Charge-carrier concentration dependence of the hopping mobility in organic materials with Gaussian disorder

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It has recently been demonstrated that the hopping mobility in semiconducting organic materials depends on the charge-carrier concentration. We have analyzed this effect within the framework of six existing semianalytical models, for the case of a Gaussian density of states (DOS). These models were either not applied earlier to the case of a Gaussian DOS, or are shown to require a major modification. The mobility is constant below a certain concentration, which decreases with increasing ratio $\delta$ of the width of the DOS over the thermal energy $k_BT$, and it increases for larger concentrations. At very high concentrations final state effects limit this increase or even give rise to a decrease. An analytical expression is given for the mobility, $\mu$, in the form of the product of the mobility in the low concentration limit times a concentration ($c$) and $\delta$-dependent enhancement factor. Depending on $c$, $\ln(\mu)$ varies approximately linearly with $1/T$ or with $1/T^2$. This finding may lead to a solution for the long-standing controversy between polaron-based and disorder-based hopping models.

I. INTRODUCTION

The mobility of charge carriers in $\pi$-conjugated organic materials is exploited in a wide range of devices, including light emitting diodes (LEDs),1 field-effect transistors (FETs),2 photoreceptors,3 and photovoltaic cells.4 Organic small molecule or polymer layers often have microstructures that can be characterized as nanocrystalline, or even amorphous. It is generally agreed that the mobility is then due to thermally assisted tunneling (“hopping”) between localized molecular states. Hopping mobilities in structurally disordered organic materials are often many orders of magnitude smaller than the mobilities due to transport via delocalized band states in crystalline inorganic semiconductors. For example, the room temperature hole mobility in typical polyphenylene-vinylene (PPV) polymer films such as used in polymer LEDs is of the order of $10^{-11}$ to $10^{-10}$ m$^2$/V s,5,6 eight to ten orders of magnitude smaller than the hole mobility in single crystalline Si.

Pioneering modeling studies of the hopping mobility ($\mu$) in disordered systems were carried out by Bässler.7 He assumed a Gaussian density of states (DOS), with width $\sigma_{\text{DOS}}$, and used Monte Carlo calculations in order to obtain the dependence of the hopping mobility on the temperature and the electrical field. In the zero-field limit, the temperature dependence of the mobility was found to be described well by $\mu \propto \exp[-(4/9)\delta^2]$, with $\delta = \sigma_{\text{DOS}}/(k_BT)$. For common hole transporting organic materials, the experimentally observed temperature dependence of the mobility leads then to $\sigma_{\text{DOS}} = 0.1$ eV.7,8 This order of magnitude is not inconsistent with results from independent studies on the degree of disorder (e.g., Ref. 9). However, $\ln(\mu)$ is for some systems better described as a linear function of $1/T$, than as a linear function of $1/T^2$. The mobility can then be expressed as $\mu \propto \exp[-E_A/(k_BT)]$, with $E_A$ an effective activation energy that is of the order of a polaron binding energy.3,10,11

Further doubts on the applicability of this so-called Gaussian disorder model were raised by the observation that the field-effect (hole) mobilities in polymer FETs are typically at least one order of magnitude larger than the hole mobility in LEDs based on the same material. Recently, TANase and co-workers showed that this can be explained as a result of a dependence of the mobility on the hole concentration.12 The authors pointed out that under typical operational conditions the carrier concentration in the accumulation channel in FETs is several orders of magnitude larger than the average carrier concentration due to the injected charges in LEDs. In FETs, the application of a high gate voltage can give rise to a concentration of 0.01–0.1 carriers per hopping site [$\sim 10^{25}$ carriers per m$^3$, with a typical site density of $10^{26}$–$10^{27}$ sites m$^{-3}$ (Ref. 12)]. In contrast, in typical 100 nm single layer organic LEDs, driven at 10 V, the effective carrier concentration is only $10^{-5}$ to $10^{-4}$. For LEDs and FETs based on the same prototypical materials, the dependence of the hole mobility on the hole density, $n$, is well described by a single function $\mu(n)$. For the polymers OC$_1$C$_{10}$PPV and P3HT (see the figure caption for the full chemical structure) this experimentally measured function is shown in Fig. 1, which was redrawn from Ref. 12. Figure 1 shows that the concentration dependence of the mobility in LEDs and FETs, based on the same materials, is given by a single continuous function. From a theoretical point of view, the carrier concentration dependence of the mobility had already been recognized by Yu et al.13

The first semianalytical model for the problem of hopping in a Gaussian DOS was presented by Baranovskii and co-workers.14,15 They argued that the hopping processes that most strongly determine the mobility are repeated hops of carriers in deep states to a so-called “transport energy level.”14 From their model, it became evident that the tem-
density of states. To this end, we make a comparison between the results obtained from five semianalytical models, the Monte Carlo results from Bässler,\textsuperscript{7} and the Master Equation results reported by Pasveer et al.\textsuperscript{16} The latter work is used as a benchmark. We discuss the semianalytical models proposed by Arkhipov et al.\textsuperscript{17} and Roichman and Tessler,\textsuperscript{18} already mentioned and we apply three other general models to the specific case of a Gaussian DOS: (i) the model introduced by Movaghar and Schirmacher,\textsuperscript{20} which involves a modified effective medium approximation, (ii) a percolation model, in the form used earlier by Vissenberg and Matters for the case of an exponential DOS,\textsuperscript{21} (iii) a model given recently by Martens et al.\textsuperscript{22} The latter two models are based on formalisms introduced by Ambegoakar et al.\textsuperscript{23} and by Mott,\textsuperscript{24} respectively.

We explain all methods in some detail in Sec. III. The mere fact that a large number of different models exists already reflects the difficulty of the problem of the hopping mobility. As emphasized by Ambegoakar et al.,\textsuperscript{23} an essential ingredient of a successful model is that it takes into account that hopping in a disordered system is not determined by the rate of “average” hops, but by the rate of those hops that are “most difficult but still relevant.” Hopping conduction is, in fact, a percolation problem. The electrochemical and electrostatic potential landscapes are highly nonuniform, showing rather flat regions and narrow bottleneck regions. There are small regions in which the current density is much larger than average. The challenge is to find out the spatial and energetic distance corresponding to the critical hops. In all models that are discussed this is done, albeit in different ways, except in the model by Roichman and Tessler.\textsuperscript{18} Within that model, the mobility is simply expressed as a sum of contributions from all possible hops, with a weight that depends on the intersite hopping rate. Such a procedure leads to quantitatively incorrect results (too high mobilities at low temperatures),\textsuperscript{23} as will be confirmed in Sec. IV for the case of a Gaussian DOS. Furthermore, we show that in the models proposed by Arkhipov et al.\textsuperscript{17} and Martens et al.\textsuperscript{22} the treatment of percolation is quantitatively not quite correct. In Secs. III and IV we discuss a simple procedure for improving both models on this issue.

Our focus is on the low-field limit, on carrier concentrations that are much smaller than 1, on cases for which the average intersite distances are much larger than the decay length of the localized wave functions, and on sufficiently low temperatures, so that $\delta > 1$. For disordered $\pi$-conjugated polymers around and below room temperature, the latter inequality is usually well obeyed. In Sec. IV we analyze the results obtained for all semianalytical models in the low-concentration limit and we give a comparison with the results from the Baranovskii model.\textsuperscript{14,15} In Sec. V, an overview is presented of semianalytically predicted carrier concentration dependences, and a comparison is made with the numerical results by Pasveer et al. We give a simple but accurate expression [Eq. (30)] for the mobility, which extends the numerical results by Bässler\textsuperscript{7} and Pasveer et al.\textsuperscript{16} by providing predictions for any site density and carrier concentration. It is valid for $\delta$ larger than 1 but smaller than the value beyond which the hopping mobility is not anymore in the nearest neighbour hopping regime, but in the variable range
We have discovered a remarkable result, viz. that for \( \delta \) larger than about 2, the mobility at the crossover carrier density, at which \( E_F = E_0 \), is to an excellent approximation equal to two times the mobility in the low carrier density limit:

\[
\frac{\mu[n(E_F = E_0)]}{\mu(n = 0)} \approx 2.
\] (2)

This is independent of the specific model used. Furthermore, the carrier concentration \( c = n / N_i \) at the crossover between the two transport regimes is (exactly) given by

\[
c(E_F = E_0) = \frac{1}{2} \exp\left(-\frac{1}{2}\delta^2\right).
\] (3)

These two results, which are proven in Appendix A, enable one to estimate the width of the DOS from the carrier concentration dependence of the mobility, measured at a fixed temperature. For example, Fig. 1 shows that for OC\(_2\)C\(_{10}\)PPV the crossover between the two transport regimes takes place around a site density of the order 10\(^{22}\) m\(^{-3}\), where the mobility is about two times the mobility at low concentrations. This corresponds to a concentration of approximately 10\(^{-4}\). From Eq. (3), one expects then that \( \delta = 4 \), so that \( \sigma_{\text{DOS}} \approx 0.1 \text{ eV} \). This is consistent with the values obtained typically from the temperature dependence of the mobility. The observation, that for the less disordered polymer P3HT the crossover takes place at higher concentrations, is also consistent with the model.

III. SEMIANALYTICAL MODELS

In all models that we consider the hopping rate \( w_{ij} \) from a site with energy \( E_i \) to a site with energy \( E_j \), at a distance \( R_{ij} \), is assumed to be given by the Miller-Abrahams rate constants:

\[
w_{ij} = n \exp\left(-2\alpha R_{ij} - \frac{E_j - E_i}{k_B T}\right) \quad \text{if } E_j > E_i,
\]

\[
w_{ij} = n \exp(-2\alpha R_{ij}) \quad \text{if } E_j < E_i,
\] (4)

where \( n_0 \) is an attempt frequency, and \( \alpha \) is the inverse of the decay length of the localized wave functions, which is taken to be equal for all sites. Equation (4) is correct if all hops are single-phonon processes. Inclusion of multiphonon processes is likely to affect the predicted temperature dependence of the mobility.\(^{26}\) A discussion of the appropriateness of the use of Miller-Abrahams hopping rates is beyond the scope of the present work (see Refs. 23 and 25). We note that Bleiбаum \( et \) \( al.\)\(^{27}\) have developed a hopping theory within which \( E_j - E_i \) is restricted to small values, and that that theory has recently been applied to the case of a Gaussian DOS.\(^{28}\) The attempt frequency depends on the electron-phonon coupling strength, the phonon density of states, and other properties of the material.\(^{23}\) The factor \( \exp(-2\alpha R_{ij}) \) is proportional to the quantum-mechanical transfer integral between the two sites, and, therefore, determines the tunnel probability for sites with equal energies. For hops to higher energy states there is an effective activation barrier that is equal to the energy difference between the two states.
The physics of the hopping process depends on the dimensionless parameters $\tilde{\delta}$, $c$, and $N_{l}^{1/3}/\alpha$, the ratio of the wave-function decay length and the average distance between nearest neighbor sites. We will represent most of our results in terms of these three parameters. Experimental studies of the mobility in systems containing conjugated small molecules in an insulating polymer matrix, as a function of the molecule concentration, have revealed values of $\alpha^{-1}$ around 0.1 nm.10 The site densities in conjugated polymers such as OC81C10$^{10}$-PPV are of the order $N_{l} \approx 10^{22} - 10^{23}$ m$^{-3}$, corresponding to average nearest neighbor intersite distances around 1 nm. A representative value of the reduced site density is thus $N_{l}/\alpha^{2} \approx 10^{-3}$.

In the remainder of this section, we give a brief outline of the semianalytical hopping models for the concentration dependence of the mobility that are considered in this paper. For practical reasons, we have chosen to name the models after the authors or first author of the publications in which the formalism is described which we follow most closely. However, as indicated already above, we emphasize that these “models” were in some cases not quite new, and are partly or entirely based on the earlier work of Mott24 and on percolation theory.

\[
\sigma(E) = \frac{4\pi}{B_{MS}} \int_{-\infty}^{\infty} g(E')dE' \int_{0}^{\infty} \frac{R^{2}}{2k_{B}T} \frac{|E-E'|-|E'-E_|}{\exp \left( \frac{2\alpha R + |E-E'|-|E'-E_|}{2k_{B}T} \right) + \frac{1}{\sigma_{l}(E')}} dR. \tag{6}
\]

The denominator of the argument in the radial integral suppresses contributions due to hopping from sites with energies far from $E_{F}$, and due to hopping to sites that are far away or for which $\sigma_{l}$ is small (hopping to sites at which carriers are effectively strongly trapped). For $B_{MS}$=1, this approach is called the effective medium approximation (see Ref. 20, and references therein). However, the EMA does not properly treat the transport problem as a long-range percolation process. The larger actual value of $B_{MS}$ effectively corrects for that.

Within the MS model, the mobility $\mu = \sigma(E)/\nu_{F}$ thus follows from Eq. (5), with Eqs. (1) and (6). This is, in principle, straightforward. However, the fact that $\sigma_{l}(E)$ is given by an integral equation, which needs to be solved iteratively, makes the evaluation of the mobility from a computational view less pleasant.

B. Vissenberg-Matters (VM) percolation model

Within the percolation model introduced by Ambegoakar et al.21 and applied earlier by Vissenberg and Matters to the case of an exponential DOS,21 the system is viewed as a random resistor network. The conductance between sites $i$ and $j$ is given by $G_{ij} = G_{0} \exp(-s_{ij})$, with $G_{0} = e^{2}\nu_{0}/(k_{B}T)$, and $s_{ij}$ is effectively strongly trapped. For $B_{MS}$=1, this approach is called the effective medium approximation (see Ref. 20, and references therein). However, the EMA does not properly treat the transport problem as a long-range percolation process. The larger actual value of $B_{MS}$ effectively corrects for that.

\[
s_{ij} = 2\alpha R_{ij} + \frac{|E_{i}-E_{j}|}{2k_{B}T} + \frac{|E_{j}-E_{i}|}{2k_{B}T} + \frac{|E_{i}-E_{j}|}{2k_{B}T}. \tag{7}
\]

This expression is obtained by expressing the equilibrium current density in terms of contributions proportional to the rates given by Eq. (4), multiplied by the initial and final state Fermi factors, taking the zero-field limit and under the condition that the most relevant hop energies are large as compared to the thermal energy $k_{B}T$.10 The occupation probabilities of the initial and final states, as given by Fermi-Dirac statistics, are properly taken into account. The total conductance is obtained by making use of percolation theory. It follows from that theory that when hopping processes between sites with decreasing $s_{ij}$ are neglected, the conductivity remains initially almost constant, until it decreases strongly at a certain critical value $s_{c}$, below which essential percolation paths are disrupted. The system may then be regarded as being broken up in effectively disconnected clusters. The conductivity is taken to be proportional to the critical conductance:

\[
\sigma = \sigma_{0} \exp(-s_{c}), \tag{8}
\]

where $\sigma_{0}$ is proportional to $G_{0}$. The critical exponent $s_{c}$ is obtained from the criterion that, after disregarding all connections for which $s_{ij} > s_{c}$, each site that is not disconnected...
The critical exponent $\nu$ in an efficient manner, we have made use of the fact that for rectangular areas the double energy integral in Eq. (11) can be evaluated analytically:

$$
\int d^3R_{ij} \int_{E_{i1}}^{E_{i2}} dE_i \int_{E_{j1}}^{E_{j2}} dE_j \left\{ \text{erf} \left[ \frac{E_{i1}}{\sqrt{2}\sigma_{\text{DOS}}} \right] - \text{erf} \left[ \frac{E_{i2}}{\sqrt{2}\sigma_{\text{DOS}}} \right] \right\}
$$

$$
\left( \text{erf} \left[ \frac{E_{j1}}{\sqrt{2}\sigma_{\text{DOS}}} \right] - \text{erf} \left[ \frac{E_{j2}}{\sqrt{2}\sigma_{\text{DOS}}} \right] \right),
$$

where $\text{erf}$ is the error function. The density of bonds is given by

$$
N_b = \int d^3 R_{ij} \int_{E_{i1}}^{E_{i2}} dE_i \int_{E_{j1}}^{E_{j2}} dE_j g(E_i)g(E_j) \theta(s_c - s_{ij}),
$$

where the $R_{ij}$ integral is over the entire space and where $\theta$ is the Heaviside unit step function. From Eq. (7), it is seen that for a given intersite distance $s_c$, only bonds contribute that are within an energy distance $U = (s_c - 2\sigma R_{ij})k_B T$ from each other, and from $E_F$. In Fig. 3, the corresponding area in the $E_i-E_j$ plane is shown. For a given temperature and carrier concentration, the critical exponent $s_c$ is obtained by solving Eq. (9) using a root finding procedure. The mobility follows then from the conductivity, given by Eq. (8), using $\mu = \sigma/(ne)$.

FIG. 3. The range of initial and final states ($E_i$ and $E_j$) that contributes to the number of bonds, $N_b$, within the Vissenberg-Matters model. As explained in the text, $U$ depends on the reduced intersite distance $s_c k_B T$ and on the critical exponent $s_c$. The subdivision of this area in a series of square regions, for which analytical expressions for $N_b$ are available [Eq. (12)], is also indicated schematically.

We wish to add a technical remark. In order to calculate $N_b(s_c)$ in an efficient manner, we have made use of the fact that for rectangular areas the double energy integral in Eq. (11) can be evaluated analytically:

$$
\int d^3R_{ij} \int_{E_{i1}}^{E_{i2}} dE_i \int_{E_{j1}}^{E_{j2}} dE_j (E_i)g(E_j)
$$

$$
= \pi N_c \int_0^{\sqrt{2} \alpha} dR R^2 \left( \text{erf} \left[ \frac{E_{i1}}{\sqrt{2}\sigma_{\text{DOS}}} \right] - \text{erf} \left[ \frac{E_{i2}}{\sqrt{2}\sigma_{\text{DOS}}} \right] \right)
$$

$$
\times \left( \text{erf} \left[ \frac{E_{j1}}{\sqrt{2}\sigma_{\text{DOS}}} \right] - \text{erf} \left[ \frac{E_{j2}}{\sqrt{2}\sigma_{\text{DOS}}} \right] \right),
$$

$N_b$ can be expressed as a sum of integrals of this type over square areas, as shown in Fig. 3. Note that the integration boundary of the double energy integral depends on $R$, so that also the boundaries of the separate square areas depend on $R$. The radial integrals were evaluated numerically. The dimensions of the edge regions in the second and fourth quadrant (gray in Fig. 3) were taken sufficiently small, and the contributions from these regions were given a weight of $1/2$.

### C. Arkhipov model

The starting assumption made within the model developed by Arkhipov and co-workers is that the first hop of a carrier at a site with energy $E$ will be to the neighbor site to which the Miller-Abrahams hopping rate is largest, i.e., the site for which the function

$$
u = 2 a R + \theta(E' - E) \frac{E' - E}{k_B T},$$

is smallest. Here, $R$ is the distance between the sites, $E'$ is the final state energy, and $\theta$ is the Heaviside unit step function. The mobility is then argued to be given by

$$\mu = \frac{e v_n}{k_B T} \int_{-\infty}^{\infty} \exp(-\langle u(E) \rangle (R^2)) h(E) dE,$$

where $\langle u(E) \rangle$ is the average $u$ value of the hop to the next site, $\langle R^2 \rangle(E)$ is the average of the square of the hopping distance to the next site, and $h(E)$ is the normalized density of occupied states [i.e., $g(E)f(E)/n$, where $f(E)$ is the Fermi-Dirac distribution function]. The function $\langle u(E) \rangle$ is shown to be given by

$$\langle u(E) \rangle = \int_{0}^{\infty} \exp\left( - \frac{n(E, u')}{B_{\text{Ark}}} \right) du',$$

where $n(E, u')$ is the average number of neighbor sites for which $u < u'$:

$$n(E, u') = \frac{4\pi}{3} \left( \frac{u'}{2\alpha} \right)^3 \int_{-\infty}^{E} g(E') dE + \int_{E}^{E + k_B T u'} g(E')$$

$$\times \left( 1 - \frac{E' - E}{k_B T u'} \right)^3 dE',$$

and in which $B_{\text{Ark}}=1$. We have introduced the latter param-
eter for reasons that are explained below. Eq. (14) is derived by assuming that the contribution to the diffusion constant due to carriers at sites with energy $E$ is given by $v_0 \exp \left[ -(u(E)) \frac{R^2}{2} \right]$, and that the diffusion constant is related to the mobility via the Einstein equation for noninteracting particles. The mobility is then obtained by integration over the initial state energy $E$. Instead of using the full expression for $\langle R^2 \rangle(E)$, given by Eq. (5) in Ref. 17, one may make use of the fact that for hopping at low carrier concentrations in a Gaussian DOS the average square hopping distance is approximately equal to the square of the average intersite distance (see the discussion of the MS model).

As in the VM model, very difficult hops are effectively disregarded, because the argument in Eq. (15) drops rapidly to zero when $u'$ attains such a high value that $n(E,u')$ becomes larger than $B_{Ark}$. Equation (15) expresses then that only neighbor states for which $n(E,u)$ is smaller than $B_{Ark}$ contribute appreciably to the mobility. Furthermore, Eq. (14) bears some similarity to Eq. (5), which gives the conductivity as obtained from the MS model. However, as compared to these earlier models, by taking $B_{Ark}=1$ the original version of the Arkhipov model focuses more strongly on short-range hopping. $B_{Ark}$ has the function of a percolation parameter, such as $B_{MS}$ or $B_{VM}$ in the MS and VM models, respectively. In the next section, we show that the model can be improved by giving $B_{Ark}$ a value that is somewhat larger than 1. Physically, this means that more difficult hops are assumed to be most relevant, so that $(u(E))$ increases and $\mu$ decreases. In our actual calculations we use $B_{Ark}=3.933$, as motivated in Sec. IV B.

We note that Arkhipov and co-workers have made an attempt to correct the model for a specific aspect of the percolation problem, viz. the fact that the model incorrectly includes the contribution of fast hops between neighbor sites that are isolated from other sites. The authors propose a correction for this (Sec. 4 of Ref. 17). However, we believe that the correction will not provide a full solution, because it only extends the analysis by considering hopping to a third site. It does not effectively increase the percolation parameter.

Minor points of criticism, for the purpose of this paper, are (i) that the model does not take final state effects into account (the model disregards that hopping cannot take place to a site that is already occupied) and (ii) that for $E_F > E_0$ (i.e., in the high concentration regime) the Einstein relation actually contains a carrier concentration dependent correction factor. In the Boltzmann regime, these deficiencies are of no practical importance.

D. Mott-type model Martens et al.

Martens et al.\textsuperscript{22} have recently formulated a model for an arbitrary DOS that uses the approach introduced by Mott for hopping in a uniform DOS.\textsuperscript{24} It is assumed that the conductivity, expressed as

$$\sigma = \sigma_0 \exp \left( -2aR^2 - \frac{E^* - E_F}{k_B T} \right),$$

is governed by conductivity-determining hops over a distance $R^*$, from $E_F$ to an energy $E^*$. The prefactor $\sigma_0$ is only a weak (algebraic) function of the temperature. $R^*$ and $E^*$ are obtained from the following criteria.

1. Each site has on average one neighbor site within a radius $R \leq R^*$, and with an energy in the range $[E_F,E^*]$.

2. $R^*$ and $E^*$ are taken such that the conductivity is minimal.

Martens et al. also introduced the option to treat hopping between sites with a finite extension. However, we will not discuss such effects here. A major simplification as compared to the three previous models is that no initial state integration is carried out. It is assumed to be sufficient to consider only hopping from states at the Fermi level.

The first criterion may loosely be interpreted as if it is assumed that each site that participates in the long-range transport process is, on average, connected to only one other site. However, percolation theory shows that more “bonds” are required per site (on average 2.8 in the VM model). One may, therefore, suspect that the same critical remark that we expressed about the Arkhipov model, viz. that it assumes a percolation factor that is too small, also applies to the Martens model. In an attempt to improve the model, we will treat the average number of sites within a sphere with radius $R^*$ and in the range $[E_F,E^*]$ as a free parameter, $B_{M}$. For a Gaussian DOS, straightforward application of the two criteria given above leads to

$$R^* = \left( \frac{3B_M}{2\pi N_i} \left[ \text{erf} \left( \frac{E^*}{\sqrt{2}\sigma_{DOS}} \right) - \text{erf} \left( \frac{E_F}{\sqrt{2}\sigma_{DOS}} \right) \right] \right)^{1/3}$$

and to the transcendental equation

$$\sqrt{\frac{8}{9\pi}} \frac{3B_M}{2\pi} \frac{1}{N_i^{1/3}} \alpha \frac{\exp \left( - \frac{(E^*)^2}{2\sigma_{DOS}^2} \right)}{\left[ \text{erf} \left( \frac{E^*}{\sqrt{2}\sigma_{DOS}} \right) - \text{erf} \left( \frac{E_F}{\sqrt{2}\sigma_{DOS}} \right) \right]^{4/3}} = \delta.$$  

Equation (19) was solved numerically. Apart from the prefactor, which is not discussed in further detail in Ref. 22, the conductivity follows then from Eq. (17). In Secs. IV A we show that, in the Boltzmann regime, this model is equivalent to the model developed earlier by Baranovskii and co-workers.\textsuperscript{14}

E. Roichman-Tessler (RT) model

Roichman and Tessler recently proposed to explain the observed dependence of the mobility on the carrier concentration from a model that applies a “mean medium approximation” (MMA).\textsuperscript{18} In the actual system that is considered, the energy at each site has a specific value, taken randomly from the DOS. However, within the MMA each site accommodates effectively the full Gaussian distribution of energy levels. The medium is thus regarded as homogeneous, and there are no bottleneck regions. Each possible hop contributes to the current density with a weight (a “velocity”) that is equal to the component of the resulting displacement parallel
to the field, multiplied by the Miller-Abrahams hopping rate. The average carrier velocity \( v_{av} \) is obtained by integration over all initial state and final state energies, with weights that are equal to the probability distribution function of initial state energies (the DOOS) and the probability distribution function of final state energies. The current density is then equal to \( J=n_e v_{av} \), with \( n \) the carrier density. All hops, upward and downward, contribute.

As shown by the authors, the field dependence of the mobility can be straightforwardly included in this model. However, we focus here on the zero-field limit, for which the mobility is given by

\[
\mu = \frac{N_e \, e \, v_0}{\alpha^2 \, k_B T} \times \int_{-\infty}^{\infty} \int_{-\infty}^{E} dE \, dE' \, g'(E) g'(E') f(E) [1 - f(E')] \exp \left( -\frac{E' - E}{k_B T} \right),
\]

(20)

where \( g'(E) = g(E)/N_e \) and \( f(E) \) is the Fermi-Dirac distribution function.

The use of the MMA yields predictions that are quite different from those obtained from the other four models. For a Gaussian DOS, the MMA predicts a temperature dependence of the mobility that is much smaller than predicted from the four other semianalytical models, as shown in Sec. IV. Important discrepancies are also found for other shapes of the DOS. We show in Appendix B that the conductivity for a system with a uniform DOS is predicted to increase linearly with \( T \), instead of being given by the Mott expression [Eq. (B1)]. We have also considered the case of an exponential DOS, of the form \([1/(k_B T_0)] \exp[E/(k_B T_0)]\) for \( E \leq 0 \), with \( k_B T_0 \) the width of the DOS. For \( T \ll T_0 \), the MMA yields a quadratic carrier concentration dependence of the conductivity, \( \sigma \propto c^2 \). However, the more sophisticated VM model \(^{20} \) yields \( \sigma \propto c^2 \), with \( p = T_0/T \).

IV. THE MOBILITY IN THE ZERO-CONCENTRATION LIMIT

A. Analytical expressions for the mobility

As mentioned in the Introduction, the first studies of the mobility in the zero-concentration limit were performed by Bässler. \(^7 \) For the specific parameter value \( N_e^{1/3}/\alpha = 0.1 \), he found that the temperature dependence of the mobility could be well described by an expression of the form \( \mu/\mu_{av} \propto \exp(-4/9) \). This result has been rationalized \(^{32} \) within a picture of the hopping conduction where the hops that most effectively determine the mobility are hops from the average thermal equilibrium energy level, \( E_0 = -\sigma_{DOS}^2/(k_B T) \), to a “transport energy level,” situated at \( E_t = -(5/9) \sigma_{DOS}^2/(k_B T) \). Baranovskii and co-workers \(^{14} \) showed that the transport level concept is indeed valid for hopping in a Gaussian DOS, in the sense that it is the final state energy to which the rate of hopping from any (deep) initial state energy is maximal. The hopping rate to higher states is smaller as a result of the higher thermal activation barrier in the expression of the Miller-Abrahams hopping rate, and the hopping rate to lower states is smaller as a result of the smaller density of final states. However, the authors showed that the actual transport level energy depends on the density of sites, and that its value is not simply proportional to \( \sigma_{DOS}^2/(k_B T) \).

Based on the transport energy level concept, Baranovskii and co-workers developed a semianalytical model for hopping in a Gaussian DOS within which the average hopping distance to a state at the transport level, \( R(E_t) \), was assumed to be given by the radius of a sphere within which there is on average one state present with an energy less than \( E_t \). \(^{14} \) Recently, the model was improved \(^{15} \) by extending the hopping volume by a factor \( B_B \). As suggested by percolation theory, the authors used \( B_B = 2.7 \). Up to this point, the Baranovskii model is mathematically equivalent to the extended version of the Martens model (Sec. III D), with \( B_M = B_B \), and for the case \( E_t = -\infty \). It applies, therefore, only to the zero-concentration limit. \( E_t \) is equal to the quantity \( E^* \) that follows from Eq. (19), and \( R(E_t) \) is equal to the quantity \( R^* \) given by Eq. (18). We remark that the authors do not consider the model assumptions to be justified for relatively high site densities or temperatures (see Ref. 15). In practice, this severely restricts the formal range of validity. \(^33 \)

With respect to the actual expression assumed for the mobility, the Baranovskii model is seemingly quite different from the Martens model. Within the latter model, the mobility is assumed to be proportional to the rate of a single critical hop, from the Fermi energy to the transport level [Eq. (17)], leading in the limit \( c \to 0 \) to

\[
\mu(0) = \frac{\sigma_0}{N_e} \exp \left( -2a R^* - \frac{E^*}{k_B T} - \frac{1}{2} \sigma_{DOS}^2 \right).
\]

(21)

We have derived this expression by using that the carrier concentration is then given by \( c = \exp(E_f/(k_B T) + \sigma_{DOS}^2/2) \). \( R^* \) is given by Eq. (18) with \( E_f = -\infty \). Within the Baranovskii model, the effective hopping rate is written as the inverse of the average waiting time for hops from all states below \( E_t \) to the transport level. Although this is a more complicated approach, the resulting expression for the mobility has a form that is quite similar to Eq. (21), \(^{15} \) viz.
The function \( \Psi \), which is of the order 1, is only weakly temperature dependent. The temperature dependence of \( \mu \) is therefore mostly determined by the exponential factor. As emphasized by Baranovskii et al.,\textsuperscript{14} Eq. (22) shows that the temperature and site density dependences of the mobility can, in general, not be factorized, because of the dependence of \( E_i \) and \( R(E_i) \) on the temperature and the site density. Our results from the other models, given below, support this conclusion.

Unfortunately, Eqs. (21) and (22) do not provide transparent expressions for the temperature dependence of the exponential factors, as a function of the reduced site density. However, such a useful result can be obtained from the VM model. In Appendix C, we show that the mobility is well approximated by

\[
\mu(0) \approx \frac{e v_0}{k_B T} R(E_i)^3 \Psi(E_i/\sigma, \delta) \exp\left( -2a R(E_i) \frac{E_i}{k_B T} - \frac{1}{2} \delta^2 \right).
\]  

(22)

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\[
\mu(0) \approx \frac{\sigma_0}{N_e} \exp\left[ -p_0 - a \delta - b \delta^2 \right],
\]

(23)

with

\[
p_0 = \left( \frac{6B_{VM} a^3 \alpha^3}{\pi N_i} \right)^{1/3},
\]

(24a)

\[
b = \left( \frac{1}{2} - \frac{d}{p_0} \right),
\]

(24b)

\( a=0.566 \) and \( d=0.680 \), provided that \( \delta \ll p_0 \). The mobility is then due to nearest neighbor hopping.\textsuperscript{34} As discussed earlier, realistic parameter values for conjugated polymers, such as PPVs, are \( \sigma_{DOS} \approx 0.1 \text{ eV} \) and \( N_i^{1/3}/\alpha=0.1 \). Equation (24) yields then \( p_0=17.5 \), so that \( \delta=0.2p_0 \) at room temperature. Equation (23) is thus valid under such conditions. Equation (23) shows that the temperature dependence and the site density dependence can only be factorized if the site density is sufficiently small, so that \( b/p_0 \ll 1 \). In that case, the mobility is proportional to \( \exp(-\alpha \sigma \lambda_m) \), where \( \lambda_m=N_i^{1/3} \) is the average inter-site distance and \( \alpha=1.748 \) for \( R=2.8 \). The prefactor of the quadratic term under the exponent is then equal to \( \frac{2}{3} \). For the typical example given above, the prefactor is slightly smaller, viz. \( 0.661 \).

The prefactor \( \sigma_0 \) in Eq. (8) for the conductivity in the VM model is not specified. Within the resistor network model, on which the VM model is based, the conductance between sites \( i \) and \( j \) depends on \( G_{ij}=G_0 \exp(-\gamma_{ij}) \), with \( G_0=e^2 v_0/(k_B T) \) (see Sec. III B). If we view the network as a cubic grid with an inter-site spacing \( N_i^{1/3} \), and if the exponential factor would be equal for all pairs \( (i,j) \), the conductivity of the network would be given by a prefactor of the order \( \sigma_0=e^2 v_0 N_i^{1/3} / (k_B T) \) times the exponential factor. We regard this as a first estimate of the prefactor, but emphasize its approximate character. The actual expression for \( \sigma_0 \) will, e.g., certainly contain the percolation factor \( B_{VM} \). The mobility is then given by

\[
\mu(0) \approx \frac{e v_0}{N_i^{2/3} k_B T} \exp(-p_0 - a \delta - b \delta^2).
\]  

(25)

The prefactor is, within a factor of order 1, equal to the prefactor given by Eq. (22) for the Baranovskii model.

B. Results from the semianalytical and numerical models

In order to facilitate making a comparison between the results from the various models that we have considered, we first represent the results of the calculations in a form that is analogous to Eq. (25), viz. as a product of a prefactor times a dimensionless exponential factor, \( \mu_{\text{red}}(0) \) (reduced mobility). The definitions of the prefactors are given in Table I. Assuming values for \( a_0 \) as estimated in the previous subsection, and taking into account that in the parameter range that we focus on, the mobility is due to nearest neighbor hopping (see Appendix C), all prefactors are equal within a factor of the order 1. The expressions for \( \mu_{\text{red}}(0) \) in the Martens and Baranovskii models are fully equivalent. We present the results using the term “MB model.” As in Eq. (23), the reduced mobilities in the limit \( \sigma_{DOS} \rightarrow \infty \) can be expressed in the form \( \mu_{\text{red}}=\exp(-p_0^*) \), with \( p_0^* \) analogous to the expression given in Eq. (24a) for the case of the VM model. These expressions for \( p_0^* \) are included in Table I.

The deviating expression for \( p_0^* \) for the RT model shows that the physics contained in the model is quite different from that contained in the other models. The same conclusion was also drawn in Appendix B from the analysis of the case of a uniform DOS. The mobility is linearly, instead of exponentially, dependent on the site density, so that this dependence is too weak for small site densities. Furthermore, the RT model predicts that in the limit of large \( \delta \) the mobility is given by

\[
\mu(0) \approx \frac{\pi N_i^{2/3} e v_0}{\alpha^2 \sigma_{DOS}} \exp\left( -\frac{1}{2} \delta^2 \right).
\]  

(26)

The temperature dependence is also much weaker than as predicted from the other models, for which the temperature dependence is more close to \( \exp(-\frac{1}{2} \delta^2) \) (see below).

The expressions for \( p_0^* \) that are given in Table I for the other models show that the role of the percolation coefficients, \( B_{\text{MS}}, B_{\text{VM}}, B_{\text{AK}}, \) and \( B_{\text{MB}} \), is to effectively reduce the density of sites. In order to make a fair comparison between the results obtained from the semianalytical models, one approach would be to make use of percolation constants that lead to equal values of \( p_0^* \). Alternatively, one could, e.g., choose the percolation constants such that for hopping in a uniform DOS the characteristic temperatures \( T_1 \) [Eq. (B2)] are equal. A comparison between Tables I and III (expressions for \( \xi \)) shows that equal percolation constants will result in different values for \( T_1 \) for the models considered. This makes it clear that the various models are different in nontrivial ways. The parameter regime in which we are most interested (intermediate temperatures, typically \( 2<\delta<6 \)) lies in between both extremes. In this paper we adopt a mixed approach. We take \( B_{\text{MS}}=B_{\text{VM}}=2.8 \), the percolation parameter used in the VM model, leading to equal values of \( p_0^* \) for the MS and VM models. Furthermore, we take \( B_{\text{MB}} \)
TABLE I. (Implicit) definitions of the reduced mobility, used in Fig. 4, and analytical expressions for the quantity $p_0^*$ defined in the text. The numerical Master Equation results obtained by Pasveer et al. (Ref. 16) do not yield an analytical expression for $p_0^*$.

<table>
<thead>
<tr>
<th>Model</th>
<th>Definition of $\mu_{\text{red}}$</th>
<th>$p_0^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS model</td>
<td>$\mu = \frac{eV_0}{k_B T} \frac{R^2}{6a_p} \mu_{\text{red}}$</td>
<td>$\left( \frac{6}{\pi a_p N_t} \right)^{1/3}$</td>
</tr>
<tr>
<td>VM model</td>
<td>$\mu = \frac{\sigma_0}{N_t} \mu_{\text{red}}$</td>
<td>$\left( \frac{6B_{\text{VB}} \alpha^3}{\pi N_t} \right)^{1/3}$</td>
</tr>
<tr>
<td>Arkhipov model$^a$</td>
<td>$\mu = \frac{eV_0}{k_B T} (R^2) \mu_{\text{red}}$</td>
<td>$\Gamma \left( \frac{4}{3} \right) \left( \frac{6B_{\text{MB}} \alpha^3}{\pi N_t} \right)^{1/3}$</td>
</tr>
<tr>
<td>Martens model</td>
<td>$\mu = \frac{\alpha_0}{N_t} \mu_{\text{red}}$</td>
<td>$\frac{6B_{\text{MB}} \alpha^3}{\pi N_t}^{1/3}$</td>
</tr>
<tr>
<td>Baranovskii model</td>
<td>$\mu = \frac{eV_0}{k_B T} R(E_1)^2 \Psi \mu_{\text{red}}$</td>
<td>$\frac{6B_{\text{MB}} \alpha^3}{\pi N_t}^{1/3}$</td>
</tr>
<tr>
<td>RT model</td>
<td>$\mu = \frac{eV_0}{N_t^{1/2} k_B T} \mu_{\text{red}}$</td>
<td>$\ln \left( \frac{\alpha}{\pi N_t} \right)^{5/3}$</td>
</tr>
<tr>
<td>Master Equation approach (Ref. 16)$^b$</td>
<td>$\mu = \frac{eV_0}{k_B T} \lambda^2 \mu_{\text{red}}$</td>
<td>—</td>
</tr>
</tbody>
</table>

$^a$ $\Gamma(4/3) \approx 0.893$. Here $\Gamma$ is the Euler gamma function.

$^b$ The parameter $\lambda$ is the inter site distance in the simple cubic lattice used.

= 1.96875, leading to a value of $T_{1}$ equal to that for the VM model. The latter choice was made somewhat ad hoc. As will be shown below, it leads $\mu_{\text{red}}(\tilde{\delta})$ to a fair agreement with the other models. In its original form, the Arkhipov model does not contain a percolation factor ($B_{\text{Ark}} = 1$). A comparison with the predicted mobilities from that model, which are too large, will enable us to judge the effect of the percolation factor.

For all semianalytical models, we have calculated $\mu_{\text{red}}$ for the reduced site densities $N_t/\alpha^3 = 10^{-2}, 10^{-3},$ and $10^{-4}$, and for the range $2 < \tilde{\delta} < 6$. We regard these parameter ranges as representative for PPV-type polymers in polymer LED devices, studied around room temperature. For the case $N_t/\alpha^3 = 10^{-3}$, $\mu_{\text{red}}$ has also been calculated using the modified Arkhipov model, with $B_{\text{Ark}} = 2.8/\Gamma(4/3)^{1/3} = 3.933$. This percolation factor leads to the same value of $p_0^*$ as the percolation factor used for the MS and VM models. For each reduced site density, we have made a least squares fit to an expression of the form of $\mu_{\text{red}}(\tilde{\delta})$ given by the exponential factor in Eq. (23). The same procedure has been followed for the numerical results presented by Pasveer et al. for the reduced density $N_t/\alpha^3 = 10^{-3}$. In the $\tilde{\delta}$ range considered, the fitted to the numerical results was in all cases excellent. Table II gives the fit parameters $p_0, a,$ and $b$. For the VM model, the table also includes the parameter values that are predicted for the high temperature and low site density limit by Eqs. (23) and (24). As expected, the agreement is excellent, except for the highest site density considered.

The data for the MS, VM, and MB models consistently show an increase of $b$ with decreasing reduced site density, with values ranging from about 0.4 to 0.5 when $N_t/\alpha^3$ is increased from $10^{-2}$ to $10^{-4}$. Qualitatively, this is expected from Eq. (24b). For the original Arkhipov model $p_0^*$ is much smaller than for the MS, VM, and MB models, because the percolation factor is effectively equal to 1. The parameter $a$ is only for the VM model quite constant in the density range considered.

In Fig. 4, $\ln(\mu_{\text{red}})$ is given for all models for the case $N_t/\alpha^3 = 10^{-3}$. In the $\tilde{\delta}$ range considered, the reduced mobilities $\mu_{\text{red}}$ as obtained from the MS, VM, modified Arkhipov, MB models, and from the Master Equation approach (Pasveer et al.) coincide within a factor of about 10. A better agreement should not be expected, as the prefactors are only equal within one order of magnitude. Furthermore, one should keep in mind that for the Arkhipov and MB models one could view the percolation parameters that are used to a certain extent as free parameters that can be varied in order to improve the agreement. We conclude, from this point of view, that the models that have been considered are essentially equivalent. In particular, the figure demonstrates that our introduction of percolation constants in the expressions for the mobility used within the Martens and Arkhipov models has indeed successfully corrected the original models. The curve that has been calculated from the original Arkhipov model, using $B_{\text{Ark}} = 1$, shows that the error to be corrected for is (in the example given) about three orders of magnitude in the mobility. More importantly, the correction leads to a higher (more negative) slope of the curves [as is expected from Eqs. (23) and (24)].
TABLE II. Results of calculations of the mobility in the low-concentration limit, for three values of the reduced site density \(N_t/\alpha^3\), calculated within various models. The reduced mobility \(\mu_{\text{red}}(0)\) is for each model defined in Table I; \(\mu_{\text{red}}(0) = \hat{s}\mu_{\text{red}}(0)\). The parameters \(p_0, a, b, p_0', a\) and \(b\) are obtained from a fit of the numerical data in the range \(2 < \hat{s} < 6\). Within parentheses, the parameters as obtained from Eq. (24) are given.

<table>
<thead>
<tr>
<th>Model</th>
<th>(N_t/\alpha^3)</th>
<th>Parameter values defining (\mu_{\text{red}}(0))</th>
<th>Parameter values defining (\mu_{\text{red}}'(0))</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS model</td>
<td>(10^{-2})</td>
<td>(p_0) 0.85 0.292 0.408</td>
<td>(p_0) 7.84 0.411</td>
</tr>
<tr>
<td></td>
<td>(10^{-3})</td>
<td>(a) 0.457 0.439</td>
<td>(a) 15.74 0.463</td>
</tr>
<tr>
<td></td>
<td>(10^{-4})</td>
<td>(b) 0.515 0.466</td>
<td>(b) 37.84 0.497</td>
</tr>
<tr>
<td>VM model</td>
<td>(10^{-2})</td>
<td>(p_0) 8.03 (8.11) 0.631 (0.566) 0.405 (0.416)</td>
<td>(p_0) 8.43 0.450</td>
</tr>
<tr>
<td></td>
<td>(10^{-3})</td>
<td>(a) 17.49 (17.49) 0.563 (0.566) 0.462 (0.461)</td>
<td>(a) 17.76 0.499</td>
</tr>
<tr>
<td></td>
<td>(10^{-4})</td>
<td>(b) 37.67 (37.68) 0.566 (0.566) 0.482 (0.482)</td>
<td>(b) 37.95 0.519</td>
</tr>
<tr>
<td>Arkhipov model ((B_{\text{Ark}}=1))</td>
<td>(10^{-2})</td>
<td>(p_0) 5.19 0.387</td>
<td>(p_0) 5.15 0.362</td>
</tr>
<tr>
<td></td>
<td>(10^{-3})</td>
<td>(a) 11.11 0.441</td>
<td>(a) 11.17 0.415</td>
</tr>
<tr>
<td></td>
<td>(10^{-4})</td>
<td>(b) 23.89 0.434</td>
<td>(b) 23.94 0.451</td>
</tr>
<tr>
<td>Modified Arkhipov model ((B_{\text{Ark}}=3.933))</td>
<td>(10^{-3})</td>
<td>(p_0) 17.67 0.348</td>
<td>(p_0) 17.56 0.438</td>
</tr>
<tr>
<td>MB model</td>
<td>(10^{-2})</td>
<td>(a) 8.43 0.574 0.372</td>
<td>(a) 8.73 0.410</td>
</tr>
<tr>
<td></td>
<td>(10^{-3})</td>
<td>(b) 16.51 1.201 0.384</td>
<td>(b) 17.94 0.499</td>
</tr>
<tr>
<td></td>
<td>(10^{-4})</td>
<td>(c) 34.29 1.679 0.403</td>
<td>(c) 36.57 0.576</td>
</tr>
<tr>
<td>RT model</td>
<td>(10^{-2})</td>
<td>(p_0) 6.24 0.377 0.230</td>
<td>(p_0) 6.19 0.244</td>
</tr>
<tr>
<td></td>
<td>(10^{-3})</td>
<td>(a) 11.24 0.377 0.230</td>
<td>(a) 11.19 0.244</td>
</tr>
<tr>
<td></td>
<td>(10^{-4})</td>
<td>(b) 15.08 0.377 0.230</td>
<td>(b) 15.03 0.244</td>
</tr>
<tr>
<td>Master Equation approach</td>
<td>(10^{-3})</td>
<td>(p_0) 19.85 0.562 0.383</td>
<td>(p_0) 20.13 0.420</td>
</tr>
</tbody>
</table>

temperature-dependent factors in the prefactor, the full temperature dependence of the mobility is given by the quantity \(\mu_{\text{red}}(0) = \hat{s}\mu_{\text{red}}(0)\). In Fig. 5, \(\ln(\mu_{\text{red}}'(0))\) is given as a function of \(\hat{s}\), for three values of \(N_t/\alpha^3\), as obtained from various models. From Eq. (25), we see that \(\mu(0) = \mu_{\text{red}}(0) = c_{\text{red}} = c_{\text{red}}(0)\), with \(\lambda_{\text{av}} = N_t^{-1/3}\) the average intersite distance. We find that, in the parameter range studied, our data can be described excellently by expressions of the form

\[
\mu_{\text{red}}(0) = \exp(-p_0' - b'\hat{s}^2),
\]

with values of the parameters \(p_0', a\) and \(b\) as given in Table II. In order to derive the width of the DOS from a measurement of the temperature dependence of the mobility in the limit of very low concentrations, one thus needs \(b'\). The table shows that the difference between \(b\) and \(b'\) is, as expected, usually quite small. Only for the MB model, for which \(b\) becomes high for small site densities, \(b'\) is much larger than \(b\).

C. Discussion

We first discuss the temperature dependence of \(\mu_{\text{red}}(0)\), characterized by the parameter \(b'\). Just like \(b\), it depends weakly on the site density. For the specific case \(N_t/\alpha^3 = 10^{-3}\), which is representative for organic semiconductors, we find \(0.44 < b' < 0.50\) for the various semianalytical models considered. The result obtained from the RT model is excluded. The value \(b' = 4/9 = 0.444\), obtained by Bässler from Monte Carlo calculations (see Sec. IV A), falls near the bottom of this interval. The value \(b' = 0.42\), obtained from the Master Equation approach, is even somewhat below the lower boundary. We discuss three issues that affect \(b'\), and contribute to its dependence on the model used.

Firstly, the prefactor in expressions of \(\mu_{\text{red}}(0)\) is not only due to a temperature dependence of the average hopping distance \(\langle R^2 \rangle\). In order to investigate this, we have evaluated within the Martens model the characteristic hopping distance \(\langle R^2 \rangle\), as a function of \(\hat{s}\). As shown in Fig. 6, \(\langle R^2 \rangle = 10^{-3}\), and smaller, \(\hat{s}\) remains close to \(\lambda_{\text{av}}\), so that the conduction remains in the nearest neighbor hopping regime. If it is assumed that the temperature dependence of the factor \(\langle R^2 \rangle\) in the mobility prefactor is roughly proportional to \(\langle R^2 \rangle^2\), \(b'\) decreases for \(N_t/\alpha^3 = 10^{-3}\) from 0.499 to 0.488 (about 2%). The correction is thus quite small. For larger (smaller) reduced site densities the correction will be larger (smaller).

Secondly, the relatively small value of \(b'\), as obtained from the numerical models, might be related to the use in these models of an ordered lattice of sites. At low temperatures, when a typical “critical” hop distance is well above the
average intersite distance, the difference with continuum models is expected to be small. However, at very high temperatures, the critical hop distance can in a discrete lattice model not be smaller than the lattice spacing. In contrast, in a continuum model it may then be smaller than the average intersite distance. Figure 6 shows that such a situation is indeed found for the Martens model. Furthermore, Fig. 4 shows that, indeed, the difference between the reduced mobilities as obtained from the semianalytical models and the Master Equation approach is largest at small \( \sigma_{DOS}/(k_B T) \). The difference is already quite small around \( \sigma_{DOS}/(k_B T) = 10^{-3} \), larger than the average intersite distance. These observations thus provide some support from the point of view that for small \( \sigma_{DOS}/(k_B T) \) the numerical calculations cannot be used as a perfect benchmark for the semianalytical calculations. However, at present we cannot make a quantitative estimate of the effect. We remark that the assumption of hopping in a system with a spatially random site distribution neglects the occurrence of a lower limit in the intersite distance. In this sense, the assumption of hopping on an ordered lattice is somewhat more physical.

A third, more fundamental issue is the suitability of the semianalytical models. It is not a priori clear how accurate the predictions from each model will be. Each model can, in principle, be applied to any shape of the DOS. However, it is presently not clear which model is most suitable for the specific case of a Gaussian DOS. In Appendix B, we have made a comparison between the various models for the case of a uniform DOS. At low temperatures, variable range hopping is then found, instead of nearest neighbor hopping. Therefore, ordering of sites on a lattice, assumed in the numerical models, is then expected to be of negligible influence. All semianalytical models lead to an identical temperature dependence of the hopping mobility, viz. the Mott expression \( \mu \propto \exp[-(T_1/T)^{1/4}] \), but the characteristic temperatures \( T_1 \) are generally different. Furthermore, for all models considered \( T_1 \) is significantly different from the value obtained from the Master Equation solution obtained by Pasveer et al. In principle, the percolation parameters could have been chosen such that all semianalytical models would yield equal values for \( T_1 \) as obtained from the Master Equation approach. However, that would have led to an even larger range of \( b' \) values for the case of a Gaussian DOS. We thus conclude that a good quantitative agreement between all models for one particular DOS does not guarantee a good agreement.
for a different DOS. For all semianalytical models a more extensive comparison with numerical predictions should be carried out, for various densities of states, to clarify their limitations.

Making an assessment of the accuracy of the predicted values for \( \mu(0) \), by making a comparison with experimental results, is hampered by the uncertainty of the effective attempt frequency \( v_0 \) in the pre-exponential factor and of the effective wave-function decay length. For PPV-based polymers such as used in LEDs, \( \sigma_{\text{DOS}} \approx 0.1 \) eV, \( \delta \approx 4 \) (room temperature), and the average inter-site distance is \( N^{-1/3}_c \approx 1.5 \text{ nm} \). Assuming a wave-function decay length \( \alpha^{-1} = 0.32 \text{ nm} \) (\( N_c/\alpha^3 = 10^{-2} \)) and taking \( v_0 = 10^{13} \text{ s}^{-1} \) (a typical phonon frequency) would lead to \( \mu(0) \approx 1.5 \times 10^{-10} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1} \). This is the experimentally observed order of magnitude of the mobility.\(^5\) However, there is presently no strong physical basis for the choice made above for \( \alpha^{-1} \) and \( v_0 \). Moreover, at least for polymers the actual situation is, of course, more complex than assumed within the model, e.g., due to the separate contributions from intrachain and interchain hopping.

V. CARRIER CONCENTRATION DEPENDENCE OF THE MOBILITY

A. Results and analysis

Figures 7(a) and 7(b) show the dependence of the reduced mobility, \( \mu_{\text{red}} \), on the carrier concentration \( c \), as calculated from the various semianalytical models that we have considered for the case \( N_c/\alpha^3 = 10^{-3} \). A comparison is given with the numerical results obtained by Pasveer et al.\(^{16}\) We have displayed the results obtained from the Roichman-Tessler (RT) model separately for reasons of clarity. We use here a log scale, instead of an ln scale, in order to facilitate making a fast comparison with experimental results such as given in Fig. 1. For clarity, we have normalized the calculated mobilities to those calculated in the low-concentration limit for the case \( \delta = 2 \). At all carrier concentrations, the RT model predicts a much smaller temperature dependence of the mobility than the other models. For concentrations below about \( 10^{-2} \), the four semianalytical models for which Fig. 7(a) gives the results yield quite similar concentration dependences of the mobility. Moreover, the curves from these models are then highly consistent with the Master Equation results obtained by Pasveer et al.\(^{16}\) This is a key result of our work.

As anticipated already in Sec. II, the carrier concentration above which the concentration dependence of the mobility becomes appreciable decreases with increasing \( \delta \). Equation (3) gives the concentrations at which the mobility is equal to two times the low-concentration mobility. These crossover points are indicated in Fig. 7(a) by vertical dashed lines. On a double-logarithmic scale, the slope of the mobility versus concentration initially increases with increasing concentration, until an inflection point and for most models a maximum is obtained above \( c = 0.01 \) or higher. For this very high concentration region, the predictions from the various models are different, as discussed further below.

Figure 8 shows that the carrier concentration dependence of the mobility [expressed in terms of the enhancement factor \( \mu_{\text{red}}(c)/\mu_{\text{red}}(0) \)] is essentially independent from the ratio \( N_c/\alpha^3 \), for concentrations below approximately 0.01. Although the figure only gives results for the Martens model, the same conclusion is obtained for the other models. This also implies that, for these concentrations, the carrier concentration dependence is not affected by the percolation factor used.

FIG. 7. Carrier concentration dependence of the reduced mobility, \( \mu_{\text{red}}(c) \), for \( \delta = 2, 4, \) and 6, with respect to \( \mu_{\text{red}}(c, \delta = 2) \). (a) Results obtained from the Movaghar-Schirmacher (MS), Vissenberg-Matters (VM), Martens, modified Arkhipov models, and Pasveer models, for \( N_c/\alpha^3 = 10^{-3} \). The vertical dashed lines indicate the concentrations at which the mobility is equal to two times the mobility in the \( c = 0 \) limit, as given by Eq. (3); (b) Results obtained from the Roichman-Tessler (RT) model and the Pasveer model, for \( N_c/\alpha^3 = 10^{-3} \). The RT* curves (dotted line) have been obtained while neglecting final state effects (see text).
We now turn to the simplest model included, the Martens model, to explain these findings. Within that model, the conductivity is determined by critical hops from $E_F$ to an energy $E^*$ and over a distance $R^*$. Such hops may be considered as the most difficult, but still relevant hops. $E^*$ and $R^*$ are such that there are within a radius $R^*$ around each site on average $B_M$ sites with an energy in the range $(E^* - E_F)$. It was already shown in Fig. 6 that, in the Boltzmann regime, $R^*$ is of the order of the average intersite distance, $\lambda_{av}$. The average number of sites within a radius $R^*$ is then $\approx 4$. This implies that the energy interval $[E_F, E^*]$ is such that is accommodates a fraction $B_M/4$ of all states. In our actual calculations, we have taken $B_M$ close to 2, so that the energy interval $[E_F, E^*]$ accommodates approximately half of all states. For very small concentrations, for which $|E_F| \gg \sigma_{DOS}$, $E^*$ will then be located near the top of the Gaussian DOS. This situation is shown schematically in Fig. 9. Let us now consider the effect of an increase of $E_F$, i.e., of the carrier concentration. As long as $E_F$ is located in the tail of the DOS, even a substantial increase of $E_F$ will only have a very small effect on $E^*$. This is due to the very large ratio $g(E^*)/g(E_F)$ between the densities of states at $E^*$ and $E_F$. Also $R^*$ will then remain essentially the same. From Eq. (17), it follows that the conductivity is then proportional to $\exp(E_F/k_BT)$, so that $\mu_{\text{red}}(c) = \gamma \exp(E_F/k_BT)/c$, with $\gamma$ a proportionality constant. Using Eq. (A2), we have $\mu_{\text{red}}(0) = \gamma \exp(-1/2s^2)$. The concentration dependence of the mobility is thus given by

$$
\frac{\mu(c)}{\mu(0)} = 1 - e^{-c\exp\left(\frac{E_F(c)}{k_BT} + \frac{1}{2s^2}\right)}.
$$

(28)

This expression is valid when the Fermi level is located in the tail of the DOS, so that the ratio $g(E^*)/g(E_F)$ is much larger than 1. The use of Eq. (28), together with Eq. (3), provides an alternative route for proving Eq. (2), which states that at $E_F = E_0$ the mobility is enhanced by a factor of 2. The full lines in Fig. 8, which represent Eq. (28), show that the approximation is excellent up to concentrations around 0.01. Equation (28) explains thus why the enhancement of the mobility is then independent of the ratio $N_f/\alpha^3$ and of the detailed value of the percolation factor used. The result is very general, as could have been anticipated already from its derivation. It is based on the general notion that there are “critical” hops. This is, in different ways, also the basis for the Movaghar-Schirmacher, Vissenberg-Matters, and Arkhipov models. All models will therefore yield essentially the same carrier concentration dependence of the mobility for concentrations that are sufficiently small, as is confirmed by Fig. 7(a).

For very high concentrations, such that $g(E^*)$ is not anymore much larger than $g(E_F)$, $E^*$ increases significantly with increasing $E_F$, so that the mobility increases less rapidly with increasing $c$. It can even decrease. In this regime, the detailed concentration dependence depends on the ratio $N_f/\alpha^3$ (see Fig. 8) and on the specific model used [see Fig. 7(a)]. The largest final state effect is found for the Martens model. Within that model, final states below $E_F$ are entirely excluded, resulting in an overestimation of final state effects. In contrast, the Arkhipov model neglects final state effects: in Eq. (16) the occupation probability of final states is not taken into account. The MS and VM models predict a reduction of the mobility enhancement that is intermediate between these two extremes. The results from these two latter models are in a fair, although not excellent, agreement with the Master Equation results.

In Fig. 10(a), we show curves of the reduced mobility, $\mu_{\text{red}}$, as a function of $\hat{\epsilon}$, for various values of the carrier concentration and for a fixed reduced site density $N_f/\alpha^3 = 10^{-3}$. The full lines have been calculated using the VM model. The MS, Arkhipov, and Martens models yield results that are basically the same. The dashed line shows $\ln(\mu_{\text{red}})$ as obtained using the VM model for the low-concentration limit, for which $\mu_{\text{red}}$ is well approximated by Eq. (23). For very small carrier concentrations $\mu_{\text{red}}$ varies then approximately quadratically with $\hat{\epsilon}$. However, for sufficiently large carrier concentrations and for sufficiently large $\hat{\epsilon}$, $\ln(\mu_{\text{red}})$ varies to a first approximation linearly with $\hat{\epsilon}$. This can be
In Fig. 10(a), the mobility as expressed by Eq. (29) is given by dotted curves. For almost the entire parameter range covered, Eq. (29) is seen to be an excellent approximation. Only for high carrier concentrations do final state effects lead to a lower mobility than expected from Eq. (29). In Fig. 10(b), a comparison is made between the mobility as a function of $\delta$, as obtained from the full VM model and as given by Eq. (29), for various reduced site densities. A fixed value was taken for the carrier concentration ($c=10^{-6}$). The approximation given by Eq. (29) is excellent, unless the reduced site density is very high. This may be understood from the fact that, as explained in Sec. IV, Eq. (23) has been derived under the condition $\delta/p_0 \ll 1$. For the case $N_s/\alpha^3=0.1$ we have $p_0=3.76$. Figure 10(b) shows that the agreement for this case is still quite good up to $\delta=6$, so that the approximation given by Eq. (29) is better than would be expected.

### B. Full and compact analytical expressions for the mobility

On the basis of these results, we propose the following full expression for the mobility:

$$
\mu(c) \equiv \frac{eV_0}{N_t^{2/3}k_BT} \Phi \times \exp \left[ -p_0 - \ln c - \left( a - \frac{E_F}{\sigma_{\text{DOS}}} \right) \delta + \frac{d}{p_0} \right].
$$

This is the central result, presented in this paper. The prefactor has essentially the form that was given in Table I for the various models considered. $\Phi$ is a dimensionless function of the order 1, which may depend slightly on $c$, $\delta$, and $N_s/\alpha^3$. It takes, e.g., a weak dependence of the average square of the hopping distance into account. $E_F$ depends only on $c$ and $\delta$. The parameters $p_0$, $a$, and $d$ only depend on $N_s/\alpha^3$. The parameter $p_0$ is a number of the order of the ratio of the average intersite distance over the wave-function localization length, multiplied by the cube root of the percolation constant. One may use the result obtained for the VM model [Eq. (24a) for $p_0$, and constant $a$ and $d$], or one may use values as derived from Table II, obtained from a fit to results from the MS, modified Arkhipov, MB models, or from the Master Equation approach. Equation (30) is a good approximation for $c \ll 1$ (otherwise final state effects will lead to a reduction of $\mu$), $\delta \gg 1$ (otherwise the unspecified temperature dependence of $\Phi$ will play a major role), and $\delta \ll p_0$ (otherwise the conduction process is in the “variable range hop-
ping” regime, instead of in the “nearest neighbor hopping” regime).

The use of Eq. (30) in a numerical device model for, e.g., an organic LED or transistor may in practice be hampered by the fact that no exact explicit analytical expression for $E_F$ as a function of $c$ and $\tilde{s}$ is available. It follows from solving the integral equation $\int \frac{dE}{E}(E_{E_F},E,T) = c N_t$, with $\int$ the Fermi-Dirac distribution function. Such a procedure may make practical implementations of Eq. (30) numerically somewhat inefficient. In Appendix D we discuss the accuracy of compact expressions of the form

$$\mu(c) \equiv \mu(0) \exp[u(2c)^{\gamma}],$$

where the exponential factor is an approximation to the enhancement factor given by Eq. (28). The parameters $u$ and $\gamma$ depend only on $\tilde{s}$, and may be chosen such as to optimize the accuracy within a certain $c$ and $\tilde{s}$ range.

C. Discussion

In this subsection we discuss two implications of our results on earlier experimental and theoretical work on the hopping mobility.

We have found that $\ln(\mu_0/\mu_\infty)$ can vary quadratically or linearly with $1/T$, depending on the experimental conditions. This result may help resolve the long-standing controversy concerning the temperature dependence of the mobility, mentioned in the Introduction. Schein et al., e.g., observed for molecularly doped polymers a linear dependence of $\ln(\mu_0/\mu_\infty)$ on $1/T$, with an activation energy of the order 0.5 eV.11 The authors interpreted this by assuming a polaron binding energy of the same order of magnitude. However, whereas Hartree-Fock calculations indeed yield polaron binding energies of the order of a few tenths of an eV, calculations based on density functional theory (DFT) yield values of the order of the order of 10–40 meV for, e.g., PPV or polythiophene, depending on the conjugation length (see Ref. 35 and references therein). On the basis of the DFT results, one may thus conclude that polaron binding energies are much smaller than the energetic disorder (width of the DOS), so that self-trapping effects can be ignored in practice.

Figure 10 shows that a $1/T$ relationship is found if the temperature dependence of the mobility is measured at a fixed and sufficiently high carrier concentration. The effective activation energy, $E_a = [E_F + 0.566 \cdot \alpha_{DOS}]$ (see Sec. VII), would be approximately equal to 0.5 eV for, e.g., $c = 10^{-6}$, $\tilde{s} \approx 5$ (i.e., $\alpha_{DOS} = 0.125$ eV if room temperature experiments are involved) and reduced site densities $N_t/a^2 = 10^{-5}$ or smaller [see Fig. 10(b)]. It is thus possible to explain the $1/T$ dependence within the Gaussian disorder model, using a realistic set of parameters. Furthermore, Schein et al. observed an increase of the activation energy with decreasing dopant concentration, from 0.4 to 0.6 eV, until saturation occurred at low concentrations. Qualitatively, this is precisely the trend that is predicted by Fig. 10(b). It would thus be of great interest to remodel this and other work from the literature within the framework of the Gaussian disorder model, including now the carrier concentration dependence of the mobility.

Our results are valid in the zero-field limit. Pasveer et al.16 have found from the Master Equation approach that the field dependence of the mobility can be expressed rather accurately in terms of a field-dependent multiplication factor, for low and intermediate fields, leading to a successful description of the experimental current density versus voltage curves of PPV-based LEDs. We believe that the combination of our Eq. (30) and Eq. (5) in Ref. 16 provides a very useful compact expression for the mobility up to intermediate fields within the Gaussian disorder model. The field ($F$) dependence of the mobility obtained by Pasveer et al. is quite dissimilar from the Poole-Frenkel factor $\exp[\gamma \sqrt{F}]$, with $\gamma$ an empirical temperature and disorder dependent parameter, used conventionally.57 Novikov et al.37 and Parris et al.38 provided further support for the latter approach by showing that the $\exp[\gamma \sqrt{F}]$ field dependence is obtained over an extended field range if it is assumed that the site energies show a certain degree of spatial correlation. These results were argued to be in good qualitative agreement with experimental findings from time-of-flight measurements (TOF) on molecularly doped polymers (see Ref. 37, and references therein).

Our work suggests that the TOF experiments should be reanalyzed, taking the carrier concentration dependence of the mobility into account. It remains to be seen to what extent an $\exp[\gamma \sqrt{F}]$ factor then still provides an appropriate description of the experimental data. Another motivation of the work by Novikov et al. and Parris et al. was to provide a hopping theory that reconciles theories based on polaronic motion and based on motion in a disordered DOS. However, if the observed $1/T$ behavior can indeed be fully understood as an effect of a carrier concentration dependence of the mobility, as discussed above, the need for a theory based on polaronic transport seems less obvious.

VI. SUMMARY, CONCLUSIONS, AND OUTLOOK

In this paper, we have analyzed the hopping mobility in systems with localized states and Gaussian disorder using various different semi-analytical models, taken from the literature. All models have in common that Miller-Abrahams hopping rates are assumed between pointlike sites. We have shown that the Movaghar-Schirmacher, Vissenberg-Matters, Baranovskii, Martens, and Arkhipov models all essentially contain Mott’s idea that the mobility is determined by certain critical “difficult but still relevant” hops. A second crucial ingredient of hopping theories, taken from percolation theory, is that each site should be “connected” to more than one (B) neighbor site, in order to make long-range transport between otherwise isolated well-conducting clusters possible. Within the Martens and Arkhipov models, this is not taken into account, and the percolation parameter $B$ is effectively set equal to 1. As a result, the predicted mobilities can be many orders of magnitude too large. We have shown that these models can be straightforwardly improved by including a percolation parameter. In the limit of zero concentration, the mobility in a Gaussian DOS is independent of the concentration. A comparison of the results from the (improved) models mentioned above, and a comparison with the numerical results obtained by Pasveer et al., has led to the conclu-
sion that the mobility can be expressed as the product of the mobility in the limit of zero carrier concentration, \( \mu(0) \), times a carrier-concentration dependent enhancement factor. Equation (30), which gives the overall result, is expected to be the basis of efficient numerical modeling of transport processes in, e.g., organic LEDs, FETs, photovoltaic cells, and in devices used for TOF measurements. We have suggested that earlier experimental results concerning the field dependence of the mobility, based on TOF experiments, and earlier theoretical models for the hopping mobility, e.g., based on polaronic transport, should be reconsidered.

From our analyses, we cannot yet express a clear preference for either the Movaghar-Schirmacher, Vissenberg-Matters, Arkhipov, or Martens model, in as far as the precision of the results is concerned. From the point of view of numerical efficiency, the Martens model is highly preferred. The double-energy integrals (over the initial states and final states) which must be evaluated within the other models makes the evaluation of \( \mu \) from these models much slower. However, the relative simplicity of the Martens model raises the question as to what extent its precision is retained outside the parameter range that we have focussed on. We have, e.g., already shown that it overestimates final state effects, so that it underestimates the mobility at very high carrier concentrations.

Future studies should make it clear as to what extent the simple model assumptions that are made within the Gaussian disorder model lead to a sufficiently precise description of the mobility in real organic materials. We emphasize that our focus on a Gaussian DOS does not imply that we feel sure that a Gaussian DOS would in all cases be the most suitable approximation to the real hole or electron DOS in an organic semiconductor. Our prime purpose has been to provide a critical comparison of the mobility for a Gaussian DOS, as obtained from different approaches. More detailed microscopic modeling of the interactions in the disordered systems of interest and more experimental studies of the electronic structure and transport properties are required to better understand the shapes of actual densities of states. We note that the mobility in FETs based on polythiophene or pentacene has been described successfully in terms of a mobility of the form \( \mu(c)=qc^r \), where the prefactor \( q \) and the exponent \( r \) are both dependent on the temperature. This expression follows for an exponential DOS.\(^{21}\) Obviously, the mobility is then not independent of the concentration in the limit of low carrier concentrations. However, it has been found by Tanase et al.\(^{12} \) and Blom et al.\(^ {39} \) that the empirical relationship \( \mu(c) = \mu(c=0,T)+qc^r \) can under certain conditions provide an adequate phenomenological description of the experimental results obtained at a given temperature in LEDs and FETs. We remark that future analyses of the mobilities in FETs, should, for any assumed DOS, consider the possible effect on the effective mobility of the rather extreme carrier density gradient in the accumulation layer.

ACKNOWLEDGMENTS

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APPENDIX A: THE MOBILITY AND CARRIER CONCENTRATION AT THE Crossover ENERGY

In this Appendix we proof Eq. (2), which states that at the crossover between the low and high carrier density regimes, the mobility is (approximately) equal to two times the mobility in the low carrier density limit. For that purpose, we first derive Eq. (3), which gives the carrier density at the crossover energy.

By definition, the crossover point is situated at \( E_F=E_0 = -\sigma_{\text{DOS}}^2/k_BT \). The carrier concentration \( c=n/N_f \) is then (exactly) given by

\[
c(E_F=E_0) = \frac{1}{N_f} \int_{-\infty}^{\infty} \frac{g(E)}{1 + \exp\left( E/k_BT + \frac{\sigma_{\text{DOS}}^2}{k_BT} \right)} dE \\
= \frac{1}{\sqrt{2\pi}\sigma_{\text{DOS}}^2} \int_{-\infty}^{\infty} dE' \exp\left( -\frac{(E')^2}{2\sigma_{\text{DOS}}^2} \right) \frac{1 + \exp\left( E'/k_BT \right)}{1 + \exp(-E'/k_BT)} \\
= \exp\left( -\frac{\sigma_{\text{DOS}}^2}{2(k_BT)^2} \right) \frac{1}{\sqrt{2\pi}\sigma_{\text{DOS}}^2} \int_{-\infty}^{\infty} dE' \exp\left( -\frac{(E')^2}{2\sigma_{\text{DOS}}^2} \right) \frac{1 + \exp(-E'/k_BT)}{1 + \exp(-E'/k_BT)} \\
= \frac{1}{2} \exp\left( -\frac{\sigma_{\text{DOS}}^2}{2(k_BT)^2} \right).
\]

(A1)
which is Eq. (3).

In the Boltzmann regime, for $E_F \ll E_0$, the density of occupied states is such that almost all carriers reside in states that are well above $E_F$. This is, e.g., evident from Fig. 2. We can use Boltzmann statistics instead of Fermi-Dirac statistics, so that the carrier concentration, $c = n/N_c$, is to a good approximation given by

$$
c \equiv \frac{1}{N_c} \int_{-\infty}^{\infty} dE \, g(E) \exp\left(-\frac{E - E_F}{k_B T}\right) = \exp\left(\frac{E_F}{k_B T} + \frac{1}{2} \frac{\sigma^2}{k_B T}\right).
$$

(A2)

Quite generally, the conductivity $\sigma$, can be written as an integral over contributions from carriers that reside at sites with energy $E$. These contributions are proportional to a function $F(E)$ that is equal to the contribution to the current density due to a single carrier at energy $E$ and to the density of occupied states (DOOS) at energy $E$. Using Boltzmann statistics in the expression for the DOOS, using Eqs. (1) and (A2), and defining $F'(E) = F(E)/[(e^\sqrt{2\pi} \alpha)]$, the mobility in the $n=0$ limit is given by

$$
\mu(n=0) = \int_{-\infty}^{\infty} dE \, F'(E) \exp\left(-\frac{E^2}{2 \sigma_{\text{DOOS}}^2}\right) \exp\left(-\frac{E - E_F}{k_B T}\right) \exp\left(\frac{E_F}{k_B T} + \frac{1}{2} \frac{\sigma^2}{k_B T}\right)
$$

$$
= \int_{-\infty}^{\infty} dE \, F'(E) \exp\left[-\frac{1}{2} \left(\frac{E - E_F}{\sigma_{\text{DOOS}} + \delta}\right)^2\right].
$$

(A3)

Within the same formalism, the mobility at the crossover point is given by

$$
\mu(n = E_0) = \int_{-\infty}^{\infty} dE \, F'(E) \exp\left(-\frac{E^2}{2 \sigma_{\text{DOOS}}^2}\right) \left[1 + \exp\left(\frac{E - E_F}{k_B T} + \frac{1}{2} \frac{\sigma^2}{k_B T}\right)\right]^{-1} \frac{1}{2} \exp\left(-\frac{1}{2} \frac{\sigma^2}{k_B T}\right).
$$

(A4)

where we have used the expression for the carrier concentration given by Eq. (3). A very good approximation of the integral in the numerator can be obtained by again using Boltzmann statistics instead of Fermi-Dirac statistics. In this case, that is permitted because the function $F'(E)$ increases very rapidly with increasing $E$ (in the energy range which contributes most). Most carriers are located in the tail of the Gaussian DOS, so that the number of low lying neighbor states to which they can hop is a very steep function of the initial state energy $E$. In view of the fast increase of $F'(E)$ with $E$, the mobility is almost completely due to carriers at energies far above $E_F$. Note that the detailed form of $F'(E)$, which will depend on the specific model used, is here of no importance. We obtain

$$
\mu(n = E_0) = \int_{-\infty}^{\infty} dE \, F'(E) \exp\left(-\frac{E^2}{2 \sigma_{\text{DOOS}}^2}\right) \left[1 + \exp\left(\frac{E - E_F}{k_B T} + \frac{1}{2} \frac{\sigma^2}{k_B T}\right)\right]^{-1} \frac{1}{2} \exp\left(-\frac{1}{2} \frac{\sigma^2}{k_B T}\right).
$$

(A5)

Straightforward rearrangement of the right-hand side of this expression leads, after comparison with Eq. (A3), to Eq. (2). Obviously, the approximation made in Eq. (A5) is only good when the DOS is sufficiently wide. From numerical calculations, using any of the methods discussed in Sec. III, we find that the approximation is excellent for $\delta > 2$.

APPENDIX B: HOPPING CONDUCTIVITY IN A UNIFORM DOS

It is instructive to make a comparison between the predictions, obtained from the various models considered in this paper, for the conductivity of a system with a uniform density of states. As shown first by Mott,24 the conductivity is then due to hopping over a wide range of distances ("variable range hopping"), and is given

$$
\sigma = \sigma_0 \exp\left[-\left(\frac{T_1}{T}\right)^{1/4}\right],
$$

(B1)

where the characteristic temperature $T_1$ can be expressed as

$$
T_1 = \xi \frac{\alpha^3}{k_B C},
$$

(B2)

where $C$ is the DOS and where $\xi$ is a dimensionless prefactor. The semianalytical models discussed in Secs. III A–III D do all correctly yield the Mott-expression, Eq. (B1). The prefactors $\xi$, which are given in Table III, are model-dependent. For each model, $\xi$ is proportional to the percolation factors used within that model. The table gives the percolation factors that are used for obtaining the graphs shown in this paper, and the corresponding numerical values. We include the result that was obtained from a numerical solution of the Master Equation by Pasveer.16

The Roichman-Tessler MMA model does not give rise to the Mott expression. Instead, we find [consistent with Eq. (6.3) in Ref. 23]
TABLE III. Prefactors $\xi$ that determine the Mott-temperature $T_1$ [see Eq. (B2)], for the models considered in this paper. $\Gamma(x)$ is the Euler-gamma function.

<table>
<thead>
<tr>
<th>Model</th>
<th>$\xi$</th>
<th>Percolation factor used in this paper</th>
<th>$\xi$ (numerical value)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Movaghar-Schirmacher (Ref. 20)</td>
<td>$\frac{24B_{MS}}{\pi}$</td>
<td>$B_{MS}=2.8^{a}$</td>
<td>21.39</td>
</tr>
<tr>
<td>Vissenberg-Matters (Ref. 21)</td>
<td>$\frac{40B_{VM}}{\pi}$</td>
<td>$B_{VM}=2.8$</td>
<td>35.65</td>
</tr>
<tr>
<td>Arkhipov (Ref. 17) (modified)</td>
<td>$\frac{24B_{Ark}}{\pi}[\Gamma(5/4)]^4$</td>
<td>$B_{Ark}=3.933$</td>
<td>20.28</td>
</tr>
<tr>
<td>Martens (Ref. 22) (modified)</td>
<td>$\frac{512B_{M}}{9\pi}$</td>
<td>$B_{M}=1.969^c$</td>
<td>35.65</td>
</tr>
<tr>
<td>Pasveer (Ref. 40)</td>
<td>$\frac{\text{C2}}{12}$</td>
<td>$\text{C2}=16.6\pm0.2^d$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$The value given in Ref. 20 is $B_{MS}=\exp(1)=2.718$. The slightly higher value that we use in our calculations leads to expressions for the mobility in the low-concentration limit that coincide with those from the VM model (see Sec. IV).

$b$The Arkhipov and Martens models have been modified to include the percolation factors $B_{Ark}$ and $B_{M}$, respectively (see the main text, Sec. III).

$c$Obtained from a $1/T^{-1/4}$ fit of $\ln(\sigma(T))$ [see Eq. (B1)]. The uncertainty given is the numerical accuracy. As the temperature interval studied was by necessity limited, it cannot be excluded that the systematic error that could arise due to a $T$-dependence of $\sigma_0$ is larger than the numerical accuracy.

$^d$The value given in Ref. 20 is $B_{MS}=\exp(1)=2.718$. The slightly higher value that we use in our calculations leads to expressions for the mobility in the low-concentration limit that coincide with those from the VM model (see Sec. IV).

APPENDIX C: THE MOBILITY IN THE ZERO CONCENTRATION LIMIT WITHIN THE VISSENBERG-MATTERS MODEL

In this Appendix, we derive Eqs. (23) and (24), which give the mobility in the zero concentration limit as obtained for a Gaussian DOS from the Vissenberg-Matters model. The reduced mobility $\mu_{red}(0)$, defined in Table I, can be written as $\exp(-p)$, where $p$ is a function of $\hat{s}$. From Eqs. (8) and (A2), one finds that in the Boltzmann regime, $\ln(\mu_{red})$ is given by

$$\ln \mu_{red}(c) = -s_c - \frac{E_F(c)}{k_BT} - \frac{1}{2} \xi^2 = p.$$  \hspace{1cm}  (C1)

We first calculate $p_0$, which provides us with the reduced mobility in the high-temperature limit $\hat{s} \to 0$. In that limit, all sites contribute to the mobility, so that (within the language of the VM model) $N_b=N_t$. The calculation of the density of bonds, $N_b$, is simplified by noting that in the Boltzmann regime almost all carriers reside in states well above $E_F$. Only energies $E_i$ and $E_j$ in the first quadrant in Fig. 3 contribute to $N_b$, so that from Eq. (12)

$$N_b = \frac{\pi}{2}N_{t}^2 \int_0^{R_0} dR \frac{R^2}{2} \left[ \text{erf} \left( \frac{E_F + (p_0 - 2 \alpha R)k_BT}{\sqrt{2}\sigma_{DOS}} \right) \right. - \left. \text{erf} \left( \frac{E_F}{\sqrt{2}\sigma_{DOS}} \right) \right]^2.$$  \hspace{1cm}  (C2)

In the high-temperature limit the factor containing the error functions approaches a step function, being equal to 0 for $R > R_{max} = p_0 / (2 \alpha)$, and equal to 4 for $R < R_{max}$. The step coincides with the upper integration boundary. Hopping processes over distances larger than $R_{max}$ do not contribute to the conductivity, whereas for smaller intersite distances bonds between states at essentially all energies contribute. Application of Eq. (9) yields then Eq. (24a) for $p_0$, so that the maximum hopping distance, $R_{max}$, is given by

$$R_{max} = \frac{3B_{VM}}{4\pi N_t} \left( \frac{\sqrt{2}\sigma_{DOS}}{k_BT} \right)^{1/3}.$$  \hspace{1cm}  (C3)

Using $B_{VM}=2.8$, we find that $R_{max}=0.874 \times N_t^{-1/3}$, from which it follows that in this low concentration and high temperature limit only nearest neighbor hopping processes contribute to the conductivity.

At finite temperatures and small carrier concentrations all sites contribute to the conductivity as long as

$$p_0 = \frac{E_F + s_0 k_BT}{\sqrt{2}\sigma_{DOS}} = \left[ p + \frac{1}{2} \hat{s}^2 \right] \frac{k_BT}{\sqrt{2}\sigma_{DOS}} \gg 1.$$  \hspace{1cm}  (C4)

From Eq. (10), it follows that then $N_t=1$. The conduction process remains then in the nearest neighbor hopping regime. We will use this result to derive $p$ at finite temperatures and show subsequently that the criterion is fulfilled for $\hat{s}/|p_0| \ll 1$. In Sec. IV A, it is shown that condition (C5) is well obeyed for parameters that are realistic for PPV-type polymers at room temperature. Furthermore, $N_t$ is for sufficiently small concentrations well approximated by only taking initial and final states above $E_F$ into account, so that from Eq. (12)
$N_b \equiv \pi N_t^2 \int_0^{r_v/2a} dR R^2 \left[ \operatorname{erf} \left( \frac{E_F + (s_c - 2aR)k_B T}{\sqrt{2} \sigma_{\text{DOS}}} \right) - \operatorname{erf} \left( \frac{E_F}{\sqrt{2} \sigma_{\text{DOS}}} \right) \right]^2. \quad (C5)

Using that $E_F \ll \sigma_{\text{DOS}}$ for sufficiently small concentrations, Eq. (C5) can be rewritten as

$$N_b \equiv \pi N_t^2 \left( \frac{\sqrt{2} \sigma_{\text{DOS}}}{2a k_B T} \right)^3 \int_0^\infty d\rho \rho^2 (\operatorname{erf}[\rho_0 - \rho] + 1)^2 \equiv \pi N_t^2 \left( \frac{\sqrt{2} \sigma_{\text{DOS}}}{2a k_B T} \right)^3 \left[ \frac{4}{3} \rho_0 - 1.595 \rho_0^2 + 1.798 \rho_0 \right]. \quad (C6)

Taking only the first three terms in the series expansion of the integral is a good approximation if $\rho_0 \gg 1$. Using $N_s=N_t$, as motivated above, the percolation criterion $N_s/N_t=R_c$, leads then straightforwardly to Eqs. (23) and (24).

### APPENDIX D: APPROXIMATE EXPLICIT EXPRESSIONS FOR THE MOBILITY ENHANCEMENT FACTOR

In Sec. V the mobility has been expressed as the product of the mobility in the zero concentration limit, $\mu(0)$, times an enhancement factor, given by Eq. (28). The use of the resulting expression Eq. (30), in the device models is not very efficient, because the Fermi energy is only an implicit function of $\varepsilon$ and $\delta$. In this Appendix we investigate the accuracy of compact models of the form given by Eq. (31), in which the enhancement factor is given as an explicit function of $\varepsilon$ and $\delta$.

The form of the compact model, given by Eq. (31), is suggested by the shape of the full curves in Fig. 8. On a double logarithmic scale, the mobility enhancement factor can be approximated by an exponential function of the carrier concentration:

$$\ln \left( \frac{\mu(c)}{\mu(0)} \right) \cong u \exp[u \ln(2c)] \Rightarrow \frac{\mu(c)}{\mu(0)} = \exp[u(2c)^v]. \quad (D1)$$

Here $u$ and $v$ are parameters that may be chosen such that the resulting expression provides an optimal fit to the full expression for the carrier concentration interval that is of most interest. A first possible choice would be to take $u$ and $v$ such that the model is exact for the concentration for which $E_F = E_0$ (where the mobility enhancement is exactly equal to 2, see Sec. II) and for $E_F=0$ ($c=0.5$, so that from Eq. (28) the mobility enhancement factor is equal to 2 $\exp(\hat{s}^2/2)$). One obtains then

$$u_1 = \frac{1}{2} \hat{s}^2 + \ln 2, \quad (D2)$$

and

$$v_1 = 2 \left( \frac{\ln(\hat{s}^2 + 4) - \ln(4)}{\hat{s}^2} \right). \quad (D3)$$

Figure 11(a) shows the accuracy of the approximation, as a function of the concentration, for $\hat{s}$ varying from 2 to 8. For applications in single layer polymer LEDs, which typically operate at $c=10^{-5}$ to $10^{-3}$, and for PPV-based light emitting polymers, with $\sigma_{\text{DOS}}/(k_B T) \approx 4$ at room temperature, the approximation is excellent. However, for the modeling of FETs, which typically operate at $c=10^{-2}$, the approximation is less accurate, in particular for large $\hat{s}$. The predicted mobility enhancement is too high. We have empirically found that, for the parameter range investigate here, an overall improvement is obtained when taking a lower enhancement factor at $c=0$, equal to $\exp((1/2)(\hat{s}^2-\hat{s}))$, so that

$$u_2 = \frac{1}{2} \hat{s}^2 - \hat{s}, \quad (D4)$$

and

$$v_2 = 2 \left( \frac{\ln(\hat{s}^2 - \hat{s} - \ln(4))}{\hat{s}^2} \right). \quad (D5)$$

It may be seen from Fig. 11(b) that in the concentration range from $10^{-6}$ to $10^{-2}$ and for $2<\hat{s}<6$ the accuracy on a log$_{10}$ scale is better than 0.15 decades. For $c>10^{-2}$ final state effects are expected to give rise to a decrease of the mobility (see Sec. V). To a certain extent, the negative error above $c=10^{-2}$ will take that effect into account, so that the approxi-
mation will actually be somewhat better than as suggested by the figure. Indeed, we have found that this second version of the compact model fits the numerical data obtained by Pasveer et al. \(^{16}\) (2 < δ < 6) within a factor of 2 or better, even for concentrations up to 10\(^{-1}\). For δ = 6, the mobility varies over almost six orders of magnitude with the concentration. On a log\(_{10}\) scale, the accuracy of this model is thus better than \(\approx 5\%\).

10. O. Bleibaum (unpublished).
15. The criterion is that \(E_R\) should be smaller than \(-\sigma_{\text{DOS}}/2.15\). For example, if \(\sigma_{\text{DOS}}/(k_B T) = 3.3(5.0)\), the model is not anymore valid when \(N_R^0/\alpha < 0.3(0.1)\).
16. We remark that the VM model is not valid at high temperatures, because, as remarked in Sec. III B, the most relevant hopping energies should be much larger than \(k_B T\). Therefore, Eq. (25) will not be good for \(\sigma_{\text{DOS}}/(k_B T) \approx 1\).
18. With “intermediate fields” we mean fields around \(F = \sigma_{\text{DOS}}/(e \lambda_{av})\), with \(\lambda_{av}\) the average intersite distance. The electrostatic energy gain for a hop along the field direction is then approximately equal to the width of the DOS.