$ has the form [143]:

$$\sigma_{dc} \propto \exp[-(T_0/T)^{1/4}],$$
$$T_0 = \beta/[kg(\varepsilon_F)\alpha^3], \tag{19}$$

where $\beta$ is a numerical factor [84].

(ii) 1971–1972: *Quantitative approach to description of VRH based on the percolation theory* [71–73]. The essence of this approach is that hopping transport is determined not by the rate of average hops, but rather by the rate of those hops that are most difficult but still relevant for long-range transport. Hopping conduction is in fact a percolation process, in which the slowest transitions still needed to provide a connected path through the system determine charge transport. The appropriate percolation problem to describe hopping transport in spatially disordered materials is the percolation problem for random sites, where the percolation radius is related to the site concentration [84]. In Section 4.4, we compare percolation results with those obtained by the averaging of rates.

(iii) 1979: *Percolation theory for VRH in the exponential DOS* [44]. Using the classical percolation approach [71–73], it was shown that in a broad range of temperatures $T$ and carrier concentrations $n$ the carrier mobility is equal to

$$\mu = \frac{\sigma_{dc}}{en} = \frac{\sigma_{dc}^0}{en} \exp\left(-\frac{\varepsilon^* - \varepsilon_F}{kT}\right), \tag{20}$$

where $\sigma_{dc}^0$ is the preexponential factor in the expression for the conductivity and $\varepsilon^*$ is the characteristic highest energy of sites contributing to charge transport [44].

Two decades later, the very same problem was addressed by the community working with ODSs, though in the frame of a less accurate theory [43]. The approaches used in Ref. [44] and in Ref. [43] are compared in Section 4.2.

Although the exponential DOS given by Eq. (4) is probably irrelevant to ODSs [61], it provides a perfect test field for theoretical studies. The exponential DOS possesses a unique feature: the four-dimensional (three spatial dimensions and energy) VRH problem in such DOS can be exactly mapped onto a purely geometrical, three-dimensional problem of percolation via spheres with distributed radii that allows an exact

solution [89]. In the exponential DOS, one can correctly obtain in the case of VRH not only the very pronounced exponential dependences of kinetic coefficients on various parameters, but also the slowly varying preexponential factors [89]. Some details to this issue are given in Section 4.2.

(iv) 1981: *Formulation of the Gaussian disorder model (GDM)* [12]. This is a decisive milestone for the theory of charge transport in ODSs [1].

(v) 1985: *Concept of the transport energy for the exponential DOS* [75]. It has been shown that VRH transport in the exponential DOS can be described in the framework of a MT model with replacing the mobility edge by a slightly temperature-dependent energy level called the TE [75, 76, 130].

(vi) 1988: *Existence of the equilibration energy $\varepsilon_\infty$ in a Gaussian DOS* [133]. It has been recognized that the equilibration energy given by Eq. (14) determines the equilibrium energy distribution of carriers in a Gaussian DOS at low concentrations $n$ [1, 133]. Herewith, the principle difference between the Gaussian and the exponential DOS was realized, that later led to the transport picture described above in Section 3.2.

(vii) 1997: *Concept of the transport energy for the Gaussian DOS* [77]. It has been shown that VRH transport in any steeply energy-dependent DOS, like a Gaussian one, can be described in the framework of a MT model with replacing the mobility edge by the TE [32, 77].

(viii) 2000: *Analytical theory for hopping transport in the Gaussian DOS in a non-trivial case of low carrier concentrations $n$* [78]. Using the concept of the TE, the dependences of carrier mobility $\mu$ on temperature $T$ and on the concentration of sites $N$ have been derived analytically for low carrier concentrations, $n \ll n_c$ [22, 32, 78]. Equation (8) was obtained with parameter $C$ slightly dependent on the concentration of sites $N$.

(ix) 2002–2003: *Theory for hopping transport in the Gaussian DOS with the mobility $\mu$ dependent on the carrier concentration $n$* [14, 63–68]. Using percolation theory [63, 64], the concept of the TE [14, 65, 66] and by semi-analytical calculations [67, 68] it has been shown that the dependence of the mobility $\mu$ on the concentration of carriers $n$ is the inherent property of the GDM. The dependences of carrier mobility $\mu$ on temperature $T$, on the concentration of sites $N$, and on the concentration of carriers $n$ have been derived analytically [14, 63–68]. The physical picture described in Section 3.2 was formulated with the decisive role of the conditions given by Eqs. (17), (18) [63, 65, 68]. At $n < n_c$ and $T > T_c$, mobility $\mu$ is independent of $n$, demonstrating $T$-dependence described by Eq. (8) with parameter $C$ dependent on concentration of sites $N$, while at $n > n_c$ and $T < T_c$, mobility $\mu$ depends on $n$ showing $T$-dependence described by Eq. (7) in the form of Eq. (20) [63, 65]. A detailed analysis of experimental data for $\mu(n)$ in the framework of the GDM has been performed [65, 66], demonstrating the ability of the GDM to account for the experimentally observed concentration-dependent mobility in ODSs.

**4.2 Percolation theory** The best way known so far to describe hopping transport in disordered systems analytically is based on the percolation theory. Let us very briefly sketch this approach for the simplest case of a lattice model in the frame of scaling arguments, closely following the classical description [84, 144]. Consider a simple lattice with random resistances between adjacent sites that can be given in the form

$$R = R_0 \exp(\xi), \tag{21}$$

where $R_0$ is a constant and the random variable $\xi$ is distributed in the interval $-\xi_0 < \xi < \xi_0$ with $\xi_0 \gg 1$. The goal is to find the DC conductivity $\sigma_{dc}$ as a function of $\xi_0$. The classical recipe for uncorrelated resistances is to search for the critical value $\xi_c$ determined via the relation

$$\int_{-\xi_0}^{\xi_c} F(\xi)\mathrm{d}\xi = x_c, \tag{22}$$

where $x_c$ is the known percolation threshold for the bond problem on the chosen lattice and $F(\xi)$ is the distribution function of exponents in Eq. (21). Taking the homogeneous distribution $F(\xi) = (2\xi_0)^{-1}$ one obtains $\xi_c = \xi_0[2x_c(b) - 1]$ [84]. The conductivity $\sigma_{dc}$ is proportional to $\exp(-\xi_c)$. Taking into account only bonds with $\xi \leq \xi_c$, one obtains a fractal percolation cluster with extremely low spatial density. Electrical current is therefore carried in a system of bonds with parameters $\xi$ slightly larger than $\xi_c$, i.e. with $\xi \leq \xi_c + K$, where $K \ll \xi_c$ is a number of the order unity [84]. Such a cluster responsible for electrical current with a finite spatial density [84] was named the 'fat percolation cluster' [145]. This philosophy [84] has recently arrived in the field of ODSs under the term 'fat percolation' [69, 88]. Scaling arguments based on the geometry of the percolation cluster responsible for charge transport provide not only the exponential dependence $\exp(-\xi_c)$, but they also yield the structure of the preexponential factor. For instance, in the case of a lattice with lattice period $l_0$ the result reads [84]

$$\sigma_{dc}(\xi_0) = A(R_0 l_0)^{-1} \xi_0^{-\nu} \exp(-\xi_c), \tag{23}$$

where $A$ is a numerical coefficient of order unity dependent on the type of the lattice, while $\nu$ is the critical index of the correlation length of a percolation cluster, independent of the short-range details such as the lattice structure. In the 3D case, its value is close to $\nu \approx 0.9$ [84].

Notably, Schönherr et al. [126] used Eq. (22) with a Gaussian distribution $F(\xi)$ of site energies and $\xi_0 = -\infty$, $x_c = 0.31$, in order to estimate the position of the energy level $\varepsilon_c$ responsible for charge transport on a simple cubic lattice with Gaussian DOS. In this case, the relevant percolation threshold is the one for the site percolation problem, since resistances ascribed to adjacent bonds are correlated via the energy of the common site. A very similar result for the simple cubic lattice was recently obtained by Cottaar et al. [88], showing that analytical calculation of Schönherr et al. [126] was correct. The obtained value $\varepsilon_c \cong -0.6\sigma$ [126] is very close to the value $\varepsilon_c \cong -0.5\sigma$ derived by Cottaar et al. [69]. However, computer simulations carried out by Schönherr et al. [126] were interpreted as in contrary to this correct analytical result, leading Schönherr et al. [126] to the conclusion that percolation theory is not suitable to describe hopping transport in a Gaussian DOS [126]. This example shows once again that conclusions based on phenomenological fitting of numerical data can sometimes be ambiguous.

The percolation problem not on a lattice, but rather in a system of random sites seems appropriate for ODSs, as illustrated in Section 2.1. Let us first consider the simplest example of a carrier hopping through a system of isoenergetic sites randomly distributed in space with some concentration $N$, so that $r = N^{-1/3} \gg \alpha$, i.e. states are strongly localized. In such a case, carriers would preferentially hop to the spatially nearest sites and therefore this transport regime is called nearest-neighbour 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 of the DOS, $\sigma$. Under this condition, the energy-dependent term in Eq. (2) does not play an essential role, and hopping rates are determined solely by the spatial distances. The local resistance between two sites separated by distance $r$ can then be described as $R(r) = R_0 \exp(2r/\alpha)$. Note that in real systems, the preexponential factor $R_0$ depends on the relative position of the energy level ascribed to the isoenergetic sites with respect to the Fermi level $\varepsilon_F$ and therefore the quantity $R_0$ depends on the concentration $n$ of carriers. The recipe for calculating electrical conductivity $\sigma_{dc}$ in such a system looks as follows [84]. In order to find the transport path, one connects sites with the relative separation smaller than some given distance $r$, and checks, whether a continuous path through the system via connected sites is formed. If such a path is absent, the value of $r$ is increased and the procedure is repeated. At some particular value $r = r_c$, a continuous path via sites with relative separations $r \leq r_c$ arises. In order to determine $r_c$, one should calculate the average number of valid bonds per site necessary for the percolation threshold [84]. Various mathematical considerations give for $r_c$ the relation [84, 146, 147]

$$\frac{4\pi}{3} N r_c^3 = B_c, \tag{24}$$

where $B_c \cong 2.735$ is the average number of connected neighbouring sites within the distance $r_c$ [148]. Scaling arguments given in paragraph 5.6 of the monograph by Shklovskii and Efros [84] then lead straightforwardly to the expression for the conductivity at low carrier concentrations

$$\sigma_{dc}(N) = A R_0^{-1} N^{1/3} (\alpha N^{1/3})^\nu \exp\left(-\frac{\gamma N^{-1/3}}{\alpha}\right), \tag{25}$$

**Review**

**Article**

Phys. Status Solidi B 251, No. 3 (2014)                                499

where $\gamma \cong 1.7351$ is determined by solving Eq. (24) for $r_c$, $A$ is a numerical coefficient of the order unity and $\nu \approx 0.9$ is the critical index of the correlation length of the percolation cluster.

This dependence $\sigma_{dc}(N)$ over several orders of magnitude has been observed in numerous experimental studies of hopping transport via impurity atoms in doped crystalline semiconductors, where the values of the localization length $\alpha$ for randomly placed impurities are well known [84]. Notably, the percolation theory for random sites does not presume any threshold concentration $N_c$ as often searched for in ODSs, but it rather provides Eq. (25), valid in particular for low concentrations $N^{-1/3} \gg \alpha$ and high temperatures, $kT > \sigma$.

The percolation approach to charge transport becomes more sophisticated if not only spatial positions of sites but also their energies and the occupation of sites are essential, which is the case if $kT$ is smaller than the energy scale of the DOS $\sigma$, and the concentration of carriers $n$ is not negligible, i.e. the distribution of site energies and the dependence $\varepsilon_F(n)$ are essential for hopping rates determined by Eq. (3). In the general case, the problem should be solved in a four-dimensional (4D) space for three spatial coordinates and energy, as typical for the VRH [84]. The important question to be answered would be: can one use the percolation criterion with $B_c \approx 2.7$ for VRH as in the case of NNH given by Eq. (24) and, if yes, how to calculate the average number of valid bonds per site in the 4D case?

There is no agreement among researchers in attempts to answer this question. Grünewald and Thomas for the exponential DOS [44] and Baranovskii et al. [63] and Rubel et al. [22] for the Gaussian DOS, used $B_c = 2.7$, while Arkhipov et al. [14] and Li et al. [149] used $B_c = 1$ for the Gaussian DOS. Furthermore, the way of calculating the average number of valid bonds per site was also different in different approaches. While Grünewald and Thomas for the exponential DOS [44] and Baranovskii et al. for the Gaussian DOS [63] used the classical recipe [73] of averaging over the sites belonging to the infinite cluster that provides percolation, Vissenberg and Matters for the exponential DOS [43] and Arkhipov et al. [14] and Coehoorn et al. [150] for the Gaussian DOS carried out the averaging over all sites in the system. It is, of course, desirable to find out what approach is more accurate.

Fortunately, the above question can be answered precisely in a special case of the exponential DOS described by Eq. (4). At the realistic condition $\varepsilon_0 > kT$, the 4D VRH problem in the exponential DOS can be mapped onto a novel geometrical 3D problem of percolation via a system of randomly placed spheres of density $N$ with exponentially distributed radii $g(r) = N \exp(-\tilde{r})$, where $\tilde{r}$ is a dimensionless radius of a sphere. The corresponding percolation problem [89] is illustrated in Fig. 8. Using the numerical solution of this purely geometrical problem for a dimensionless density, $\tilde{N}_c \approx 0.219$ [89], one obtains an accurate result for the VRH problem in the exponential DOS. This solution allows one to find out, which approach from the previously reported in the literature provides most accurate results. In Fig. 9, we compare the results obtained by Grünewald and Thomas [44] and
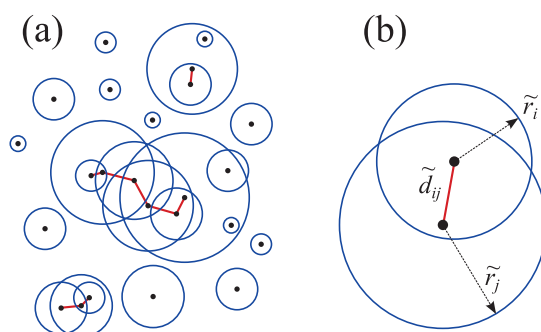


**Figure 8** The system of spheres of different radii (a) and the connection criterion (b). $\tilde{r}_i$, $\tilde{r}_j$ are dimensionless radii of randomly placed spheres; $\tilde{d}_{ij}$ is the dimensionless distance between spheres considered as connected [89] (reproduced with permission from [89]; Copyright 2013 by the American Physical Society).

those obtained by Vissenberg and Matters [43] with the exact analytical solution [89]. In this figure, we also plot the results of the analytical description based on the concept of TE suggested by Oelerich et al. [61] in order to calculate the carrier mobility $\mu$ at arbitrary concentration of carriers $n$.

All analytical solutions mentioned above can be represented as

$$\mu = \mathbf{A} \frac{\nu_0 e}{n \varepsilon_0 \alpha} \left[ \mathbf{B} \frac{n}{8} \left( \frac{\alpha \varepsilon_0}{kT} \right)^3 \right]^{\varepsilon_0/kT}, \qquad (26)$$

where $\mathbf{A}$ and $\mathbf{B}$ are factors different for different approaches to be checked. Table 1 lists the different approaches and the corresponding values of $\mathbf{A}$ and $\mathbf{B}$. Note that in all cases, these values are either constants or slowly varying functions of $\varepsilon_0/kT$ so that the strong dependencies on system parameters are equal in all solutions.

In Fig. 9, each data set is normalized to its value at $kT = 0.3\varepsilon_0$, so that only deviations in the temperature dependencies are shown. It is clear from the figure, that the result
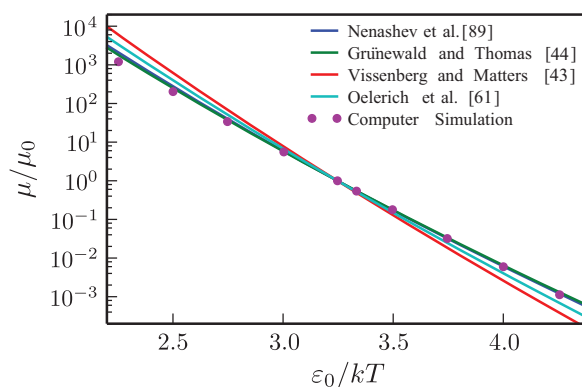


**Figure 9** Normalized mobility values obtained from computer simulation and Eq. (26) for the different analytical solutions, at $N^{1/3}\alpha = 0.3$ and $n/N = 0.001$ (reproduced with permission from [89]; Copyright 2013 by the American Physical Society).

**Table 1** Values of **A** and **B** in Eq. (26) for the different compared expressions for the mobility $\mu$. $\widetilde{C}$ is an unknown numerical coefficient, $\nu \approx 0.875$ and $\widetilde{N}_c \approx 0.219$ are known from percolation theory [89, 151] and $B_c = 2.7$ is a percolation threshold taken from Ref. [84].

| Article | **A** | **B** |
|---|---|---|
| Nenashev et al. [89] | $0.36 \left( \frac{kT}{\varepsilon_0} \right)^\nu$ | $\frac{1}{\widetilde{N}_c}$ |
| Oelerich et al. [61] | $\frac{B_c}{2\pi}$ | $\frac{4\pi}{3B_c} \frac{27}{\exp(3)}$ |
| Vissenberg and Matters [43] | $\widetilde{C}$ | $\frac{\pi}{B_c}$ |
| Grünewald and Thomas [44] | $\frac{1}{3}$ | $\frac{4\pi}{3B_c} \frac{68}{27}$ |

of Grünewald and Thomas [44] and the exact analytical solution by Nenashev et al. [89] show very similar dependences on temperature, and that they match the simulation results. This is particularly remarkable not only because the result of Grünewald and Thomas [44] was the first one among those obtained via percolation theory for the VRH in the exponential DOS, but mainly because it was based on a simplified approach with a percolation threshold $B_c = 2.7$ for overlapping spheres with equal sizes, an approach proven so far to be valid only for NNH and not for VRH. The result of Nenashev et al. [89] based on the geometrical problem with distributed sizes of spheres agrees with the simulation results even better. The comparison in Fig. 9 shows that the approach for the description of the VRH based on the transport-energy concept (usually less accurate than percolation theory) suggested by Oelerich et al. [61] and applied in Section 6 to systems with Gaussian DOS is close to the exact solution. The approach by Vissenberg and Matters [43] has already been shown as not in perfect agreement with simulation results [32, 152].

Although the result of Grünewald and Thomas [44] is very close to that of Nenashev et al. [89], the two approaches were fundamentally different to each other. Nenashev et al. [89] did not use the number of bonds per site as a percolation criterion. As shown by the difference between the results of the two percolation approaches, [44] and [43], the number of bonds is a non-trivial quantity to use when sites are not equivalent. One can view the good agreement of the results by Grünewald and Thomas with the precise numerical and analytical solutions by Nenashev et al. [89] as supporting for the classical averaging procedure suggested by Pollak [73] and used by Grünewald and Thomas [44] for the exponential DOS and by Baranovskii et al. [63] for the Gaussian DOS. This information is important for applying percolation theory to systems with other shapes of the DOS.

Recently Cottaar et al. [88] claimed that the theory by Vissenberg and Matters [43] predicts that the activation energy for charge transport diverges at $T \to 0$ and suggested to reanalyze mobilities in OFETs using their theory for exponential DOS from Ref. [88]. Two remarks seem worthwhile in this respect. First: Cottaar et al. [88] considered percolation on regular lattices and obtained the activation energy for charge transport dependent on the choice of the lattice

structure. It is, however, not clear, what particular regular lattice structure should be taken for spatially disordered ODSs. Second: the activation energy in the theory by Vissenberg and Matters [43] along with that in the more accurate theory by Grünewald and Thomas [44] does not diverge at $T \to 0$. Indeed, the carrier mobility described by Eq. (26) can be represented in the form

$$\mu = A \frac{v_0 e}{n \varepsilon_0 \alpha} \exp\left( -\frac{\varepsilon^* - \varepsilon_F}{kT} \right), \tag{27}$$

with activation energy $\varepsilon^* - \varepsilon_F = \varepsilon_0 \ln[8/Bn(kT/\alpha\varepsilon_0)^3]$. With decreasing temperature $T$, the activation energy apparently decreases. At $kT \simeq \varepsilon_0 n^{1/3}\alpha$, the activation energy becomes smaller than $\varepsilon_0$. At lower temperatures, the Mott law given by Eq. (19) is valid for the temperature dependence of the carrier mobility.

If the DOS is different from the exponential one (e.g. Gaussian with energy scale $\sigma$) the universal solution for $\mu(n)$ is also possible, though only for lattice models [84, 89]. A scaling approach to charge transport on a regular lattice with Gaussian distribution of site energies was recently addressed by Cottaar et al. [69]. The main result is the expression for the charge carrier mobility as a function of the fraction of occupied sites $c$ and temperature $T$,

$$\mu(T, c) = B \frac{e\omega_0}{N^{2/3} kTc} \left( \frac{kT}{\sigma} \right)^\lambda \exp\left( \frac{\varepsilon_F(T, c) - \varepsilon^*}{kT} \right). \tag{28}$$

Here, $B$ and $\lambda$ are parameters assumed to be independent of $T$ and $c$. These two parameters were determined by fitting Eq. (28) to the mobility data obtained in numerical simulations [69]. As a result, it has been concluded that $\lambda$ depends on the choice of the lattice structure (SC or fcc) and on the form of the hopping transition rates (Miller–Abrahams or Marcus equations) [69].

Almost literally following the derivation from the monograph by Shklovskii and Efros [84] one can show analytically [89] that in a lattice model with lattice constant $l_0$, carrier mobility is described by the equation

$$\mu(T, n) \simeq \frac{e\omega_0}{kTl_0 n} \left( \frac{kT}{\sigma} \right)^\nu \exp\left( \frac{\varepsilon_F(T, n) - \varepsilon^*}{kT} \right) \tag{29}$$

with $\omega_0 = v_0 \exp(-2l_0/\alpha)$. The quantity $\nu$ in Eq. (29) is the universal critical index of the correlation length of the percolation cluster. In 3D, $\nu = 0.875 \pm 0.008$ [151]. One should keep in mind that the theory leading to Eq. (29) is based only on the long-range geometrical structure of the percolation cluster independent of the model details at shorter scales than the correlation length of such cluster [84, 89]. Comparison between Eqs. (28) and (29) suggests that $\lambda$ of Cottaar et al. is equal to the critical index of the correlation length $\nu$, which does not depend on the choice of the lattice (SC or fcc) and on the type of hopping rates (Miller–Abrahams or Marcus equations). This example shows once again that analytical

Phys. Status Solidi B 251, No. 3 (2014)

**Review**

**Article**

501

theories are advantageous as compared to fitting of numerical data.

Equation (26) is valid for not very low temperatures: $kT/\varepsilon_0 > (n\alpha^3/8N_c)^{1/3}$ [89]. These temperatures are far above those, at which the well known Mott law for the VRH given by Eq. (19) is expected. Mott law is valid at temperatures satisfying the strong inequality $kT(T_0/T)^{1/4} \ll \varepsilon_0$, where $kT_0 = 1/[g(\varepsilon_F)\alpha^3]$. Using the estimate $g(\varepsilon_F) \approx n/\varepsilon_0$, one obtains the condition $kT/\varepsilon_0 \ll (n\alpha^3)^{1/3}$ for the validity of the Mott's law. Clearly, the latter condition is fulfilled at much lower temperatures than those determined by the condition $kT/\varepsilon_0 > (n\alpha^3/8N_c)^{1/3}$ necessary for the validity of Eq. (26).

Percolation theory for VRH in systems with Gaussian DOS was developed in Refs. [63, 64] (some typos in [63] were corrected in Chapter 6 of Ref. [32]). Under the conditions $n > n_c$ and $T < T_c$, where $n_c$ and $T_c$ are determined by Eqs. (17) and (18), respectively, the result is equivalent to Eq. (20). However, percolation theory is mathematically elaborative, yielding results via a set of complicated integrals [44, 63, 64]. Therefore, in the following Section 4.3 we present a more transparent analytical approach to describe VRH. In fact, percolation theory applied to the exponential and Gaussian forms of the DOS shows that sites with energies in the vicinity of a particular energy level $\varepsilon^*$ dominate charge transport at realistic experimental conditions [44, 63, 64]. This conclusion can be supported by a transparent derivation [76, 77, 132], that leads to the concept of the so-called TE, which will be used below to describe the VRH charge transport in ODSs.

**4.3 The concept of the transport energy (TE)** A powerful theoretical method, complementary to the percolation theory, for description of hopping transport in systems with steeply energy-dependent DOS is the concept of the TE. Initially this approach was developed for systems with the exponential DOS [75, 76] and was later extended for systems with other energy spectra, for instance, with a Gaussian DOS [77]. The essence of the TE approach is the ability to describe hopping transport via sites distributed in space and energy in full analogy with the MT model by replacing the mobility edge in the MT model with some particular energy level [75–77], as shown in Figs. 1–3. Dependences of the mobility $\mu$ on $T$, $N$, $n$ will be derived in this report with the help of the TE approach.

The high importance of the TE concept for the description of charge transport in ODSs can be illustrated by the following example. Already in 1982 Rudenko and Arkhipov [153] calculated the dependence $\mu(T)$ in the framework of the MT model for a Gaussian DOS and derived it in the form of Eq. (8) with $C = 1/\sqrt{2}$. Although the very same dependence had been known due to computer simulations in the GDM since 1981 [126], the possibility to derive this result for hopping transport in the GDM analytically had not been recognized by the community working with ODSs before Eq. (8) has been theoretically derived using the TE approach [78]. Instead, many researchers in the field of ODSs used the averaging of hopping rates in order to describe charge

transport in ODSs, although the latter approach can hardly be treated as appropriate for the description of hopping transport [71–73, 84], as shown in Section 4.4.

Let us derive the position of the TE in the Gaussian DOS using optimization (not averaging!) of hopping rates [76, 77, 132]. Consider a carrier in a state with energy $\varepsilon_i$. According to Eqs. (2) and (3), the typical rate of a downward hop of such a carrier to a localized state deeper in energy is [132]

$$\nu_{\downarrow} = \nu_0 \exp\left[-\frac{2r(\varepsilon_i)}{\alpha}\right], \tag{30}$$

where

$$r(\varepsilon) = \left[\frac{4\pi}{3} \int_{-\infty}^{\varepsilon} g(\varepsilon')[1 - f(\varepsilon', \varepsilon_F)]d\varepsilon'\right]^{-1/3}. \tag{31}$$

The typical rate of an upward hop of such a carrier to a localized state with energy $\varepsilon_x > \varepsilon_i$ is

$$\nu_{\uparrow}(\varepsilon_i, \varepsilon_x) = \nu_0 \exp\left[-\frac{2r(\varepsilon_x)}{\alpha} - \frac{\delta}{kT}\right], \tag{32}$$

where $\delta = \varepsilon_x - \varepsilon_i > 0$. This expression is not exact. The considered distance, $r(\varepsilon_x)$ is based on all empty states with energies deeper than $\varepsilon_x$. For the Gaussian DOS, this is equivalent to considering a slice of energy with the width of the order $\sigma$. This works for a DOS that varies slowly compared to $kT$, 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 released easily 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 out the energy $\varepsilon_x$, which provides the fastest typical hopping rate for charge carrier placed initially at energy $\varepsilon_i$. The corresponding energy $\varepsilon_x$ is determined by the condition

$$\frac{\partial \nu_{\uparrow}(\varepsilon_i, \varepsilon_x)}{\partial \varepsilon_x} = 0. \tag{33}$$

It is easy to show [76, 77] that the target energy $\varepsilon_x$ determined by Eq. (33) does not depend on the initial energy $\varepsilon_i$ and hence is universal for given parameters $N\alpha^3$ and $\sigma/kT$ and can be considered as the TE $\varepsilon_t$. It means that from states below $\varepsilon_t$ carrier transitions essential for charge transport occur to the vicinity of $\varepsilon_t$, while transitions from states with energies higher than $\varepsilon_t$ occur downwards in energy. This is the essence of the concept of the TE. After relaxation towards $\varepsilon_t$ the behaviour of charge carriers resembles the MT mode [131] with the TE $\varepsilon_t$ playing the role of the mobility edge [75–77]. Energy relaxation of a carrier in a Gaussian DOS is shown schematically in Fig. 10 [77, 78]. The TE is then determined by [132]

$$\varepsilon_t = \sigma x(N\alpha^3, \sigma/kT, \varepsilon_F/kT), \tag{34}$$
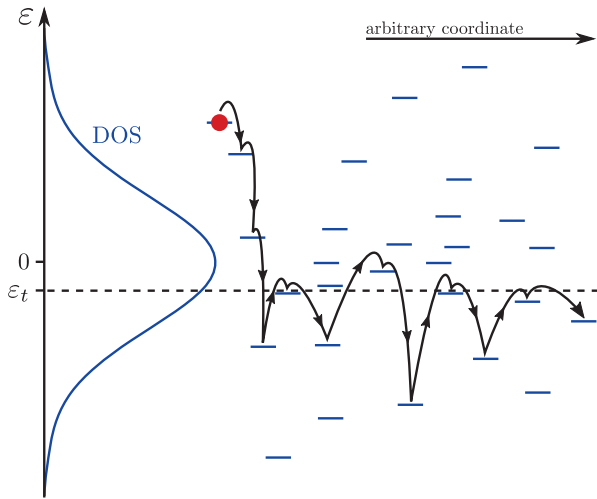
**Figure 10** Schematic picture of carrier energy relaxation via the transport energy in a Gaussian DOS (reproduced with permission from [78]; Copyright 2000 by the American Physical Society).

where $x(N\alpha^3, \sigma/kT, \varepsilon_F/kT)$ is the solution of the equation

$$\left[1+\exp\left(\frac{\varepsilon_F-\sigma x}{kT}\right)\right]\left[\int_{-\infty}^{x/\sqrt{2}}\frac{e^{-t^2}}{1+\exp(\varepsilon_F-\sqrt{2}\sigma t/kT)}\,dt\right]^{4/3}$$
$$= (9\sqrt{2\pi}B_c^{-1}N\alpha^3)^{-1/3}\frac{kT}{\sigma}\exp\left(-\frac{x^2}{2}\right). \qquad (35)$$

The factor $B_c = 2.735$ [148] in this expression accounts for the percolation nature of the hopping transport, i.e. for the necessity to provide a continuous path via sites with corresponding distances as described in Section 4.2.

Numerical solution for the TE via Eq. (35) for realistic values of the parameters $\sigma/kT = 4$ and $N\alpha^3 = 0.01$ is shown in Fig. 5. This result is remarkable in at least two respects. First, it shows that for the realistic parameters, the TE is situated in a close vicinity of the maximum of the Gaussian DOS, as was already assumed in the literature [1, 154] though without rigorous justification. Second, the result of Eq. (35) shows that the TE is essentially independent of the concentration of charge carriers $n$, up to rather high concentrations $n \approx 0.05N$ [132].

Researchers often come to the conclusion on the position of the energy responsible for charge transport in a Gaussian DOS via the following arguments. Assuming that mobility is limited by the activation of carriers from the equilibrium energy $\varepsilon_\infty$ to the vicinity of some energy $\varepsilon_B$ and using for the activation energy the value $C^2\sigma^2/kT$ with $C = 2/3$, as deduced from Eq. (8), they come to the conclusion that the energy responsible for charge carrier motion in a Gaussian DOS, i.e. the TE, is equal to $\varepsilon_B \simeq -(\sigma^2/kT) + 4/9(\sigma^2/kT) = -5/9(\sigma^2/kT)$ [1, 155–157]. The position of this energy $\varepsilon_B$ is shown in Fig. 5 by the arrow. Our calculations of the TE given above show, however, that the energy level $\varepsilon_B$ has nothing to do with the real position of the TE.

A question might arise on why the activation energy $C^2\sigma^2/kT \approx (1/2)\sigma^2/kT$ for the carrier mobility in Eq. (8) is so different from the value $\sigma^2/kT$, which could be derived if activation from the equilibration energy $\varepsilon_\infty = -\sigma^2/kT$ to the TE $\varepsilon_t \approx 0$ is considered. The answer to this question is the following. In the thermal equilibrium, not all carriers have energies equal to $\varepsilon_\infty = -\sigma^2/kT$, but carrier energies are distributed around this level as shown in Fig. 4. Carriers with energies in the upper part of the distribution contribute more to transport than carriers from the lower part of the distribution, since activation to the transport level $\varepsilon_t \approx 0$ is easier for carriers with higher energies. Because this contribution to transport properties is more pronounced for carriers with energies above $\varepsilon_\infty = -\sigma^2/kT$, the effective activation energy $(1/2)\sigma^2/kT$ is essentially smaller than $\varepsilon_t - \varepsilon_\infty \approx \sigma^2/kT$. This result will be derived in Section 5.

An important question that should be asked with respect to the above derivation of the TE $\varepsilon_t$ is how sharp the maximum provided by Eq. (33) is at realistic model parameters. For exponential and steeper than exponential DOS functions, it has been shown that the energy width of the transport path around the TE is rather narrow at realistic parameters [77]. If the energy distance from $\varepsilon_\infty$ and/or $\varepsilon_F$ to $\varepsilon_t$ is larger than the energy scale of the DOS $\sigma$ the description based on the TE concept is reasonable, since the energy width of the transport path around $\varepsilon_t$ is smaller than the activation energy for charge transport.

After the concept of the TE had been proven valid for systems with Gaussian DOS [77] various derivations of the TE were suggested [19, 63–66, 158, 159], which give for $\varepsilon_t$ slightly different values. While the derivation of the TE in Refs. [63, 64, 132] was based on the percolation criterion with $B_c = 2.7$, the value $B_c = 1.0$ was used in Refs. [158–160]. In Refs. [65, 66] a slightly different derivation of the TE has been suggested as compared to Refs. [76, 77, 132]. When analyzing different derivations of the TE one should pay attention not only to the value of $\varepsilon_t$, but also to the way how TE is used for calculations of transport coefficients.

It would be interesting to find a method to study the position of the TE via Monte Carlo simulations. Cleve et al. [82] suggested to determine the position of the TE by tracing the energies of most frequently targeted sites in hopping transitions. This algorithm has been used in several numerical studies [54, 155, 161]. Hartenstein and Bässler [155] recognized, however, that due to oscillations of carriers between spatially and energetically close sites the most frequently targeted energy is not the energy essential for charge transport. The effect of oscillations for the most frequently targeted sites has been addressed in analytical studies [159] and in computer simulations [54]. Very recently a comprehensive study of this effect has been provided by Mendels and Tessler [20]. Therefore, the algorithm suggested by Cleve et al. is not suitable to find the position of the TE. One can find more details in Ref. [20].

Another important issue is the validity of the concept of the TE not only for uncorrelated systems like the GDM considered above, but also for systems with space – energy

Phys. Status Solidi B 251, No. 3 (2014)

Review

Article

503

correlations, like, for instance, the CDM. Using the algorithm by Cleve et al. [82], Novikov and Malliaras [161] came to the conclusion that the TE does not exist for systems with correlated disorder. In contrast, Cottaar et al. [88] found the position of TE (called $E_{\text{crit}}$ in Ref. [88]) for systems with correlated disorder. The question about the validity of the TE concept for systems with correlated disorder apparently needs more attention.

Without providing further details, we would like to emphasize that for steeply energy-dependent DOS, such as the Gaussian or exponential DOS, the concept of the TE helps a lot to get a clear insight into the underlying physical processes responsible for charge transport.

### 4.4 Deficiency of the rate averaging

Although the percolation theory and the concept of the TE have been widely used in the field of inorganic disordered semiconductors since the 1970s and 1980s, respectively, theories in ODSs are often based on the averaging of hopping rates highlighted in Paper I. Furthermore, averaging of rates is also often used for calculations of injection currents in the hopping regime [162]. It therefore seems instructive to briefly describe the deficiency of the rate averaging emphasized already in the classical literature on hopping transport [71–73, 84].

### 4.4.1 Energetically degenerate random sites

Consider the simplest example, discussed above in Section 4.2, of a carrier hopping through a system of isoenergetic sites randomly distributed in space with some concentration $N$. The correct solution for the dependence of carrier conductivity $\sigma_{\text{dc}}$ and mobility $\mu = \sigma_{\text{dc}}/(ne)$ on the concentration of sites $N$ is provided by the percolation theory, as given by Eq. (25). Sometimes, it is claimed in the field of ODSs that the carrier mobility $\mu(N)$ is determined by the ensemble-averaged hopping rate. The average transition rate is obtained by weighting the rate $\nu(r)$ with the probability density to find a neighbour at some particular distance $r$ and by integrating over all possible distances:

$$\langle \nu \rangle = \int_0^\infty \nu_0 \exp\left(-\frac{2r}{\alpha}\right) 4\pi r^2 N \mathrm{d}r = \pi \nu_0 N \alpha^3. \tag{36}$$

Assuming that this average hopping rate describes the mobility and conductivity, one comes to the conclusion that $\mu$ and $\sigma_{\text{dc}}$ are proportional to $N$ [163–166]. However, experiments evidence an exponential dependence of $\mu$ on $N$ [2, 98–101].

The difference in $N$-dependences between Eqs. (36) and (25) is apparent. The belief of some researchers in the validity of the procedure based on the averaging of hopping rates is so strong that the agreement between Eq. (25) and the experimental data is sometimes considered accidental [167]. It seems, therefore, instructive to emphasize the following. The magnitude of the average rate in Eq. (36) is dominated by the rare configurations of very compact pairs of sites with separations of the order of the localization length $\alpha$. Such pairs allow very fast carrier transitions with the rate $\nu_0$, thus dominating the average value $\langle \nu \rangle$ given by Eq. (36). However,

carriers cannot move over considerable distances by using only such compact pairs. Therefore, the magnitude of the average transition rate is irrelevant for carrier mobility in the hopping regime [71–73, 84].

### 4.4.2 Disorder-enhanced diffusion

Some disordered systems possess much higher diffusion coefficients of electronic excitations than their crystalline counterparts, as known for aromatic molecular crystals, such as naphtalene or pirene [28, 168, 169]. A possible explanation of this effect [170] highlighted in Paper I [1] is relevant to the topic of the current report. Therefore, we consider the corresponding model in more detail following Refs. [170, 171].

A cubic lattice with energetically degenerate sites is set up. The rate of a transition from a filled site $i$ to a neighbouring empty site $j$ is determined by the overlap factor $\Gamma_{ij}$,

$$\nu(\Gamma_{ij}) = \nu_0 \exp(-2\Gamma_{ij}). \tag{37}$$

Fluctuations in the intersite couplings are introduced by splitting the overlap parameter $\Gamma_{ij}$ into two terms characteristic for sites $i$ and $j$: $\Gamma_{ij} = \Gamma_i + \Gamma_j$, where $\Gamma_i$ and $\Gamma_j$ are assumed to vary randomly and uncorrelated following a Gaussian distribution

$$p(\Gamma) = (2\pi\delta^2)^{-1/2} \exp\left[-\frac{(\Gamma - \Gamma')^2}{2\delta^2}\right]. \tag{38}$$

Concomitantly the distribution of the overlap parameters $\Gamma_{ij}$ has the form

$$P(\Gamma) = \left(2\pi\Sigma^2\right)^{-1/2} \exp\left[-\frac{(\Gamma - \Gamma_0)^2}{2\Sigma^2}\right] \tag{39}$$

with $\Gamma_0 = 2\Gamma'$ and $\Sigma = 2^{1/2}\delta$. The parameters $\delta$ and $\Sigma$ characterize the extent of the so-called non-diagonal disorder [1]. This disorder was suggested to be responsible for the enhancement of the diffusion coefficient $D(\Sigma)$ as compared to ordered systems with $D(0) \equiv D(\Sigma = 0)$ [1, 170].

It was assumed that to first-order approximation one can describe the diffusion enhancement by replacing the distribution of overlap factors by the ensemble-averaged diffusion coefficient using the distribution of the overlap parameters $\Gamma_{ij}$ described by Eq. (39) [1, 170]. Such averaging leads to the result [171]

$$\langle D(\Sigma) \rangle = D(0) \exp(2\Sigma^2). \tag{40}$$

(In Refs. [1, 96, 170] the relation $\langle D(\Sigma) \rangle = D(0) \exp(\Sigma^2/2)$ was derived based on the probably misprinted equation $\langle D \rangle \propto \langle \exp[-2P(\Gamma)] \rangle$.)

Percolation theory applied to the same problem prescribes that $D(\Sigma)/D(0)$ is proportional to the quantity $\nu(\Gamma_c)/\nu(\Gamma_0)$, where $\Gamma_c$ is determined by a condition similar

to Eq. (22) for uncorrelated bonds [171]

$$\int_0^{\Gamma_c} P(\Gamma)\mathrm{d}\Gamma = x_c(b). \qquad (41)$$

More details about the norm in Eq. (39) and not-negative values of $\Gamma$ can be found in Ref. [171]. Using $x_c(b) \simeq 0.25$ for a sc lattice, one obtains for $\Sigma \leq 3$

$$D_{\mathrm{perc}}(\Sigma) = D(0) \exp(1.34\Sigma). \qquad (42)$$

Let us compare the results given by Eq. (40) based on the rate averaging with those given by Eq. (42) based on the percolation theory for some value of $\Sigma$. For instance, at $\Sigma = 3$, Eq. (40) predicts the disorder-enhanced increase in the diffusion coefficient by more than a factor of $10^7$, while percolation theory predicts such an increase by approximately a factor of 60. This huge discrepancy is due to the fact that rate averaging overestimates the contribution of rare configurations with high transition rates. Percolation theory does not possess such a deficiency describing appropriately transport processes in disordered systems with broad distribution of local transition rates.

Notably, in the above formulation of the GDM [1], properties of the neighbouring bonds were correlated [171]. For instance, the mathematical treatment based on Eq. (39) for the distribution $P(\Gamma)$ of uncorrelated overlap parameters $\Gamma_{ij} = \Gamma_i + \Gamma_j$ is not equivalent to the treatment using the distributions $p(\Gamma)$ for quantities $\Gamma_i$ and $\Gamma_j$, because in the latter formulation, parameters $\Gamma_{ij}$ for bonds belonging to the same site $i$ (or $j$) are correlated to each other [171]. For instance, if some value $\Gamma_i$ is occasionally much larger than the average quantity $\Gamma'$, the values of the overlap parameters $\Gamma_{ij}$ for all six neighbours of site $i$ on a cubic lattice are probably higher than the average value $\Gamma_0$. Similar correlations between neighbouring bonds arise also if one takes into account the distribution of site energies [73]. Therefore, application of a bond percolation to the lattice models should be taken with caution. A site percolation problem is more suitable for the GDM, as already mentioned in Section 4.2.

## 5 Nontrivial case: mobility $\mu$ independent of carrier concentration $n$

As explained in Section 3, the carrier mobility $\mu$ always depends on the carrier concentration $n$ if the DOS depends on energy exponentially or weaker. Furthermore, $\mu$ always depends on $n$, even if the DOS is steeper than the exponential one, though for carrier concentrations $n > n_c$, where $n_c$ is given by Eq. (17). Therefore, the regime with $\mu$ dependent on $n$ looks trivial. It will be considered in Section 6. Here we would like to start with the theory for the concentration-independent $\mu$ that is possible only for a DOS steeper than the exponential one and for carrier concentrations $n < n_c$ as shown in Figs. 6 and 7. Low carrier concentrations are characteristic for time-of-flight measurements and they are often met in OLEDs. One can find experimental data for this case, for instance, in Ref. [26].

### 5.1 Dependences of $\mu$ on temperature, $T$ and on the site concentration, $N$

Assume first that the transient time $t_{\mathrm{tr}}$, necessary for a carrier to travel through a sample, is larger than the time $\tau_{\mathrm{rel}}$, necessary for carriers to relax towards equilibration energy $\varepsilon_\infty$, and charge transport therefore takes place under the equilibrium conditions. As described in Section 4.3 and illustrated in Fig. 10, the carrier jumps limiting the transient time are those that bring a carrier upwards in energy to the vicinity of the TE $\varepsilon_t$. These jumps are succeeded by the downward jumps to the spatially nearest sites with deeper energies. The energy corresponding to such a spatially close site is determined solely by the DOS. Therefore, in order to calculate the drift mobility $\mu$, it is correct to average the times of upward hopping transitions over energy states below $\varepsilon_t$, since only these states are essential for charge transport in the thermal equilibrium [22, 78]. Hops downwards in energy from the level $\varepsilon_t$ occur exponentially faster than upward hops towards $\varepsilon_t$. Therefore, one can neglect the former in the calculation of the average time $\langle t \rangle$. The carrier drift mobility can be then evaluated as [78]

$$\mu \simeq \frac{e}{kT} \frac{r^2(\varepsilon_t)}{\langle t \rangle}, \qquad (43)$$

where $r(\varepsilon_t)$ is determined by Eqs. (31), (34), (35), (1), and it is assumed that the relation between the carrier mobility $\mu$ and the diffusion coefficient $D$ is given by the conventional Einstein relation

$$\mu = \frac{e}{kT} D \qquad (44)$$

valid for non-degenerate conditions in the thermal equilibrium. The average hopping time has the form [22, 78]

$$\langle t \rangle = \int_{-\infty}^{\varepsilon_t} \mathrm{d}\varepsilon g(\varepsilon) \nu_0^{-1} \exp\left[\frac{2r(\varepsilon_t)}{\alpha} + \frac{\varepsilon_t - \varepsilon}{kT}\right]$$
$$\times \left[\int_{-\infty}^{\varepsilon_t} \mathrm{d}\varepsilon g(\varepsilon)\right]^{-1}. \qquad (45)$$

This equation averages the times of upward hops from sites with energies $\varepsilon$ toward sites with energies in the vicinity of $\varepsilon_t$ over all sites below $\varepsilon_t$. The probability for a carrier to have the starting energy $\varepsilon$ is determined by the probability in the previous jump to fall down from $\varepsilon_t$ onto this energy level $\varepsilon$. Since carriers jump downwards to the spatially closest sites, the energies of starting sites in the upward hops are determined solely by the DOS function.

Equations (43) and (45) determine $\mu$ up to a numerical coefficient, i.e. up to a preexponential factor, as typical for treatments based on the concept of the TE $\varepsilon_t$. However, they allow one to obtain the exponential terms in the expression for the carrier drift mobility in a system with the Gaussian

Phys. Status Solidi B 251, No. 3 (2014) 505

Review

Article
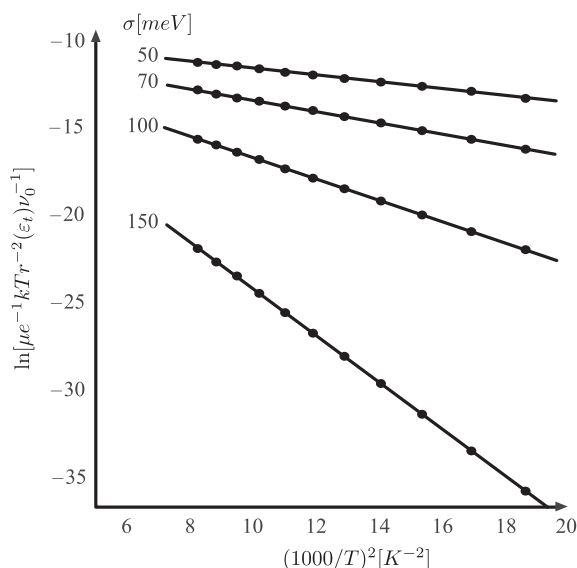


**Figure 11** Temperature dependence of zero-field mobility in organic semiconductors at low $n < n_c$ obtained via Eq. (46) for different disorder energy scales $\sigma$ at $N\alpha^3 = 0.01$ (reproduced with permission from [172]; Copyright 2006 by Springer).

DOS using Eqs. (1), (34), (35) [22, 78]

$$
\ln\left[\mu\left(\frac{er^2(\varepsilon_t)\nu_0}{kT}\right)^{-1}\right]
$$
$$
= -\frac{\varepsilon_t}{kT} - \frac{1}{2}\left(\frac{\sigma}{kT}\right)^2 - \left[\frac{4\sqrt{\pi}}{3B_c}N\alpha^3\int_{-\infty}^{\varepsilon_t/\sigma\sqrt{\pi}}e^{-t^2}dt\right]^{-1/3}.
$$
(46)

It is Eq. (46) that determines the dependences of the carrier drift mobility on the parameters $N\alpha^3$ and $\sigma/kT$.

Let us first analyze the temperature dependence of $\mu$. In Fig. 11, the obtained dependences of the drift mobility on temperature at $N\alpha^3 = 0.01$ are shown for several values of $\sigma$. Eq. (46) confirms the validity of Eq. (8), though with the coefficient $C$ slightly dependent on the value of the parameter $N\alpha^3$. In computer simulations, the value $N\alpha^3 = 0.008$ was chosen and $C \simeq 0.69$ was obtained [126]. Equation (46) predicts a very close value $C \simeq 0.68$. However, at $N\alpha^3 = 0.02$ we obtain from Eq. (46) a different value $C \simeq 0.62$, which shows that this coefficient in Eq. (8) depends on the value of the parameter $N\alpha^3$ as expected for the VRH transport. Very similar data for $C$ were obtained in several other papers [63–66]. The choice of the numerical coefficient $C$ in Eq. (8) is important for the estimation of the energy disorder parameter $\sigma$ from the comparison with experimental data for $\mu(T)$. This parameter is not universal, being dependent on $N\alpha^3$.

Keeping the value $kT/\sigma$ as a parameter, the dependence of $\mu$ on the product $N\alpha^3$ can be represented in the form [22]

$$
\mu(N) \propto \exp\left[-\Gamma\left(N\alpha^3\right)^{-p}\right].
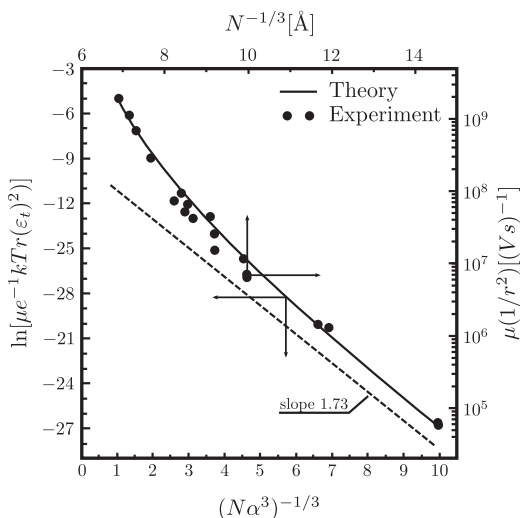$$
(47)
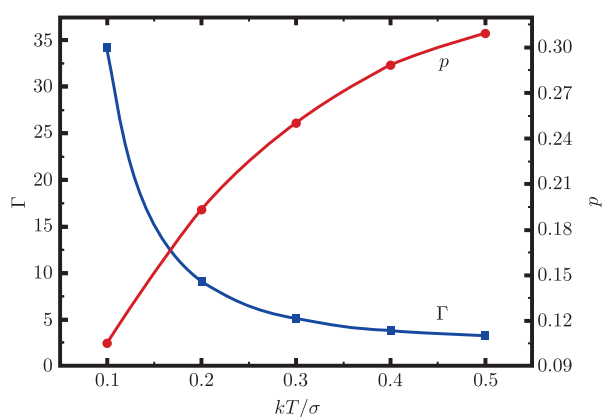


**Figure 12** Temperature dependences of parameters $\Gamma$ and $p$ in Eq. (47) (reproduced with permission from [22]; Copyright 2004 by the American Physical Society).

The width $\sigma$ of the DOS in various ODSs, particularly in doped polymers varies from 0.065 to 0.150 eV depending on the kind of dopant, dopant concentration and host polymers, while the temperature in the experimental studies usually ranges between 200 and 350 K [26]. Hence, the values of the parameter $kT/\sigma$ in the experimental studies fall between 0.1 and 0.5. The values of the parameters $p$ and $\Gamma$ that provide the best fit for the solution of Eq. (46) in the form of Eq. (47) are plotted in Fig. 12 for this range of $kT/\sigma$. The data was calculated for $0.001 < N\alpha^3 < 1.0$. It is clear from Fig. 12 that for low enough temperatures the values of the parameter $p$ are less than $1/3$. This is expected for the VRH transport mechanism based on the interplay between the spatial and energy factors in the exponent of the transition probability given by Eq. (2). The energy-dependent terms in Eq. (2) diminish the effect of the spatially dependent terms and lead to a weaker dependence of the carrier mobility on $N\alpha^3$ as compared to the NNH regime with $p = 1/3$ as given by Eq. (25), in which only the spatial terms determine the mobility.

In Fig. 13, the values of $\ln(\mu)$ obtained by solving Eq. (46) are plotted as a function of $N^{-1/3}$ along with experimental data for the drift mobility in TNF/PVK and TNF/PE from Ref. [173]. In such plots, it is not possible to fit the data by a straight line in the whole range of concentrations. This obvious curvature in the experimental data has often been ignored. Using Eq. (5) with $r = N^{-1/3}$ one can describe the experimentally measured dependence $\mu(N)$ only in a limited range of $N$ [2, 98–101]. If one instead uses Eq. (46), one comes to the estimates $1.0\,\text{Å} < \alpha < 3.0\,\text{Å}$ for the localization length of electron states in various molecularly doped polymers [22], which deviate from those based on the simplified Eq. (5) with $r = N^{-1/3}$.

The slope given by the percolation theory for the purely geometrical case of the NNH in the form of Eq. (25) is shown in Fig. 13 by the dashed line. This result is valid in the case $(N\alpha^3)^{-1/3} \gg \sigma/kT$ when energy disorder affects transport properties much less than the spatial disorder does. In this case, the dependence given by Eq. (47) with $\Gamma \simeq 1.73$ and $p \simeq 1/3$ is expected [22]. This limiting case can serve as a

**Figure 13** Concentration dependence of the drift mobility evaluated from Eq. (46) for $kT/\sigma = 0.3$ (solid line) and the one observed in the experiment (circles) for TNF/PE and TNF/PVK [173] (reproduced with permission from [22]; Copyright 2004 by the American Physical Society).

check for the validity of any transport theory. For instance, transport theories leading to Eq. (47) with $1.056 < \Gamma < 1.076$ and $p = 1/3$ as in Ref. [174] should be treated with caution since the deviation from the correct result ($\Gamma \simeq 1.73$) achieves several orders of magnitude at small values of ($N\alpha^3$).

## 5.2 Transition from dispersive to non-dispersive transport: Calculation of the relaxation time $\tau_{\rm rel}$

One of the most remarkable results for energy relaxation of charge carriers in the Gaussian DOS is the existence of the equilibration energy $\varepsilon_\infty$ given by Eq. (14), as described in Section 3.2. This situation is in contrast to the case of the exponential DOS, where in the empty system at low temperatures a charge carrier always relaxes downwards in energy, and mobility depends on time, as discussed in Section 3.1. In the Gaussian DOS, a charge carrier relaxes from high-energy states downwards in energy only until it arrives at the equilibration energy $\varepsilon_\infty$, even in an empty system without any interaction between relaxing carriers [1, 12, 28, 133].

The energy relaxation of carriers in a Gaussian DOS studied by numerical simulation was described in detail in Paper I. In computer simulations [1], noninteracting carriers were initially distributed uniformly over states in the Gaussian DOS, and their energy relaxation was traced. The temporal evolution of the energy distribution of noninteracting carriers relaxing within a Gaussian DOS is shown in Fig. 4. Initially the energy distribution of carriers coincides with that of the DOS. In course of time, the distribution moves downwards until its maximum $\varepsilon_{\rm d}(t)$ arrives at the energy $\varepsilon_\infty$. The time required to reach this equilibrium distribution (called the relaxation time) $\tau_{\rm rel}$ is of key importance for the analysis of experimental results [96, 126, 133]. At times smaller than $\tau_{\rm rel}$, charge transport is dispersive, and transport coeffi-

cients, such as the carrier drift mobility, essentially depend on time. At times larger than $\tau_{\rm rel}$, the energy distribution of charge carriers stabilizes around the equilibration energy $\varepsilon_\infty$ even in a dilute system with non-interacting carriers. In the latter regime, transport coefficients are time-independent. In other words, at $t \approx \tau_{\rm rel}$ dispersive transport is succeeded by the nondispersive (also called Gaussian) transport behaviour. This is one of the most important results for charge carrier transport in disordered organic media [1]. While at short times dispersive current transients were observed in such materials, at long times transport characteristics are nondispersive, time-independent and hence they can be well characterized and described, in contrast to analogous quantities in the inorganic disordered materials with exponential DOS. In the latter materials, transport coefficients in dilute systems are always dispersive (time dependent), as shown in Section 3.1. Very interesting data on the dispersive and nondispersive features of the carrier mobility were obtained on P3HT systems [175–178]. While in regioregular structures with less amount of disorder transport coefficients do not depend on time except at very short time scales (small $\tau_{\rm rel}$), in regiorandom structures with high amount of disorder dispersive features with the time-dependent transport coefficients have been observed (large $\tau_{\rm rel}$) [175–178]. Transition from dispersive to non-dispersive transport regimes has been experimentally observed also in PF-TAA co-polymers [19].

It has been established by computer simulations in systems with a Gaussian DOS that $\tau_{\rm rel}$ strongly depends on temperature:

$$\tau_{\rm rel}(T) \propto \exp\left[\left(B\frac{\sigma}{kT}\right)^2\right], \tag{48}$$

where the numerical coefficient $B$ is close to unity: $B \simeq 1.1$ [1, 96, 126, 133]. Apparently, the relaxation time $\tau_{\rm rel}$, at which a transition from dispersive to nondispersive transport takes place, depends on the ratio $\sigma/kT$ more strongly than the carrier drift mobility $\mu$, as expressed by the difference in the coefficients $C$ and $B$ in Eqs. (8) and (48), respectively. This has an important consequence that a time-of-flight signal produced by a packet of charge carriers drifting across a sample of some given length must become dispersive above a certain degree of disorder, i.e. below a certain temperature at otherwise constant system parameters, because eventually $\tau_{\rm rel}$ will exceed the carrier transient time [96]. Some analytical theories [127, 128] already indicated the difference between the coefficients $B$ and $C$, although they predicted $C > B$ in contrast to the simulation results. Therefore, a consequent analysis of $\tau_{\rm rel}$ is desirable.

The concept of the TE $\varepsilon_t$ described in Section 4.3 provides a perfectly transparent way to calculate $\tau_{\rm rel}$. At times smaller than $\tau_{\rm rel}$, energy relaxation of carriers in a Gaussian DOS occurs in analogy to the MT model with TE playing the role of the mobility edge [77, 78]. In other words, exchange of carriers between localized states below $\varepsilon_t$ takes place via their activation to the vicinity of $\varepsilon_t$. In this relaxation mode, the maximum of the carrier energy distribution coincides with

**Review**

**Article**

Phys. Status Solidi B 251, No. 3 (2014)                                                      507

the so-called demarcation energy $\varepsilon_d(t)$ that gradually dives in course of time, in analogy to the case of the exponential DOS described in Section 3.1. States above $\varepsilon_d(t)$ release the carriers towards $\varepsilon_t$ within the time $t$. These carriers are recaptured by all localized states below $\varepsilon_t$. States with energies below $\varepsilon_d(t)$ hardly can release carriers within the time $t$. Therefore, carriers are continuously energetically redistributing from states with energies above $\varepsilon_d(t)$ into states with energies below $\varepsilon_d(t)$, in full analogy with the standard MT model [75, 131]. Since the Gaussian DOS is a rapidly decaying function of energy, most carriers below $\varepsilon_d(t)$ are distributed in the states with energies close to $\varepsilon_d(t)$. This is the reason for the maximum of the carrier energy distribution diving with time $t$ as clearly seen at $t < \tau_{rel}$ in Fig. 4.

Consider the case $\varepsilon_\infty < \varepsilon_t$, which corresponds to any reasonable choice of materials parameters $N\alpha^3$ and $kT/\sigma$ [77]. After generation of carriers in a non-equilibrium situation, the carrier energy distribution moves downwards in energy with its maximum $\varepsilon_d(t)$ logarithmically dependent on time $t$ [78]. States above $\varepsilon_d(t)$ achieve thermal equilibrium with $\varepsilon_t$ at time $t$, while states below $\varepsilon_d(t)$ have little chance to exchange carriers with states in the vicinity of $\varepsilon_t$ at time $t$, and hence the occupation of these deep energy states does not correspond to the equilibrium occupation. The system of non-interacting carriers comes into thermal equilibrium when the time-dependent energy $\varepsilon_d(t)$ crosses the equilibration level $\varepsilon_\infty$ determined by Eq. (14). The corresponding time is the relaxation time $\tau_{rel}$ [78]. At this time, the dispersive transport regime is replaced by the Gaussian transport [78]. As long as relaxation of carriers occurs via thermal activation to the level $\varepsilon_t$, the relaxation time $\tau_{rel}$ is determined by the activated transitions from the equilibration level $\varepsilon_\infty$ to the TE $\varepsilon_t$ [78]. Hence, $\tau_{rel}$ is given by the expression [78]

$$\tau_{rel}(T) = \nu_0^{-1} \exp\left[\frac{2r(\varepsilon_t)}{\alpha} + \frac{\varepsilon_t - \varepsilon_\infty}{kT}\right], \qquad (49)$$

where $r(\varepsilon)$ is determined by Eq. (31). Since the value $\varepsilon_t$ of the TE depends on the magnitude of the parameter $N\alpha^3$, the coefficient $B$ in Eq. (48) should also depend on $N\alpha^3$ [78]. However, the main term in Eq. (49) responsible for the temperature dependence of $\tau_{rel}$ is $\varepsilon_\infty(T)$ determined by Eq. (14). From Eqs. (14) and (49) one obtains $\tau_{rel}(T) \sim \exp[(B(\sigma/kT))^2]$ with $B \approx 1.0$ in good agreement with computer simulations [1, 96, 133].

The results for $\mu(T)$ and for $\tau_{rel}(T)$ easily and transparently obtained analytically in the form of Eqs. (8) and (48) with coefficients $C \approx 0.7$ and $B \approx 1.0$ are in good agreement with those obtained previously via computer simulations [1, 96]. They illustrate how valuable is the analytical approach based on the TE concept. In the following Section 6, we exploit this approach in order to calculate the carrier mobility at arbitrary concentrations of carriers $n$.

## 6 General case: mobility $\mu$ dependent on carrier concentration $n$
While the first theoretical description of the concentration-dependent mobility $\mu(n)$ in systems with
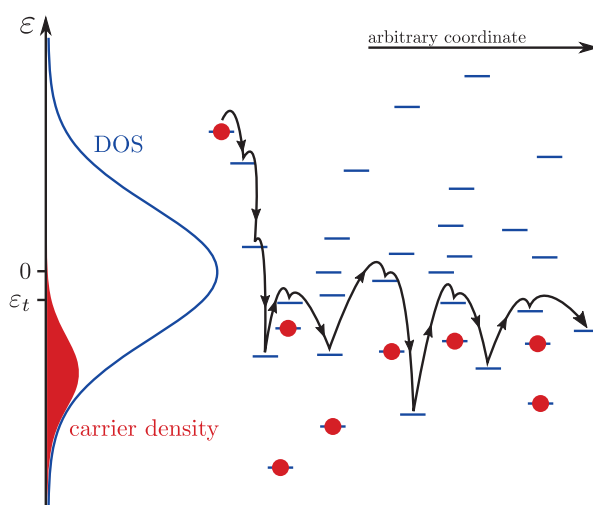


**Figure 14** Schematic picture of carrier motion via activation to the transport energy in a system with non-negligible occupation of localized states.

Gaussian DOS was performed in the framework of the percolation theory [63, 64], it was very soon recognized that the approach based on the concept of the TE is perfectly suitable to describe the $n$-dependent mobility in the GDM [65]. Furthermore, the TE approach was used successfully [65, 66] to account for the experimental data on the $n$-dependent mobility in ODSs [37]. In order to keep the theory for $\mu(n)$ compatible with the description for $\mu$ at low $n$ in Section 5, we use below the concept of the TE extending it for arbitrary $n$ values.

In Section 5.1, it was explained that the time decisive for the drift motion of charge carriers is determined by hopping transitions from states below $\varepsilon_t$ towards states in the vicinity of $\varepsilon_t$ [22, 32, 78]. One should average these times appropriately, i.e. ascribe correct probability densities to the hopping times responsible for the upward hops of carriers towards $\varepsilon_t$. The probability to have some particular starting energy $\varepsilon < \varepsilon_t$ for activated transition towards $\varepsilon_t$ is determined by the probability to fall down from $\varepsilon_t$ onto the energy level $\varepsilon$ in a previous step. In the empty system at low $n$ where states responsible for hopping transport are poorly populated, the latter is determined solely by the DOS distribution, as expressed in Eq. (45). At $n > n_c$ one should take into account explicitly the filling probabilities $f(\varepsilon, \varepsilon_F)$ of the localized states determined by the Fermi function given by Eq. (9). Transitions of carriers between localized states in a Gaussian DOS with finite concentration $n$ are shown schematically in Fig. 14. In order to calculate the carrier mobility, one should replace the DOS function $g(\varepsilon)$ by the product $g(\varepsilon)[1 - f(\varepsilon)]$ in the equations of Section 5 [61].

One additional modification of the equations given in Section 5.1 should be performed for treating systems with arbitrary $n$ values. In Eq. (43) for the carrier mobility at $\varepsilon_F < \varepsilon_\infty$ the relation between mobility $\mu$ and diffusivity $D$ in the form of the conventional Einstein relation (44) was used. This is justified because at low population of states

responsible for transport, the Boltzmann approximation is valid. At high concentrations $n$, at which $\varepsilon_F > \varepsilon_\infty$, one should use the generalized Einstein relation [179, 180]

$$\mu = eD\frac{1}{n}\frac{\partial n}{\partial \varepsilon_F}, \tag{50}$$

which, in the case of hopping transport within the DOS $g(\varepsilon)$, takes the form [181]

$$\mu = \frac{e}{kT}DF_{ER}\left[T, g(\varepsilon), n\right], \tag{51}$$

where the dimensionless functional $F_{ER}$ is determined as [181]

$$F_{ER}\left[T, g(\varepsilon), n\right]$$
$$= \frac{\int_{-\infty}^{\infty}d\varepsilon g(\varepsilon)\exp[(\varepsilon-\varepsilon_F)/kT]/(1+\exp[(\varepsilon-\varepsilon_F)/kT])^2}{\int_{-\infty}^{\infty}d\varepsilon g(\varepsilon)1/1+\exp[(\varepsilon-\varepsilon_F)/kT]}. \tag{52}$$

Replacing the DOS function $g(\varepsilon)$ by the product $g(\varepsilon)[1 - f(\varepsilon)]$ [61] in the equations of Section 5, and using Eqs. (51), (52), one comes to the result

$$\mu \simeq \frac{e}{kT}F_{ER}\frac{r^2(\varepsilon_t)}{\langle t \rangle}, \tag{53}$$

with $r(\varepsilon_t)$ determined by Eq. (31) and $\langle t \rangle$ given by the expression [61]

$$\langle t \rangle = v_0^{-1}\frac{\int_{-\infty}^{\varepsilon_t}\exp[(2B_c^{1/3}r(\varepsilon_t)/\alpha)+(\varepsilon_t-\varepsilon)/(kT)]g(\varepsilon)[1-f(\varepsilon)]d\varepsilon}{\int_{-\infty}^{\varepsilon_t}g(\varepsilon)[1-f(\varepsilon)]d\varepsilon}, \tag{54}$$
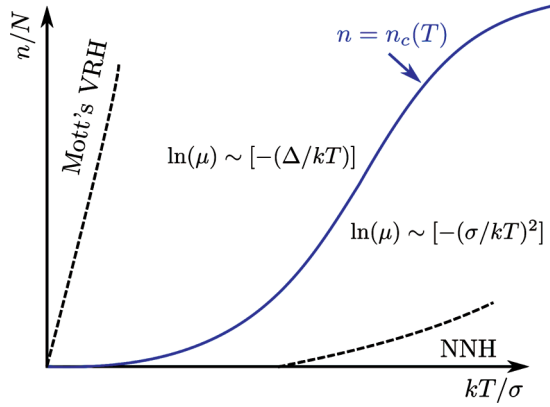
where $\varepsilon_t$ is determined by the equation [61]

$$\frac{2}{3}\left(\frac{4\pi}{3B_c}\right)^{-1/3}\frac{kT}{\alpha}\left[\int_{-\infty}^{\varepsilon_t}[1-f(\varepsilon, \varepsilon_F)]g(\varepsilon)d\varepsilon\right]^{-4/3}$$
$$\times [1 - f(\varepsilon_t, \varepsilon_F)]g(\varepsilon_t) = 1. \tag{55}$$

From these equations one straightforwardly obtains the equation for the carrier mobility [61]

$$\mu \simeq v_0\frac{e}{kT}\frac{3B_cF_{ER}}{4\pi r(\varepsilon_t)n_t}\exp\left(-\frac{2B_c^{1/3}}{\alpha}r(\varepsilon_t) - \frac{\varepsilon_t - \varepsilon_F}{kT}\right) \tag{56}$$

with $n_t$ determined as

$$n_t = \int_{-\infty}^{\varepsilon_t}f(\varepsilon, \varepsilon_F)g(\varepsilon)d\varepsilon. \tag{57}$$



**Figure 15** Regions in the $(n, T)$ plane corresponding to different conduction regimes for hopping in a Gaussian DOS (reproduced with permission from [182]; Copyright 2008 by Wiley).

For the case of the Gaussian DOS at low concentrations $n < n_c$, at which the Fermi level $\varepsilon_F$ is situated below the equilibration energy $\varepsilon_\infty$, one can easily obtain the $n$-independent mobility $\mu$ using the general set of Eqs. (51)–(57). In the low-concentration regime, the Boltzmann approximation for the Fermi distribution can be applied yielding

$$f(\varepsilon) = \left[1 + \exp\frac{(\varepsilon - \varepsilon_F)}{kT}\right]^{-1} \approx e^{\varepsilon_F/kT}e^{-\varepsilon/kT}. \tag{58}$$

In this case, in accord with Eq. (57), $n_t \propto \exp(\varepsilon_F/kT)$. Inserting this result for $n_t$ into Eq. (56) cancels the concentration-dependent Fermi energy in this equation. The functional $F_{ER}$ can be replaced by unity in the Boltzmann case [181]. Since the TE $\varepsilon_t$ is independent of $n$ at low concentrations [132], the expression for the mobility, Eq. (56), loses its $n$-dependence completely in the nondegenerate case, for which the Boltzmann approximation is valid. Note that this approximation is never valid for the purely exponential DOS given by Eq. (4) with $\varepsilon_0 > kT$, while it is valid for any DOS steeper than the exponential one in the case $\varepsilon_F < \varepsilon_\infty$.

The general picture for $\mu(n, T)$ is sketched in Fig. 15 [182]. The curve $n = n_c(T)$ corresponding to the condition given by Eq. (17) separates two regimes [32, 63, 182]: at $n < n_c(T)$ mobility does not depend on $n$ having temperature dependence $\ln \mu(T) \propto -(C\sigma/kT)^2$ with $C$ slightly dependent on $N\alpha^3$ in accord with Eqs. (8) and (46), while at $n > n_c(T)$ mobility demonstrates an Arrhenius $T$-dependence given by Eq. (7) with the activation energy $\Delta \simeq \varepsilon_t - \varepsilon_F$ strongly dependent on the concentration of carriers $n$ due to the dependence $\varepsilon_F(n)$ [63, 32, 182]. At $kT \gg \sigma$ the former regime turns into the nearest-neighbour-hopping (NNH), also called $r$-percolation [84], with mobility dependent on the concentration of sites $N$ in accord with Eq. (25), while at $kT(T_0/T)^{1/4} \ll \sigma^2/|\varepsilon_F|$ with $T_0 \simeq 1/[kg(\varepsilon_F)\alpha^3]$ charge transport appears in the Mott's VRH regime with a mobility described by Eq. (19).

In Section 4.2, the exact solution of the VRH problem in the framework of the percolation theory was presented

Phys. Status Solidi B 251, No. 3 (2014)                                                                    509

Review

Article
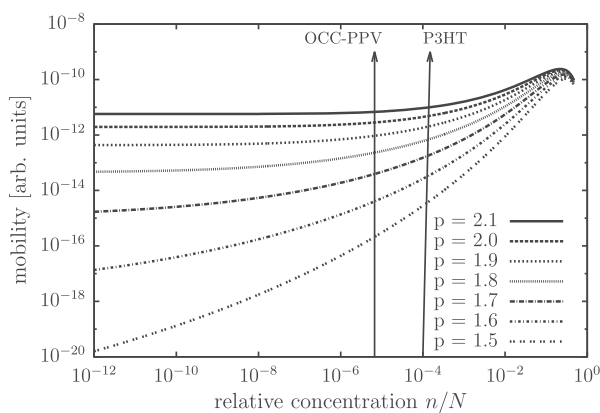


**Figure 16** Calculated mobility as a function of the relative charge carrier concentration $n/N$ for different DOS exponents $p$ in Eq. (59). The experimental results for $n_c/N$ from Refs. [38, 39] are indicated as vertical arrows (reproduced with permission from [61]; Copyright 2012 by the American Physical Society).

for systems with the exponential DOS [89]. The result of Eqs. (51)–(57) agrees with this solution if the exponential DOS is inserted into this set of equations [61], as illustrated in Fig. 9.

It is worth noting that the validity of the Eqs. (51)–(57) for the description of hopping charge transport is not restricted to a Gaussian or exponential DOS. The equations are valid for any single-scale spectrum of the form

$$g(\varepsilon) = \frac{N}{Q} \exp\left[\left(-\frac{|\varepsilon|}{\sigma}\right)^p\right], \quad p \geq 1, \qquad (59)$$

where $N$ is the total concentration of localized states and $\sigma$ is the energy scale of the DOS. In order to keep consistency with Eq. (4), we consider only negative energies counted from some reference level $\varepsilon = 0$ that in the case of the exponential DOS corresponds to the mobility edge. At $p = 1$ Eq. (59) coincides with Eq. (4), while at $p = 2$ it describes the low-energy half of the Gaussian DOS given in Eq. (1). Since charge transport takes place in the energy range below the TE, $\varepsilon_t$, with $\varepsilon_t < 0$ even for Gaussian DOS, restriction to the low-energy part of the DOS is well justified. The normalization condition

$$\int_{-\infty}^{0} g(\varepsilon)\mathrm{d}\varepsilon = N \qquad (60)$$

demands $Q = \sigma \cdot \Gamma(p^{-1} + 1)$ [61].

In Fig. 16, the dependences $\mu(n)$ calculated via Eqs. (51)–(57) are shown for different values of the exponent $p$ in Eq. (59) [61]. The parameters $\sigma/kT$ and $N\alpha^3$ were chosen according to Refs. [38, 39]: $\sigma = 0.112\sqrt{2}\,\mathrm{eV}$, $T = 293$ K, $N = 3 \times 10^{20}\,\mathrm{cm}^{-3}$ and $\alpha = 0.16$ nm. By the arrows in Fig. 16, the concentrations $n_c$ are indicated, below which the experimentally studied mobilities demonstrated the independence of $n$ [38, 39]. This result evidences that the DOS exponents of $p < 1.8$ in Eq. (59) cannot match

the experimental data, since in the experiments mobility becomes independent of $n$ at much higher values $n_c$ [38, 39] than a DOS with $p < 1.8$ would allow. For simplicity the factor $F_{ER}$ was taken equal to unity for calculations of the theoretical data in Fig. 16 [61] since the emphasis was put on the values of $n_c$ at which Eq. (44) is still valid.

A question might arise with respect to the different structures of the exponential terms in Eqs. (56) and (20). While the former equation contains the term $-2B_c^{1/3}r(\varepsilon_t)/\alpha$, in the latter one such a term is absent, although we claim that both approaches should lead to the same value for the carrier mobility $\mu$. The reason for the difference in the structure of these exponential terms is the difference in the definition of the transport energies $\varepsilon_t$ and $\varepsilon^*$ in these two cases. While in the framework of the percolation approach [44, 63, 64, 71–73], leading to Eq. (20), the whole 'exponential difficulty' has been encoded by the percolation exponent containing only energy terms, in the approach based on the TE described in Section 4.3, energy and spatial terms in the exponents were explicitly carried through the derivations. This does not mean that the percolation approach is erroneous, rather that one should pay attention not only to the term 'TE', but also to the way of using this TE for calculations of measurable quantities, such as the carrier mobility $\mu$. It is apparent that the energy level $\varepsilon^*$ in Eq. (20), as derived for the exponential DOS in Ref. [44] and for the Gaussian DOS in Refs. [63, 64], in the framework of the percolation theory is situated higher than the level $\varepsilon_t$ derived in Section 4.3 and used in Eq. (56) eliminating the difference in the exponential terms in these equations.

**7 Dependence of transport coefficients on electric field $F$** So far we discussed transport phenomena in ODSs at low values of electric fields $F$, at which the mobility and the diffusion coefficient of charge carriers do not depend on $F$. In this section, we discuss the situations, at which transport coefficients in ODSs become $F$-dependent.

Three effects are usually discussed with respect to the field dependence of the charge carrier kinetic coefficients in organic semiconductors [1, 26–29]. One of them is the apparent decrease of the drift mobility with rising field at low $F$ and relatively high temperatures [1, 4, 26–29, 183, 184]. The second one is the strong increase of the drift mobility with rising field at higher $F$. The third effect is the strong field dependence of the diffusion coefficient $D$ at rather low fields $F$, at which carrier mobility remains field-independent and charge transport occurs in the Ohmic regime [185]. The subsections below deal with these three effects.

**7.1 Negative differential conductivity at low fields $F$: an artefact** The apparent decrease of carrier mobility with rising field strength $F$ at low $F$ and high temperatures, though sometimes assumed as an inherent property of ODSs [1, 4, 26–29, 183, 184], has been shown experimentally [186, 187] and theoretically [188] to be an artefact. Experimental data showing the puzzling decrease of the mobility with rising field at low $F$ [1] was obtained by the

time-of-flight technique, in which charge carriers are created close to one surface of a sample and the transient time $\tau_{\mathrm{tr}}$ is measured, which is necessary for charge carriers to reach the opposite surface of the sample of a given thickness $L$. The drift mobility is then calculated as

$$\mu = \frac{L}{\tau_{\mathrm{tr}} F}. \tag{61}$$

However, at high temperatures and low electric fields, the current transients in the time-of-flight experiments are determined also by diffusion of charge carriers, not only by their drift [186–188]. Therefore, one strongly overestimates the real magnitude of the carrier mobility at small $F$ using the drift formula (61). It is the presence of the field strength in the denominator of Eq. (61) that leads to the apparent 'decrease' of the mobility at increasing $F$ [186, 188]. If one uses at low fields $F$ and high temperatures the diffusion approach instead of Eq. (61), no decrease of the mobility with increasing field can be recognized [188].

This observation does not exclude the possibility of the negative differential conductivity (NDC) in the hopping regime. Böttger and Bryksin [189] and Shklovskii with coworkers [190, 191] have suggested a detailed theory for the NDC in the hopping regime in various systems, particularly those with Gaussian DOS [191]. Recent theoretical results on the NDC in the hopping regime can be found in Ref. [192]. The effect of the NDC is, however, to be expected at high fields [190, 191]. This regime succeeds the very strong increase of the mobility with rising field and does not precede it at lower fields.

### 7.2 Concept of the effective temperature
Results for the dependence of the carrier mobility $\mu$ on the strength of the electric field $F$ in the Gaussian DOS were given in Paper I [1] in the form

$$\mu(F) = \mu_0 \exp\left\{ -\left( \frac{2}{3} \frac{\sigma}{kT} \right)^2 \right\}$$
$$\times \exp\left\{ \widetilde{C} \left[ \left( \frac{\sigma}{kT} \right)^2 - \widetilde{B} \right] \sqrt{F} \right\}. \tag{62}$$

This equation is one of the most widely used in the context of organic semiconductors [35], although it merely represents a parametrization of numerical results obtained in a restricted range of physical parameters. Among other features, this expression predicts for $\sigma/kT < \sqrt{\widetilde{B}}$ an exponentially strong decrease of the carrier mobility with rising field at any field strength, which can hardly be justified. Usually experimentally measured dependences $\mu(F)$ are compared to Eq. (62) in an attempt to determine material parameters [193–195]. In Eq. (62), $\mu_0$ is a field-independent prefactor and $\widetilde{B} = 2.25$ for $\Sigma < 1.5$ and $\widetilde{B} = \Sigma^2$ for $\Sigma \geq 1.5$, with $\Sigma$ being the numerical parameter of the so-called non-diagonal disorder responsible for the variation of the intersite coupling

on a lattice [1]. For a spatially random distribution of sites, this extra parameter $\Sigma$ would correspond to the additional random distribution of localization parameters $\alpha$.

Description of the dependence $\mu(F)$ in the form of Eq. (62) may be considered as not convenient, since it contains the strength of electric field $F$ with the corresponding dimension under the square root in the exponent. The parameters in the exponent, determining $\mu(F)$, should have a dimensionless form. The only way to express $F$ in a dimensionless form is to build a ratio $eFL/\widehat{E}$, where $L$ has a dimension of length and $\widehat{E}$ has a dimension of energy. With respect to $\widehat{E}$ the only possible candidates in the GDM are $kT$, $\sigma$, or some combination of these parameters. With respect to $L$, the most often considered option is the typical distance between hopping sites $N^{-1/3}$. For instance, Nemeth-Buchin et al. [196] suggested the parameter $eFN^{-1/3}/\sigma$ for the dimensionless electric field. Dunlap et al. [197] mentioned that in a system with uncorrelated energies the only length scale is the mean interdopant spacing, $L \simeq N^{-1/3}$. In Paper I [1], it has already been mentioned that the description of $\mu(F)$ by Eq. (62) is an approximation since the proper scaling quantity in the exponent 'is the effective field $F^{\mathrm{eff}} = eF\triangle x_{ji}/(2kT)$ rather than the applied electric field itself' [1]. Not specifying the quantity $\triangle x_{ji}$, it was mentioned that the coefficient $\widetilde{C}$ in Eq. (62) is proportional to $N^{-1/6}$. Herewith it was assumed that $\widehat{E} \simeq kT$ and $L \simeq N^{-1/3}$, i.e. that the dimensionless parameter responsible for the field dependence of the mobility $\mu(F)$ has the structure $eFN^{-1/3}/kT$.

A rather similar approach to determine $\mu(F)$, as compared to Paper I [1], was used by Pasveer et al. [16], who also numerically determined $\mu(F)$ in a lattice model and fitted the results by the analytical formula

$$\mu(T, n, F) \approx \mu(T, n)\phi(T, F), \tag{63}$$

where $\phi(T, F)$ is a function independent of the carrier density:

$$\phi(T, F) = \exp\left\{ 0.44 \left[ \left( \frac{\sigma}{kT} \right)^{3/2} - 2.2 \right] \right.$$
$$\left. \times \left[ \sqrt{1 + 0.8 \left( \frac{Fea}{\sigma} \right)^2} - 1 \right] \right\}, \tag{64}$$

where $a$ is the lattice constant. The latter parameter is analogous to the intersite distance $N^{-1/3}$ in the GDM with spatially random distribution of sites. Besides predicting that mobility decreases exponentially with rising field at $\sigma/kT < 2.2^{2/3}$, which is in line with Eq. (62), this expression suggests once again that the decisive length scale for the dimensionless field is the intersite distance.

In the following, we show that another length scale, namely the localization length $\alpha$, can be decisive for the field dependence of carrier mobility, as well known for inorganic non-crystalline semiconductors, in which field-dependent

Phys. Status Solidi B 251, No. 3 (2014)

Review
Article

511
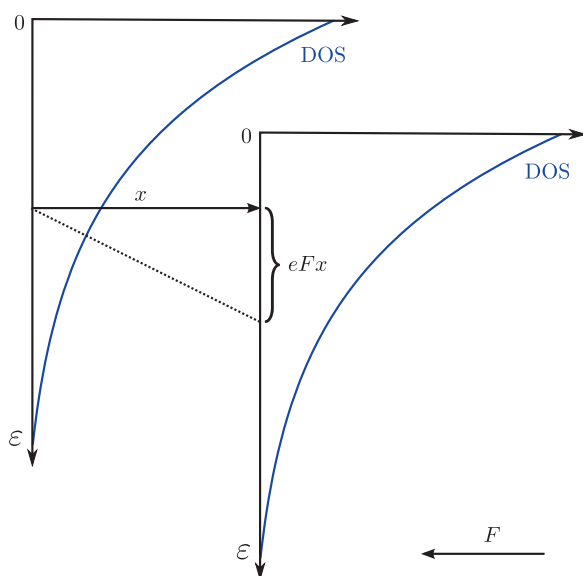


**Figure 17** Tunnelling transition of a charge carrier affected by a strong electric field. Traveling the distance $x$, the carrier acquires the energy $eFx$, where $F$ is the strength of the electric field and $e$ is the elementary charge (reproduced with permission from [82]; Copyright 1995 by the American Physical Society).

mobility in the hopping regime has been in the focus of intensive experimental and theoretical research for decades. This interest was implied by observations of a strong nonlinearity in the field dependences of the dark conductivity [198, 199], of the photoconductivity [200], and of the charge carrier drift mobility [198, 201, 202] at high electric fields.

Shklovskii [79] has recognized that strong electric field plays for hopping conduction a role similar to that of temperature. In order to calculate the carrier mobility at high fields, it was suggested to replace temperature $T$ in the dependence $\mu(T)$ for low fields by the function $\mu(T_{\mathrm{eff}})$ with $T_{\mathrm{eff}}$ in the form [79]

$$T_{\mathrm{eff}} = \frac{eF\alpha}{2k}. \tag{65}$$

A very similar result was later obtained for hopping energy relaxation of carriers through band tails at very low temperatures and high electric fields [203]. Furthermore, it was shown that one can calculate the field dependence of the stationary photoconductivity by replacing the laboratory temperature $T$ in formulas for the low-field theory by an effective temperature $T_{\mathrm{eff}}$ given by Eq. (65) [130].

It is easy to understand why the electric field plays a role similar to that of temperature for hopping conduction. 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 illustrated in Fig. 17. Hence, carriers can move faster at higher fields. From the figure, it is clear that a carrier can increase its energy with respect to the starting level by the amount $\varepsilon = eFx$ in a hopping event over a

distance $x$ in the direction prescribed by the field without any thermal activation. However, the process resembles a thermal activation. The analogy becomes closer if one expresses the transition rate for the hop as

$$\nu(x) = \nu_0 \exp\left(-\frac{2x}{\alpha}\right) \equiv \nu_0 \exp\left[-\frac{\varepsilon}{kT_{\mathrm{eff}}(F)}\right], \tag{66}$$

where $T_{\mathrm{eff}}(F)$ is given by Eq. (65). It has been checked numerically for systems with exponential DOS that this effective activation induced by the electric field produces a Boltzmann tail described by $T_{\mathrm{eff}}(F)$ in the energy distribution of carriers [80, 81].

Experiments are carried out at finite temperatures, and the question arises on whether the concept of the effective temperature is also valid in the presence of both factors, finite $T$ and high $F$. For systems with exponential DOS, the validity of this concept at finite $T$ has been confirmed in numerical studies of the steady-state energy distribution of carriers [80, 81], of the steady-state hopping conductivity, and of the transient energy relaxation of carriers [82]. The validity of the effective temperature approach has also been confirmed for the energy distribution of carriers and their mobility in systems with the Gaussian DOS [83]. The concept has been shown to work for systems with and without space-energy correlations. From the numerical results for uncorrelated systems, one can conclude that the effective temperature can be modeled as

$$T_{\mathrm{eff}}(T, F) = \left[T^{\beta} + \left(\gamma \frac{eF\alpha}{k}\right)^{\beta}\right]^{1/\beta} \tag{67}$$

with $\beta = 1.54 \pm 0.2$ and $\gamma = 0.64 \pm 0.2$ [83].

Remarkably, the validity of the concept of the effective temperature with very close numerical parameters has been reported on the basis of experimental study on the inorganic disordered material a-Si:H [204]. This quantitative agreement between experimental data and Eq. (67) could mean that in the material studied in Ref. [204], the distribution of localized states can be described by the GDM.

No analytical theory is known for the effective temperature described by Eq. (67). It is, however, easy to show that this expression with parameter $\beta = 1$, as sometimes suggested in the literature [205, 206] cannot be valid. Suppose that conductivity $\sigma_{\mathrm{dc}}$ depends solely on $T_{\mathrm{eff}}(T, F)$, so that

$$\frac{d\sigma_{\mathrm{dc}}}{dF} = \frac{d\sigma_{\mathrm{dc}}}{dT_{\mathrm{eff}}} \frac{dT_{\mathrm{eff}}}{dF}. \tag{68}$$

In the Ohmic transport regime at $F \ll kT/e\alpha$, the conductivity $\sigma_{\mathrm{dc}}$ must be field-independent, implying that $dT_{\mathrm{eff}}/dF \to 0$ as $F \to 0$. The function described by Eq. (67) with $\beta = 1$ obviously does not fulfill this condition [82]. However, any function with $\beta > 1$ suits the Ohmic transport regime at $F \ll kT/e\alpha$.

### 7.3 Field dependence of the diffusion coefficient $D$ at low fields: decisive energy level $\varepsilon_{\mathrm{dif}} = -2\sigma^2/kT$

The field-dependent diffusion in ODSs has first been studied in computer simulations by Richert et al. [185] who showed that the longitudinal (along the field direction $Z$) diffusion coefficient $D_z$ is strongly dependent on the strength of the electric field $F$ already at such low fields, at which the carrier mobility $\mu$ remains field independent, i.e. in the Ohmic regime. This result was interpreted in analytical calculations by Bouchaud and Georges [207], who considered hopping of carriers in a one-dimensional (1D) system of equidistant sites with spacing $b$ using transition rates

$$\nu_{i,i\pm1} = \nu_0 \exp\left( \frac{\Delta_{i\pm1,i} \pm eFb}{2kT} \right) \tag{69}$$

with $\Delta_{i,i\pm1} = \Delta_{i\pm1,i}$ distributed according to $g(\Delta_{i,j})$ given by Eq. (1). Apparently, such rates are different to those given by Eq. (2). This model is called the random-barrier model (RBM) in contrast to the GDM model described by Eqs. (1) and (2), which is often called the random-energy model (REM). Bouchaud and Georges [207] suggested for the field-dependent part of the diffusion coefficient in the RBM expression $D(F) - D(0) \propto F \exp(3\sigma^2/[8(kT)^2])$, which they claimed to be precisely the dependence found in Ref. [185]. Remarkably this expression predicts a linear field dependence, nonanalytic at low fields. Later, the authors of Ref. [185] studied the quantity $D(F) - D(0)$ by computer simulations in more detail [208] and found a quadratic dependence of $D(F) - D(0)$ on $F$ at low fields and no turnover to a linear field dependence as predicted by Bouchaud and Georges [207]. The question arises on whether this discrepancy in the field dependences of the diffusion coefficient between the computer simulations [208] and analytical calculations [207] is due to different models, RBM (Ref. [207]) against REM (Ref. [208]) or it is due to different space dimensionalities considered in these two approaches (1D in analytical calculations [207]) against 3D in computer simulations [208]).

This question has been answered by Nenashev et al. [91, 92], who showed that nonanalytic linear field dependence of the diffusion coefficient $D(F) - D(0) \propto F$ at low $F$ is a peculiarity of the 1D systems independent of the model, i.e. it is inherent for both 1D RBM and 1D REM. 1D systems will be discussed in more detail in Section 8. Here we instead turn to 3D and 2D systems.

The effect of the field-dependent diffusion in systems with traps has first been treated analytically in all detail by Rudenko and Arkhipov [153] in the framework of the MT model, which includes capture of free carriers by traps, emission of trapped carriers into conducting states, and free motion (Brownian motion plus drift in the electric field) of carriers in the conduction band, as shown in Fig. 18. Carriers captured by traps cannot move, while carriers in the conducting states are accelerated by the electric field, which causes a field-dependent spatial spread of the carrier distribution along the field direction. Rudenko and Arkhipov [153]
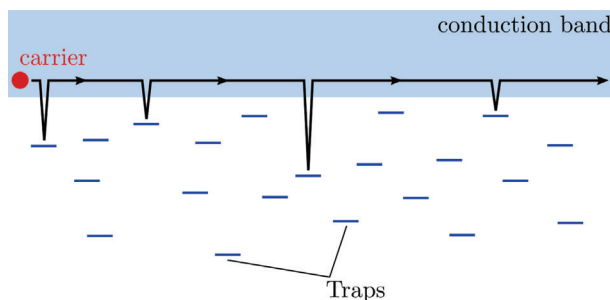


**Figure 18** A sketch of the multiple-trapping process (reproduced with permission from [92]; Copyright 2010 by the American Physical Society).

assumed that transport takes place in quasiequilibrium, i.e. that the distribution function changes slowly in comparison to the rate of exchange between traps and the conducting states, considering only the direction of electric field. Nenashev et al. [92] extended this theoretical treatment by releasing it from the assumption of quasiequilibrium and considering not only the longitudinal diffusion coefficient but also the transversal one.

Since hopping transport in the Gaussian DOS resembles the MT kind of carrier motion (with TE replacing the mobility edge), as shown in Section 4.3, it is not at all surprising that the effect of the field-induced diffusion is valid also for the hopping transport mode. The origin of the field-dependent diffusion can be understood qualitatively with the aid of a spatiotemporal picture of the carrier distribution sketched in Fig. 19. The small dots indicate the distribution of carriers after some definite number of jumps, assuming that all carriers start at the same time $t = 0$ from the same point. In order to get the spatial distribution of carriers at some fixed time $t^*$, one may 'project' these dots from the starting point to the line $t = t^*$. The direction of the projection is determined by the drift velocity. When the drift velocity is equal to zero (no electric field, the left part of Fig. 19), the spatial distribution of carriers at $t = t^*$ does not
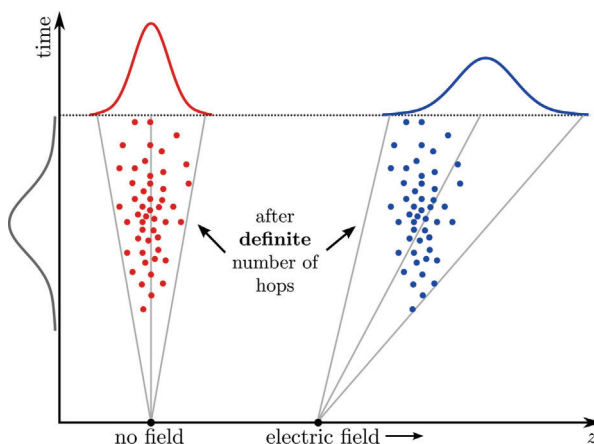


**Figure 19** A sketch of a spatiotemporal distribution of carriers after some definite number of jumps (reproduced with permission from [92]; Copyright 2010 by the American Physical Society).

**Review**
**Article**

Phys. Status Solidi B 251, No. 3 (2014)                                           513

depend on the distribution of times spent by carriers in order to perform the fixed number of jumps. On the contrary, in the case of drift caused by the electric field (the right part of Fig. 19), this distribution in times 'projects' onto the line $t = t^*$, which gives rise to the broadening of the spatial distribution at $t = t^*$. This broadening is the reason for the enhancement of the diffusion coefficient due to the electric field.

The consideration above shows that fluctuations in delays of jumps are responsible for the field-induced diffusion. These fluctuations can be especially pronounced for systems with a broad distribution of site energies, like the GDM, because jumps from energetically deep sites to transport sites demand exponentially long times. This crucial role of sites with deep energies leads to the following result derived analytically by Nikitenko et al. [90] and by Nenashev et al. [92]. The field-dependent diffusion in the GDM is determined by sites with energies in the vicinity of the level

$$\varepsilon_{\mathrm{dif}} = -2\sigma^2/kT. \tag{70}$$

This characteristic energy level arises due to the interplay between two competing factors. Energy states, which are shallower than $\varepsilon_{\mathrm{dif}}$ do not keep carriers long enough to determine the spatial spreading, while states with energies deeper than $\varepsilon_{\mathrm{dif}}$ in the Gaussian DOS are too rare to affect the spreading essentially. In Ref. [92], the interested reader can find the quantitative derivation of Eq. (70) along with the proof that the behavior of the field-dependent diffusion coefficient at low $F$ is analytic: $D(F) - D(0) \propto F^2$, in both 3D and 2D.

Let us estimate the position of the energy level $\varepsilon_{\mathrm{dif}}$ determined by Eq. (70) for real materials. Taking the estimate $\sigma \simeq 0.1\,\mathrm{eV}$, well-accepted for most ODSs, we arrive at the value $\varepsilon_{\mathrm{dif}} \simeq -8\sigma$ for room temperature. This very deep position of $\varepsilon_{\mathrm{dif}}$ can play a crucial role not only for computer simulations, but also for real samples, as discussed in Sections 9 and 10. Nenashev et al. [92] performed computer simulations in order to study the finite-size effects. They showed that in order to get reliable results for the field-dependent diffusion at reasonably low temperatures, one needs to perform simulations on enormously large systems. The system was modeled as a lattice of $L^2$ (2D) or $L^3$ (3D) sites with lattice constant $b$ and site energies $\varepsilon$ distributed randomly according to Eq. (1). Periodic boundary conditions were applied in all directions. Hops inside a square of $7 \times 7$ sites (2D) or a cube of $7 \times 7 \times 7$ sites (3D), centered at each starting site were allowed. The simulation proceeded as follows. A packet of noninteracting carriers was allowed to move through the lattice until a fixed time $t$ has passed. The mobility $\mu$ was calculated from the average distance that carriers had moved along the direction of the field while the longitudinal diffusion coefficient $D_z$ was calculated from the width of the carrier packet,

$$\mu = \frac{\langle z \rangle}{Ft}, \quad D_z = \frac{\langle z^2 \rangle - \langle z \rangle^2}{2t}. \tag{71}$$
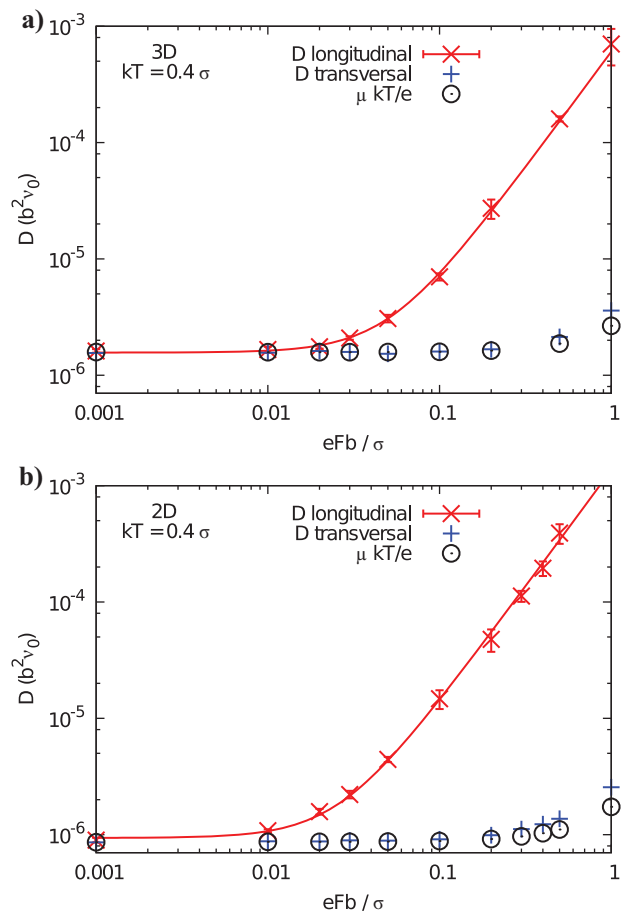
**Figure 20** The diffusion coefficient along and perpendicular to the field, and the mobility $\mu$ scaled by $kT/e$ as a function of the field strength, (a) in 3D and (b) in 2D. At small fields all three quantities are equal, implying that the Einstein relation is valid (reproduced with permission from [92]; Copyright 2010 by the American Physical Society).

The number of sites in the simulated arrays was $700^3$ in 3D and $15\,000^2$ in 2D. Simulation results for the diffusion coefficients parallel and perpendicular to the electric field are shown in Fig. 20, along with the data for the carrier mobility (scaled with $kT/e$). The localization length was chosen equal to $\alpha = 0.2b$. A packet consisting of 1000 charge carriers was simulated for each data point and the simulation results were averaged over five different realizations of disorder. It is seen that all three of the plotted quantities are equal at extremely low fields, which means that Einstein relation given by Eq. (44), is valid. With rising electric field, the longitudinal diffusion coefficient increases drastically at low fields, while the mobility and the transversal diffusion coefficient remain field-independent up to much higher fields. The solid line shows a fit to the longitudinal diffusion coefficient by a square trial function

$$D_z(F, T) = A(T)F^2 + D_0(T). \tag{72}$$
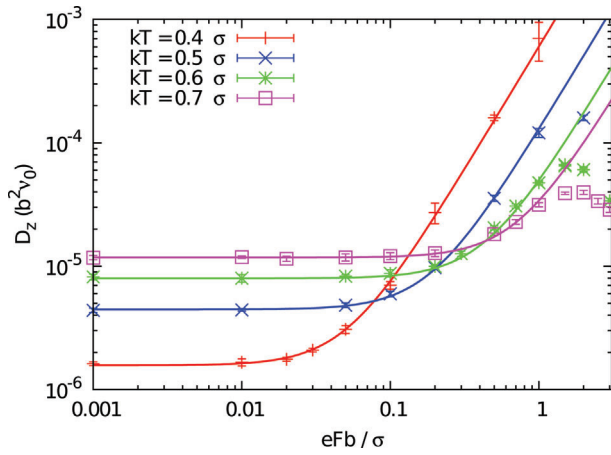
**Figure 21** The longitudinal diffusion coefficient $D_z$ for hopping in 3D, as a function of the applied electric field $F$. The solid lines show the best fit to the square function (72) (reproduced with permission from [92]; Copyright 2010 by the American Physical Society).



**Figure 22** Diffusion coefficient $D_z$ (at the field $eFd = 0.5\sigma$) and mobility $\mu$ (at low field) in a 3D system where sites with energies below $E_c$ are absent. The temperature is $kT = 0.33\sigma$ (reproduced with permission from [92]; Copyright 2010 by the American Physical Society).

The square function well fits the data in agreement with the results of previous simulations [208]. The effect of temperature on the longitudinal field-dependent diffusion coefficient in 3D is illustrated in Fig. 21. The data are fitted with the square trial functions, Eq. (72), shown in the figure by solid lines. The decrease in $D_z(F)$ at very high fields for the two highest temperatures is due to the trivial saturation effect meaning that at very high fields, $eFb \approx \sigma$, energetically deep sites become inefficient. In the following, we focus on the field dependence of $D_z$ at field magnitudes lower than those, at which $D_z$ starts to decrease with increasing field.

The importance of the deep in energy states for the field-dependent diffusion is demonstrated in Fig. 22, where the values of $D_z$ (at $eFb = 0.5\sigma$) and of $\mu$ (at low fields) for temperature $kT = 0.3\sigma$ are given when calculated with a cutoff of the DOS below some energy $E_c$ [92]. In these calculations, the normalization of the DOS was kept while the states with energies below $E_c$ were excluded from the simulation. The mobility is almost unaffected by the cutting as long as $E_c \leq -4\sigma$, while the diffusion coefficient drastically decreases when sites with much smaller energies, around $-6\sigma$, are removed. The result for the mobility $\mu$ is not surprising. It has been predicted in the analytical theory [78] that the hopping mobility in the Gaussian DOS for the diluted set of carriers is determined by sites with energies in the close vicinity of $\varepsilon_\infty = -\sigma^2/kT$ as discussed in Section 3. For $kT = 0.33\sigma$, this energy is $\varepsilon_\infty = -3\sigma$, which explains the data for $\mu$ in Fig. 22. The result for the diffusion coefficient in Fig. 22 shows that rare sites with even lower energies than $\varepsilon_\infty$ cause the strong dependence of the diffusion coefficient on the electric field. As discussed above, the most important sites for the field-dependent diffusion have energies around $\varepsilon_{dif} = -2\sigma^2/kT$, which is much deeper than $\varepsilon_\infty$. This result agrees with the data shown in Fig. 22: for $kT = 0.33\sigma$, $\varepsilon_{dif} = -6\sigma$. The diffusion coefficient changes drastically when a few sites with energies below $-5.5\sigma$ are removed, while mobility starts changing only when $E_c$ is in
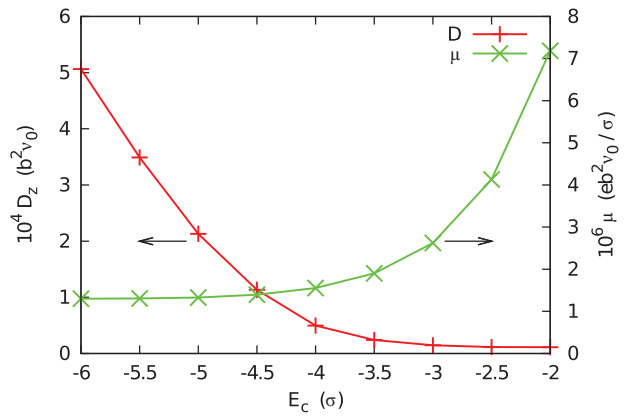
the vicinity of $\varepsilon_\infty$. In the simulations, a lattice of $700^3$ sites was used [92]. There are typically no sites with energies below $-6\sigma$ in such a system. Therefore, the data for $D_z(F)$ at $kT = 0.33\sigma$ cannot be considered as reliable in the whole simulated range of electric fields. For $kT = 0.4\sigma$, energies around $\varepsilon_{dif} = -5\sigma$ were present in the simulations, and thus results for $kT \geq 0.4\sigma$ can be considered as reliable for the lattice of $700^3$ sites. Too small numbers of sites $N$ in simulated arrays is a common problem of Monte Carlo simulations of the effects related to carrier diffusion in a Gaussian DOS [209]. We discuss the consequences of the finite-size effects for simulations as well as for real samples in Sections 9 and 10, respectively.

All results and estimates in this section were based on the Boltzmann statistics, which is justified if the Fermi level $\varepsilon_F$ is far below the energies of the sites that make a major contribution to the field-dependent diffusion, i.e. below $\varepsilon_{dif} = -2\sigma^2/kT$. A simple calculation shows that the carrier concentration $n_{dif}$ corresponding to the position of the Fermi level at $\varepsilon_F = -2\sigma^2/kT$ is

$$n_{dif} \simeq N \exp\left[-\frac{3\sigma^2}{2(kT)^2}\right], \tag{73}$$

where $N$ is the concentration of sites. The theory considered above presumes that $n \ll n_{dif}$. In this limit, the diffusion coefficient does not depend on carrier concentration $n$. At larger concentrations, $n \gg n_{dif}$, sites with energies $\varepsilon_{dif} = -2\sigma^2/kT$ are essentially occupied. In the latter case, they cannot efficiently capture the moving charge carriers and the contribution of such sites to the diffusion process is suppressed. Therefore, in the case $n \gg n_{dif}$, the difference $D_z(F) - D(0)$ decreases with increasing $n$ [92]. All effects related to the field dependences of $\mu$ and $D$ discussed above become particularly specific in the 1D case considered in the following Section 8.

Phys. Status Solidi B 251, No. 3 (2014)

515

**Review**

**Article**

**8 Theoretical treatment of charge transport in one-dimensional organic disordered systems** In many cases, hopping transport in 1D systems can be described theoretically with much higher precision than hopping transport in 3D systems. Provided the rates for hopping transitions between localized states and the DOS function are known, the problem of calculating the transport coefficients can often be solved exactly. Using this advantage of the precise theoretical description, one can clarify various transport phenomena discovered experimentally.

1D systems represent not only a test field for theoretical research. Much attention has also been devoted to experimental study of charge transport in 1D systems, such as the columnar discotic liquid-crystalline glasses, due to their potential technical applications for electrophotography and as transport materials in light-emitting diodes [210, 211]. Dielectric measurements have clarified that charge transport in most of such materials is extremely anisotropic [212] and that it is reasonable to describe transport as a 1D process [213]. The values of conductivity along and perpendicular to the discotic columns differ in such materials by up to three orders of magnitude [212]. Experimentally observed dependences of the conductivity on the frequency and strength of applied electric field, and on temperature show that incoherent hopping of charge carriers is the dominant transport mechanism in such materials [129, 212, 213]. Moreover, it has been found reasonable to describe transport of charge carriers as a hopping process via molecules arranged in spatially ordered 1D chains with Gaussian distribution of site energies given by Eq. (1) [129, 197, 213]. Let us first consider, following [188, 213], the simplest case allowing only hops to the nearest neighbours and assuming that 1D chains of localized states are spatially regular. In such a case, one can omit the $r$-dependence of transition probabilities using the effective preexponential factor $\nu_0$ that includes the term $\exp(-2b/\alpha)$, where $b$ is the distance between the neighbouring sites on the conducting chain. The Miller–Abrahams transition rates obtain the form [188, 213]

$$\nu_{ij} = \nu_0 \exp\left(-\frac{\varepsilon_j - \varepsilon_i + |\varepsilon_i - \varepsilon_j|}{2kT}\right). \tag{74}$$

Other forms of transition probabilities have also been considered in the literature. Seki and Tachiya [214] studied 1D conduction with transition rates described by Marcus law that takes into account also polaron effects [215]. Another, symmetric form was also used in order to analyze analytically the field and temperature dependences of the hopping conductivity in 1D systems [188, 197, 213]

$$\nu_{i\pm1,i} = \nu_0 \exp\left(-\frac{\varepsilon_{i\pm1} - \varepsilon_i}{2kT}\right). \tag{75}$$

Remarkably, there is no consensus among researchers on the very basic properties of 1D transport, as for instance, the temperature dependence of the carrier mobility. While Eq. (8) is usually obtained for $\mu(T)$, there is no agreement

on the magnitude of the coefficient $C$ in this formula. Ochse et al. [129] used the three-dimensional value $C \simeq 2/3$ for columnar systems with 1D transport, while Bleyl et al. [213] obtained $C \simeq 0.9$ in computer simulation for the 1D case with asymmetric transition probabilities. Analytic calculations by Dunlap et al. [197] for symmetric probabilities predicted $C \simeq 1$. The value of $C$ in Eq. (8) is decisive for characterization of the disorder parameter $\sigma$ via comparison with experimental data in 1D systems, and therefore precise knowledge of the coefficient $C$ in Eq. (8) is desirable. Let us address the analytical formulas, which allow one to calculate exactly transport coefficients in 1D systems.

**8.1 Exact equations for the nearest-neighbour hopping in 1D systems** The steady-state drift velocity of charge carriers in 1D periodic systems with the number of sites in the period $N$ and the distance $b$ between the nearest sites on the chain can be written exactly using the general solution found by Derrida [216]

$$v = \frac{Nb(1 - \prod_{k=0}^{N-1}(\nu_{k+1,k})/(\nu_{k,k+1}))}{\sum_{k=0}^{N-1} \nu_{k,k+1}^{-1}(1 + \sum_{i=1}^{N-1} \prod_{j=1}^{i}(\nu_{k+j,k+j-1})/(\nu_{k+j,k+j+1}))}. \tag{76}$$

This formula was used by Dunlap et al. [197] to study the drift mobility in 1D system with symmetric transition rates (75). The drift mobility $\mu$ is related to the steady-state velocity $v$ via $\mu = v/F$.

The drift mobility is usually obtained experimentally by the time-of-flight technique [1], in which charge carriers pass only once through a sample of finite thickness (no periodic behaviour), and drift mobility is calculated by dividing the sample length $Nb$ by the mean transit time $\langle t_{0N} \rangle$ and electric field $F$:

$$\mu = \frac{Nb}{\langle t_{0N} \rangle F}. \tag{77}$$

Murthy and Kehr [217, 218] derived an analytical expression for the mean transit time through a given chain of $N$ sites:

$$\langle t_{0N} \rangle = \sum_{k=0}^{N-1} \nu_{k,k+1}^{-1} + \sum_{k=0}^{N-2} \nu_{k,k+1}^{-1} \sum_{i=k+1}^{N-1} \prod_{j=k+1}^{i} \frac{\nu_{j,j-1}}{\nu_{j,j+1}}. \tag{78}$$

This formula gives the transit time for a charge carrier that starts on site 0 and finishes on site $N$. The time is averaged over many transits through the same chain with given values of transition probabilities $\nu_{ij}$.

One should be cautious with application of Eqs. (77) and (78) at low electric fields. Even without electric field, carriers starting at site 0 will pass through the finite system solely due to the diffusion process. At low fields, diffusion dominates the motion and it would be erroneous to use Eq. (77). It is Eq. (77) that brought many researchers to the hardly acceptable conclusion about the mobility rising with decreasing

field at low $F$ and high $T$ discussed in Section 7.1. More appropriate in such a case is the estimate of the mobility via the diffusion coefficient [188]

$$D = \frac{N^2 b^2}{2\langle t_{0N}\rangle}, \tag{79}$$

with the appropriate form of the Einstein relation for $\mu$.

### 8.2 Mobility and diffusivity in the 1D GDM for the nearest-neighbour hopping (NNH)

Using the exact equations above, one obtains the following result for the RBM with transition rates given by Eq. (69) [91, 216]

$$\mu = \frac{2v_0 b}{F} \exp\left[-\frac{\sigma^2}{8(kT)^2}\right] \sinh\left(\frac{eFb}{2kT}\right), \tag{80}$$

$$D = b^2 v_0 \exp\left[-\frac{\sigma^2}{8(kT)^2} - \frac{|eF|b}{2kT}\right]$$
$$+ b^2 v_0 \exp\left[\frac{\sigma^2}{8(kT)^2}\right] \sinh\left(\frac{|eF|b}{2kT}\right). \tag{81}$$

While Eq. (80) for the carrier mobility in the RBM gives at low $F$ an expected analytic (quadratic) behavior as function of $F$, Eq. (81) predicts a linear, non-analytic behavior for the carrier diffusion coefficient $D$ at low $F$. The latter equation confirms the statement of Bouchaud and Georges [207] on the non-analytic behaviour of $D$ in the 1D RBM at low fields, though the coefficient in this linear field dependence given by Eq. (81) differs from the result of Bouchaud and Georges, who claimed $D(F) - D(0) \propto |F| \exp(3\sigma^2/[8(kT)^2])$ [207].

With respect to the 1D GDM with transition rates given by Eq.(74), the result for the infinite chain at low fields, $|eFb| \ll kT$, and small temperatures, $kT \ll \sigma$, reads [91]

$$\mu \simeq \frac{eb^2 v_0}{2kT} \exp\left[-\left(\frac{\sigma}{kT}\right)^2\right] \left(1 + \frac{|eF|b}{2kT} + \frac{e^2 F^2 b^2}{6(kT)^2}\right), \tag{82}$$

$$D \simeq \frac{b^2 v_0}{2} \exp\left[-\left(\frac{\sigma}{kT}\right)^2\right] + \frac{|eF|b^3 v_0}{2kT}$$
$$+ \frac{e^2 F^2 b^4 v_0}{8(kT)^2} \exp\left[\left(\frac{\sigma}{kT}\right)^2\right]. \tag{83}$$

From the latter expressions, it is obvious that there is a cusp at $F = 0$ for both $\mu(F)$ and $D(F)$. The dependence $D(F)$ demonstrates a linear behaviour for very small fields, $|eFb| \ll kT \exp[-(\sigma/kT)^2]$, when the first two terms in Eq. (83) are dominating, and a parabolic behaviour for intermediate fields, $kT \exp[-(\sigma/kT)^2] \ll |eFb| \ll kT$, when the third term is dominating.

In the limit of the very low fields, $F \to 0$ one obtains from Eqs. (82) and (83) the conventional Einstein relation

and the result for the mobility

$$\mu(T) = \frac{e}{kT} D(T) = \frac{v_0 b^2 e}{2kT} \exp\left[-\left(\frac{\sigma}{kT}\right)^2\right]. \tag{84}$$

This result is in good agreement with the computer simulations by Bleyl et al. [213] and with the analytical calculations by Dunlap et al. [197], although the latter analytical calculations were carried out for correlated systems (CDM) with symmetric transition rates described by Eq. (75). This shows that in 1D systems, Eq. (8) with $C \simeq 1$ is correct and even stable against the choice of the form of the transition rates.

The structure of the exponential term in Eq. (84) can be easily understood without exact calculations. In the infinite chain with Gaussian DOS, the average resistivity per unit length is finite and there exists a characteristic value of the resistance that determines the overall chain resistivity [219]. The corresponding energy $\varepsilon_{t:1D} = +\sigma^2/(kT)$ is in some respects similar to the TE $\varepsilon_t$ introduced in Section 4.3 for 3D systems. In order to estimate $\varepsilon_{t:1D}$, let us first consider the probability for a site to have an energy above $\varepsilon$: $p(\varepsilon) = (1/2)(1 - \mathrm{erf}(\varepsilon/\sqrt{2\sigma^2}) \approx (\sigma/\sqrt{2\pi\varepsilon^2}) \exp(-\varepsilon^2/2\sigma^2)$. Therefore, the product

$$2[1 - p(\varepsilon)]\left(-\frac{dp(\varepsilon)}{d\varepsilon}\right) \approx \frac{2}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{\varepsilon^2}{2\sigma^2}\right)$$

is the probability distribution that one of the energies of a pair of sites is below $\varepsilon$ whereas the upper energy lies at the energy $\varepsilon$, i.e. it gives the distribution of the resistances. In the upper DOS tail, the average resistance (containing $\varepsilon$) is therefore obtained by integrating the function [219]

$$\varphi = \exp\left[\frac{1}{2}\left(\frac{\sigma}{kT}\right)^2\right] \exp\left(\frac{\varepsilon}{kT}\right) \exp\left(-\frac{\varepsilon^2}{2\sigma^2}\right). \tag{85}$$

The integrand is sharply peaked at the energy $\varepsilon_{t:1D} = \sigma^2/kT$. The resistivity exponent at this energy is $(1/2)\sigma^2/(kT)^2 + \varepsilon_{t:1D}/kT - (1/2)\varepsilon_{t:1D}^2/\sigma^2 = \sigma^2/(kT)^2$, i.e. it provides the exponential term for the mobility (proportional to the inverse resistivity) in the form of Eq. (84).

Note that the derivation above is valid only at the low carrier concentration $n$, at which the position of the Fermi level can be described by equation [63, 64]:

$$\varepsilon_F = -\frac{1}{2}\left(\frac{\sigma^2}{kT}\right) - kT \ln\left(\frac{N}{n}\right). \tag{86}$$

If the concentration of carriers $n$ is higher than $n_c$ determined by Eq. (17) and the Fermi level is situated above the equilibration energy $\varepsilon_\infty = -\sigma^2/kT$, the temperature dependence of the carrier mobility becomes weaker and the numerical coefficient $C$ in Eq. (8) becomes smaller than unity. The latter feature has been observed in computer simulations by Pasveer et al. [220], who simulated carrier hopping via nearest neighbouring sites on a regular chain assuming the Fermi

**Review**

**Article**

Phys. Status Solidi B 251, No. 3 (2014)

517

level at energy $\varepsilon = 0$, i.e. in the maximum of the Gaussian DOS. A dependence described by Eq. (8) with $C \approx 0.84$ was obtained in Ref. [220] at not very low temperatures (though Pasveer et al. [220] interpreted their data by Eq. (8) with $C = 1$, as had been known from the literature for the 1D systems at small $n$). Apparently, increasing the concentration $n$ weakens the temperature dependence of the carrier mobility. This effect is similar to that described in Section 6.

### 8.3 Mobility in the 1D GDM beyond the NNH
So far, we considered hopping in 1D chains of sites taking into account carrier transitions only between the nearest sites. The question arises on how transitions to further neighbours on the chain can modify the obtained results. The VRH philosophy tells us that the temperature dependence of the conductivity and that of the carrier drift mobility should be determined at low temperatures by transitions of charge carriers to further neighbours than the nearest ones. The effect of such long-distance tunnelling transitions on the temperature dependences of the kinetic coefficients in 1D systems was studied analytically by Zvyagin et al. [219] and via computer simulations by Kohary et al. [221] and by Pasveer et al. [220]. Zvyagin et al. [219] showed that transitions to $m$ neighbours in each direction lead to the asymptotic temperature dependence of carrier mobility described by Eq. (8) with $C = \sqrt{(m+1)/2m}$. For instance, hopping to the second nearest neighbours ($m = 2$) leads to Eq. (8) with $C = \sqrt{3/4}$. However, this asymptotic behavior with $C = \sqrt{(m+1)/2m}$ can hardly be achieved at realistic conditions. Zvyagin et al. [219] have shown that even at $(\sigma/kT)^2 \simeq 100$, the coefficient $C$ in Eq. (8) is close to $C \simeq 0.8$.

An analogous result on the weak effect of the distant transitions has been obtained by computer simulations [221]. Kohary et al. [221] simulated hopping transport in 1D GDM in the frame of the Monte Carlo algorithm using transition rates in the form of Eq. (2) instead of Eq. (74) that was used for the nearest-neighbour hopping. In these simulations the lattice constant $b = 0.36$ nm was chosen as realistic for discotic liquid-crystalline glasses, and the values of parameter $\alpha$ in Eq. (2) were varied between 0.1 and 0.3 nm. Transitions to six neighbours in each direction were allowed in the simulation procedure. The distant transitions were shown to rather slightly affect the transport coefficients. Even for a high value of the localization length $\alpha = 0.2$ nm, which makes the distant hops favourable, the magnitude of the coefficient $C \simeq 0.9$ in Eq. (8) is not much different from its value for the nearest-neighbour hopping. Thus exact analytic solutions obtained in previous sections, taking into account only the nearest-neighbour hopping, give reasonable values for transport coefficients [221].

Pasveer et al. [220] numerically studied the effect of the distant hopping transitions in the framework of the approach based on the Master equation and came to a different conclusion as compared to that of Zvyagin et al. [219] and of Kohary et al. [221]. Calculations of Pasveer et al. [220] evidence a drastic effect of the long-range transitions, which almost eliminate the temperature dependence of the carrier mobil-

ity. There is one obvious feature that makes the approach of Pasveer et al. [220] different to treatments in Refs. [219, 221]. Pasveer et al. [220] assumed the Fermi level at energy $\varepsilon = 0$, i.e. at the maximum of the Gaussian DOS, while Zvyagin et al. [219] and Kohary et al. [221] studied unoccupied systems with the Fermi level situated below the equilibration energy $\varepsilon_\infty$, i.e. at carrier concentrations smaller than $n_c$ determined by Eq. (17). The dependence $\mu(T)$ weakens with rising concentration $n$ in accord with the results given in Sections 6 and 8.2.

## 9 Deficiency of computer simulations: Finite size effects
Computer simulations belong to the strongest tools in studying charge transport in ODSs often providing valuable information on various effects, as shown, for instance, in Paper I [1]. In order to be capable of providing such information, numerical calculations should fulfill some demands, which we briefly discuss in this Section. Of course, the unavoidable demand to computer calculations is that calculations should be based on a correct algorithm. This demand is usually fulfilled in most Monte Carlo simulations and numerical calculations based on solutions of various master equations. Another very important demand is that the simulated arrays of sites should be representative for the effects under study. This demand is sometimes not fulfilled. The corresponding issues have already been discussed in the previous sections of the current report. Therefore, they are only briefly summarized in this Section for those readers, who are particularly interested in numerical simulations.

### 9.1 Simulating mobility and energy relaxation in 3D systems
In previous sections of the current report, it was shown that different energy regions in the Gaussian DOS are responsible for different physical effects. For instance, states with energies around the level $\varepsilon_\infty = -\sigma^2/kT$ determined by Eq. (14) are responsible for the carrier mobility at low carrier concentrations $n$. It was also explained in Section 5 that relaxation of carriers towards this level is responsible for the transition from the dispersive transport regime with a time-dependent carrier mobility to the non-dispersive regime with constant mobility. In order to study these effects by computer simulations, the size of the simulated arrays of sites should be large enough in order to represent sites with energies in the vicinity of $\varepsilon_\infty$. This is, however, not always the case. For instance, it has been recognized in computer simulations on a system of $70 \times 30 \times 30$ sites that mean energy of non-interacting carriers in the GDM attains after energy relaxation at $\sigma/kT > 6$ an asymptotic value [126]. The simulated activation energy of carrier mobility, if counted from that asymptotic value, would lead to the very high energy position of the transport level in drastic discrepancy to the value predicted for the transport level by the percolation theory. The conclusion that this result clearly argues against viewing transport across an energy distribution of hopping sites in terms of a percolation concept [126] seems however ambiguous since the asymptotic value for the mean energy was probably caused by a too small size of the simulated

array of sites. In another example, the Gaussian DOS has been rejected relying on simulations of carrier relaxation and recombination for the parameter range $6kT < \sigma < 10kT$ since the dispersive kinetics was reproduced only in a too narrow time window as compared to experiments [47]. However, even taking the lowest limit $\sigma = 6kT$ one comes to the probability of $N \exp(-18) \simeq N \times 10^{-8}$ to find sites with energies around $\varepsilon_\infty = -\sigma^2/kT$ among the $N$ sites in the simulated array. In other words, the arrays in the simulations should contain at least $10^8$ sites in order to make the results of simulations reliable. Since the simulated arrays seem to contain a less amount of sites, the results of such simulations can hardly serve for conclusions about the validity or invalidity of the Gaussian DOS or about applicability of the percolation theory to charge transport in the GDM.

### 9.2 Simulating mobility in 1D systems
As shown in Section 8, carrier mobility in long 1D regular chains in the GDM is determined by the energy states in the vicinity of the level $\varepsilon_{t:1D} = \sigma^2/kT$. Therefore, states with energies in the vicinity of $\varepsilon_{t:1D}$ should be present in the simulated arrays of sites in order to obtain reliable results for $\mu(T)$. This is, however, not always the case. For instance, Pasveer et al. [220] numerically simulated the carrier mobility in 1D GDM and obtained for the case of nearest-neighbour hopping a kink in the dependence $\mu(T)$. At $(\sigma/kT)^2 < 18$, the curve $\mu(T)$ is steeper than at $(\sigma/kT)^2 > 18$. This observation looks remarkable. Indeed, if one would use the simulated dependence $\mu(T)$ in order to determine $\sigma$ by comparison between the simulated data and the experimental results [129], one would obtain different $\sigma$ values for the same system if using the data at $(\sigma/kT)^2 < 18$, or at $(\sigma/kT)^2 > 18$. The reason for the different simulated $\mu(T)$ dependences at different $\sigma/kT$ values is the finite size of the simulated system that contained only 10 000 sites [220]. As explained in Section 8 following Ref. [219], the decisive energy level determining $\mu(T)$ in the infinite 1D system is $\varepsilon_{t:1D} = \sigma^2/kT$. For $(\sigma/kT)^2 < 18$ sites with decisive energies in the vicinity of $\varepsilon_{t:1D} = \sigma^2/kT$ were statistically present in the simulated array of 10 000 sites. This decisive energy $\varepsilon_{t:1D} = \sigma^2/kT$ increases with decreasing temperature and at $(\sigma/kT)^2 > 18$ this energy level was statistically not represented in the array of the simulated 10 000 sites [220]. In such a case, sites with energies smaller than $\varepsilon_{t:1D} = \sigma^2/kT$ determined $\mu(T)$ and this dependence became weaker as evidenced in the numerical calculations [220]. This example illustrates once again that numerical results should be taken with caution if not supported by reasonable theoretical concepts.

### 9.3 Simulating diffusion in the GDM
As shown in Section 7.3, the field-induced diffusion of carriers in the GDM is determined by energy states in the vicinity of the level $\varepsilon_{dif} = -2\sigma^2/kT$. The DOS parameter $\sigma$ in ODSs is of the order 0.1 eV [1, 28]. Therefore, at room temperature, this energy $\varepsilon_{dif} = -2\sigma^2/kT$ is situated very deep in the tail of the DOS, around $-8\sigma$. This fact raises very severe demands to the size of the system in computer simulations for carrier

diffusion in ODSs. In order to have the decisive traps with $\varepsilon \approx \varepsilon_{dif} = -2\sigma^2/kT$ in a simulation at room temperature, one needs approximately $\exp[2\sigma^2/(kT)^2] \approx 10^{14}$ sites. Such huge arrays were not yet simulated. Numerical results in Paper I [1] and in Ref. [185] were obtained on systems containing $70^3$ sites, being reliable only for $kT > 0.55\sigma$. Simulations in Ref. [92] were carried out on systems of $700^3$ sites being reliable only for $kT > 0.40\sigma$.

### 10 Mesoscopic effects
So far we discussed the dependences of the carrier mobility and diffusivity on temperature $T$, on the concentration of localized states $N$, on the carrier concentration $n$, and on the magnitude of the applied electric field $F$. There is, however, another important parameter that can drastically affect the measured kinetic coefficients, namely the geometrical size $L$ of the sample under study. For instance, if the system size is so small that energy regions indicated in previous sections as decisive for various physical effects are statistically not present in the system because of its too small size, description of kinetic effects for charge transport should be essentially modified. In such cases, the results for transport coefficients are determined not by the decisive energies $\varepsilon_\infty = -\sigma^2/kT$, $\varepsilon_{t:1D} = +\sigma^2/kT$, $\varepsilon_{dif} = -2\sigma^2/kT$, but by the deepest energies in 3D or by the highest energies in 1D, which are still statistically present in the sample in accord with the sample size. This is the essence of the mesoscopic physical effects. Let us briefly discuss the consequences of such effects.

If the size of the 3D sample is so small, or the ratio $\sigma/kT$ is so large that sites with energies $\varepsilon_\infty = -\sigma^2/kT$ are statistically not present in the system, transport coefficients would always be dependent on the carrier concentration $n$ even at low $n$, since the condition $\varepsilon_F > \varepsilon_\infty$ necessary for the $n$-dependence of the mobility would be fulfilled at any $n$. Furthermore, the relaxation time $\tau_{rel}$ necessary for carrier mobility to achieve a stable time-independent value would always depend on the concentration of carriers $n$. The temperature dependence of carrier mobility at times larger than $\tau_{rel}$ will always be given by the Arrhenius law with activation energy $\Delta \simeq \varepsilon_t - \varepsilon_F$ as described in Section 6 for $\varepsilon_F > \varepsilon_\infty$. This dependence is weaker than the one given by Eq. (8).

If in 1D the size of the sample is so small, or the ratio $\sigma/kT$ is so large that sites with energies $\varepsilon_{t:1D} = +\sigma^2/kT$ are statistically not present in the system, the temperature dependence of the carrier mobility would always be weaker than that for the infinite chains. The latter statement has already been evidenced by analytical calculations [188] and computer simulations [221, 220].

If the size of the sample in 3D is so small, or the ratio $\sigma/kT$ is so large that sites with energies $\varepsilon_{dif} = -2\sigma^2/kT$ are statistically not present in the system, the field-induced diffusion coefficient would have the magnitude lower than expected for infinitely large samples. Moreover, it will always depend on the concentration of carriers $n$.

Remarkably, for conditions at which sites with energies in the vicinity of $\varepsilon_\infty = -\sigma^2/kT$ responsible for carrier mobility $\mu$ are statistically present in the system while sites

**Review**

**Article**

Phys. Status Solidi B 251, No. 3 (2014)                                                                 519

in the vicinity of $\varepsilon_{dif} = -2\sigma^2/kT$ responsible for the diffusion coefficient $D$ are statistically absent, the ratio $\mu/D$ should depend not only on carrier concentration $n$ as given by Eq. (50), but at $\varepsilon_F < \varepsilon_\infty$ also on the size of the system.

Mesoscopic effects responsible for the dependences of the carrier mobility and of the diffusion coefficient on sample thickness $L$ need to receive more attention. Some results obtained by computer simulations can be found in Ref. [222]. Since there is not much study on this topic yet, we conclude the discussion here with the following qualitative remark. For studying carrier mobility in ODSs in time-of-flight experiments, as described in Paper I [1], thick samples are usually favoured in order to obtain clear charge transients for estimating the transient time $\tau_{tr}$ necessary for calculating $\mu$ in the given material via Eq. (61). However, for fabrication of devices like OLEDs, OFETs and OSCs, thin samples are used as compared to those studied in time-of-flight experiments. Due to mesoscopic effects, the carrier mobilities and diffusion coefficients in device samples fabricated from the same material could essentially deviate from the values measured in time-of-flight experiments. Furthermore, the transport coefficients in the mesoscopic regime should fluctuate from sample to sample [92].

**11 GDM or CDM?** One of the most important issues with respect to theoretical description of charge transport in ODSs is the question on whether possible correlations between spatial positions of localized states and their energies should be taken into account (CDM), or such correlations could be neglected (GDM).

Generally speaking, correlations between energies and spatial positions of localized states should be present in ODSs. Already in one of the first studies of ODSs, Silinsh [110] argued that energy disorder in such systems is due to polarization of the matrix. This is the long-range effect that should cause correlations. Furthermore, several studies of the carrier mobility in molecularly doped polymers have evidenced that the energy width $\sigma$ of the DOS depends on the presence of dipolar additives and on the dipole moments of either the transport or the host molecules, or both [1, 7, 223–227].

More arguments in favour of correlations came from studies of the field-dependent mobility $\mu(F)$. Novikov and Vannikov [228] showed that dipole traps could account for the observed dependence $\mu(F)$ and studied the energy landscape in a dipolar glass [229]. Gartstein and Conwell [24] argued that a spatially correlated potential is needed to describe the observed effects in a wide range of electric fields. Correlations were suggested to arise due to the interaction of charge carriers with permanent dipoles or to molecular density fluctuations [24]. Dunlap et al. [197] strengthened this point by rigorous calculations of the dependence $\mu(F)$ in 1D and showed that $\mu(F)$ observed in molecularly doped polymers is accounted for by the interaction of charge carriers with randomly distributed permanent dipoles. Novikov et al. [25] supported this conclusion by numerical simulations in 3D case.

Yu et al. [230] pointed out that conjugated polymers, in contrast to molecularly doped polymers, usually do not have permanent dipole moments. Correlations between energies and spatial positions of localized states are nevertheless possible due to the steric restoring force for thermal fluctuations of the molecular geometry responsible for energy levels [230]. Novikov and Vannikov [231] suggested a model of a quadrupole glass for ODSs without permanent dipoles.

On the other hand, Pasveer et al. [16] claimed that their theoretical analysis of the field-dependent carrier mobility in such polymers as NRS-PPV and $OC_1C_{10}$-PPV does not indicate that there is a need to assume a certain spatial energy correlation, as suggested before [24, 25, 197, 230]. A similar conclusion, at least with respect to the PPV-based materials was suggested by Bouhassoune et al. [232]. There are indications that while the GDM can serve as an appropriate model for polymers, small-molecular ODSs are better described by the CDM [233].

Schein and Tyutnev [234] recently analyzed temperature dependences of the low-field mobility $\mu(T)$ in a series of molecularly doped polymers with different concentrations of dipoles varying in a broad range. No significant dependence of the parameter $\sigma$ responsible for $\mu(T)$ in accord with Eq. (8) on the concentration of dipoles has been evidenced in this study. This is a strong argument against the polarization nature of disorder and hence against the CDM. Novikov and Vannikov [235] argued that at least some contribution to the magnitude of $\sigma$ should be due to polarization energies, which favours the CDM.

Apparently more research is needed in order to answer the question on whether the GDM presented in Paper I [1] is adequately applicable to describe charge transport in ODSs, or whether this model should be replaced by the CDM. A possible result is that some ODSs can be analyzed in the framework of the GDM, while other ODSs are better described by the CDM. For instance, polymers and low-molecular-weight ODSs could have different properties with respect to space-energy correlations [233]. No final conclusion to this issue seems currently possible. A theoretical description based on the concept of TE may be valid also for the CDM [88].

**12 Polaron effects** Although the GDM is widely used to describe charge transport in ODSs, polaron effects not included in the GDM are often discussed as affecting charge transport in such materials. Usually the model of small polarons is employed that takes into account interactions between a localized carrier and molecular vibrations in the close vicinity of the localization centre. Thus a quasiparticle polaron is formed by a charge associated with molecular distortion. When a charge carrier appears on some localized state, the atomic matrix can reorganize gaining some energy $E_p$. The more flexible is the matrix, the more pronounced are polaron effects, i.e. the higher the $E_p$ value. A soft molecular structure of ODSs is favourable for polaron formation. Therefore, sometimes charge carriers in ODSs are called polarons even in the case when the reorganization energy $E_p$

of the matrix is not considered [47]. Many theoretical studies have been devoted to polaron effects in ODSs. Starting from interpreting experiments in terms of the adiabatic to nonadiabatic small polaron crossover [184, 236, 237] the research has later been focused on the interplay between the roles of the matrix reorganization characterized by the energy $E_p$ and of the energy disorder characterized by the scale of the DOS $\sigma$ [238–241].

As clearly described by Fishchuk et al. [242], models based solely on polaron effects without disorder cannot account for the broad variety of experimental observations in ODSs. For instance, disorder is necessary to account for the transition from nondispersive to dispersive transport regimes upon lowering temperature [242]. Furthermore, if the observed activation energy of the carrier mobility in ODSs in the range between 0.3 and 0.6 eV would be determined solely by the reorganization energy $E_p$, the values for $E_p$ in the range between 0.6 and 1.2 eV would be necessary. These large values of $E_p$ are in drastic contradiction to the $E_p \simeq 0.15$ eV as an upper limit of the polaron binding energy for the crystalline counterparts of the ODSs [242, 243]. Moreover, the large $E_p$ would lead to the assumption of an unreasonably large value for the transfer integrals necessary to account for the typical values of the carrier mobility $\mu$ in disorder-free materials [184, 236, 242]. The transfer integrals should be assumed in the order of 1 eV, which is unrealistic for organic materials with a weak van der Waals intermolecular coupling [28].

However, it has been demonstrated in several reports [244–246] that for some organic systems the polaron formation should be taken into account and that the observed temperature dependence of the carrier mobility is due to the superposition of disorder and polaron effects . Bässler et al. [244] suggested that in such a case 'the effective zero-electric-field ($F \to 0$) Arrhenius activation energy of the mobility $E_{aeff}$ can be approximated by a sum of the disorder and polaron contributions $E_{aeff}^m(F \to 0) = E_a^{pol} + E_{aeff}^{dis} = E_p/2 + (8/9)\sigma^2/kT$, where $E_a^{pol}$ and $E_{aeff}^{dis}$ are the polaronic and disorder contributions, respectively, and $\sigma$ is the width of the DOS distribution' [242]. The following expression for the temperature dependence of the zero-field mobility has been suggested [244]

$$\mu(T) \propto \exp\left(-\frac{E_p}{2kT}\right) \exp\left[-A\left(\frac{\sigma}{kT}\right)^2\right], \qquad (87)$$

with $A = 4/9$.

The problem that polaron-based models for ODSs required unreasonably high values for transfer integrals [238, 239] has been resolved in a model with correlated disorder (CDM) [247]. By calculations similar to those of Novikov et al. [25] it has been shown that the temperature dependence of the zero-field mobility in the CDM can be represented by Eq. (87). The value $A = 0.31$ has been deduced for $\sigma = 80$ meV and $E_p = 150$ meV [247]. Using the effective media approximation (EMA) Fishchuk et al. [242] obtained the value $A = 1/8$ for the case of a strong polaron contribution as

compared to disorder effects, i.e. for $E_p > \sigma$. A comparison between the results of Parris et al. [247] and Fishchuk et al. [242] suggests that coefficient $A$ in Eq. (87) should depend on the ratio $E_p/\sigma$.

Using EMA, Fishchuk et al. [248] performed further study of the polaron effects in ODSs with the key result that the concentration dependence of the carrier mobility $\mu(n)$ is sensitive to the strength $E_p$ of the polaron effects in the way that the larger is $E_p$, the less pronounced is the dependence $\mu(n)$. On the other hand, Cottaar et al. [69] compared mobilities calculated via percolation theory on a simple cubic lattice with nearest-neighbour hopping for two cases: (i) using Miller–Abrahams hopping rates (no polaron effects); (ii) using Marcus hopping rates (with polaron effect), and found no difference for the dependence $\mu(n)$ in these two cases. This result has been considered [69] at variance to that of Fishchuk et al. [248]. Very recently, Fishchuk et al. [249] developed, also for a simple cubic lattice with nearest-neighbour hopping, a generalized EMA approach, which is superior to their previous treatment [248] since it is applicable with arbitrary polaron activation energy as compared to the energy disorder parameter $\sigma$. This comprehensive theoretical study confirms the previous analytical result by Fishchuk et al. [248] that the value of $E_p$ affects the dependence $\mu(n)$, at least for the way of calculations (called in Ref. [249] 'averaging A') that seems to be preferred by the authors of Ref. [249]. This result has been opposed [249] to that of Cottaar et al. [69]. One should, however, keep in mind that results obtained by the percolation theory [69] are valid at low temperatures, while those obtained by the EMA approach [249] are valid at higher temperatures. Apparently, more research to this topic is desirable.

A question might arise on how to find out experimentally whether polaron effects are essential or not in a material under study. The following recipe can be suggested. One should measure the temperature dependence of carrier mobility at low concentrations $n$. If this dependence is of Arrhenius type as described by Eq. (7), polaron effects are essential. If carrier mobility at low concentrations $n$ demonstrate a temperature dependence described by Eq. (8), polaron effects for the charge transport are less pronounced than disorder effects. Note that at high carrier concentrations $n > n_c$, Arrhenius behaviour is expected even without polaron effects [63, 32], as described in Section 3.2.

**13 Summary** (i) Probably the most remarkable conclusion, to which one comes when looking at the development of the theory for charge transport in ODSs in the past decades, is the capability of the simple model suggested by Heinz Bässler in Paper I [1] and in the even older review paper [12] to account for the pronounced dependences of transport coefficients on temperature, on the applied electric field, on the concentration of localized states, and on the concentration of charge carriers, in good agreement with experimental results. It looks almost miraculous that such a simple model, in which complicated morphology of a disordered organic system is replaced by

Phys. Status Solidi B 251, No. 3 (2014)

521

Review

Article

a set of randomly distributed point-like localization centres with Gaussian distribution of energies (GDM), can describe almost all experimentally observed features related to charge transport in ODSs. The similarity of these features observed experimentally in chemically and morphologically different systems called, in fact, for a universal model. This call has apparently been adequately replied in Paper I [1] by suggesting the VRH in the GDM as the dominant transport mechanism. Future theoretical studies would hopefully clarify, why the experimentally observed features are so similar in chemically and morphologically very different systems, as polymers and low-molecular-weight organic materials with a broad variety of chemical compositions. With respect to the recent trend of further simplifying the GDM by using lattice models with hopping between the nearest sites, one could remark that such attempts do not look promising since ODSs do not have a periodic structure, while theoretical results depend essentially on this structure and on the particular choice of the lattice.

(ii) While the theoretical description of the VRH in the frame of the GDM has mostly been focused on phenomenological fitting of numerical results, the current report emphasizes that well-approved theoretical tools, like the percolation theory, the concept of the TE, the concept of the effective temperature, etc., which have been used successfully for decades to describe the VRH in inorganic disordered semiconductors, are well applicable for description of charge transport in ODSs. Using these tools, one can easily derive the dependences of carrier mobility on temperature (with different forms of the temperature dependence for different concentrations of carriers), on the concentration of carriers, on the applied electric field, on the concentration of localized states, on the size of samples under study and on other parameters. These tools make phenomenological fitting of numerical data unnecessary.

(iii) Among the not yet clarified issues, one could highlight the question on whether the GDM or the CDM (correlated disorder model) is more realistic for ODSs and the question on the role of polaron effects for charge transport in ODSs. Furthermore, one should surely step out of the simplest set of phenomenological assumptions, which is the basis for the GDM and CDM. The appropriate description of the relation between the chemical structure and charge dynamics is a real challenge for future theories. The molecular electronic structure and the relative positions and orientations of neighbouring molecules should be appropriately taken into account, along with thermal fluctuations contributing to the transfer integrals for charge transport. Some already existing theoretical attempts in this direction were left out of the scope in our review. The goal of the current report is to highlight the well approved and useful theoretical tools applicable to GDM (and also partly to CDM), which have not yet been addressed in Paper I.

## References

[1] H. Bässler, Phys. Status Solidi B **175**, 15 (1993).
[2] W. Gill, J. Appl. Phys. **43**, 5033 (1972).
[3] L. A. Schein, A. Peled, and D. Glatz, J. Appl. Phys. **66**, 686 (1989).
[4] M. Abkowitz, Philos. Mag. B **65**, 817 (1992).
[5] A. Y. Kryukov, A. C. Saidov, and A. V. Vannikov, Thin Solid Films **209**, 84 (1992).
[6] P. M. Borsenberger and J. Shi, Phys. Status Solidi B **191**, 461 (1995).
[7] P. M. Borsenberger, W. T. Gruenbaum, and E. H. Magin, Physica B **228**, 226 (1996).
[8] C. W. Tang and S. A. Van Slyke, Appl. Phys. Lett. **51**, 913 (1987).
[9] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, and A. B. Holmes, Nature **347**, 539 (1990).
[10] A. R. Brown, C. P. Jarrett, D. M. de Leeuw, and M. Matters, Synth. Met. **88**, 37 (1997).
[11] G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and A. J. Heeger, Science **270**, 1789 (1995).
[12] H. Bässler, Phys. Status Solidi B **107**, 9 (1981).
[13] H. C. F. Martens, P. W. M. Blom, and H. F. M. Schoo, Phys. Rev. B **61**, 7489 (2000).
[14] V. I. Arkhipov, P. Heremans, E. V. Emelianova, G. J. Adriaenssens, and H. Bässler, J. Phys.: Condens. Matter **14**, 9899 (2002).
[15] C. Tanase, P. W. M. Blom, D. M. de Leeuw, and E. J. Meijer, Phys. Status Solidi A **201**, 1236 (2004).
[16] W. F. Pasveer, J. Cottaar, C. Tanase, R. Coehoorn, P. A. Bobbert, P. W. M. Blom, D. M. de Leeuw, and M. A. J. Michels, Phys. Rev. Lett. **94**, 206601 (2005).
[17] V. I. Arkhipov, P. Heremans, E. V. Emelianova, and H. Bässler, Phys. Rev. B **71**, 045214 (2005).
[18] N. I. Craciun, J. Wildeman, and P. W. M. Blom, Phys. Rev. Lett. **100**, 056601 (2008).
[19] W. C. Germs, J. J. M. van der Holst, S. L. M. van Mensfoort, P. A. Bobbert, and R. Coehoorn, Phys. Rev. B **84**, 165210 (2011).
[20] D. Mendels and N. Tessler, J. Phys. Chem. C **117**, 24724 (2013).
[21] A. Miller and E. Abrahams, Phys. Rev. **120**, 745 (1960).
[22] O. Rubel, S. D. Baranovskii, P. Thomas, and S. Yamasaki, Phys. Rev. B **69**, 014206 (2004).
[23] J. L. Bredas, D. Beljonne, V. Coropceanu, and J. Cornil, Chem. Rev. **104**, 4971 (2004).
[24] Yu. N. Gartstein and E. M. Conwell, Chem. Phys. Lett. **245**, 351 (1995).
[25] S. V. Novikov, D. H. Dunlap, V. M. Kenkre, P. E. Parris, and A. V. Vannikov, Phys. Rev. Lett. **81**, 4472 (1998).
[26] P. M. Borsenberger, E. H. Magin, M. van der Auweraer, and F. C. de Schryver, Phys. Status Solidi A **140**, 9 (1993).
[27] M. van der Auweraer, F. C. de Schryver, P. M. Borsenberger, and H. Bässler, Adv. Mater. **6**, 199 (1994).
[28] M. Pope and C. E. Swenberg, Electronic Processes in Organic Crystals and Polymers (Oxford University Press, Oxford, 1999).

[29] G. Hadziioannou and P. F. van Hutten (eds.), Semiconducting Polymers (John Wiley & Sons, New York, 2000).

[30] C. Brabec, V. Dyakonov, J. Parisi, and N. Sariciftci (eds.), Organic Photovoltaics: Concepts and Realization (Springer, Berlin, 2003).

[31] W. Bruetting (ed.), Physics of Organic Semiconductors (Wiley-VCH, Weinheim, 2005).

[32] S. Baranovski (ed.), Charge Transport in Disordered Solids with Applications in Electronics (John Wiley & Sons, Chichester, 2006).

[33] M. Schwoerer and H. C. Wolf (eds.), Organic Molecular Solids (Wiley-VCH, Weinheim, 2007).

[34] S. S. Sun and L. Dalton (eds.), Organic Electronic and Optoelectronic Materials and Devices (CRC Press, Boca Raton, 2008).

[35] N. Tessler, Y. Preezant, N. Rappaport, and Y. Roichman, Adv. Mater. **21**, 2741 (2009).

[36] G. Meller and T. Grasser (eds.), Organic Electronics (Springer, Berlin, 2010).

[37] B. Maennig, M. Pfeiffer, A. Nollau, X. Zhou, K. Leo, and P. Simon, Phys. Rev. B **64**, 195208 (2001).

[38] C. Tanase, E. Meijer, P. Blom, and D. de Leeuw, Phys. Rev. Lett. **91**, 216601 (2003).

[39] C. Tanase, P. Blom, and D. de Leeuw, Phys. Rev. B **70**, 193202 (2004).

[40] K. Schulze, M. Riede, E. Brier, E. Reinold, P. Bäuerle, and K. Leo, J. Appl. Phys. **104**, 074511 (2008).

[41] S. Alesi, G. Brancolini, I. Viola, M. L. Capobianco, A. Venturini, N. Camaioni, G. Gigli, M. Melucci, and G. Barbarella, Chem. Eur. J. **15**, 1876 (2009).

[42] G. Juška, K. Genevičius, N. Nekrašas, and G. Sliaužys, Phys. Status Solidi **7**, 980 (2010).

[43] M. C. J. M. Vissenberg and M. Matters, Phys. Rev. B **57**, 12964 (1998).

[44] M. Grünewald and P. Thomas, Phys. Status Solidi B **94**, 125 (1979).

[45] E. J. Meijer, C. Tanase, P. W. M. Blom, E. van Veenendaal, B. H. Huisman, D. M. de Leeuw, and T. M. Klapwijk, Appl. Phys. Lett. **80**, 3838 (2002).

[46] C. Tanase, E. Meijer, P. Blom, and D. de Leeuw, Org. Electron. **4**, 33 (2003).

[47] J. Nelson, Phys. Rev. B **67**, 155209 (2003).

[48] A. Salleo, T. W. Chen, A. R. Völkel, Y. Wu, P. Liu, B. S. Ong, and R. A. Street, Phys. Rev. B **70**, 115311 (2004).

[49] J. Nelson, S. Choulis, and J. Durrant, Thin Solid Films **451–452**, 508 (2004).

[50] T. Anthopoulos, C. Tanase, S. Setayesh, E. J. Meijer, J. C. Hummelen, P. W. M. Blom, and D. M. Leeuv, Adv. Mater. **16**, 2174 (2004).

[51] P. W. M. Blom, C. Tanase, D. M. de Leeuw, and R. Coehoorn, Appl. Phys. Lett. **86**, 092105 (2005).

[52] N. Sedghi, D. Donaghy, M. Raja, S. Badriya, S. Higgins, and W. Eccleston, J. Non-Cryst. Solids **352**, 1641 (2006).

[53] M. Estrada, I. Mejía, A. Cerdeira, J. Pallares, L. Marsal, and B. Iñiguez, Solid-State Electron. **52**, 787 (2008).

[54] J. Gonzalez-Vazquez, J. Anta, and J. Bisquert, Phys. Chem. Chem. Phys. **11**, 10359 (2009).

[55] M. Tachyia and K. Seki, Phys. Rev. B **82**, 085201 (2010).

[56] J. Montero and J. Bisquert, J. Appl. Phys. **110**, 043705 (2011).

[57] R. A. Street, K. W. Song, J. E. Northrup, and S. Cowan, Phys. Rev. B **83**, 165207 (2011).

[58] W. C. Germs, K. Guo, R. A. J. Janssen, and M. Kemerink, Phys. Rev. Lett. **109**, 016601 (2012).

[59] J. J. Brondijk, W. S. C. Roelofs, S. G. J. Mathijssen, A. Shehu, T. Cramer, F. Biscarini, P. W. M. Blom, and D. M. de Leeuw, Phys. Rev. Lett. **109**, 056601 (2012).

[60] M. Schubert, E. Preis, J. C. Blakesley, P. Pingel, U. Scherf, and D. Neher, Phys. Rev. B **87**, 24203 (2013).

[61] J. O. Oelerich, D. Huemmer, and S. D. Baranovskii, Phys. Rev. Lett. **108**, 226403 (2012).

[62] R. Coehoorn and P. A. Bobbert, Phys. Status Solidi A **209**, 2354 (2012).

[63] S. D. Baranovskii, I. P. Zvyagin, H. Cordes, S. Yamasaki, and P. Thomas, Phys. Status Solidi B **230**, 281 (2002).

[64] S. D. Baranovskii, I. P. Zvyagin, H. Cordes, S. Yamasaki, and P. Thomas, J. Non-Cryst. Solids **299**, 416 (2002).

[65] R. Schmechel, Phys. Rev. B **66**, 235206 (2002).

[66] R. Schmechel, J. Appl. Phys. **93**, 4653 (2003).

[67] S. Shaked, S. Tal, Y. Roichman, A. Razin, S. Xiao, Y. Eichen, and N. Tessler, Adv. Mater. **15**, 913 (2003).

[68] Y. Roichman and N. Tessler, Synth. Met. **135 & 136**, 443 (2003).

[69] J. Cottaar, L. J. A. Koster, R. Coehoorn, and P. A. Bobbert, Phys. Rev. Lett. **107**, 136601 (2011).

[70] A. J. Mozer, N. S. Sariciftci, A. Pivrikas, R. Österbacka, G. Juška, L. Brassat, and H. Bässler, Phys. Rev. B **71**, 035214 (2005).

[71] B. I. Shklovskii and A. L. Efros, Sov. Phys. JETP **33**, 468 (1971).

[72] V. Ambegaokar, B. I. Halperin, and J. S. Langer, Phys. Rev. B **4**, 2612 (1971).

[73] M. Pollak, J. Non-Cryst. Solids **11**, 1 (1972).

[74] F. R. Shapiro and D. Adler, J. Non-Cryst. Solids **74**, 189 (1985).

[75] D. Monroe, Phys. Rev. Lett. **54**, 146 (1985).

[76] S. D. Baranovskii, P. Thomas, and G. J. Adriaenssens, J. Non-Cryst. Solids **190**, 283 (1995).

[77] S. D. Baranovskii, T. Faber, F. Hensel, and P. Thomas, J. Phys. C **9**, 2699 (1997).

[78] S. D. Baranovskii, H. Cordes, F. Hensel, and G. Leising, Phys. Rev. B **62**, 7934 (2000).

[79] B. I. Shklovskii, Sov. Phys. Semicond. **6**, 1964 (1973).

[80] S. Marianer and B. I. Shklovskii, Phys. Rev. B **46**(20), 13100 (1992).

[81] S. D. Baranovskii, B. Cleve, R. Hess, and P. Thomas, J. Non-Cryst. Solids **164**, 437 (1993).

[82] B. Cleve, B. Hartenstein, S. D. Baranovskii, M. Scheidler, P. Thomas, and H. Bässler, Phys. Rev. B **51**, 16705 (1995).

[83] F. Jansson, S. D. Baranovskii, F. Gebhard, and R. Österbacka, Phys. Rev. B **77**, 195211 (2008).

[84] B. I. Shklovskii and A. L. Efros, Electronic Properties of Doped Semiconductors (Springer, Berlin, 1984).

[85] A. L. Efros and B. I. Shklovskii, J. Phys. C **8**, L49 (1975).

[86] S. D. Baranovskii, A. L. Efros, B. L. Gelmont, and B. I. Shklovskii, J. Phys. C **12**, 1023 (1979).

[87] H. C. F. Martens, I. N. Hulea, I. Romijn, H. B. Brom, W. F. Pasveer, and M. A. J. Michels, Phys. Rev. B **67**, 121203 (R) (2003).

[88] J. Cottaar, R. Coehoorn, and P. A. Bobbert, Phys. Rev. B **85**, 245205 (2012).

[89] A. V. Nenashev, F. Jansson, J. O. Oelerich, D. Huemmer, A. V. Dvurechenskii, F. Gebhard, and S. D. Baranovskii, Phys. Rev. B **87**, 235204 (2013).

Phys. Status Solidi B 251, No. 3 (2014)

Review
Article

523

[90] V. R. Nikitenko, H. von Seggern, and H. Bässler, J. Phys.: Condens. Matter **19**, 136210 (2007).

[91] A. V. Nenashev, F. Jansson, S. D. Baranovskii, R. Österbacka, A. V. Dvurechenskii, and F. Gebhard, Phys. Rev. B **81**, 115203 (2010).

[92] A. V. Nenashev, F. Jansson, S. D. Baranovskii, R. Österbacka, A. V. Dvurechenskii, and F. Gebhard, Phys. Rev. B **81**, 115204 (2010).

[93] T. M. Clarke and J. R. Durrant, Chem. Rev. **110**, 6736 (2010).

[94] C. Deibel and V. Dyakonov, Rep. Prog. Phys. **73**, 096401 (2010).

[95] S. D. Baranovskii, M. Wiemer, A. V. Nenashev, F. Jansson, and F. Gebhard, J. Phys. Chem. Lett. **3**, 1214 (2012).

[96] H. Bässler, in: Advances in Disordered Semiconductors – Vol.2, edited by H. Fritzsche and M. Pollak (World Scientific, Singapore, 1990), pp. 491–520.

[97] M. Abkowitz, M. Stolka, and M. Morgan, J. Appl. Phys. **52**, 3453 (1981).

[98] S. J. Santos Lemus and J. Hirsch, Philos. Mag. B **53**, 25 (1986).

[99] G. Pfister, Phys. Rev. B **16**, 3676 (1977).

[100] J. Hirsch, J. Phys. C **12**, 321 (1979).

[101] D. M. Pai, J. F. Yanus, and M. Stolka, J. Phys. Chem. **88**, 4714 (1984).

[102] D. M. de Leeuw, Synth. Met. **55**, 3597 (1993).

[103] O. Marinov, M. J. M. J. Deen, and R. Datars, J. Appl. Phys. **106**, 064501 (2009).

[104] I. Lange, J. C. Blakesley, J. Frisch, A. Vollmer, N. Koch, and D. Neher, Phys. Rev. Lett. **106**, 216402 (2011).

[105] S. Yogev, E. Halpern, R. Matsubara, M. Nakamura, and Y. Rosenwaks, Phys. Rev. B **84**, 165124 (2011).

[106] J. C. Blakesley, M. Schubert, R. Steyrleuthner, Z. Chen, A. Facchetti, and D. Neher, Appl. Phys. Lett. **99**, 183310 (2011).

[107] H. P. D. Lanyon, Phys. Rev. **130**, 134 (1963).

[108] A. Sussman, J. Appl. Phys. **38**, 2738 (1967).

[109] F. Gutmann and L. E. Lyons, Organic Semiconductors (Wiley, New York, 1967).

[110] E. A. Silinsh, Phys. Status Solidi A **8**, 817 (1970).

[111] S. D. Baranovskii and A. L. Efros, Sov. Phys. Semicond. **12**, 1328 (1978).

[112] J. J. Kwiatkowski, J. Nelson, H. Li, J. L. Bredas, W. Wenzel, and C. Lennartz, Phys. Chem. Chem. Phys. **10**, 1852 (2008).

[113] Y. Nagata and C. Lennartz, J. Chem. Phys. **129**, 034709 (2008).

[114] A. Lukyanov and D. Andrienko, Phys. Rev. B **82**, 193202 (2010).

[115] S. D. Baranovskii, M. Zhu, T. Faber, F. Hensel, P. Thomas, M. B. von der Linden, and W. F. van der Weg, Phys. Rev. B **55**, 16226 (1997).

[116] S. D. Baranovskii, F. Hensel, K. Ruckes, P. Thomas, and G. J. Adriaenssens, J. Non-Cryst. Solids **190**, 117 (1995).

[117] P. Bozsoki, S. D. Baranovskii, P. Thomas, and S. C. Agarwal, Phys. Status Solidi C **1**, 113 (2004).

[118] H. Bässler, G. Schönherr, M. Abkowitz, and D. M. Pai, Phys. Rev. B **26**, 3105 (1982).

[119] P. M. Borsenberger, J. Appl. Phys. **68**, 6263 (1990).

[120] P. M. Borsenberger, L. Pautmeier, and H. Bässler, J. Chem. Phys. **94**, 5447 (1991).

[121] G. Horowitz, in: Semiconducting Polymers, edited by G. Hadziioannou and P.F. van Hutten (Wiley-VCH, Weinheim, 2000), chap. 14, pp. 463–514.

[122] J. D. Ferry, L. D. Grandine, and E. R. Fitzgerald, J. Appl. Phys. **24**, 911 (1953).

[123] D. L. Huber, J. Chem. Phys. **78**, 2530 (1983).

[124] U. Larsen, Phys. Lett. A **105**, 307 (1984).

[125] U. Larsen, Phys. Rev. B **32**, 1772 (1985).

[126] G. Schönherr, H. Bässler, and M. Silver, Philos. Mag. B **44**, 369 (1981).

[127] M. Grünewald, B. Pohlmann, B. Movaghar, and D. Würtz, Philos. Mag. B **49**, 341 (1984).

[128] B. Movaghar, M. Grünewald, B. Ries, H. Bässler, and D. Würtz, Phys. Rev. B **33**, 5545 (1986).

[129] A. Ochse, A. Kettner, J. Kopitzke, J. H. Wendorff, and H. Bässler, Phys. Chem. Chem. Phys. **1**, 1757 (1999).

[130] B. I. Shklovskii, E. I. Levin, H. Fritzsche, and S. D. Baranovskii, in: Advances in Disordered Semiconductors, Vol. 3 (World Scientific, Singapore, 1990), pp. 161–191.

[131] J. Orenstein and M. Kastner, Solid State Commun. **40**, 85 (1981).

[132] J. O. Oelerich, D. Huemmer, M. Weseloh, and S. D. Baranovskii, Appl. Phys. Lett. **97**, 143302 (2010).

[133] B. Ries, H. Bässler, M. Grünewald, and B. Movaghar, Phys. Rev. B **37**, 5508 (1988).

[134] I. H. Campbell, D. L. Smith, C. J. Neef, and J. P. Ferraris, Appl. Phys. Lett. **75**, 841 (1999).

[135] O. Tal, Y. Rosenwaks, Y. Preezant, N. Tessler, C. K. Chan, and A. Kahn, Phys. Rev. Lett. **95**, 256405 (2005).

[136] K. Celebi, P. Jadhav, K. Milaninia, M. Bora, and M. Baldo, Appl. Phys. Lett. **93**, 083308 (2008).

[137] W. So, D. Lang, V. Butko, X. Chi, J. Lashley, and A. Ramirez, J. Appl. Phys. **104**, 054512 (2008).

[138] W. L. Kalb, S. Haas, C. Krellner, T. Mathis, and B. Batlogg, Phys. Rev. B **81**, 155315 (2010).

[139] J. Puigdollers, A. Marsala, S. Cheylanb, C. Voza, and R. Alcubilla, Org. Electron. **11**, 1333 (2010).

[140] W. S. C. Roelofs, S. G. J. Mathijssen, R. A. J. Janssen, D. M. de Leeuw, and M. Kemerink, Phys. Rev. B **85**, 085202 (2012).

[141] A. Fuchs, T. Steinbrecher, M. S. Mommer, Y. Nagata, M. Elstner, and C. Lennartz, Phys. Chem. Chem. Phys. **14**, 4259 (2012).

[142] V. Rühle, A. Lukyanov, F. May, M. Schrader, T. Vehoff, J. Kirkpatrick, B. Baumeier, and D. Andrienko, J. Chem. Theory Comput. **7**, 3335 (2011).

[143] N. F. Mott, Philos. Mag. **19**, 835 (1969).

[144] S. Kirkpatrick, Phys. Rev. Lett. **27**, 1722 (1971).

[145] J. C. Dyre and T. B. Schrøder, Rev. Mod. Phys. **72**, 873 (2000).

[146] N. W. Dalton, C. Domb, and M. F. Sykes, Proc. Phys. Soc. **83**, 496 (1964).

[147] C. Domb and N. W. Dalton, Proc. Phys. Soc. **89**, 859 (1966).

[148] C. D. Lorenz and R. M. Ziff, J. Chem. Phys. **114**, 3659 (2001).

[149] L. Li, S. Van Winckel, J. Genoe, and P. Heremans, Appl. Phys. Lett. **95**, 153301 (2009).

[150] R. Coehoorn, W. F. Pasveer, P. A. Bobbert, and M. A. J. Michels, Phys. Rev. B **72**, 155206 (2005).

[151] C. D. Lorenz and R. M. Ziff, Phys. Rev. E **57**, 230 (1998).

[152] S. D. Baranovskii, O. Rubel, and P. Thomas, Thin Solid Films **487**, 2 (2005).

[153] A. I. Rudenko and V. I. Arkhipov, Philos. Mag. B **45**, 177 (1982).

[154] F. Neumann, Y. A. Genenko, and H. von Seggern, J. Appl. Phys. **99**, 013704 (2006).

[155] B. Hartenstein and H. Bässler, J. Non-Cryst. Solids **190**, 112 (1995).

[156] C. Tanase, Unified Charge Transport in Disordered Organic Field-Effect Transistors and Light-Emitting Diodes, PhD thesis, University of Groningen (2005).

[157] L. Fumagalli, M. Binda, D. Natali, M. Sampietro, E. Salmoiraghi, and P. Di Gianvincenzo, J. Appl. Phys. **104**, 084513 (2008).

[158] A. Kadashchuk, Y. Skryshevskii, A. Vakhnin, N. Ostapenko, V. I. Arkhipov, E. V. Emelianova, and H. Bässler, Phys. Rev. B **63**, 115205 (2001).

[159] V. I. Arkhipov, E. V. Emelianova, and G. J. Adriaenssens, Phys. Rev. B **64**, 125125 (2001).

[160] L. Li, G. Meller, and H. Kosina, Appl. Phys. Lett. **92**, 013307 (2008).

[161] S. V. Novikov and G. G. Malliaras, Phys. Status Solidi B **243**, 387 (2006).

[162] V. I. Arkhipov, U. Wolf, and H. Bässler, Phys. Rev. B **59**, 7514 (1999).

[163] V. I. Arkhipov and H. Bässler, Philos. Mag. Lett. **67**, 343 (1993).

[164] V. I. Arkhipov and H. Bässler, Philos. Mag. B **68**, 425 (1993).

[165] V. I. Arkhipov and H. Bässler, Philos. Mag. Lett. **69**, 241 (1994).

[166] V. I. Arkhipov and H. Bässler, Philos. Mag. B **70**, 59 (1994).

[167] B. Ries, H. Bässler, and M. Silver, Philos. Mag. B **54**, 141 (1986).

[168] H. Bässler and K. Abt, J. Chem. Phys. **47**, 4007 (1967).

[169] H. Bässler, J. Chem. Phys. **49**, 5198 (1968).

[170] L. Pautmeier, B. Ries, R. Richert, and H. Bässler, Chem. Phys. Lett. **143**, 459 (1988).

[171] S. D. Baranovskii, H. Cordes, K. Kohary, and P. Thomas, Philos. Mag. B **81**, 955 (2001).

[172] S.D. Baranovskii and O. Rubel, in: Handbook of Electronic and Photonic Materials, edited by S. Kasap and P. Capper (Springer, Berlin, Heidelberg, 2006), pp. 161–186.

[173] W. Gill, in: Proceedings of the Fifth International Conference on Amorphous and Liquid Semiconductors, edited by J. Stuke and W. Brenig (Taylor and Francis, London, 1974), p. 901.

[174] V. I. Arkhipov, E. V. Emelianova, and H. Bässler, Philos. Mag. B **81**, 985 (2001).

[175] R. Österbacka, A. Pivrikas, G. Juška, K. Genevičius, K. Arlauskas, and H. Stubb, Curr. Appl. Phys. **4**, 534 (2004).

[176] A. J. Mozer, G. Dennler, N. S. Sariciftci, M. Westerling, A. Pivrikas, R. Österbacka, and G. Juška, Phys. Rev. B **72**, 035217 (2005).

[177] A. Pivrikas, R. Österbacka, G. Juška, K. Arlauskas, and H. Stubb, Synth. Met. **155**, 242 (2005).

[178] A. Pivrikas, N. S. Sariciftci, G. Juška, and R. Österbacka, Prog. Photovolt. Res. Appl. **15**, 677 (2007).

[179] R. A. Smith, Semiconductors (University Press, Cambridge, 1978).

[180] N. W. Aschcroft and D. Mermin, Solid State Physics (Holt, Reinhart and Winston, New York, 1988).

[181] Y. Roichman and N. Tessler, Appl. Phys. Lett. **80**, 1948 (2002).

[182] I. P. Zvyagin, Phys. Status Solidi C **5**, 725 (2008).

[183] A. Peled and L. B. Schein, Chem. Phys. Lett. **153**(5), 422 (1988).

[184] L. B. Schein, Philos. Mag. B **65**, 795 (1992).

[185] R. Richert, L. Pautmeier, and H. Bässler, Phys. Rev. Lett. **63**, 547 (1989).

[186] A. Hirao, H. Nishizawa, and M. Sugiuchi, Phys. Rev. Lett. **75**, 1787 (1995).

[187] G. Juška, K. Genevičius, K. Arlauskas, R. Österbacka, and H. Stubb, Phys. Rev. B **65**, 233208 (2002).

[188] H. Cordes, S. D. Baranovskii, K. Kohary, P. Thomas, S. Yamasaki, F. Hensel, and J. H. Wendorff, Phys. Rev. B **63**, 094201 (2001).

[189] H. Böttger and V. V. Bryksin, Phys. Status Solidi B **96**, 219 (1979).

[190] N. Van Lien and B. I. Shklovskii, Solid State Commun. **38**, 99 (1981).

[191] E. I. Levin and B. I. Shklovskii, Solid State Commun. **67**, 233 (1988).

[192] A. V. Nenashev, F. Jansson, S. D. Baranovskii, R. Österbacka, A. V. Dvurechenskii, and F. Gebhard, Phys. Rev. B **78**, 165202 (2008).

[193] P. M. Borsenberger and J. J. Fitzgerald, J. Phys. Chem. **97**, 4815 (1993).

[194] H. Kageyama, K. Ohnishi, S. Nomura, and Y. Shirota, Chem. Phys. Lett. **277**, 137 (1997).

[195] F. Laquai, G. Wegner, and H. Bässler, Philos. Trans. R. Soc. A **365**, 1473 (2007).

[196] A. Nemeth-Buchin, C. Juhasz, V. Arkhipov, and H. Bässler, Philos. Mag. B **74**, 295 (1990).

[197] D. H. Dunlap, P. E. Parris, and V. M. Kenkre, Phys. Rev. Lett. **77**, 542 (1996).

[198] C. E. Nebel, R. A. Street, N. M. Johnson, and C. C. Tsai, Phys. Rev. B **46**(11), 6803 (1992).

[199] A. Nagy, M. Hundhausen, L. Ley, G. Brunst, and E. Holzenkämpfer, J. Non-Cryst. Solids **164**, 529 (1993).

[200] R. Stachowitz, W. Fuhs, and K. Jahn, Philos. Mag. B **62**, 5 (1990).

[201] H. Antoniadis and E. A. Schiff, Phys. Rev. B **43**, 13957 (1991).

[202] K. Murayama, H. Oheda, S. Yamasaki, and A. Matsuda, Solid State Commun. **81**, 887 (1992).

[203] M. Grünewald and B. Movaghar, J. Phys. C, Condens. Matter **1**, 2521 (1989).

[204] T. Aoki, N. Ohrui, C. Fujihashi, and K. Shimakawa, Philos. Mag. Lett. **88**, 9 (2008).

[205] V. I. Arkhipov, E. V. Emelianova, and G. J. Adriaenssens, J. Appl. Phys. **93**, 6150 (2003).

[206] B. N. Limketkai, P. Jadhav, and M. A. Baldo, Phys. Rev. B **75**, 113203 (2007).

[207] J. P. Bouchaud and A. Georges, Phys. Rev. Lett. **63**, 2692 (1989).

[208] L. Pautmeier, R. Richert, and H. Bässler, Philos. Mag. B **63**, 587 (1991).

[209] S. Raj Mohan, M. P. Singh, and M. P. Joshi, J. Phys. Chem. C **116**, 2555 (2012).

[210] A. Bacher, I. IBleyl, C. H. Erdelen, D. Haarer, W. Paulus, and H. W. Schmidt, Adv. Mater. **9**, 1031 (1997).

[211] T. Christ, B. Glüsen, A. Greiner, A. Kettner, R. Sander, Stümpflen, V. Tsukruk, and J. H. Wendorf, Adv. Mater. **9**, 48 (1997).

[212] N. Boden, R. J. Bushby, J. Clements, B. Movaghar, K. J. Donovan, and T. Kreouzis, Phys. Rev. B **52**, 13274 (1995).

Phys. Status Solidi B 251, No. 3 (2014)

Review
Article

525

[213] I. Bleyl, C. Erdelen, H. W. Schmidt, and D. Haarer, Philos. Mag. B **79**, 463 (1999).
[214] K. Seki and M. Tachiya, Phys. Rev. B **65**, 014305 (2001).
[215] R. A. Marcus, J. Chem. Phys. **24**, 966 (1956).
[216] B. Derrida, J. Stat. Phys. **31**, 433 (1983).
[217] K. P. N. Murthy and K. W. Kehr, Phys. Rev. A **40**, 2082 (1989).
[218] K. P. N. Murthy and K. W. Kehr, Phys. Rev. A **41**, 1160 (1990).
[219] I. P. Zvyagin, S. D. Baranovskii, K. Kohary, H. Cordes, and P. Thomas, Phys. Status Solidi B **230**, 227 (2002).
[220] W. F. Pasveer, P. A. Bobbert, and M. A. J. Michels, Phys. Status Solidi C **1**, 164 (2003).
[221] K. Kohary, H. Cordes, S. D. Baranovskii, P. Thomas, S. Yamasaki, F. Hensel, and J. H. Wendorff, Phys. Rev. B **63**, 094202 (2001).
[222] N. A. Korolev, V. R. Nikitenko, and D. V. Ivanov, Semiconductors **45**, 230 (2011).
[223] P. M. Borsenberger and H. Bässler, J. Chem. Phys. **95**, 5327 (1991).
[224] P. M. Borsenberger and H. Bässler, Phys. Status Solidi B **170**, 291 (1992).
[225] P. M. Borsenberger and M. B. O'Regan, Chem. Phys. **200**, 257 (1995).
[226] P. M. Borsenberger, W. T. Gruenbaum, and E. H. Magin, Physica B **228**, 233 (1996).
[227] Y. Shen, K. Diest, M. H. Wong, B. R. Hsieh, D. H. Dunlap, and G. G. Malliaras, Phys. Rev. B **68**, 081204 (2003).
[228] S. V. Novikov and A. V. Vannikov, Chem. Phys. Lett. **182**, 598 (1991).
[229] S. V. Novikov and A. V. Vannikov, J. Phys. Chem. **99**, 14573 (1995).
[230] Z. G. Yu, D. L. Smith, A. Saxena, R. L. Martin, and A. R. Bishop, Phys. Rev. Lett. **84**, 721 (2000).
[231] S. V. Novikov and A. V. Vannikov, Mol. Cryst. Liq. Cryst. **361**, 89 (2001).
[232] M. Bouhassoune, S. L. M. van Mensfoort, P. A. Bobbert, and R. Coehoorn, Org. Electron. **10**, 437 (2009).
[233] S. L. M. van Mensfoort, V. Shabro, R. J. de Vries, R. A. J. Janssen, and R. Coehoorn, J. Appl. Phys. **107**, 113710 (2010).
[234] L. B. Schein and A. Tyutnev, J. Phys. Chem. C **112**, 7295 (2008).
[235] S. V. Novikov and A. V. Vannikov, J. Phys. Chem. **113**, 2532 (2009).
[236] L. B. Schein, D. Glatz, and J. C. Scott, Phys. Rev. Lett. **65**, 472 (1990).
[237] L. T. Pautmeier, J. C. Scott, and L. B. Schein, Chem. Phys. Lett. **197**, 568 (1992).
[238] V. M. Kenkre and D. H. Dunlap, Philos. Mag. B **65**, 831 (1992).
[239] D. H. Dunlap and V. M. Kenkre, Chem. Phys. **178**, 67 (1993).
[240] Yu. N. Gartstein and E. M. Conwell, Chem. Phys. Lett. **217**, 41 (1994).
[241] Z. G. Soos, S. Bao, J. M. Sin, and G. W. Hayden, Chem. Phys. Lett. **319**, 631 (2000).
[242] I. I. Fishchuk, A. Kadashchuk, H. Bässler, and S. Nešpůrek, Phys. Rev. B **67**, 224303 (2003).
[243] E. A. Silinsh and V. Capek, Organic Molecular Crystals: Interaction, Localization, and Transport Phenomena (AIP Press, New York, 1994).
[244] H. Bässler, P. M. Borsenberger, and R. J. Perry, J. Polym. Sci. B, Polym. Phys. **32**, 1677 (1994).
[245] B. Hartenstein, H. Bässler, S. Heun, P. Borsenberger, M. Van der Auweraer, and F. C. De Schryyer, Chem. Phys. **191**, 321 (1995).
[246] E. H. Magin and P. M. Borsenberger, J. Appl. Phys. **73**, 787 (1993).
[247] P. E. Parris, V. M. Kenkre, and D. H. Dunlap, Phys. Rev. Lett. **87**, 126601 (2001).
[248] I. I. Fishchuk, V. I. Arkhipov, A. Kadashchuk, P. Heremans, and H. Bässler, Phys. Rev. B **76**, 045210 (2007).
[249] I. I. Fishchuk, A. Kadashchuk, S. T. Hoffmann, S. Athanasopoulos, J. Genoe, H. Bässler, and A. Köhler, Phys. Rev. B **88**, 125202 (2013).