

# Scaling theory for percolative charge transport in molecular semiconductors: Correlated versus uncorrelated energetic disorder

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We recently introduced a scaling theory for charge transport in molecular semiconductors with uncorrelated Gaussian energetic disorder, considering Miller-Abrahams as well as Marcus hopping and different lattice structures [Cottaar *et al.*, *Phys. Rev. Lett.* **107**, 136601 (2011)]. A compact expression was derived for the dependence of the charge-carrier mobility on temperature and carrier concentration. We show here that for Miller-Abrahams hopping the theory can also be applied to non-Gaussian energetic disorder, without parameter changes. Moreover, we show how it can be applied to correlated energetic disorder as obtained from randomly oriented molecular dipoles, which experiments suggest to be often more suitable. The same compact expression still describes the charge-carrier mobility, with new parameter values as determined from numerically exact results. The critical scaling exponent for correlated disorder is about twice as large as for uncorrelated disorder, which is caused by a different topology of the percolating network. The temperature dependence of the mobility for correlated disorder is significantly weaker than for uncorrelated disorder, while the carrier-concentration dependence is slightly weaker, due to small deviations of the density of states from a Gaussian. We indicate how comparison with experiments could distinguish between the different models.

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## I. INTRODUCTION

Disordered organic molecular semiconductors play an important role in organic electronics, with applications in devices such as organic light-emitting diodes.<sup>1,2</sup> Predictive modeling of devices using these semiconductors requires a thorough understanding of the charge transport, which occurs by thermally assisted tunneling—hopping—of charge carriers between neighboring molecules, which are the transport sites. This transport is characterized by the charge-carrier mobility  $\mu$  (the average velocity of a charge carrier divided by the applied electric field), which depends on the temperature  $T$ , carrier concentration  $c$ , and electric field  $F$ . An important factor determining  $\mu$  is the density of states (DOS), i.e., the distribution of site energies. These energies may be correlated; for example, if the electrostatic potential distribution is caused by randomly oriented dipoles,<sup>3</sup> which we will call “dipole-correlated disorder” for short. It has been shown through experimental current-voltage characteristics that, depending on the material, either uncorrelated or dipole-correlated energetic disorder is more appropriate.<sup>4-6</sup>

For uncorrelated Gaussian energetic disorder and low carrier concentrations, the mobility  $\mu$  was determined numerically by Bäessler<sup>7</sup> using a Monte Carlo (MC) simulation of a single charge carrier on a simple cubic (SC) lattice with Miller-Abrahams (MA) hopping rates.<sup>8</sup> The low carrier-concentration case for dipole-correlated disorder has also been studied using both MC simulation<sup>9,10</sup> and a semianalytic method.<sup>11</sup> It was later realized that the dependence of  $\mu$  on the carrier concentration plays a crucial role.<sup>12,13</sup> This dependence was determined numerically for uncorrelated disorder using a master-equation approach, leading to a parametrization of the mobility function  $\mu(T, c, F)$ , by Pasveer *et al.*<sup>14</sup> An analogous parametrization for dipole-correlated disorder was obtained by Bouhassoune *et al.*<sup>15</sup>

More insight into the transport process has been obtained using percolation theories based on the concept of a single critical bond in the system, from which semianalytical expressions for  $\mu(T, c)$  at  $F = 0$  have been derived.<sup>16-19</sup> However, none of these theories accurately describes the results of numerical simulations. In Ref. 20 we developed a scaling theory based on the concept of fat percolation,<sup>21</sup> which states that not just one but several critical bonds must be taken into account. We have shown that this scaling theory accurately describes  $\mu(T, c)$  for uncorrelated disorder, not only for the SC lattice and MA hopping considered in Ref. 14 but also for a face-centered-cubic (fcc) lattice and Marcus hopping.<sup>22</sup> In the present work, we will extend and apply the scaling theory to densities of states other than the uncorrelated Gaussian one, focusing especially on dipole-correlated energetic disorder. This wide applicability of the scaling theory demonstrates its very general character.

In Sec. II, we describe the hopping transport model and its mapping onto a random-resistor network. In Sec. III, we discuss the scaling theory introduced in Ref. 20. This theory can be used to obtain  $\mu$  from this random-resistor network, leading to an explicit formula for  $\mu(T, c)$ . In Sec. IV we demonstrate that for MA hopping the scaling theory as developed in Ref. 20 can be applied to different DOS types. Moreover, we show and discuss results for the dependence of  $\mu$  on the temperature and carrier concentration for the case of correlated disorder for both MA and Marcus hopping. Finally, Sec. V contains the conclusions and an outlook on the application of our results.

## II. HOPPING TRANSPORT AND THE RANDOM-RESISTOR NETWORK

We consider the mobility of charge carriers with nearest-neighbor hopping between the sites of a lattice having site

density  $N_t$ , which we take to be either SC or fcc. We take periodic boundary conditions. Each site has an energy  $E_i$ , which is the energy of a charge carrier occupying site  $i$ . These site energies can be spatially uncorrelated or correlated. In the uncorrelated case, we take the DOS  $g(E)$  to be Gaussian with standard deviation  $\sigma$ ,  $g(E) = \exp(-E^2/2\sigma^2)/\sqrt{2\pi}\sigma$ . We will later also consider other types of DOS. It has been shown that for uncorrelated energetic disorder moderate positional disorder does not have a strong effect on  $\mu$ , since it is a second-order effect.<sup>7,20</sup> We expect the same to hold for correlated energetic disorder and will therefore not consider positional disorder in the present work.

For correlated energy disorder, we consider an energy landscape generated by placing a randomly oriented dipole  $\mathbf{d}_i$  with fixed magnitude  $d$  at every site  $i$ . The site energies then follow from the electrostatic potential of these dipoles:

$$E_i = - \sum_{j \neq i} \frac{e \mathbf{d}_j \cdot (\mathbf{R}_j - \mathbf{R}_i)}{\varepsilon |\mathbf{R}_j - \mathbf{R}_i|^3}, \quad (1)$$

where  $\varepsilon$  is the electrical permittivity of the material,  $e$  is the elementary charge, and  $\mathbf{R}_i$  is the position of site  $i$ . The minimum image convention is used to take into account the periodic boundary conditions in the calculation of the electrostatic potential. An appropriate choice of  $d$  then yields a DOS that is approximately a Gaussian with standard deviation  $\sigma$  (see the Appendix). There is now a correlation between the energies of two sites, with a correlation function asymptotically decreasing as  $1/R$  with the intersite distance  $R$ .<sup>10</sup>

Carriers can hop from an occupied site  $i$  to an unoccupied neighboring site  $j$ . Any physical rate should satisfy detailed balance and can therefore be written as

$$\omega_{ij} = \omega_{\text{symm}}(|\Delta E_{ij}|) \exp(-\Delta E_{ij}/2k_B T), \quad (2)$$

where  $k_B T$  is the thermal energy and  $\Delta E_{ij} \equiv E_j - E_i - e\mathbf{F} \cdot (\mathbf{R}_j - \mathbf{R}_i)$  is the energy difference between the sites, with  $\mathbf{F}$  the applied electric field. The symmetric part of the hopping rate  $\omega_{\text{symm}}(|\Delta E|)$  determines the type of hopping. For Marcus hopping we have<sup>22</sup>

$$\omega_{\text{symm}}(|\Delta E|) = \omega_0 \exp(-\Delta E^2/4E_r k_B T), \quad (3)$$

where  $E_r$  is the reorganization energy (the energy gain of the atomic arrangement of a molecule adapting to the presence of a charge) and

$$\omega_0 \equiv \frac{J_0^2}{\hbar} \sqrt{\frac{\pi}{E_r k_B T}} \exp(-E_r/4k_B T), \quad (4)$$

with  $J_0$  the transfer integral. For MA hopping we have<sup>8</sup>

$$\omega_{\text{symm}}(|\Delta E|) = \omega_0 \exp(-|\Delta E|/2k_B T), \quad (5)$$

where  $\omega_0$  is now a temperature-independent prefactor. We will give all results for  $\mu$  in units of the prefactor  $\omega_0$ , where we should keep in mind that for Marcus hopping  $\omega_0$  depends on  $T$  and  $E_r$ .

The charge-carrier mobility  $\mu$  can be determined by solving the hopping problem numerically using the master-equation (ME) method.<sup>14</sup> We will use these ME results as a benchmark and to determine the parameter values in the scaling theory discussed below. This approach takes into account the dominant

effect of Coulomb interactions, which is to prevent two carriers from occupying one site. Longer-range Coulomb interactions are not relevant at the carrier concentrations considered here of at most a few percent. This was shown by Zhou *et al.* for uncorrelated disorder<sup>23</sup> and by van der Holst *et al.* for correlated disorder.<sup>24</sup> We note that these works show that at higher concentration, around 10%, these interactions cannot be neglected.

By linearizing in the electric field  $F$ , the problem of finding  $\mu$  can be mapped onto that of finding the network conductivity of a random-resistor network on the same lattice,<sup>16</sup> with the conductance  $G_{ij}$  of the bond between sites  $i$  and  $j$  given by

$$G_{ij} = \frac{e^2 \omega_{\text{symm}}(|\Delta E_{ij}|)}{4k_B T \cosh \left[ \frac{E_i - E_F}{2k_B T} \right] \cosh \left[ \frac{E_j - E_F}{2k_B T} \right]} \quad (6a)$$

$$\approx \frac{e^2 \omega_{\text{symm}}(|\Delta E_{ij}|)}{k_B T} \exp \left( \frac{E_F}{k_B T} - \frac{E_i + E_j}{2k_B T} \right), \quad (6b)$$

where  $E_F$  is the Fermi energy. The approximation Eq. (6b) is valid for sufficiently low  $E_F$ , as compared to the energies of the sites that are relevant for the charge transport. For uncorrelated Gaussian disorder, this holds for carrier concentrations  $c \lesssim 0.03$ .<sup>20</sup> We will see further on that for correlated disorder the requirement is that  $c \lesssim 0.01$ .

### III. SCALING THEORY FOR THE CHARGE-CARRIER MOBILITY

We will now discuss the scaling theory introduced in Ref. 20 to obtain the carrier mobility  $\mu$  from the random-resistor network. We consider the problem from a percolation-theory standpoint. There is a percolation threshold  $p_{\text{bond}}$ , such that the portion  $p_{\text{bond}}$  of bonds with highest conductivity just forms an infinitely large connected network, the percolating network.<sup>16</sup> We define the critical conductance  $G_{\text{crit}}$  as the lowest conductance occurring in this network.  $G_{\text{crit}}$  and  $p_{\text{bond}}$  are related through  $\Phi(G_{\text{crit}}) = 1 - p_{\text{bond}}$ . Here,  $\Phi(G)$  is the cumulative distribution function (CDF) of the distribution of bond conductances, i.e.,  $\Phi(G)$  is the probability that a randomly chosen bond has a conductance lower than or equal to  $G$ .

The key concept in linking  $G_{\text{crit}}$  to the charge-carrier mobility  $\mu$  is the notion of fat percolation, first introduced by Dyre and Schröder,<sup>21</sup> which states that the mobility is determined not only by the critical bond, but also by the bonds with conductance close to that of the critical bond. In our scaling theory, we assume that  $\mu$  only depends on the *amount* of these bonds. This amount is given by  $f(G_{\text{crit}})$ , where  $f(G) \equiv d\Phi/dG$  is the probability density function (PDF) of the conductance distribution. Since percolation can be viewed as a critical phenomenon, with a critical point at  $T = 0$ , we propose as a scaling ansatz for the dependence of the mobility on  $G_{\text{crit}}$  and  $f(G_{\text{crit}})$  a power-law form, which is expected to be valid in a scaling regime around the critical point, i.e., at finite but not too high temperatures. Dimensional analysis then leads us to consider the following form:<sup>20</sup>

$$\mu = A \frac{1}{N_t^{2/3} e c} G_{\text{crit}} [G_{\text{crit}} f(G_{\text{crit}})]^\lambda, \quad (7)$$

where in general the prefactor  $A$  and the critical exponent  $\lambda$  depend on the DOS and the type of hopping and lattice, but *not* on  $T$  or  $c$ . These parameters can be determined from fits to numerically exact ME results. This equation holds only in the scaling regime, i.e., at a sufficiently low temperature or, equivalently, a sufficiently large disorder strength  $\sigma$ . Outside this regime, a large range of conductances determines the mobility and the full distribution  $f(G)$  becomes relevant, not only  $f(G_{\text{crit}})$ . The analysis in Ref. 20 has shown that the scaling regime corresponds to  $\hat{\sigma} \equiv \sigma/k_B T \gtrsim 2$  for a Gaussian DOS and uncorrelated disorder, which means that the scaling theory has a wide applicability range.

To apply Eq. (7) we must explicitly determine  $G_{\text{crit}}$  and  $f(G_{\text{crit}})$ . We first consider MA hopping. Using Eq. (5) in Eq. (6b) gives

$$G_{ij} = \frac{e^2 \omega_0}{k_B T} \exp\left(\frac{E_F - \max(E_i, E_j)}{k_B T}\right). \quad (8)$$

Consider now the *site* percolation problem, instead of the bond percolation problem. There is a *site* percolation threshold  $p_{\text{site}}$ , such that the bonds in between the portion of sites  $p_{\text{site}}$  with lowest energy just form a percolating network. Similar to the critical conductance  $G_{\text{crit}}$ , we define the critical energy  $E_{\text{crit}}$  as the maximum energy occurring in this network. From Eq. (8) we see that the bonds connecting these sites are exactly the bonds of highest conductivity, and so *the site percolating network is identical to the bond percolating network*. Since a site has a probability  $p_{\text{site}}$  to be in the percolating network, a bond has probability  $p_{\text{bond}} = p_{\text{site}}^2$  (for uncorrelated energy disorder). The critical energy  $E_{\text{crit}}$  can now be linked directly to the percolation threshold  $p_{\text{bond}}$ :

$$\sqrt{p_{\text{bond}}} = p_{\text{site}} = \Gamma(E_{\text{crit}}) \equiv \int_{-\infty}^{E_{\text{crit}}} g(E) dE, \quad (9)$$

where  $\Gamma(E)$  is the CDF of the density of states. From Eq. (8) we see that  $G_{\text{crit}}$  and  $E_{\text{crit}}$  are related by

$$G_{\text{crit}} = \frac{e^2 \omega_0}{k_B T} \exp\left(\frac{E_F - E_{\text{crit}}}{k_B T}\right). \quad (10)$$

The conductance distribution function  $f(G)$  can be derived from Eq. (8) and the DOS  $g(E)$ . Using Eq. (9) we then obtain

$$f(G_{\text{crit}}) = \frac{2k_B T}{G_{\text{crit}}} g(E_{\text{crit}}) \sqrt{p_{\text{bond}}}. \quad (11)$$

Combining Eqs. (7), (10), and (11) yields the following expression for the charge-carrier mobility  $\mu$ , valid only for MA hopping:

$$\mu(T, c) = A \frac{e \omega_0}{N_t^{2/3} k_B T c} [2k_B T g(E_{\text{crit}}) \sqrt{p_{\text{bond}}}]^\lambda \times \exp\left(\frac{E_F(T, c) - E_{\text{crit}}}{k_B T}\right). \quad (12)$$

Since the topology of the percolating network is determined purely by site percolation, it does not depend on the DOS as long as the energetic disorder is uncorrelated. Consequently, for uncorrelated disorder, the parameters  $A$ ,  $\lambda$ , and  $p_{\text{bond}}$  do not depend on the DOS either. In fact, site percolation is a standard problem and values of  $p_{\text{bond}}$  can be found in general percolation literature.<sup>25</sup> We note that  $E_{\text{crit}}$  *does* depend on the DOS,

but can be determined straightforwardly from  $p_{\text{bond}}$  using Eq. (9). This means that for uncorrelated disorder, Eq. (12) can predict the mobility for MA hopping for any DOS without any change in the parameters. We note that if  $g(E_{\text{crit}}) \approx 0$ , i.e., if there are very few sites around  $E_{\text{crit}}$  available, Eq. (12) only holds at very low temperatures. This is because it is only at these temperatures that the few sites close to  $E_{\text{crit}}$  determine the transport. Such a situation may occur, for example, in host-guest systems for guest concentrations at the crossover in between the low guest-concentration regime in which the guest molecules act as traps and the high guest-concentration regime in which the transport takes place via direct hopping between the guest sites. For correlated disorder the topology of the percolating network does depend on the DOS. Hence, the parameters  $A$ ,  $\lambda$ , and  $p_{\text{bond}}$  will in this case also depend on the DOS. However, for this case we will not explicitly construct the percolating network, but apply an approach explained in the next section.

The discussion above does not hold for Marcus hopping, because in that case the bond percolating network is not identical to the site percolating network. However, just like for MA hopping the dependence of  $G_{ij}$  on  $E_i$  and  $E_j$  can be written in the form  $\exp[-E(E_i, E_j)/k_B T]$ , where  $E$  is an energy function of  $E_i$  and  $E_j$  that does not depend on  $T$  or  $c$ . Consequently, Eq. (10) still holds, although there is now no straightforward relationship between  $E_{\text{crit}}$  and the DOS, such as Eq. (9) for the case of MA hopping. Therefore, Eq. (11) no longer holds, but it can be analytically shown that  $G_{\text{crit}} f(G_{\text{crit}})$  is still independent of  $c$  and scales linearly with  $T$ . Consequently, we find the following expression for  $\mu$ , valid for both Marcus and MA hopping:<sup>20</sup>

$$\mu(T, c) = B \frac{e \omega_0}{N_t^{2/3} W c} \left(\frac{W}{k_B T}\right)^{1-\lambda} \times \exp[(E_F(T, c) - E_{\text{crit}})/k_B T], \quad (13)$$

where the prefactor  $B$  depends on the DOS, the lattice, and the type of hopping, but not on  $T$  or  $c$ . The parameter  $W$  is a measure for the width of the DOS. For the Gaussian DOS we choose  $W = \sigma$ ; other shapes of the DOS will be discussed in the next section. The choice of  $W$  is in a sense arbitrary, but a different definition would simply result in a different value of the prefactor  $B$ .

#### IV. RESULTS

To apply the theory derived in the previous section, we must determine the various fitting parameters. In the case of uncorrelated disorder, the parameters  $p_{\text{bond}}$ ,  $E_{\text{crit}}$ ,  $G_{\text{crit}}$ , and  $f(G_{\text{crit}})$  can be found by explicitly determining the percolating network for large lattices by numerical techniques. We then fit Eq. (7) to the carrier mobility as determined from ME calculations at various temperatures  $T$  and carrier concentrations  $c$ , with  $A$  and  $\lambda$  as fitting parameters. The prefactor  $B$  in Eq. (13) then follows directly from the value of  $A$ . The validity of this approach was demonstrated in Ref. 20. The obtained parameter values for the two different lattices and hopping types are listed in Table I. The dependence of these parameters on the reorganization energy  $E_r$  in the case of Marcus hopping is discussed at the end of this section. This

TABLE I. Bond percolation threshold  $p_{\text{bond}}$ , prefactor  $A$ , critical exponent  $\lambda$  in Eqs. (7) and (12), prefactor  $B$ , and critical energy  $E_{\text{crit}}$  in Eq. (13), for uncorrelated Gaussian disorder. Results are given for Miller-Abrahams (MA) and Marcus hopping, and simple cubic (SC) and fcc lattices. The last column gives the value  $C$  in an optimal fit of the low carrier-concentration mobility  $\mu_0(T)$ , as given by Eq. (16), to  $\exp(-C\hat{\sigma}^2)$  in the range  $2 \leq \hat{\sigma} \leq 6$ , with  $\hat{\sigma} = \sigma/k_B T$ . The number of digits given in each entry is compatible with the accuracy with which the parameters could be obtained. All values were taken from Ref. 20.

Lattice	Hopping	$E_r[\sigma]$	$p_{\text{bond}}$	$A$	$\lambda$	$B$	$E_{\text{crit}}[\sigma]$	$C$
SC	MA	N/A	0.097	2.0	0.97	0.47	-0.491	0.44
SC	Marcus	$\infty$	0.139	1.8	0.85	0.66	-0.766	
SC	Marcus	10	0.131	1.8	0.85	0.63	-0.748	0.69
SC	Marcus	3	0.118	1.8	0.85	0.59	-0.709	0.49
SC	Marcus	1	0.104	1.8	0.85	0.51	-0.620	0.44
fcc	MA	N/A	0.040	8.0	1.09	0.7	-0.84	0.40
fcc	Marcus	$\infty$	0.058	8.0	1.10	1.2	-1.11	
fcc	Marcus	10	0.054	8.0	1.10	1.1	-1.09	0.66
fcc	Marcus	3	0.048	8.0	1.10	1.0	-1.06	0.45
fcc	Marcus	1	0.042	8.0	1.10	0.8	-0.98	0.40

table was already given in Ref. 20, but is included here in order to facilitate comparison with the results obtained for correlated energetic disorder, discussed below.

In Fig. 1(a) we show the validity of Eq. (12) by plotting the temperature dependence of the mobility for MA hopping with uncorrelated disorder for three different types of DOS: a Gaussian, an exponential, and a constant DOS. In all three cases,  $W$  is a measure for the width of the DOS. For the Gaussian DOS,  $W = \sigma$  is the standard deviation. For the exponential DOS  $W = k_B T_0$  is the decay energy:  $g(E) = \exp(E/k_B T_0)/k_B T_0$  for  $E \leq 0$  and  $g(E) = 0$  for  $E > 0$ . For the constant DOS  $W$  is half the size of the energy region in which the DOS is nonzero:  $g(E) = 1/2W$  for  $-W \leq E \leq W$  and  $g(E) = 0$  otherwise. The results of Eq. (12) (lines) describe the ME results (symbols) very well for  $W/k_B T \gtrsim 2$ ,

using the *same* values  $A = 2.0$ ,  $\lambda = 0.97$ , and  $p_{\text{bond}} = 0.097$  [which determines  $E_{\text{crit}}$  through Eq. (9)] for each type of DOS.

We will consider the exponential DOS in more detail, because this type of DOS is often used in analyzing the mobility of organic field-effect transistors (OFETs).<sup>26</sup> Applying Eq. (13) to this case gives

$$\mu(T, c) = B \frac{e\omega_0}{N_t^{2/3} k_B T_0 c} \left( \frac{T_0}{T} \right)^{1-\lambda} \times \left( \frac{\exp(E_{\text{crit}}/k_B T_0) c}{\Gamma(1 - T/T_0)\Gamma(1 + T/T_0)} \right)^{T_0/T}, \quad (14)$$

where  $\Gamma(z) \equiv \int_0^\infty dy \exp(-y)y^{z-1}$  and Eq. (2) in Ref. 26 was used to express  $E_F$  in terms of  $c$ . For MA hopping on an SC lattice, we have from Eq. (9)  $E_{\text{crit}} = -1.17k_B T_0$  leading to  $\exp(E_{\text{crit}}/k_B T_0) = 0.32$ . We compare this to the result given by Vissenberg and Matters (VM)<sup>26</sup> for MA hopping:

$$\mu(T, c) = \sigma_{0, \text{VM}} \frac{e}{N_t c} \left( \frac{\pi N_t (T_0/T)^3 c}{(2\alpha)^3 B_c \Gamma(1 - T/T_0)\Gamma(1 + T/T_0)} \right)^{T_0/T}, \quad (15)$$

where  $\sigma_{0, \text{VM}}$  is a conductivity prefactor and the critical number  $B_c \approx 2.8$ . Equation (15) was derived within a percolation analysis of variable-range hopping (VRH) on a randomly and uniformly distributed collection of sites, with a decay length  $\alpha^{-1}$  of the wave functions localized at the sites. We note that the concentration dependence in Eqs. (14) and (15) is the same. The temperature dependence is similar in the sense that the dominant factor is Arrhenius-like,  $\mu(T) \propto \exp[-E_a/k_B T]$ , with an activation energy  $E_a$ . In our case we have  $E_a = E_{\text{crit}} - E_F$  [see Eq. (13)], whereas in the VM case  $E_a = k_B T_0 \ln[\pi N_t (T_0/T)^3 / (2\alpha)^3 B_c] - E_F$ . We note that the value of  $E_a$  in our approach converges to a finite value for  $T \rightarrow 0$ , while in the VM case it diverges to infinity. It could be worthwhile to reanalyze mobilities in OFETs with the present theory.

We now consider correlated energy disorder. Figure 2 shows that the topologies of the percolating networks for uncorrelated and correlated disorder are very different. Shown are the

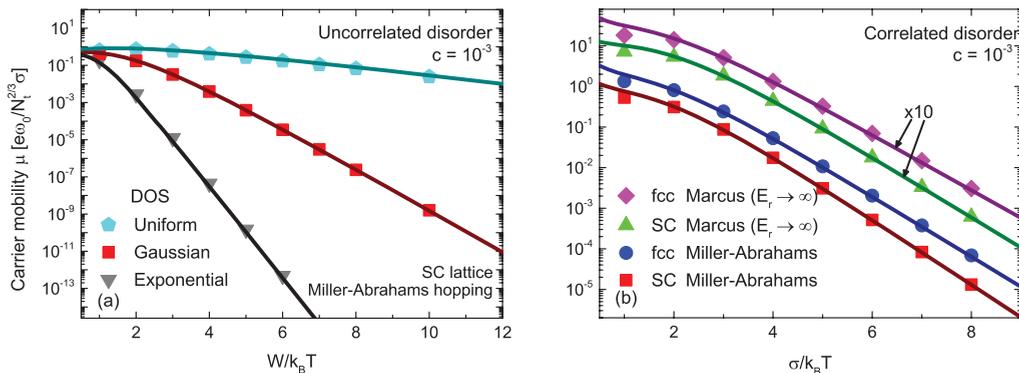


FIG. 1. (Color online) (a) Dependence of the charge-carrier mobility  $\mu$  on the temperature  $T$  for different densities of states (DOS), uncorrelated disorder, an SC lattice, MA hopping, and carrier concentration  $c = 10^{-3}$ . In all cases  $W$  is a measure for the width of the DOS. Symbols: master-equation (ME) results. Curves: scaling theory, Eq. (12), with  $A = 2.0$  and  $\lambda = 0.97$  for all three curves, and  $E_{\text{crit}}$  determined from Eq. (9) with  $p_{\text{bond}} = 0.097$ . (b) Dependence of  $\mu$  on  $T$  for different lattices and hopping rates, with dipole-correlated disorder and  $c = 10^{-3}$ . Symbols: ME. Curves: scaling theory, Eq. (13), with values of  $B$ ,  $\lambda$ , and  $E_{\text{crit}}$  as given in Table II. For clarity the mobilities for Marcus hopping have been multiplied by 10. The error in the ME results is smaller than the symbol sizes.

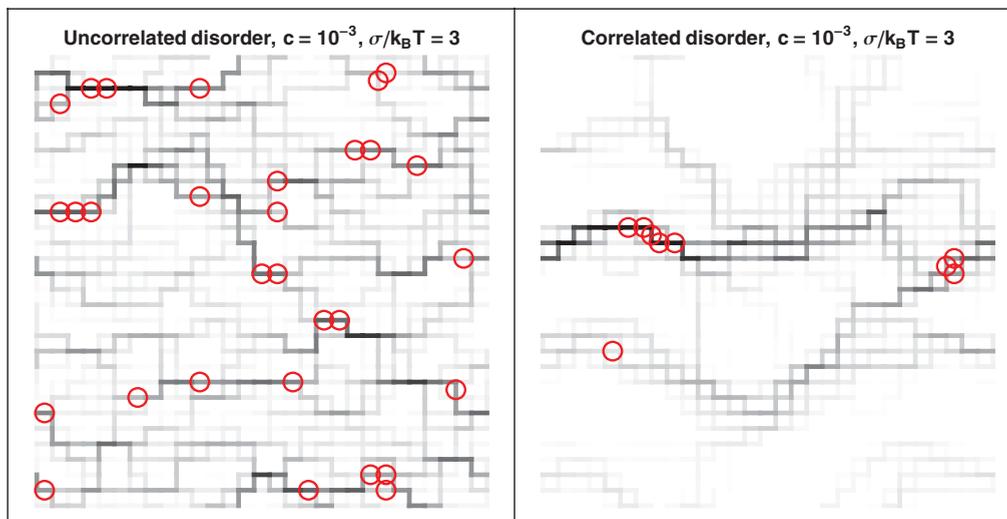


FIG. 2. (Color online) Normalized current (line opacity) in bonds of a  $30 \times 30$  square lattice with uncorrelated Gaussian energetic disorder (left) and dipole-correlated energetic disorder (right), both with standard deviation  $\sigma$ . The red circles indicate bonds with a power dissipation of at least 30% of the maximum power dissipation. The results shown are for Marcus hopping with reorganization energy  $E_r \rightarrow \infty$ ,  $c = 10^{-3}$ , and  $\sigma/k_B T = 3$ . A small electric field has been applied from left to right.

bond current distributions on a two-dimensional square lattice, for uncorrelated (left) and dipole-correlated (right) Gaussian disorder. Also shown are the critical bonds, i.e., those bonds at which most power is dissipated. We see that the correlated case is very different from the uncorrelated case: both the high-current bonds and the critical bonds are much more clustered. This clustering makes it almost impossible in the case of correlated disorder to use a percolation analysis as described above to determine  $p_{\text{bond}}$ ,  $E_{\text{crit}}$ ,  $G_{\text{crit}}$ , and  $f(G_{\text{crit}})$  for three-dimensional lattices with the typical sizes of  $100 \times 100 \times 100$  sites that we used. In order to circumvent this problem, we applied Eq. (13) to this case and fitted the parameters  $B$ ,  $\lambda$ , and  $E_{\text{crit}}$  directly to this expression. The results for the two different lattices and hopping types are listed in Table II. The values of the parameter  $p_{\text{bond}}$  and  $A$  are not included in the table, since they are not used in this approach. We note that the different topology of the percolating network for correlated and uncorrelated disorder is reflected in the value of the critical exponent  $\lambda$ , which is around two for correlated disorder and around unity for uncorrelated disorder.

TABLE II.  $\lambda$ ,  $B$ , and  $E_{\text{crit}}$  for dipole-correlated disorder. The last column gives the value  $C$  in an optimal fit of  $\mu_0(T)$ , as given by Eq. (17), to  $\exp(-C\hat{\sigma}^2)$  in the range  $2 \leq \hat{\sigma} \leq 6$ .

Lattice	Hopping	$E_r[\sigma]$	$\lambda$	$B$	$E_{\text{crit}}[\sigma]$	$C$
SC	MA	N/A	2.0	0.36	-1.26	0.33
SC	Marcus	$\infty$	1.7	0.43	-1.37	
SC	Marcus	10	1.7	0.42	-1.37	0.61
SC	Marcus	3	1.7	0.38	-1.37	0.38
SC	Marcus	1	1.7	0.29	-1.37	0.32
fcc	MA	N/A	2.2	0.78	-1.43	0.31
fcc	Marcus	$\infty$	2.2	1.1	-1.56	
fcc	Marcus	10	2.2	1.1	-1.56	0.60
fcc	Marcus	3	2.2	1.0	-1.56	0.38
fcc	Marcus	1	2.2	0.7	-1.56	0.31

The validity of Eq. (13) with the parameter values obtained above for the case of dipole-correlated disorder is shown in Fig. 1(b). This figure shows the temperature dependence of the mobility for SC and fcc lattices with MA hopping and Marcus hopping for  $E_r \rightarrow \infty$ . As in Fig. 1(a) we observe a very good agreement between the results of the scaling theory and the ME results for  $\hat{\sigma} \gtrsim 2$ .

Of special interest is the temperature dependence of the mobility at low carrier concentration  $c \rightarrow 0$ , i.e., the mobility of a single noninteracting carrier. For uncorrelated Gaussian disorder we find, starting from Eq. (13),<sup>20</sup>

$$\begin{aligned} \mu_0(T) &= B \frac{e\omega_0}{N_t^{2/3} \sigma} \hat{\sigma}^{1-\lambda} \exp[-E_{\text{crit}}/k_B T] \\ &\times \lim_{c \rightarrow 0} \frac{\exp[E_F(T, c)/k_B T]}{c} \\ &= B \frac{e\omega_0}{N_t^{2/3} \sigma} \hat{\sigma}^{1-\lambda} \exp[-\hat{\sigma}^2/2 - E_{\text{crit}}/k_B T]. \end{aligned} \quad (16)$$

This expression does not apply to the dipole-correlated case because the DOS is not exactly Gaussian for that case. Instead, make use of Eq. (A5) to obtain

$$\mu_0(T) \approx B \frac{e\omega_0}{N_t^{2/3} \sigma} \hat{\sigma}^{1-\lambda} \exp[-0.56\hat{\sigma}^{1.9} - E_{\text{crit}}/k_B T] \quad (17)$$

for correlated disorder. This is an approximate expression because Eq. (A5) is an approximation of the exact limit Eq. (A4). We remind the reader that in the case of Marcus hopping  $\omega_0$  depends on  $T$  via Eq. (4), leading to an additional temperature dependence that is not explicitly shown in Eqs. (16) and (17).

The temperature dependence of the mobility in the limit of zero carrier density and zero electric field is often expressed as  $\mu_0(T) \propto \exp(-C\hat{\sigma}^2)$ . We find that this provides a quite accurate description of Eqs. (16) and (17) when considering a limited temperature range  $2 \leq \hat{\sigma} \leq 6$ . To facilitate the comparison with earlier work, we have included the value of  $C$  in such a fit in Tables I and II, taking into account the

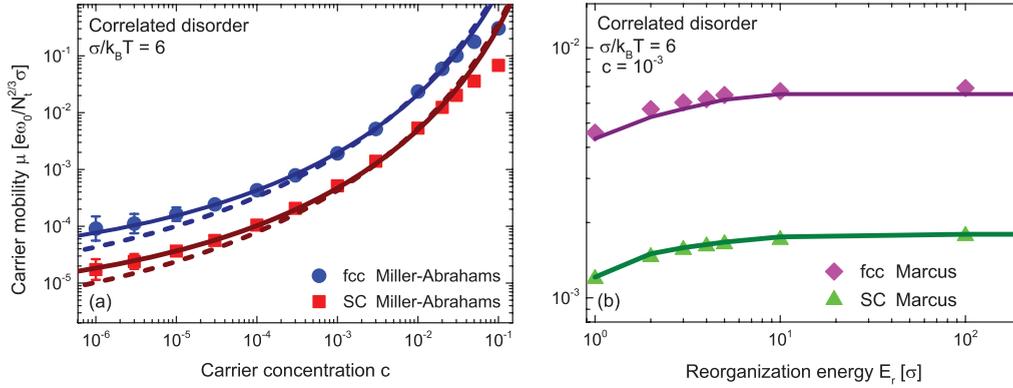


FIG. 3. (Color online) (a) Dependence of  $\mu$  on  $c$  for different lattices, with correlated disorder, MA hopping, and  $\sigma/k_B T = 6$ . Symbols: ME results. Curves: scaling theory, Eq. (13), with values of  $B$ ,  $\lambda$ , and  $E_{\text{crit}}$  as given in Table II. The dashed curves assume the DOS to be perfectly Gaussian, while the solid curves use the corrected form, Eq. (A3). (b) Dependence of  $\mu$  on the reorganization energy  $E_r$  for different lattices, with correlated disorder, Marcus hopping,  $\sigma/k_B T = 6$ , and  $c = 10^{-3}$ . Interpolation was used to determine  $B$  at values of  $E_r$  not listed in Table II.

dependence of  $\omega_0$  on  $T$  for the case of Marcus hopping. We note that for correlated disorder the much lower value of  $E_{\text{crit}}$  leads to a significantly weaker temperature dependence, i.e., a lower value of  $C$ . This is consistent with the results found in Ref. 15. For the case of an SC lattice with uncorrelated Gaussian disorder and MA hopping, the obtained value of  $C$  (0.44) is similar to the best-fit value  $C = 4/9$  found from an MC simulation of this system by Bässler.<sup>7</sup> This result is often interpreted as if the temperature dependence of the mobility is determined by the rate of hops from the average carrier energy  $-\sigma^2/k_B T$  to a “transport level” with an energy around  $-(5/9)\sigma^2/k_B T$ . We note that the origin of the similar factor  $\exp[-(1/2)\delta^2]$  in Eq. (16) is very different: it originates from the limit taken in deriving this equation and results purely from the physics of carriers obeying Boltzmann statistics in a Gaussian DOS, not from the transport properties.

We now turn to the carrier-concentration dependence of the mobility. From Eq. (13) it follows that this dependence is given by  $\mu \propto \exp[E_F(T, c)/k_B T]/c$  and so does *not* contain any parameters depending on the type of hopping, lattice, or DOS. This was verified for uncorrelated Gaussian disorder in Ref. 20. The concentration dependence for dipole-correlated disorder is also found to be well described by Eq. (13), but is slightly different from that obtained for uncorrelated Gaussian disorder, because the DOS is now not exactly Gaussian. This leads to a slightly different dependence of  $E_F$  on  $c$ . We use Eq. (A3) to describe the DOS [note that this is itself an approximation of Eq. (A1)]. In Fig. 3(a) we show that the mobility obtained in this way describes the ME results very well. For comparison, the results found using a perfectly Gaussian DOS are also shown (dashed curves). We note that for the case of correlated disorder Eq. (13) is accurate for  $c \lesssim 0.01$ , compared to  $c \lesssim 0.03$  for uncorrelated disorder.<sup>20</sup> For larger values of  $c$  the assumption of low Fermi energy, which was used to derive Eq. (6b), no longer holds. Since the critical energy  $E_{\text{crit}}$  for the case of correlated disorder is lower than for uncorrelated disorder, the assumption of low Fermi energy breaks down at a lower concentration than for uncorrelated disorder. Our results for the concentration dependence of the mobility are again consistent with those in Ref. 15, where the

concentration dependence for dipole-correlated disorder was found to be slightly weaker than for uncorrelated disorder.

Finally, we investigate the dependence of  $\mu$  on the reorganization energy  $E_r$  for Marcus hopping and correlated disorder. For the case of uncorrelated disorder, this dependence was studied in Ref. 20. It was found that for uncorrelated disorder the parameter values of  $A$  and  $\lambda$  could be taken constant (see Table I). However, for correlated disorder we cannot apply the same approach, because we do not know the value of  $A$ . Instead, we keep  $\lambda$  constant and fit  $B$  and  $E_{\text{crit}}$  to ME calculations, using Eq. (13). The results are listed in Table II. Interestingly, no dependence of  $E_{\text{crit}}$  on  $E_r$  is found, contrary to the case of uncorrelated disorder (compare with Table I). In other words, the dependence of  $\mu$  on  $E_r$  occurs only via the prefactor  $B$ . This can be understood by considering the effect of  $E_r$  on the hopping rates, as given by Eq. (3): a large value reduces the hopping rate when the energy difference between the sites involved is large. This energy difference is diminished by the correlation of the energy levels, thus reducing the effect of the reorganization energy. The validity of these results is demonstrated in Fig. 3(b), which shows the dependence of the mobility on the reorganization energy for dipole-correlated disorder. We must keep in mind here that there is an additional dependence on  $E_r$  through the prefactor  $\omega_0$ ; see Eq. (4). If this prefactor is taken into account, the expected decrease of the mobility with increasing  $E_r$  is found.

## V. CONCLUSIONS AND OUTLOOK ON APPLICATIONS

We have developed a very general scaling theory for percolative charge transport in disordered molecular semiconductors, describing the dependence of the charge-carrier mobility on temperature and carrier concentration. The theory is valid in a scaling regime corresponding to a wide temperature range that includes most relevant cases. We have studied, in particular, the differences between uncorrelated Gaussian energetic disorder and correlated energetic disorder caused by randomly oriented dipoles. The topology of the percolating network for correlated disorder is quite different than for uncorrelated disorder, which is reflected in a different value of the critical

exponent  $\lambda$  in the theory. The temperature dependence of the mobility for correlated disorder is significantly weaker than for uncorrelated disorder, due to the significantly lower value of the critical site energy  $E_{\text{crit}}$  of the percolating network. The carrier-concentration dependence for correlated disorder is slightly weaker, due to the fact that the density of states is not perfectly Gaussian.

The theory can be applied to many different situations. We have demonstrated how it can be applied to uncorrelated and dipole-correlated energetic disorder, Miller-Abrahams and Marcus hopping, and simple cubic and face-centered-cubic lattices. The mobility can be obtained for all these cases by applying Eq. (13) and simply looking up the appropriate values of the parameters  $\lambda$ ,  $E_{\text{crit}}$ , and  $B$  in Table I or II. In the case of dipole-correlated disorder one should keep in mind that the DOS is not perfectly Gaussian, which affects the dependence of the Fermi energy  $E_F$  on the carrier concentration, and thereby the carrier-concentration dependence of the mobility. A parametrization of the exact DOS for this case is given by Eq. (A3). For uncorrelated disorder and Miller-Abrahams hopping it is even possible to obtain the mobility for any shape of the DOS using Eq. (12), with values of  $A$  and  $\lambda$  as found in Table I.  $E_{\text{crit}}$  can be easily calculated from Eq. (9), with the value of  $p_{\text{bond}}$  found in Table I. No such straightforward formula is known for Marcus hopping in a non-Gaussian DOS; Eq. (13) applies to this case, but the parameters  $\lambda$ ,  $E_{\text{crit}}$ , and  $B$  have to be determined specifically for each DOS.

To determine which model correctly describes the underlying physics, it is important to develop methods to use experimental data to distinguish between Miller-Abrahams and Marcus hopping, and between correlated and uncorrelated disorder. We note that the concentration dependence is nearly identical for all cases and so cannot be used for this purpose. The temperature dependence is different for every case and so can, in principle, be used to distinguish between models. However, typically experiments take place in the range  $2 \leq \sigma/k_B T \leq 6$ , in which for all cases the temperature dependence is well described by  $\mu_0(T) \propto \exp[-C(\sigma/k_B T)^2]$  for some  $C$ . The value of  $C$  alone is not enough to tell apart all cases (see Tables I and II). We expect that the field dependence of the mobility, which has been determined for Miller-Abrahams hopping<sup>14,15</sup> but has yet to be determined for Marcus hopping, may make it possible to fully distinguish between the different models.

Another possibility to distinguish between models is to consider the time- or frequency-dependent ac mobility as probed in transient experiments. In such experiments charge-carrier relaxation effects give rise to a time-dependent current density, which reflects the finite time needed for the carriers to relax to the dynamic thermal equilibrium distribution. Recently, Germs *et al.* found that the energy  $E_{\text{crit}}$  as obtained from the present scaling theory in Ref. 20 for the case of MA hopping in an SC lattice is close to the effective ‘‘conduction’’ energy level that may be used in a multiple-trapping model describing charge-carrier relaxation in a hole-transporting polyfluorene-based polymer.<sup>27</sup> The differential capacitance of the sandwich-type metal/polymer/metal devices was found to be very sensitive to the value of  $E_{\text{crit}}$ . This suggests that it will be possible to validate the predicted values of

$E_{\text{crit}}$  as obtained in this paper from analyses of ac current density in, e.g., admittance, dark-injection, or time-of-flight experiments. The finding that  $E_{\text{crit}}$  is much lower for systems with correlated disorder than for systems with uncorrelated Gaussian disorder suggests that the ac response of systems with correlated disorder is less strongly affected by relaxation effects. Quantitative analyses of the ac response are thus expected to provide a method for probing the presence of spatial correlation between the energy levels in disordered organic semiconductors.

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## APPENDIX: DENSITY OF STATES FOR DIPOLE-CORRELATED DISORDER

We consider the DOS  $g(E)$  for a lattice site in a dipole-induced correlated energy landscape. For convenience we put this site at the origin. In Ref. 28, Novikov and Vannikov derived that

$$g(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dy \exp[iyE + S(y)], \quad (A1)$$

$$S(y) \equiv \sum_j \ln \left[ \frac{\sin(yz_j)}{yz_j} \right], \quad z_j \equiv \frac{ed}{\varepsilon R_j^2},$$

where  $i = \sqrt{-1}$  and the summation runs over all other lattice sites  $j$ . Note that this yields different densities of states for SC and fcc lattices, though the differences are minor.

Since the main contribution to the integral is from small values of  $y$ , it is useful to replace  $S(y)$  by its Taylor expansion around  $y = 0$ :<sup>28</sup>

$$S(y) = -\frac{A}{6} \left( \frac{edyN_t^{2/3}}{\varepsilon} \right)^2 + O(y^4), \quad A \equiv \sum_j (R_j N_t^{1/3})^{-4}. \quad (A2)$$

For the SC lattice we have  $A \approx 16.532$  and for the fcc lattice  $A \approx 15.962$ . Using only this term in Eq. (A1) and setting  $d = (\sqrt{3}/A)\sigma\varepsilon/eN_t^{2/3}$  yields a Gaussian DOS with standard deviation  $\sigma$ . It is possible to refine this approximation by continuing the expansion and parametrizing the resulting DOS, yielding

$$g(E) \approx \frac{0.383}{\sigma} \exp(-0.44|E/\sigma|^{2.11}), \quad (A3)$$

which is accurate to within 10% for  $-4\sigma \leq E \leq 4\sigma$  for both SC and fcc lattices.

Finally, we determine the limit necessary to describe the carrier mobility at low concentration  $c \rightarrow 0$  in Eq. (17):

$$\lim_{c \rightarrow 0} \frac{\exp[E_F(T, c)/k_B T]}{c} = \left[ \int_{-\infty}^{\infty} dE g(E) \exp(-E/k_B T) \right]^{-1} = \exp[-S(i/k_B T)], \quad (A4)$$

where  $g(E)$  is given by Eq. (A1) and the resulting double integral is solved using contour integration. Note that using

only the first term in the Taylor expansion as given by Eq. (A2) yields the usual  $\exp(-\delta^2/2)$  dependence for the Gaussian DOS. Unfortunately, continuing this expansion is not fruitful because it diverges for large values of  $\gamma$ . For this reason we choose to parametrize the result of evaluating  $S$  explicitly using

Eq. (A1), leading to

$$\lim_{c \rightarrow 0} \frac{\exp[E_F(T, c)/k_B T]}{c} \approx \exp(-0.56\delta^{1.9}), \quad (\text{A5})$$

which is accurate to within 20% for  $\delta \leq 7$  for both SC and fcc lattices. This result has been used in Eq. (17).

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