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Scaling Theory for Percolative Charge Transport in Disordered Molecular Semiconductors

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We present a scaling theory for charge transport in disordered molecular semiconductors that extends percolation theory by including bonds with conductances close to the percolating one in the random-resistor network representing charge hopping. A general and compact expression is given for the charge mobility for Miller-Abrahams and Marcus hopping on different lattices with Gaussian energy disorder, with parameters determined from numerically exact results. The charge-concentration dependence is universal. The model-specific temperature dependence can be used to distinguish between the hopping models.

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Disordered organic molecular semiconductors (OMSs) are widely used in organic devices such as organic light-emitting diodes [1,2]. Charge transport in these materials occurs by hopping of charge carriers between neighboring molecules. Understanding the effect of disorder on the dependence of the charge mobility μ (the average velocity of a charge carrier divided by the electric field) on temperature T and carrier concentration c is crucial for modeling the electronic processes in organic light-emitting diodes. In the Gaussian disorder model, proposed by Bässler, the disorder in these semiconductors is modeled by a Gaussian distribution of on-site energies [3]. This model provides a description of the T dependence of μ for vanishing carrier concentration. It was later shown that the dependence of μ on c actually plays a crucial role [4,5]. Based on a numerically exact approach, a parametrization of the mobility function $\mu(T, c)$ was constructed by Pasveer *et al.* [6]. However, this approach did not provide fundamental understanding of the form of this function. Furthermore, it is debated whether the Miller-Abrahams (MA) hopping rates [7] used in that work are appropriate for OMSs. Finally, it is not clear what the effect of the particular lattice (simple cubic) used is on the results.

Recent first-principles studies of charge transport in the OMS tris(8-hydroxyquinoline) aluminum (Alq_3) [8–10], with morphologies determined from molecular-dynamics simulations, indicate that the molecular energies indeed follow a Gaussian distribution and that hopping occurs between nearest-neighbor molecules on a random lattice. Marcus hopping rates [11] were used with transfer integrals and a reorganization energy E_r (the energy gain of the atomic arrangement of a molecule adapting to the presence of a charge) determined from quantum-chemical calculations.

Charge transport in OMSs can be analytically described by effective-medium [12–14] and percolation theories [15–18]. The hopping system is then often considered as a random-resistor network. The idea of percolation theories is that at low temperatures, when due to the disorder the spread in resistances is large, the conductivity is determined by a single critical bond in this network. This critical bond has a conductance G_{crit} such that all bonds with conductance $G \geq G_{\text{crit}}$ just form a percolating cluster [15]. However, the results of percolation theories do not agree quantitatively with the numerically exact results [18], the reason being that also bonds with conductances *around* G_{crit} influence the conductivity. Dyre and Schrøder introduced the term "fat percolation" for this and applied this concept to ac conduction [19].

In this Letter, we develop a scaling theory based on the concept of fat percolation that accurately describes the mobility function $\mu(T, c)$. Our goal is twofold: (i) to provide fundamental understanding of charge transport in OMSs and (ii) to provide a general and compact expression for $\mu(T, c)$ that can be used in the modeling of organic devices. The parameters in this expression are found from numerically exact results obtained with the master-equation (ME) method, explained in Ref. [6]. At the considered carrier concentrations of at most a few percent, the ME method properly accounts for the dominant effect of Coulomb interactions, which is to prevent the presence of two carriers on one site. We consider MA as well as Marcus rates with nearest-neighbor hopping and an uncorrelated Gaussian energy disorder with width σ. The influence of the lattice structure is investigated by considering next to simple cubic also fcc lattices and the effect of lattice disorder on the transfer integrals.

The mapping of the hopping problem onto a random-resistor network [15] leads, for the case of small F that we will consider, to bond conductances

$$G_{ij} = G(E_i, E_j) = \frac{e^2 \omega_{ij}^{\rm symm}(|\Delta E_{ij}|)}{4k_B T \cosh[\frac{E_i - E_F}{2k_B T}]\cosh[\frac{E_j - E_F}{2k_B T}]} \quad (1a)$$

$$\approx \frac{e^2 \omega_{ij}^{\rm symm}(|\Delta E_{ij})|}{k_B T} \exp\left(\frac{E_F}{k_B T} - \frac{E_i + E_j}{2k_B T}\right), \quad (1b)$$

where E_F is the Fermi energy, which is determined by T and c through the Gauss-Fermi integral, e the electronic charge, and k_B Boltzmann's constant; $\omega_{ij}^{\rm symm} = \omega_{ji}^{\rm symm}$ are symmetric hopping rates that depend in a way specified below on the energy difference $\Delta E_{ij} = E_j - E_i$ between sites j and i. The approximation Eq. (1b) is valid for sufficiently low E_F, which, as we will see later, corresponds to $c \lesssim 0.03$. The mobility μ follows by applying a voltage $V = FL$ over a slab of thickness L of this network and determining the current by applying Kirchhoff's laws. For a square lattice (for demonstration purposes, two-dimensional) and Marcus hopping rates with $E_r \to \infty$, the current and dissipated power thus obtained are shown in Fig. 1. At a high temperature [Fig. 1(a)], the current and power distributions are very homogeneous. At a low temperature [Fig. 1(c)], there is one percolating path visible, where a single critical bond with conductance $G_{\rm crit}$, indicated by the arrow, dissipates almost all the power and therefore almost fully determines the current. In standard percolation theory, the conductivity is taken to be proportional to $G_{\rm crit}$. However, at intermediate temperatures [Fig. 1(b)], there are multiple bonds with conductances around $G_{\rm crit}$ contributing to the dissipation and determining the current. This is the essence of fat percolation.

Inspired by this, we now proceed as follows. At not too high temperatures, only a small number of bonds with conductances close to $G_{\rm crit}$ determine the network conductivity. This number is to a good approximation quantified by $f(G_{\rm crit})$, where $f(G)$ is the conductance probability density function. As a consequence, the mobility μ can then depend only on $G_{\rm crit}$ and $f(G_{\rm crit})$. From a dimensional analysis and its definition, it follows that μ must be of the form $\mu = G_{\rm crit} h[G_{\rm crit} f(G_{\rm crit})]/N_t^{2/3} ec$, with h some dimensionless function that depends on the type of hopping and lattice and N_t the site density. Since percolation is a critical phenomenon, we take as a scaling ansatz for h a power law expression, leading to

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

where the prefactor A and the critical exponent λ depend on the type of hopping and lattice but *not* on T or c.

In Fig. 2, we validate the above scaling ansatz (solid curve) by a direct comparison of the T dependence of μ with numerically exact results obtained by using the ME method (symbols). Marcus hopping is used with $E_r \to \infty$, a simple cubic lattice, and a carrier concentration of $c = 10^{-2}$ carriers per site. Expressions for $G_{\rm crit}$ and $f(G_{\rm crit})$ are given below. The numerical data can be excellently fitted by Eq. (2) for $\sigma/k_B T \gtrsim 1$ with $A = 1.8$ and $\lambda = 0.85$. We also include in Fig. 2 the results of standard percolation theory (dotted curve). It is clear that the scaling approach leads to an enormous improvement. For $\sigma/k_B T \lesssim 1$, not only $f(G_{\rm crit})$ but the whole distribution $f(G)$ becomes important, and the approach fails. In this region, the mobility is accurately given by a simple effective-medium theory [12] (dashed curve).

To explicitly determine $G_{\rm crit}$ and $f(G_{\rm crit})$, we must specify $\omega_{ij}^{\rm symm}$ in Eq. (1). For Marcus hopping rates [11], we have $\omega_{ij}^{\rm symm} = \omega_0 \exp(-\Delta E_{ij}^2/4E_r k_B T)$, with $\omega_0 = (J_0^2/\hbar)\sqrt{\pi/E_r k_B T}\exp(-E_r/4k_B T)$ and J_0 the transfer integral. For MA rates [7], we have $\omega_{ij}^{\rm symm} = \omega_0 \exp(-|\Delta E_{ij}|/2k_B T)$, where ω_0 is now a temperature-independent factor times J_0^2. All results for μ are given in terms of ω_0, where we should remember that in the Marcus

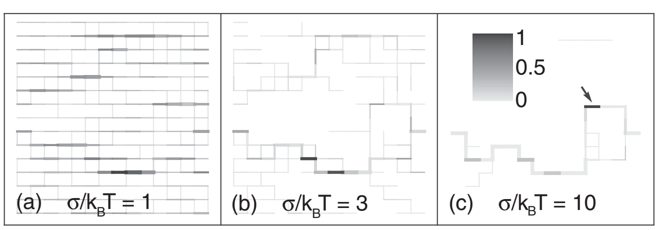

FIG. 1. Normalized current (line thickness) and dissipated power (line opacity; see the legend) in bonds of a 15×15 square lattice of sites with Gaussian energy disorder of width σ. The results shown are for Marcus hopping with reorganization energy $E_r \to \infty$, carrier concentration $c = 10^{-5}$, and three different temperatures T. A small electric field is applied from left to right. The arrow indicates the critical bond.

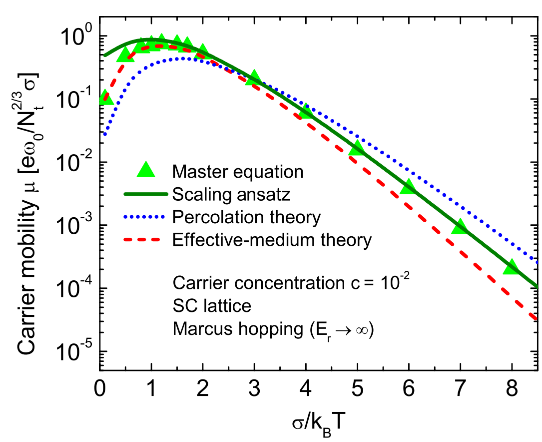

FIG. 2 (color online). Dependence of mobility μ on T for Marcus hopping with $E_r \to \infty$ on a simple cubic (SC) lattice, for $c = 10^{-2}$. Green triangles: ME. Green solid curve: Scaling ansatz, Eq. (2), with $A = 1.8$ and $\lambda = 0.85$. Blue dotted curve: Standard percolation theory, scaled to match the ME mobility at $\sigma/k_B T = 3$. Red dashed curve: Effective-medium theory [Eq. (5.4) in Ref. [12]].

case ω_0 depends on T and E_r. Later, we will allow J_0 and hence ω_0 to vary per bond to account for lattice disorder.

We are now ready to derive an expression for $G_{\rm crit}$. For a given lattice, we can find $G_{\rm crit}$ by adding bonds of decreasing conductivity until a percolating cluster is formed. We note that the dependence of the bond conductivity $G(E_i, E_j)$ on E_i and E_j in Eq. (1b) is of the form $\exp[-E(E_i, E_j)/k_{\rm B}T]$ for both MA and Marcus hopping, where E is an energy function of E_i and E_j that does not depend on T or c. We can then conclude that instead of considering $G_{\rm crit}$ we can also consider the critical value $E_{\rm crit}$ of $E(E_i, E_j)$, which does not depend on T or c either. We now find

$$G_{\rm crit} = \frac{e^2\omega_0}{k_{\rm B}T}\exp\{[E_{\rm F}(T, c) - E_{\rm crit}]/k_{\rm B}T\}. \quad (3)$$

The values of the critical energy $E_{\rm crit}$ for the different types of hopping and lattices are listed in Table I. It may be verified that for MA and Marcus hopping $E_{\rm crit}$ and $E_{\rm crit} + E_r/4$, respectively, are the highest energies of sites participating in the critical bonds.

We also need an expression for $f(G_{\rm crit})$. By constructing the distribution of conductances from Eq. (1b), we find

$$G_{\rm crit}f(G_{\rm crit}) = \frac{D}{\hat{\sigma}}, \quad (4)$$

where D is a constant that does not depend on T or c, and $\hat{\sigma} \equiv \sigma/k_{\rm B}T$. Combining Eqs. (2)–(4) yields a general and compact expression for the mobility according to our scaling theory:

$$\mu_0(T) = B\frac{e\omega_0}{N_t^{2/3}\sigma}\hat{\sigma}^{1-\lambda}\exp\left(-\frac{1}{2}\hat{\sigma}^2 - \frac{E_{\rm crit}}{kT}\right), \quad (5a)$$

$$\mu(T, c) = \mu_0(T)\frac{1}{c}\exp\left(\frac{E_{\rm F}(T, c)}{k_{\rm B}T} + \frac{1}{2}\hat{\sigma}^2\right), \quad (5b)$$

TABLE I. Percolation threshold $p_{\rm c}$, prefactor A, and critical exponent λ in Eq. (2), and prefactor B and critical energy $E_{\rm crit}$ in Eq. (5a), for MA and Marcus hopping on SC and fcc lattices. For Marcus hopping, A and λ are in good approximation independent of the reorganization energy E_r. The last column gives the value C in a fit $\mu_0(T) \propto \exp(-C\hat{\sigma}^2)$ to Eq. (5a) in the range $2 \leq \hat{\sigma} \leq 6$, with $\hat{\sigma} = \sigma/k_{\rm B}T$.

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

where $B \equiv AD$ and $\mu(T, c) \rightarrow \mu_0(T)$ when $c \rightarrow 0$. This mobility function can be readily used to compute device characteristics in a drift-diffusion approach [20].

From fits to the ME results, we have determined the parameters A, B, and λ, listed in Table I, for the two different types of hopping and lattices. We also include the value of the percolation threshold $p_{\rm c}$, i.e., the fraction of participating bonds when percolation just occurs. Figure 3 shows that in all four cases the quality of the fit is excellent. In the case of Marcus hopping, the parameters depend on the reorganization energy E_r. However, we found that A and λ depend only weakly on E_r; the values of A and λ for $E_r \rightarrow \infty$ given in Table I can also safely be used at finite E_r. The dependence of the percolation threshold $p_{\rm c}$ on E_r cannot be neglected, but $p_{\rm c}$ can be found from a percolation analysis, not requiring ME calculations. The values of $p_{\rm c}$ for different E_r are listed in Table I, as well as the resulting values of B and $E_{\rm crit}$. For typical values of T and c, Fig. 4(a) shows that the dependence of μ on E_r is well described by this approach. We note that the dependence of ω_0 on E_r leads to a net decrease of μ with E_r.

We now consider the effect of lattice disorder, which is caused by the random molecular packing in OMSs [8,9,21]. Because of the exponentially decaying wave functions, we vary the transfer integral J_0 per bond according to $J_{0,ij} = \exp(u_{ij})J_0$, where $u_{ij} = u_{ji}$ is uniformly distributed between $-\Sigma$ and Σ, with the parameter Σ controlling the lattice disorder strength. It is not *a priori* clear that Eq. (5) can be applied, but we can still determine $G_{\rm crit}$ and $f(G_{\rm crit})$ from a percolation analysis and apply Eq. (2), assuming no dependence of A and λ on Σ. The results of this approach are compared with ME results for typical values of T and c in Fig. 4(b); we see that the scaling theory still provides an excellent description of the mobility, even for large disorder $\Sigma = 6$. We also note that for $\Sigma \lesssim 3$ the mobility is almost independent of Σ, so that Eq. (5), valid for $\Sigma = 0$, can still be applied in this case.

An important conclusion drawn from Eq. (5b) is that the dependence of μ on c is in all cases given by $\exp[E_{\rm F}(T, c)/k_{\rm B}T]/c$, containing no parameters depending

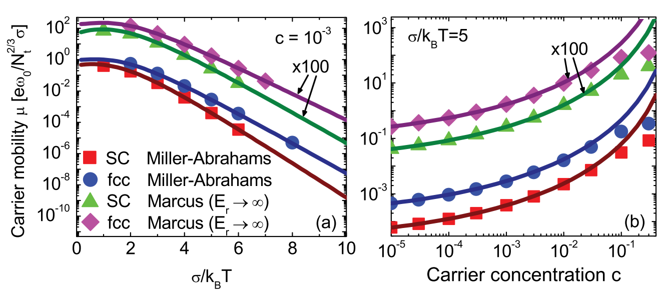

FIG. 3 (color online). (a) Dependence of μ on T for different hopping rates and lattices, for a typical c. (b) Dependence on c, for a typical $\sigma/k_{\rm B}T$. Symbols: ME. Curves: Scaling theory, Eq. (5), with values of B, λ, and $E_{\rm crit}$ as given in Table I. For clarity, all mobilities for Marcus hopping are multiplied by 100.

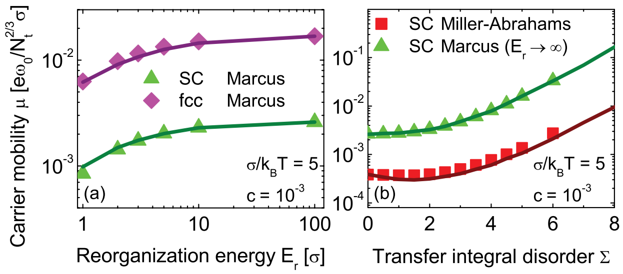

FIG. 4 (color online). (a) Dependence of μ on E_r for Marcus hopping and different lattices. (b) Dependence of μ on transfer-integral disorder strength Σ for Miller-Abrahams and Marcus hopping on a SC lattice. Symbols: ME. Curves: Scaling ansatz, Eq. (2), with values of A and λ as given in Table I. Typical values for σ/k_BT and c are chosen.

on the type of hopping or lattice. For MA hopping, this dependence was already found in Ref. [18]. We now conclude that it also holds for Marcus hopping, at variance with a previous claim [14]. We note that our conclusion agrees with the numerically exact mobilities, as shown in Fig. 3(b). The above dependence is valid for $c \lesssim 0.03$; for higher concentrations, the assumption of low Fermi energy used in deriving Eq. (1b) no longer holds.

It has become common to fit the temperature dependence of the mobility in organic semiconductors at low carrier concentration $c \to 0$ to $\mu_0(T) \propto \exp(-C\hat{\sigma}^2)$. From Eq. (5a), we find that the general form is actually $\mu_0(T) \propto T^\gamma \exp(-b\hat{\sigma}^2 - a\hat{\sigma})$ with $b = 1/2$ and a and γ depending on the type of hopping and lattice. For MA hopping, we have $a = E_{crit}/\sigma$ and $\gamma = \lambda - 1$, while for Marcus hopping, accounting for the T dependence of ω_0, $a = (E_{crit} + E_r/4)/\sigma$ and $\gamma = \lambda - 3/2$. In Ref. [18], an expression of the above form was found with $a = 0.566$ and $\gamma = -1$ for variable-range MA hopping, with, in agreement with the present result, $b = 1/2$ for nearest-neighbor hopping. However, the sign of a found by us for MA hopping (see E_{crit} in Table I) is *opposite* to that in Ref. [18], leading to a significantly different T dependence. The finding that in the range $2 \leq \hat{\sigma} \leq 6$ the numerical results for MA hopping on a simple cubic lattice can be fitted with $\mu_0(T) \propto \exp(-C\hat{\sigma}^2)$ with $C \approx 0.42$–0.44 [3,6] can now be understood as a good fit to the general expression in this range, with a negative a. Optimal fits of the results for the considered cases in Table I (except for Marcus hopping with $E_r \to \infty$) to $\ln\mu_0(T) \propto -C\hat{\sigma}^2$ in this range yield values for C given in the last column. The spread in the values shows that, when applied to experimental results, such fits could be used to distinguish between different types of hopping.

In conclusion, we have shown that charge transport in molecular semiconductors with uncorrelated Gaussian energy disorder is excellently described by a scaling theory based on fat percolation. A general and compact expression was given for the temperature and carrier-concentration dependence of the charge mobility, with parameters explicitly determined for Miller-Abrahams and Marcus hopping on different lattices. We have demonstrated the robustness of the results to lattice disorder. The obtained carrier-concentration dependence is universal. The temperature dependence is model-specific and can therefore be used to distinguish between different hopping models. We envisage that the scaling theory developed in this work can also be applied to other percolation problems.

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