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Electron-hole recombination in disordered organic semiconductors: Validity of the Langevin formula

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Accurate modeling of electron-hole recombination in organic light-emitting diodes (OLEDs) is essential for developing a complete description of their functioning. Traditionally, the recombination rate is described by the Langevin formula, with a proportionality factor equal to the sum of the electron and hole mobilities. In the disordered organic semiconductors used in OLEDs these mobilities have been shown to depend strongly on the carrier densities and on the electric field. Moreover, the energetic disorder leads to percolating pathways for the electron and hole currents, which may or may not be correlated. To answer the question whether the Langevin formula is still valid under such circumstances we perform Monte Carlo simulations of the recombination rate for Gaussian energetic disorder. We vary the disorder energy, the temperature, the densities, and mobility ratio of electrons and holes, the electric field, and the type of correlation between the electron and hole energies. We find that at zero electric field the Langevin formula is surprisingly well obeyed, provided that a change in the charge-carrier mobilities due to the presence of charge carriers of the opposite type is taken into account. Deviations from the Langevin formula at finite electric field are small at the field scale relevant for OLED modeling.

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I. INTRODUCTION

Organic light-emitting diodes (OLEDs) are very promising efficient light sources in display and lighting applications. Commercial OLED pixelated displays as well as large-area OLED white-light sources are presently entering the market. An essential process in OLEDs is the recombination of an electron and a hole, leading to the emission of a photon. In the emitting organic semiconductor the electrons and holes move toward each other under the influence of an external electric field and their mutual attractive Coulomb interaction. The rate of recombination, R, is defined as the total number of electron-hole recombination events per second and per unit volume. Already in 1903, Langevin[1,2] gave an expression for this recombination rate,

$$R_{\mathrm{Lan}} = \frac{e(\mu_{\mathrm{e}} + \mu_{\mathrm{h}})}{\epsilon_{\mathrm{r}}\epsilon_0} n_{\mathrm{e}} n_{\mathrm{h}} \equiv \gamma_{\mathrm{Lan}} n_{\mathrm{e}} n_{\mathrm{h}}, \qquad (1)$$

where e is the unit charge, n_{e} and n_{h} are the electron and hole densities, and μ_{e} and μ_{h} are the electron and hole mobilities, respectively; ϵ_0 is the vacuum permeability, ϵ_{r} is the relative dielectric constant of the semiconductor, and γ_{Lan} is the Langevin bimolecular recombination rate factor.

One of the underlying assumptions in the derivation of this expression is that the mean-free path of the charge carriers λ is much smaller than the thermal capture radius $r_{\mathrm{c}} = e^2/(4\pi\epsilon_{\mathrm{r}}\epsilon_0 k_{\mathrm{B}} T)$, where T is the temperature and k_{B} is the Boltzmann's constant. For the disordered organic semiconductors used in OLEDs charge transport takes place by hopping between molecules or conjugated segments of a π-conjugated polymer, which we will call "sites," and the mean-free path is on the order of the intersite distance $a \approx 1-2$ nm. At room temperature and with a relative dielectric constant $\epsilon_{\mathrm{r}} \approx 3$, typical for organic semiconductors, the thermal capture radius is $r_{\mathrm{c}} \approx 18.5$ nm. Hence, the assumption $\lambda \ll r_{\mathrm{c}}$ is valid.

Another assumption made in deriving Eq. (1) is that charge-carrier transport occurs homogeneously throughout the semiconductor. This is, however, in general not the case. Due to the percolative nature of charge transport in energetically disordered organic semiconductors, the current distribution has a highly inhomogeneous filamentary structure, with differences in local current densities that can vary over many orders of magnitude.[3–7] This raises the question whether Eq. (1) is still valid under such conditions. Another issue that plays a role in this context is the possible correlation between the on-site energies of holes and electrons. In the case of correlation between on-site electron and hole energies, the current filaments of the electrons and holes overlap. One would then intuitively expect a larger recombination rate than in the case of uncorrelated or even anticorrelated energies. Correlation between electron and hole energies occurs when the energetic disorder is caused by fluctuations in the local polarizability of the semiconductor or by differences in the length of conjugated segments. Anticorrelation between electron and hole energies occurs when the disorder is caused by fluctuations in the local electrostatic potential. In the present paper we will study both extremes of perfect correlation and perfect anticorrelation. In reality, the situation will be intermediate.

A further complication arises when the recombination occurs in the presence of an external electric field because the electron and hole mobilities have an electric-field dependence. Moreover, it has become clear in recent years that under typical operating conditions of OLEDs the dependence of the mobilities on the charge-carrier densities is even more important than their dependence on the electric field.[8,9] This raises the question whether it is possible to use the Langevin expression Eq. (1) by including these dependencies in the mobilities occurring in the expression.

Giving an analytical description of recombination under such complicating circumstances is impossible and one therefore has to resort to numerical methods. Various aspects of recombination in disordered semiconductors have been studied in the 1990s by using Monte Carlo (MC) simulations.[10–12] The on-site energies in these simulations are randomly drawn from a Gaussian distribution. Using Miller-Abrahams hopping rates,[13] Albrecht and Bässler[10,11] have calculated the MC recombination cross section and from that the bimolecular recombination rate factor γ. They find that the ratio between γ and γ_{Lan} from Eq. (1) is almost independent of temperature but increases with electric field. Gartstein *et al.*[12] have calculated the ratio between the MC and the Langevin recombination cross section. At room temperature, they find a slight decrease followed by an increase in this ratio with increasing electric field for Miller-Abrahams hopping rates and a decrease for polaronic hopping rates.[14,15] These authors find a weak dependence of this ratio on temperature at low electric field, developing into a considerable temperature dependence at high electric field. Both these MC studies consider the recombination of only two carriers, where one of the carriers is fixed at a particular site in a simulation box and the other carrier is released at a random site located upfield in a plane orthogonal to the electric field. Therefore, these simulations correspond to the case of vanishing electron and hole densities.

More involved MC simulations of recombination were very recently performed by Groves and Greenham.[16] In these simulations both electrons and holes are allowed to hop with polaronic hopping rates, in the presence of an external electric field, and the density of electrons and holes is varied. Like in the previous MC simulations[10–12] the on-site energies are drawn from a Gaussian distribution. Perfect correlation between hole and electron energies at a site is assumed. After recombination of an electron-hole pair, the electron and hole are reintroduced into the simulation box at random sites, guaranteeing constant prescribed charge-carrier densities. The ratio R/R_{Lan} is studied, where the charge-carrier mobilities in the Langevin expression Eq. (1) are determined by separate MC simulations of only one type of charge carrier at the same density as in the MC simulations with recombination. Considerable deviations (up to about 40%) from the Langevin expression are found.[16] Effects of anisotropy and blends of electron- and hole-transporting materials are also considered in that work but these will not be considered in the present work, which will focus on isotropic and homogeneous recombination.

Accurate modeling of OLEDs requires an adequate description of the recombination rate in such devices. Obviously, it would be attractive to have available an efficient, yet sufficiently precise way of including recombination in a device model, instead of needing to calculate the recombination rate for every specific situation with time-consuming MC simulations. One of the objectives of the present work is to make a first step into this direction. We will investigate the recombination process with MC simulations for an isotropic and homogeneous organic semiconductor, varying the disorder energy of the Gaussian disorder, the temperature, the densities of electrons and holes, the mobility ratio of electrons and holes, the electric field, and the type of correlation between electron and hole energies. As in the MC studies discussed above[10–12,16] we will study the validity of the Langevin expression Eq. (1). Since Miller-Abrahams hopping rates have been used in successful modeling studies by us of hole-only devices,[9] we will also use these hopping rates in our study. We assume that the bound state of an electron and hole residing on the same site has a sufficiently low energy so that spontaneous unbinding of such state into an electron-hole pair cannot occur. When this energy is not low enough, it is known that deviations from the Langevin expression occur.[17]

We remark that it has been argued by several authors[18–20] that the energetic disorder in organic semiconductors should be spatially correlated. One of the situations for which this would occur is when the energetic disorder is caused by random dipolar fields. Such correlation leads to a strongly enhanced electric-field dependence of the mobility.[18–20] We have recently performed modeling studies of current-voltage characteristics of hole-only devices of a derivative of PPV (Ref. 21) and of a polyfluorene-based copolymer,[22] both with spatially uncorrelated and correlated Gaussian disorder. These models are commonly called the Gaussian disorder model (GDM) and the correlated disorder model, respectively. These studies have led to the conclusion that the intersite distance as found from a fit assuming uncorrelated disorder is more realistic than that found from a fit assuming correlated disorder. Therefore, we will consider in this work spatially uncorrelated disorder.

Like Groves and Greenham,[16] we find rather large deviations from the Langevin expression if the electron and hole mobilities in the Langevin expression are taken to be those of the electrons and holes separately at their respective densities. On the other hand, we find that the Langevin expression describes our MC recombination rates surprisingly well if the electron and hole mobilities are taken to be those in exactly the double-carrier situation studied. In the case of an externally applied electric field we find deviations from the Langevin expression that can be attributed to the electric-field dependence of the mobilities. However, these deviations are small for the electric-field strengths relevant for OLEDs. All these findings can open the way to efficient and accurate modeling of double-carrier devices.

The paper is built up as follows. In the next section we discuss our Monte Carlo procedure. In Sec. III we present various results of our Monte Carlo studies. In Sec. IV we discuss our results and present our conclusions.

II. MONTE CARLO METHOD

We model the localized electronic states in the organic semiconductor by a three-dimensional cubic lattice with lattice constant a. Periodic boundary conditions are taken in all three Cartesian directions. We assume that the hopping of

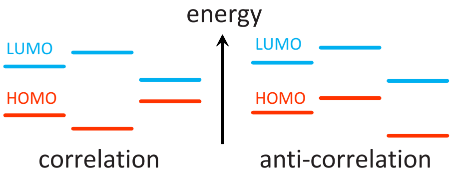

FIG. 1. (Color online) The different types of correlation between on-site electron and hole energies considered in this work, reflected in the energies for the lowest-unoccupied molecular orbital and highest-unoccupied molecular orbital. Left/right: correlated/anticorrelated electron and hole energies.

charge carriers from one localized state to another is a thermally assisted tunneling process with coupling to a bath of acoustical phonons. The hopping rate from site i to site j is then of the Miller-Abrahams form[13]

$$W_{ij,q} = \nu_{0,q} \exp\left[-2\alpha R_{ij} - \frac{E_{j,q} - E_{i,q}}{k_B T} \right], \quad \text{for } E_{j,q} \geq E_{i,q}, \tag{2a}$$

$$W_{ij,q} = \nu_{0,q} \exp[-2\alpha R_{ij}], \quad \text{for } E_{j,q} < E_{i,q} \tag{2b}$$

with q the charge of the hopping charge carrier ($q=-e$ for electrons and $q=e$ for holes), $\nu_{0,q}$ the intrinsic attempt-to-jump frequency of carrier q, α the inverse localization length of the localized wave functions, and R_{ij} the distance between sites i and j. The energy $E_{i,q}$ of charge q at site i contains a random contribution, a contribution $qFR_{ij,x}$ due to an electric field F applied in the x direction, and a contribution due to the interaction with all the other charges in the system. We take $\alpha = 10/a$ and allow hopping to the 26 nearest neighbors, which is a good approximation for derivatives of PPV at room temperature.[9]

The random contribution to the energy $E_{i,q}$ is drawn from a Gaussian density of states (DOS),

$$g(E) = \frac{1}{\sqrt{2\pi}\sigma a^3} e^{-E^2/2\sigma^2}. \tag{3}$$

The disorder energy σ is the width of the Gaussian DOS and is, in this work, taken equal for electrons and holes. As explained in Sec. I, we distinguish two cases for the correlation between on-site electron and hole energies: (1) perfect correlation and (2) perfect anticorrelation; see Fig. 1. In case (1) the random part of the hole on-site energy is taken equal to that of the electron on-site energy while in case (2) the random part of the hole on-site energy is taken opposite to that of the electron on-site energy. Therefore, it is energetically advantageous for an electron and a hole to reside on the same site in case (1) while in case (2) this is disadvantageous.

The energy $E_{i,q}$ also contains the Coulomb interaction energy U_i with all other charges. For practical reasons we use a finite-range variant of the Coulomb potential,

$$f_c(R_{ij}) = \begin{cases} \dfrac{1}{4\pi\epsilon_r\epsilon_0}\left(\dfrac{1}{R_{ij}} - \dfrac{1}{R_c}\right), & 0 < R_{ij} \leq R_c \\ 0, & R_{ij} > R_c \end{cases} \tag{4}$$

with R_c as cutoff radius. We will always use a value of R_c that is large enough to have no influence on the final results. The interaction energy U_i is taken as

$$U_i = \sum_{j \neq i} q_i q_j f_c(R_{ij}), \tag{5}$$

where q_i and q_j are the charges of the interacting carriers at sites i and j ($q_j=0$ if there is no charge at site j). We assume that due to strong on-site Coulomb repulsion the presence of two equal charges at a site is not allowed.

When an electron and a hole are on neighboring sites, the hopping of the hole to the electron or vice versa is always assumed to be downward in energy, such that the hopping rate will be given by Eq. (2). After such a process, the electron and hole are removed from the system and reintroduced randomly on empty sites according to an equilibrium distribution determined by the random contribution to the site energies (excluding the contribution from the electric field and the Coulomb interaction with other charges). Reintroduction of the electron and hole guarantees that the electron and hole densities are kept fixed. We note that our method of reintroduction is slightly different from that of Groves and Greenham, who choose random empty sites for reintroducing the electron and hole and then take new random energies of these sites according to the equilibrium density of occupied states.[16] Both methods of reintroduction are of course artificial. In a real OLED, electrons and holes approach each other from opposite electrodes. One can argue what method of reintroduction gives the most accurate description of the real situation. An alternative would be reintroduction of the electron and hole at completely randomly chosen sites. If the electrons and holes are energetically relaxed before they recombine, which should be the case for sufficiently low densities of electrons and holes, the precise way of reintroduction should become irrelevant. We will come back to this issue in the next section and show that our main conclusion is not affected by the choice of the reintroduction procedure.

Our simulations proceed as follows. First, a cubic simulation box is filled with a prescribed number of electrons and an equal number of holes. After that, hops of electrons and holes are chosen with weights determined by the hopping rates Eq. (2). A hopping time is chosen from an exponential distribution with an inverse decay time equal to the sum of all possible hopping rates. After a sufficiently long equilibration time, counting of the number of recombination events starts. This proceeds until a sufficiently accurate result for the recombination rate is obtained.

We use two different methods of calculating carrier mobilities. In the first method, which corresponds to that of Groves and Greenham,[16] we fill our simulation box with exactly the same number of charge carriers of one type as we have in the double-carrier simulation. We then apply a small electric field (or apply the same field as in the double-carrier simulation) and obtain the current by counting the number of

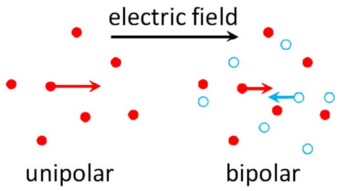

FIG. 2. (Color online) The two methods of calculating mobilities in this work. In the unipolar method we consider the presence of only one type of carrier and calculate its mobility. In the bipolar method we consider the presence of both types of carriers (open blue circles: electrons and solid red circles: holes) and calculate both their mobilities. In the bipolar method the mobilities of one carrier type are smaller than in the unipolar method because of the additional Coulomb interactions with the other carrier type. The figure indicates the typical situation in which almost all carriers are trapped in energetically deep-lying states in the Gaussian density of states, with only a few carriers that are mobile and contribute to the conduction.

hops in the field direction. From the current, we straightforwardly obtain the mobilities μ_{uni} of each carrier type in this "unipolar" system. We remark that the results obtained in this way are equivalent to those of Zhou *et al.*[23] In the second method, we take our double-carrier simulation, apply a small electric field (or apply the same field as in the double-carrier simulation) and calculate the current contribution of each carrier type separately. Accordingly, we obtain μ_{bi} of each carrier type in this "bipolar" system. We have sketched these two methods of calculating the mobilities in Fig. 2. Using these differently calculated mobilities in the Langevin expression Eq. (1) we obtain recombination rates that we will call $R_{\mathrm{Lan,uni}}$ and $R_{\mathrm{Lan,bi}}$, respectively.

III. RESULTS

In our simulations we have used the following parameters: $a=1.6$ nm, $\nu_{0,\mathrm{h}}=3.5\times10^{20}$ s^{-1}, and $\epsilon_{\mathrm{r}}=3$ (typical for organic semiconductors). The values for a and $\nu_{0,\mathrm{h}}$ are those found in Ref. 9 from a fit of the GDM to measured current-voltage characteristics for a PPV derivative {poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-*p*-phenylene vinylene], OC$_1$C$_{10}$-PPV}. The simulation box has a size of $100\times100\times100$ sites. Averages are performed over several (typically 20) different configurations of the Gaussian disorder, from which an error estimate is obtained. The following values for the cutoff radius of the finite-range Coulomb potential of Eq. (4) were found to be sufficient: $R_{\mathrm{c}}=19.2$, 32, and 64 nm for the electron and hole densities $n_{\mathrm{e}}=n_{\mathrm{h}}=10^{-3}$, 10^{-4}, and 10^{-5} carriers per site, respectively.

In Fig. 3 we investigate the effect of disorder on the ratio R/R_{Lan} of the zero-field ($F=0$) MC recombination rate R and the Langevin recombination rate R_{Lan}, given by Eq. (1). In Figs. 3(a), 3(c), and 3(e) we display R/R_{Lan} as a function of disorder energy σ for equal electron and hole hopping frequencies ($\nu_{0,\mathrm{e}}=\nu_{0,\mathrm{h}}$), at room temperature ($T=300$ K), using three different electron and hole densities in a range typical for OLEDs: (a) $n_{\mathrm{e}}=n_{\mathrm{h}}=10^{-3}$, (c) 10^{-4}, and (e) 10^{-5} carriers per site. In Figs. 3(b), 3(d), and 3(f) the corresponding unipolar and bipolar mobilities are displayed. Results are shown for correlated as well as anticorrelated disorder. In Fig. 4 we investigate the effect of taking different mobilities of electrons and holes. In Figs. 4(a), 4(c), and 4(e) we display R/R_{Lan} as a function of the ratio $\nu_{0,\mathrm{e}}/\nu_{0,\mathrm{h}}$ between the electron and hole hopping frequencies in Eq. (2), at room temperature, using three different disorder energies: (a) $\sigma=50$, (c) 100, and (e) 150 meV. The density of electrons and holes is $n_{\mathrm{e}}=n_{\mathrm{h}}=10^{-4}$ carriers per site. In Figs. 4(b), 4(d), and 4(f) the corresponding mobilities are displayed.

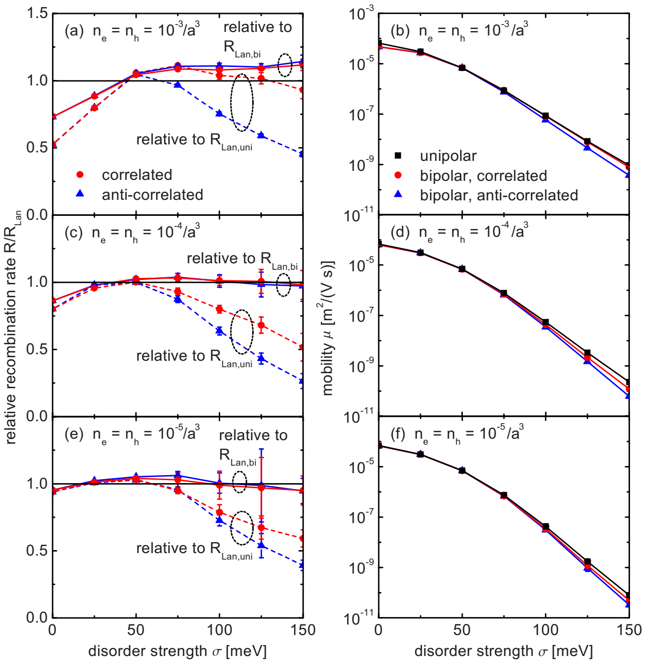

FIG. 3. (Color online) [(a), (c), and (e)]: Zero-field recombination rate R relative to the Langevin recombination rate R_{Lan} as a function of disorder energy σ, at temperature $T=300$ K and three different electron and hole densities n_{e} and n_{h}. Red circles/blue triangles: correlated/anticorrelated electron and hole energies. Solid/dashed lines: Langevin recombination rate calculated with bipolar/unipolar mobilities. [(b), (d), and (f)]: Corresponding unipolar (black squares) and bipolar mobilities.

With the unipolar mobilities used in the Langevin formula Eq. (1) ($R_{\mathrm{Lan,uni}}$) substantial deviations are found from the simulated recombination rates. As expected (see Sec. I), the recombination rate for correlated electron and hole energies is larger than for anticorrelated electron and hole energies. Surprisingly, however, the deviations from the simulated recombination rates almost completely disappear when the bipolar mobilities are used in the Langevin formula ($R_{\mathrm{Lan,bi}}$). Only for the largest density, $n_{\mathrm{e}}=n_{\mathrm{h}}=10^{-3}$ carriers per site, some deviations are observed. This is not unexpected since the average distance between electrons and holes is then smaller than the thermal capture radius. Also surprisingly, $R/R_{\mathrm{Lan,bi}}\approx1$ both for correlated and anticorrelated disorders, when the corresponding bipolar mobilities are inserted in the Langevin formula. We note that the bipolar mobilities $\mu_{\mathrm{bi,corr}}$ and $\mu_{\mathrm{bi,anticorr}}$ are *different* for the cases of correlated and anticorrelated electron and hole energies whereas the unipolar mobilities μ_{uni} are the same. A very important conclusion that we draw from these results is that *the Langevin formula is still valid when the appropriate mobilities are used.*

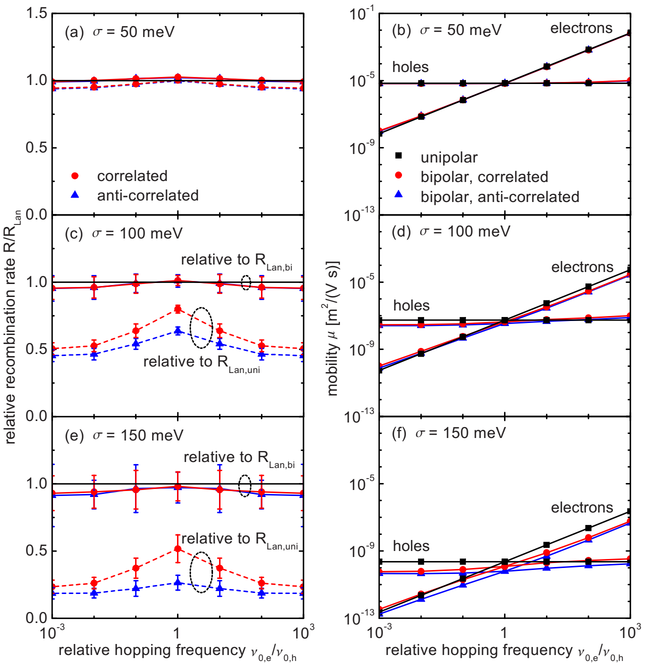

FIG. 4. (Color online) [(a), (c), and (e)]: Zero-field recombination rate R relative to the Langevin recombination rate R_{Lan} as a function of relative hopping frequency ratio $\nu_{0,\mathrm{e}}/\nu_{0,\mathrm{h}}$ of electrons and holes, at temperature $T=300$ K, electron and hole densities $n_{\mathrm{e}}=n_{\mathrm{h}}=10^{-4}/a^3$, and three different disorder energies. [(b), (d), and (f)]: Corresponding electron and hole mobilities. Symbols and lines as in Fig. 3.

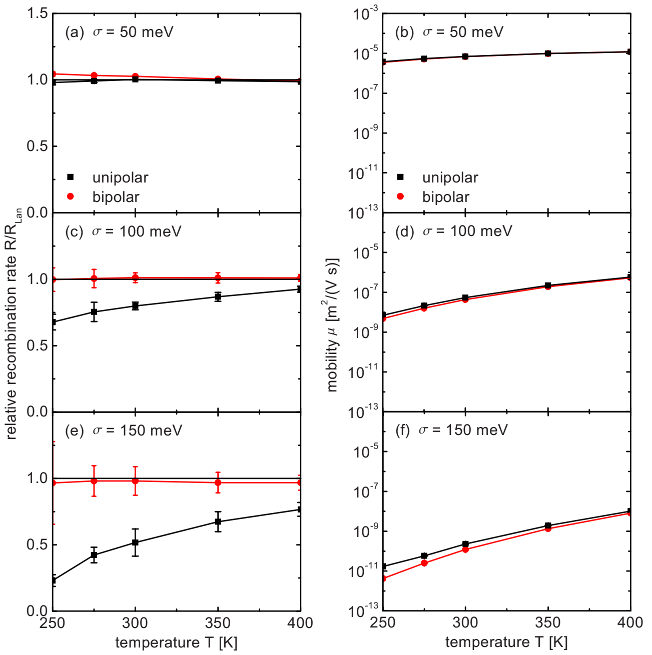

FIG. 5. (Color online) [(a), (c), and (e)]: Zero-field recombination rate R relative to the Langevin recombination rate R_{Lan}, calculated for correlated electron and hole energies, as a function of temperature T, at electron and hole densities $n_{\mathrm{e}}=n_{\mathrm{h}}=10^{-4}/a^3$ and three different disorder energies. Red circles/black squares: Langevin recombination rate calculated with bipolar/unipolar mobilities. [(b), (d), and (f)]: Corresponding mobilities.

This conclusion is further supported by Fig. 5, in which we investigate the temperature dependence of R/R_{Lan} and the corresponding mobilities for three different disorder energies: [(a) and (b)] $\sigma=50$, [(c) and (d)] 100, and [(e) and (f)] 150 meV. The density of electrons and holes is $n_{\mathrm{e}}=n_{\mathrm{h}}=10^{-4}$ carriers per site and correlated electron and hole energies are taken. Again, with unipolar mobilities substantial differences are found between the Langevin and the simulated recombination rates whereas with bipolar mobilities these differences disappear completely.

To check the influence of the specific way of reintroducing the electron and hole after a recombination event, we performed room-temperature simulations with random reintroduction of electrons and holes, for $n_{\mathrm{e}}=n_{\mathrm{h}}=10^{-4}$ carriers per site, varying disorder strengths, and correlated electron and hole energies; see Fig. 6. As expected, we find larger bipolar mobilities (by about a factor 8 for $\sigma=150$ meV) but if we use these mobilities in the Langevin expression Eq. (1), R/R_{lan} becomes indistinguishable from the values found with reintroduction according to an equilibrium distribution [the latter are the same as in Fig. 3(c)]. Hence, the specific reintroduction mechanism does not affect the above conclusion.

Finally, we investigate the electric-field dependence of the recombination rate. Figure 7 shows the ratio $R/R_{\mathrm{Lan,bi}}$ and the corresponding bipolar mobilities as a function of the electric field F, at room temperature, for three different electron and hole densities and three different disorder energies: [(a) and (b)] $\sigma=50$, [(c) and (d)] 100, and [(e) and (f)] 150 meV. Correlated electron and hole energies are taken. We now observe that some deviations between the Langevin and the simulated recombination rates occur. In the limit of vanishing carrier densities such deviations were already observed in the MC simulations of Albrecht and Bässler[10,11] and Gartstein *et al.*,[12] who suggested that these can be attributed to “field-induced mobility anisotropy.”[12] Moreover, the electric-field dependence of the charge-carrier mobility leads in the original Langevin problem to a gradient in the charge-carrier density around a recombination site, leading to a nonzero diffusion contribution that has to be taken into account.[24] The deviations from the Langevin recombination rate that we observe increase with increasing disorder energy σ. This is in agreement with the increase in the electric-field dependence of the mobility with increasing σ.[9] Interestingly, we observe that the electric-field dependence of $R/R_{\mathrm{Lan,bi}}$ has only a weak dependence on the charge-carrier density, which is in agreement with the observation that the electric-field dependence can be included in the mobility by a density-independent prefactor.[9] We note that in Fig. 7 the electric field was applied along an axis of the cubic lattice [the (100) direction]. We observed that different dependencies at high electric field $[F \gg \sigma/(ea)]$ are found when applying the field along the (111) direction, due to the increasing anisotropy in the mobility tensor with electric field. However, the relevant region for OLED modeling is $F < \sigma/(ea)$. In this region, the deviations from the Langevin prediction remain quite modest.

IV. DISCUSSION AND CONCLUSIONS

We have performed Monte Carlo simulations of electron-hole recombination in a homogeneous and isotropic disor-

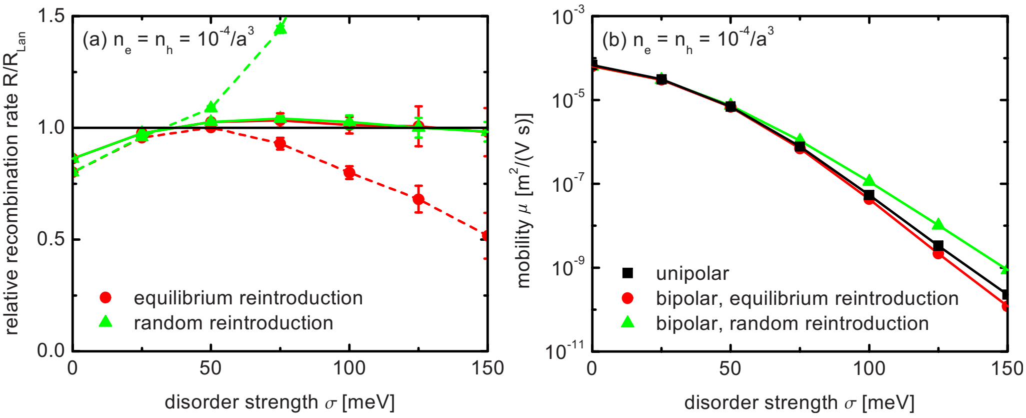

FIG. 6. (Color online) (a): Zero-field recombination rate R relative to the Langevin recombination rate R_{Lan} as a function of disorder strength σ, at temperature $T=300$ K, electron and hole densities $n_{\mathrm{e}}=n_{\mathrm{h}}=10^{-4}/a^3$, and correlated electron and hole energies, calculated for different reintroduction procedures of electrons and holes. Red circles/green triangles: equilibrium/random reintroduction. Solid/dashed lines: Langevin recombination rate calculated with bipolar/unipolar mobilities. (b): Corresponding unipolar (black squares) and bipolar mobilities.

dered organic semiconductor, including all aspects that are relevant for this process: disorder, finite densities of electrons and holes, Coulomb interactions, an applied electric field, different mobilities of electron and holes, and different types of correlation between on-site electron and hole energies. We come to the important conclusion that at zero applied electric field the Langevin expression for the recombination rate is very accurate if the appropriate charge-carrier mobilities are used, i.e., the charge-carrier mobilities as calculated in exactly the bipolar system studied. These mobilities are different from the corresponding mobilities as calculated in a unipolar system with only one charge-carrier type present. In particular, the unipolar mobilities are higher than the bipolar mobilities. The reason for this is that in the bipolar system the additional Coulomb interactions with the oppositely charged carriers lead to an increased effective disorder, resulting in a lower mobility; see Fig. 2. In the bipolar system, the mobilities for the case of correlated electron and hole energies are larger than for the case of anticorrelated electron and hole energies. We attribute this to the larger effect of state filling for the correlated case as compared to the anticorrelated case since electrons and holes compete for low-energy sites. Because state-filling effect increase the mobility, this leads to a higher mobility for the correlated case. This higher mobility then leads to a higher recombination rate. Apparently, this higher recombination rate can be fully accounted for by the Langevin expression. This means that the filamentary structure of the electron and hole current as mentioned in Sec. I does not lead to a breakdown of the Langevin expression, provided that the appropriate mobilities are used.

In order to better understand this result, we considered the distribution of the frequency of recombination events at each site as a function of the random part of the on-site energy of the site, at a disorder energy $\sigma=100$ meV, room temperature, electron and hole densities $n_{\mathrm{e}}=n_{\mathrm{h}}=10^{-4}$ carriers per site, zero electric field, and equal electron and hole mobilities; see Fig. 8. It turns out that in the case of correlated electron and hole energies this distribution has two components; see Fig. 8(a). The first component peaks at a low energy and is approximately proportional to the density of occupied states (DOOS) of electrons and holes. The second, roughly equally large, component peaks at higher energies. Analysis of our simulations shows that a typical recombination process occurs by a mobile carrier approaching an immobile carrier of opposite charge. The last step involves either the hopping of the mobile carrier to the site of the immobile carrier or the hopping of the immobile carrier to the site of the mobile carrier. Since for both possibilities this last step is downward in energy they have equal weights. The first possibility leads to the first component in the distribution and the second possibility to the second component. As

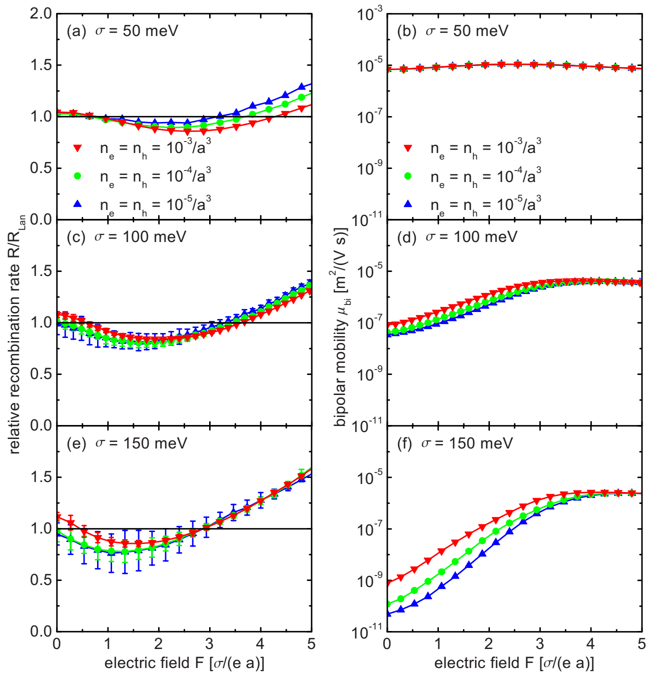

FIG. 7. (Color online) [(a), (c), and (e)]: Recombination rate R relative to the Langevin recombination rate $R_{\mathrm{Lan,bi}}$, calculated with bipolar mobilities and correlated electron and hole energies, as a function of electric field F, at temperature $T=300$ K, at three different electron and hole densities, and three different disorder energies. [(b), (d), and (f)]: Corresponding bipolar mobilities.

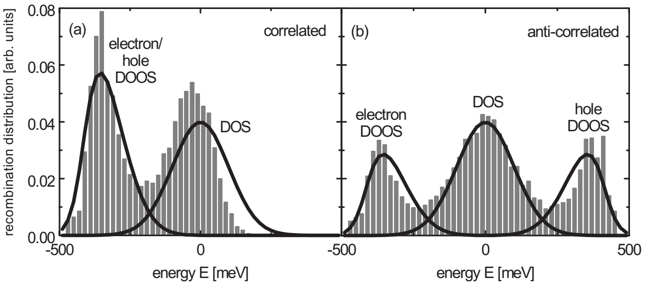

FIG. 8. Bars: distribution of the frequency of recombination events at sites as a function of the random part of the energy of the sites, at disorder energy $\sigma=100$ meV, temperature $T=300$ K, zero field, and densities $n_e=n_h=10^{-4}/a^3$ for (a) correlated and (b) anticorrelated electron and hole energies. Lines: DOOS of electrons and holes and Gaussian DOS. One disorder configuration was used and the total number of recombination events was 67133 and 66817 for the correlated and anticorrelated case, respectively.

compared to the Gaussian DOS, the second component is shifted downward in energy because the mobile charge approaches the immobile charge preferentially via a low-energy site.

In the case of anticorrelated electron and hole energies the distribution has three components; see Fig. 8(b). The third component is the mirror image of the first component of the correlated case and arises because for anticorrelated electron and hole energies a high-energy site for an electron is at the same time a low-energy site for a hole. The sum of the first and third component is now approximately equally large as the second, middle, component. The middle component now becomes symmetric and is closer to the Gaussian DOS than in the correlated case.

The consequence of the above analysis is that the location of sites at which recombination events preferentially take place does not coincide with the location of the current filaments of electrons or holes. Rather, these locations coincide with, or are neighbors of, energetically low-lying sites for electrons or holes. Hence, the conclusion from this analysis is that, whereas current filaments play a primary role in determining the mobility of electrons and holes, they do not play a primary role in determining the location at which recombination events take place.

We remark that in the present work we have taken equal electron and hole densities and equal disorder energies for electrons and holes, and we have only studied the extremes of correlated and anticorrelated on-site electron and hole energies. We expect, however, that our conclusion about the validity of the Langevin expression, with the appropriate mobilities inserted, will also hold in the general case of arbitrary electron and hole densities, different disorder energies for electrons and holes, and an arbitrary correlation between electron and hole energies.

This important conclusion opens the way to simplified and accurate modeling of the recombination rate in OLEDs. In order to realize such modeling, the effect of the reduction in the mobility caused by the enhanced effective disorder due to the random Coulomb field should be quantified. This could possibly be done along the lines set out by Arkhipov *et al.*,[25] who calculated the increase in the effective disorder energy due to Coulomb interactions with dopant ions. In order to make a first step into this direction, we calculated for a disorder energy $\sigma=150$ meV, temperature $T=300$ K, electron and hole densities $n_e=n_h=10^{-3}$ carriers per site, zero electric field, and equal electron and hole mobilities the distribution of the energies $E_{i,q}$ in our simulations, including all Coulomb interactions. We find that this is a Gaussian distribution with a width σ_{eff} that is slightly larger than σ. For the unipolar case we find $\sigma_{\text{eff,uni}}=161\pm2$ meV whereas for the bipolar case we find $\sigma_{\text{eff,bi,corr}}=171\pm1$ meV for correlated and $\sigma_{\text{eff,bi,anticorr}}=173\pm1$ meV for anticorrelated electron and hole energies, respectively. For lower densities $n_e=n_h=10^{-4}$ carriers per site and otherwise the same parameters the corresponding values are $\sigma_{\text{eff,uni}}=152\pm1$ meV, $\sigma_{\text{eff,bi,corr}}=154\pm1$ meV, and $\sigma_{\text{eff,bi,anticorr}}=154\pm1$ meV. As expected, we have $\sigma_{\text{eff,uni}}<\sigma_{\text{eff,bi,corr}}\approx\sigma_{\text{eff,bi,anticorr}}$. We find that with these values and with the parametrization of the GDM mobility as given in Ref. 9 the differences observed in the mobilities in Fig. 3(b) and 3(d) can be quite well explained. In order to properly account for state-filling effects one should then for $\mu_{\text{bi,corr}}$ take *twice* the carrier density taken for $\mu_{\text{bi,anticorr}}$. We remark that despite the fact that the additional energetic disorder caused by the random Coulomb field is smaller for lower carrier densities, the effect on the mobilities is not necessarily smaller since at lower carrier densities the dependence of the mobility on the disorder energy is larger.[9,26] As a matter of fact, the effect observed in Figs. 3(b), 3(d), and 3(f) does not strongly depend on the density. Of course, at extremely low densities [not reached yet for $n_e=n_h=10^{-5}$ in Fig. 3(f)], the effect of the Coulomb interactions on the charge-carrier mobilities should disappear. We intend to perform a more complete analysis of these issues in future work. One of the additional issues that should be analyzed is the fact that the contribution to the energetic disorder from the random Coulomb field will be spatially correlated, which means that the total effective energetic disorder cannot be treated purely within the GDM.

In the presence of an applied electric field, our simulations show deviations from the Langevin recombination rate, which can be attributed to field-induced mobility anisotropy[12] and to a nonzero diffusion contribution caused by the electric-field dependence of the mobilities. These deviations show only a weak dependence on the electron and hole densities. In the range of electric fields relevant for OLEDs the deviations are quite modest.

Our conclusions are expected to have important consequences for calculations of the width of the recombination zone in OLEDs. The inclusion of the carrier-density dependence in the electron and hole mobilities leads to a narrowing of the calculated recombination zone in OLEDs since the mobility of charge carriers entering the recombination zone decreases due to the reduced carrier density caused by recombination. Moreover, "behind" the recombination zone the mobility of charge carriers of one type decreases further due to their now very strongly reduced density.[27] According to the present work, an additional reduction in the carrier mobilities in and behind the recombination zone should occur by the increased effective disorder due to the random Coulomb field of the carriers of the opposite sign. This should lead to a further reduction in the calculated width of the recombination zone.

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