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Charge transport in disordered organic host–guest systems: effects of carrier density and electric field

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Abstract

We investigate charge transport in disordered organic host–guest systems with a bimodal Gaussian density of states (DOS). The energy difference between the two Gaussians defines the trap depth. By solving the Pauli master equation for the hopping of charge carriers on a regular lattice with site energies randomly drawn from the DOS, we obtain the dependence of the charge-carrier mobility on the relative guest concentration, the trap depth, the energetic disorder, the charge-carrier density and the electric field. At small and high guest concentrations, our work provides support for recent semi-analytical model results on the dependence of the mobility on the charge-carrier density at zero field. However, at the cross-over between the trap-limited and trap-to-trap hopping regimes, where the mobility attains a minimum, our results can almost be one order of magnitude larger than predicted semi-analytically. Furthermore, it is shown that field-induced detrapping can contribute strongly to the electric-field dependence of the mobility. A simple analytical expression is provided which describes the effect. This result can be used in continuum drift-diffusion models for charge transport in devices such as organic light-emitting diodes.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Understanding charge-carrier transport in disordered organic host–guest systems is vital because of their application in various electronic devices. For different purposes, these systems are used in organic light-emitting diodes (OLEDs): to harvest both singlet and triplet excitons [1] to decrease injection barriers [2, 3] and to tune the emission color [4]. Host–guest systems have also been used to obtain light amplification [5] in materials used for optical data storage and image processing [6] in xerography [7] and in organic field-effect transistors [8]. Apart from intentional doping, guest molecules can be present unintentionally because of non-ideal preparation processes.

The charge-carrier mobility in host–guest systems is substantially influenced by the guest if the energy of the HOMO (highest occupied molecular orbital) and/or LUMO (lowest unoccupied molecular orbital) of the guest molecule lies within the energy gap of the host. Time-of-flight (TOF) experiments [9–15] have revealed that there are then four transport regimes (see figures 1(a)–(d)). For very small guest concentrations the presence of guest molecules will not significantly affect the charge transport (figure 1(a)). Beyond a certain critical guest concentration, charge-carrier trapping at the guest molecules gives rise to a decrease of the mobility with increasing relative guest concentration, x (figure 1(b)). In the absence of disorder, the trap-limited mobility, $\mu(x)$, is described by the Hoesterey–Letson (HL) [16] expression

$$\mu(x) = \frac{\mu(0)}{1 + x\exp(\Delta/k_{\mathrm{B}}T)}, \qquad (1)$$

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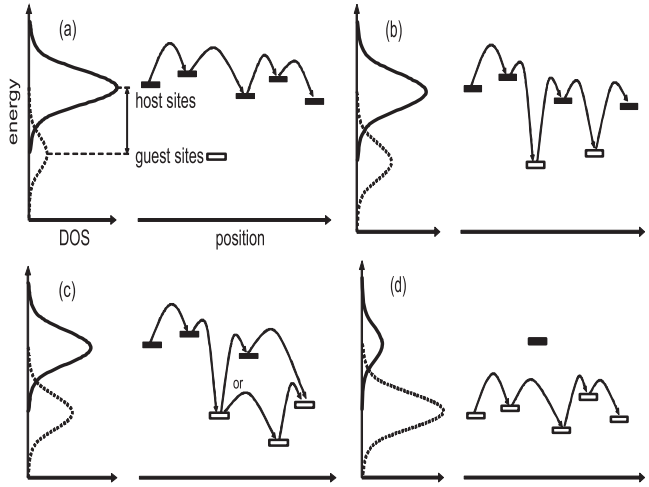

Figure 1. Different hopping regimes in a disordered host–guest system. (a) Hopping via host sites (no influence of guest); (b) hopping via host sites in the presence of a small amount of guest sites (trap-limited transport); (c) hopping via both host and guest sites; (d) hopping via guest sites. The DOS of host (solid lines) and guest (dotted lines) and the offset Δ in between are schematically indicated.

where $\mu(0)$ is the trap-free mobility, Δ is the trap depth, k_B is the Boltzmann constant and T is the temperature. At a sufficiently large guest concentration the average distance between the guest molecules can become sufficiently small, so that both host and guest molecules participate in the charge-carrier transport (figure 1(c)). Whether this cross-over regime is actually reached depends on the extensions of the localized wavefunctions of the host and guest molecules (see section 2). For very large guest concentrations the mobility is then predominantly due to hopping between the guest molecules (figure 1(d)).

Various theoretical studies, using semi-analytical [17–20] and Monte Carlo [21] methods, have been carried out to understand the dependence of the charge-carrier mobility in host–guest systems on the material parameters (host and guest density, trap depth, width of the host and guest DOS) and on the experimental conditions (temperature, carrier density and electric field). The carrier-density dependence was studied only recently, motivated by recent experimental and theoretical proofs of the importance of that effect in pure systems [22–24]. Using semi-analytical approaches based on effective-medium theory (EMT) and percolation theory, Coehoorn found that the effect can also be very important in host–guest systems [19]. It was shown that the effect can provide an explanation for experimental results obtained by Borsenberger *et al* [11] who deduced from TOF studies trap-limited mobilities of the form $\mu(x) \propto x^{-n}$, with (depending on the material investigated) n larger or smaller than the value of 1 expected from equation (1).

In spite of this progress, there are several unresolved questions concerning the mobility in host–guest systems with a bimodal Gaussian DOS. Firstly, the semi-analytical model calculations of the carrier-density dependence of the mobility, at arbitrary guest densities, have not yet been compared with numerically exact solutions of the hopping problem. In particular, it is of interest to investigate the mobility in the cross-over regime between the trap-limited and trap-to-trap hopping regimes (figure 1(c)), around the minimum in the mobility. The mobility may then be expected to be underestimated by effective-medium approaches, as any statistical variation of the local guest concentration (towards a larger *and* towards a smaller concentration) will lead to a larger local mobility. Secondly, only limited studies have been carried out on the electric-field dependence of the mobility. From TOF experiments [10, 12, 21] it is known that in the presence of guest molecules the electric-field dependence of the mobility is much stronger than in pure host systems. So far, the field dependence has only been studied by Fishchuk *et al* [17] using the EMT, for small guest concentrations and in the low carrier-density limit. The combined effect of the carrier-density and electric-field dependence of the mobility has not yet been studied theoretically.

In this paper, we present the results of numerically exact calculations of the hopping mobility in host–guest systems, from which we address both issues discussed above. We focus on parameters which are most realistic for materials and experimental conditions typical for OLED applications. For example, the width, σ, of the Gaussian DOS is $\sim$0.10 eV, so that $\sigma/(k_B T) \sim 4$ at room temperature. A comparison is made with the semi-analytical EMT results given in [19]. The agreement is shown to be excellent in the trap-limited and guest-to-guest transport regimes, but not in the mixed cross-over regime. As already anticipated above, the mobility is then significantly larger than was obtained from the EMT results. It will be argued that this is highly relevant to the modeling of transport in the emissive layers of realistic small-molecule OLED materials. Furthermore, we analyze the field dependence of the mobility and show that it can be strongly enhanced compared to the mobility that would be expected on the basis of a simple 'thermal detrapping' model. An analytical expression for the additional factor, describing 'field-induced detrapping', is shown to provide a quite accurate description of the results.

In section 2, we introduce the theoretical methods, including a master-equation (ME) approach and a percolation method. The ME approach used is comparable to that employed previously to study transport in pure materials, i.e. with a monomodal Gaussian DOS [23]. In section 3, we give results for the dependence of the mobility on the guest concentration, the carrier density and the electric field for a bimodal Gaussian DOS with different values of the trap depth and of the width of the host and guest Gaussian DOS. A summary and conclusions are given in section 4.

2. Theory

2.1. Hopping model

We treat the host–guest systems, with a total molecular site density N_t, as an array of sites on a regular cubic lattice, with site energies which are randomly drawn from a bimodal Gaussian density of states with a relative concentration x of guest sites:

$$g(\epsilon) = (1 - x)g_h(\epsilon) + x g_g(\epsilon), \qquad (2a)$$

$$g_{\mathrm{h}}(\epsilon) = \frac{1}{\sqrt{2\pi}\sigma_{\mathrm{h}}a^3}\exp\left(-\frac{\epsilon^2}{2\sigma_{\mathrm{h}}^2}\right), \tag{2b}$$

$$g_{\mathrm{g}}(\epsilon) = \frac{1}{\sqrt{2\pi}\sigma_{\mathrm{g}}a^3}\exp\left(-\frac{(\epsilon+\Delta)^2}{2\sigma_{\mathrm{g}}^2}\right), \tag{2c}$$

with σ_{h} and σ_{g} the widths of the DOS of host and guest, respectively, and with $a = N_{\mathrm{t}}^{1/3}$ the lattice constant. The center of the DOS of the guest is offset with respect to the center of the DOS of the host by $-\Delta$ ($\Delta > 0$), the mean trap depth. The effect of positional disorder has been investigated for a pure system by Bässler [25] and was found not to influence the mobility at small electric field. For a finite electric field it was found that there is almost no influence if this disorder is below a certain critical value. In the modeling of charge transport in derivatives of poly-*para*-phenylene-vinylene (PPV) it was found that it is not necessary to include the effect of positional disorder [23]. Therefore, we will also disregard positional disorder in the present work. The systems considered below have typical sizes of 100^3 lattice sites, which is large enough to avoid finite-size effects.

The hopping between sites is described as a thermally assisted tunneling process. Coupling to a bath of acoustical phonons is assumed, leading to a hopping rate from site i to j of the Miller–Abrahams form [26]:

$$W_{ij} = \nu_0 \exp\left(-2\alpha R_{ij} - \frac{\varepsilon_{ij} + |\varepsilon_{ij}|}{2k_{\mathrm{B}}T}\right), \tag{3}$$

where ν_0 is a hopping attempt rate, $\mathbf{R}_{ij} \equiv \mathbf{R}_j - \mathbf{R}_i$ is the distance vector between sites i and j, $\varepsilon_{ij} \equiv \varepsilon_j - \varepsilon_i - eER_{ij,x}$, E is the electric field (applied in the x direction), e is the charge of the carriers and α is the inverse wavefunction localization length. We consider the case of equal localization lengths of host and guest wavefunctions and take $\alpha^{-1} = 0.1 \times a$, as in [23]. Charge-carrier hopping to a maximum distance of $2\sqrt{3}\times a$ is considered, involving 124 sites around a central site. For $\Delta = 23k_{\mathrm{B}}T$, $\sigma_{\mathrm{h}} = \sigma_{\mathrm{g}} = 4k_{\mathrm{B}}T$, $p = 10^{-4}$ carriers per site, and varying guest concentration we did a test calculation within the percolation approach for a maximum hopping distance of $5\sqrt{3} \times a$, involving 1331 sites around a central site, and found no significant difference in the mobility. This demonstrates that our maximum hopping distance is large enough. Our study does not include the very low temperature and/or very large disorder parameter range within which variable-range hopping over distances much larger than a is important. The mobility of the charge carriers is determined from a numerical solution of the Pauli master equation or a numerical solution of a percolation problem. Both approaches are discussed in detail in sections 2.2 and 2.3.

In general, the host and guest wavefunction localization lengths are different. Such a situation has been studied by Coehoorn using an effective-medium theory [19]. The ratio of localization lengths determines the location of the minimum in the mobility (cross-over regime, figure 1(c)). As we will see below, the approach followed in [19] for determining the cross-over guest concentration is quite accurate. Hence, we refer to this reference for a discussion of this issue. If the polarizabilities of the host and guest molecules are different, the dielectric permittivity of the medium will change upon changing the concentration of the guest and as a result the localization length α^{-1} will change. Some experimental results [7] indicate that this effect can occur. However, we will leave this out of consideration. We will also disregard changes in the polarizabilities under the application of an applied electric field, since such nonlinear effects are negligible for the considered field strengths.

2.2. Master-equation approach for calculating the mobility

In a stationary situation, the Pauli master equation for the hopping process on a lattice of sites becomes

$$\sum_{j\neq i}\left[-W_{ij}\,p_i(1-p_j) + W_{ji}\,p_j(1-p_i)\right] = 0, \tag{4}$$

where p_i is the probability that site i is occupied by a charge, W_{ij} is given by equation (3) and where the factor $1 - p_i$ accounts, in a mean-field approximation, for the fact that only one carrier can occupy a site, due to the strong on-site Coulomb repulsion. We neglect the Coulomb interaction between carriers on different sites. As shown by Cottaar and Bobbert, the use of the mean-field approximation in ME calculations of the mobility in a monomodal Gaussian DOS is very accurate, also for the case of a finite carrier density [27]. Recently, Zhou *et al* carried out an explicit Monte Carlo simulation for transport in a Gaussian DOS at finite carrier densities including the Coulomb interaction between carriers on different sites [28]. It was found that only at densities exceeding 0.01 carriers per site the effect of the Coulomb interaction becomes noticeable. We performed a test Monte Carlo simulation including Coulomb interactions between the charge carriers for a set of realistic parameters ($\Delta = 6k_{\mathrm{B}}T$, $\sigma_{\mathrm{h}} = \sigma_{\mathrm{g}} = 3k_{\mathrm{B}}T$, $x = 0.1$, $p = 10^{-3}$ carriers per site) and compared the results with those of the master equation for a range of electric fields and found that the differences in the calculated mobility are within the error bars. We therefore conclude that the effect of the Coulomb interaction is insignificant in realistic situations.

We solve equation (4) for the occupational probabilities p_i by an iteration procedure outlined in [29] and [23], for sites on a cubic lattice, as described in section 2.1, and employing periodic boundary conditions. Once the occupational probabilities p_i are found, the charge-carrier mobility μ can be calculated from

$$\mu = \frac{\sum_{i,j,i\neq j} W_{ij}\,p_i(1-p_j)R_{ij,x}}{pVE}, \tag{5}$$

where $p = \sum_i p_i/V$ is the average charge-carrier density and V is the system volume. The summations are over all sites in the box considered. In the iteration scheme the convergence of both p_i (for all i) and μ is checked. For a number of different disorder configurations the mobility is evaluated and averaged until this average is known with a precision better than 10%.

2.3. Percolation model for calculating the mobility

For systems with large trap depths, Δ, no stable solutions could be obtained using the ME approach. For such cases, we have used a percolation model for calculating the mobility. The model is valid in the limit of small electric fields. The hopping mobility can then be conveniently obtained from a calculation of the conductivity of a random-conductor network in which the conductance between two nodes i and j is given by [30]

$$G_{ij} = G_0 \exp\left(-2\alpha R_{ij} - \frac{|\varepsilon_i - \varepsilon_F| + |\varepsilon_j - \varepsilon_F| + |\varepsilon_j - \varepsilon_i|}{2k_BT}\right), \quad (6)$$

where ε_F is the Fermi energy and $G_0 = e^2\nu_0/(k_BT)$. For a given charge-carrier density, p, ε_F is determined by the condition

$$p = \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) \frac{1}{\exp[(\varepsilon - \varepsilon_F)/k_BT] + 1}, \quad (7)$$

where $g(\varepsilon)$ is given by equation (2*a*).

The conductivity of the system can be calculated either by numerically solving Kirchhoff's equations for the whole network, or by estimating the 'typical' two-site conductance using effective-medium [31] or percolation techniques [30, 32]. We have followed the latter approach. Apart from a prefactor of order unity the conductivity of the system is then given by

$$\Sigma \sim \frac{G_c}{a}. \quad (8)$$

G_c is the so-called critical percolation conductance of the network. The mobility follows from the conductivity using the equation

$$\mu = \frac{\Sigma}{ep} \sim \frac{G_c}{epa}. \quad (9)$$

We determine G_c by considering the conductance of a large enough box-shaped conductor network in between two electrodes, from which successively the connections with increasing conductance are eliminated. G_c is then the last conductance which is eliminated before the conductance of the total system goes to zero, so that there is no percolating cluster anymore which connects the two electrodes.

3. Results and discussion

3.1. Small electric fields—comparison with semi-analytical results

In this subsection, a comparison is given between our numerically exact results with those obtained from semi-analytical approaches, including the EMT results presented in [19], restricting ourselves to small electric fields. As discussed in section 1, the transport regime in which we are most interested is the cross-over regime between trap-limited transport and trap-to-trap transport, where the mobility attains a minimum. We have studied this regime using the percolation model, which also for large trap depths is found to provide

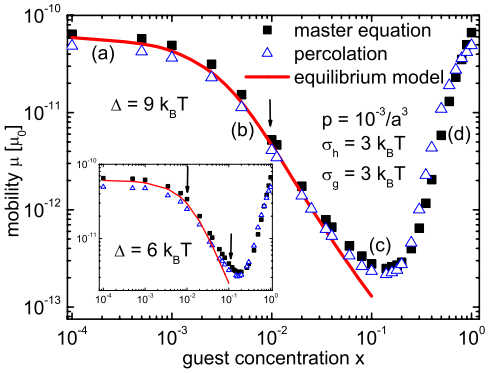

Figure 2. Dependence of the mobility on the guest concentration x obtained with the master-equation (squares) and percolation (triangles) approach, for a host–guest system with a carrier density $p = 10^{-3}/a^3$, with a host and guest DOS of width $\sigma_h = \sigma_g = 3k_BT$, and a trap depth $\Delta = 9k_BT$ (main panel) and $\Delta = 6k_BT$ (inset). Lines: results following from the equilibrium model. The different hopping regimes (a)–(d) of figure 1 are indicated in the main panel.

stable solutions. In order to establish the precision of that model, which contains an unknown prefactor of the order of unity (see section 2.3), figure 2 gives a comparison with the results from the ME approach. The figure shows the guest-concentration dependence of the small-field mobility, expressed in units of $\mu_0 = a^2\nu_0 e/\sigma_h$, for equal widths of the host and guest DOS, $\sigma_h = \sigma_g = 3k_BT$, at two different trap depths, $\Delta = 6k_BT$ and $9k_BT$, at a carrier concentration (pa^3) equal to 10^{-3}. The four transport regimes, which were already discussed in section 1 (see figures 1(a)–(d)), are clearly visible. The results obtained with the percolation approach are in very good agreement with the ME results. We conclude from figure 2 that the trend predicted by the percolation approach is correct and that the prefactor only slightly depends on the guest concentration. This conclusion is supported by analyses for other choices of the material parameters and the charge-carrier concentration. The full lines in the figure ('equilibrium model') will be discussed in section 3.2.

In figure 3 we depict the guest-concentration dependence of the normalized small-field mobility calculated within the ME and percolation approach for a system for which $\sigma_h = \sigma_g = 4k_BT$, for three different trap depths, and for a carrier concentration of 10^{-4}. At room temperature, the trap depth $\Delta_0 = 11.512k_BT$ corresponds to an energy of 0.30 eV. For large trap depths only the results from the percolation model are shown, as the ME approach did not lead to well-converged results around the mobility minimum. The dashed lines give the dependence of the charge-carrier mobility on guest concentration for different trap depths, as given in figure 4(c) of [19], which are calculated for exactly the same parameters. The latter results were obtained within the Movaghar–Schirmacher (MS) effective-medium model. In the trap-limited and in the guest-to-guest transport regimes, the agreement with the MS model results is very good. However, close to the mobility minimum the MS model yields a significant underestimation of the mobility.

The observed underestimation of the mobility near the mobility minimum may be viewed as a failure of the

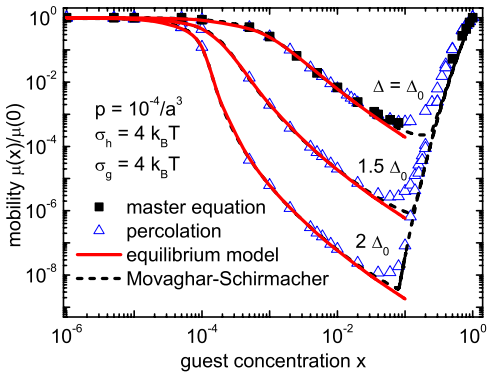

Figure 3. Dependence of the mobility on the guest concentration x, normalized by the mobility at $x = 0$, obtained with the master-equation (squares) and percolation (triangles) approach, for a host–guest system with a carrier density $p = 10^{-4}/a^3$, with a host and guest DOS of width $\sigma_h = \sigma_g = 4k_BT$, and three different trap depths, with $\Delta_0 = 11.512k_BT$. Dashed lines: results from [19] obtained with the Movaghar–Schirmacher model. Solid lines: results following from the 'equilibrium model'.

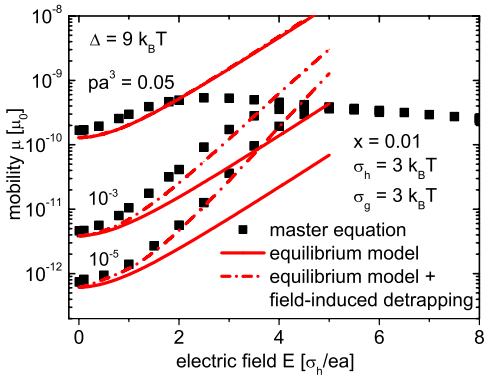

Figure 4. Dependence of the mobility on the electric field E for a host–guest system with a guest concentration $x = 0.01$, with a host and guest DOS of width $\sigma_h = \sigma_g = 3k_BT$, and a trap depth $\Delta = 9k_BT$, for three different carrier concentrations. Squares: master-equation results. Solid lines: 'equilibrium model'. Dashed–dotted lines: 'equilibrium model' with field-induced detrapping. For a carrier concentration of 10^{-3} the parameters are the same as for the point indicated by the arrow in the main panel of figure 2.

effective-medium approach to properly consider the actual percolating pathways. Random statistical variations of the local guest concentration around the mobility minimum, to smaller *and* to larger concentrations, lead to regions with an enhanced mobility. We believe that this finding is relevant to the precise modeling of transport in high-performance small-molecule OLEDs, containing host–guest-type matrix-dye emissive layers. The range of trap depths studied, from 0.30 to 0.60 eV, corresponds to values typically encountered in such systems. Furthermore, the dye concentration in such systems typically ranges from 1 to 10%. Figure 3, and also previous experimental work [9–15], shows that the cross-over to guest-to-guest hopping can coincide with this concentration range.

In [19] it was shown that a very good agreement is obtained in the trap-limited regime between the mobilities calculated with the Movaghar–Schirmacher model, taking into account a finite carrier density $p = 10^{-6}/a^3$, and the results of the time-of-flight measurements of the mobility of [11]. Since in this regime the present results agree very well with those of [19] we can conclude that our results also agree with these measurements.

3.2. Electric-field dependence of the mobility

Figure 4 shows the electric-field dependence of the mobility as obtained from the ME approach (squares) for a system with $\sigma_h = \sigma_g = 3k_BT$ and with $\Delta = 9k_BT$, as in the main panel of figure 2, for a guest concentration $x = 0.01$ (indicated in figure 2 by an arrow). The system is thus well in the trap-limited regime. The values of Δ, σ_h and σ_g are equal to those used in [17], in order to facilitate making a comparison with these results (see below). Results are given for charge-carrier concentrations equal to 10^{-5}, 10^{-3} and 5×10^{-2}.

At small fields, the mobility is strongly carrier-density-dependent, as already predicted from the EMT [19]. The mobility increases with increasing field, until it attains a maximum at a field of the order $\sigma_h/(ea) = 1$, depending on the charge-carrier density. When $Eea/\sigma_h \gg 1$, the mobility decays as $\mu \propto 1/E$, as then only energetically downward hopping along the direction of the electric field takes place, leading to an electric-field-independent carrier velocity. We analyze the lower-field parts of the curves by first considering the simplest possible model within which the mobility in the trap-limited regime is viewed as a result of the transport of carriers which are thermally excited from trap to host sites, to an extent determined by assuming thermal equilibrium. The same assumption underlies the HL relationship (equation (1)) for the case of delta-function-shaped host and guest densities of states. This thermal detrapping 'equilibrium model' may be generalized to host–guest systems with a bimodal Gaussian DOS by first calculating, for a certain carrier density p, the Fermi energy, and then calculating the carrier density p_h in the host DOS from

$$p_h = (1 - x) \int_{-\infty}^{\infty} d\varepsilon g_h(\varepsilon) \frac{1}{\exp[(\varepsilon - \varepsilon_F)/k_BT] + 1}. \quad (10)$$

Within the framework of this model, the carrier-density and field-dependent mobility is given by the fraction of carriers which populates host states times the host mobility at the corresponding carrier density:

$$\mu(T, p, E) = \frac{p_h}{p} \mu_h(T, p_h, E). \quad (11)$$

The dependence of the mobility on the carrier density, electric field and temperature in a pure host system was already calculated with the ME approach in [23], where the following parameterization scheme was introduced:

$$\mu_h(T, p_h, E) \approx \mu(T, p_h) f(T, E), \quad (12)$$

with

$$\mu(T, p) = \mu_0(T) \exp[\tfrac{1}{2}(\hat{\sigma}^2 - \hat{\sigma})(2pa^3)^\delta], \quad (13a)$$

$$\mu_0(T) = \mu_0\, c_1\, \exp\left[-c_2\hat{\sigma}^2\right], \tag{13b}$$

$$\delta \equiv 2\frac{\ln\left(\hat{\sigma}^2 - \hat{\sigma}\right) - \ln(\ln 4)}{\hat{\sigma}^2}, \tag{13c}$$

$$\mu_0 \equiv \frac{a^2\, \nu_0\, e}{\sigma}, \tag{13d}$$

and

$$f(T, E) = \exp\left[0.44(\hat{\sigma}^{3/2} - 2.2)\left(\sqrt{1 + 0.8\left(\frac{Eea}{\sigma}\right)^2} - 1\right)\right], \tag{14}$$

with $c_1 = 1.8 \times 10^{-9}$, $c_2 = 0.42$ and $\hat{\sigma} = \sigma/k_\mathrm{B}T$, where in this case $\sigma = \sigma_\mathrm{h}$. In figures 2 and 3, the full curves give the mobility as predicted from this 'equilibrium model' at zero field. It is seen that in the trap-limited regime the model then provides an excellent prediction for the mobility. In figure 4, the predictions as obtained from the 'equilibrium model' are also indicated by the full curves. Only for the highest carrier concentration considered, 0.05, is the agreement reasonable. In that case, the situation is almost equal to that for the pure host system, since all traps are filled. For the two lower carrier concentrations considered, the simple 'equilibrium model' severely underestimates the field dependence of the mobility. We attribute this to field-induced detrapping of carriers, which was neglected in the 'equilibrium model'.

We have developed a simple model to take field-induced detrapping into account by noting that, as a result of the applied field, carriers trapped on a guest site i are not in equilibrium with carriers on host sites with a mean energy which is displaced by an energy Δ, but (to a first approximation) with carriers at host sites j with mean energies which are different from Δ by an amount $-e\mathbf{R}_{ij}\cdot\mathbf{E}$, where $\mathbf{E}$ is the electric-field vector. As we focus in this paper on transport at relatively large temperatures, i.e. on the nearest-neighbor hopping transport regime, we argue that to a good first approximation R_{ij} may be taken equal to the average intersite distance, a (see also figure 6 in [24]). On a cubic lattice, three different detrapping processes can then be distinguished: detrapping from a guest to a host site (i) along the electric field, (ii) opposite to the electric field, and (iii) perpendicular to the electric field (with a weight four times that of the other two processes). Therefore, we propose to describe the increase of the mobility by field-induced detrapping by inserting in equation (10) the following *effective* field-dependent host DOS:

$$g_{h,\mathrm{eff}}(\epsilon, E) = \frac{1}{\sqrt{2\pi}\sigma_\mathrm{h}a^3}\frac{1}{6}\left\{\exp\left(-\frac{(\epsilon - Eea)^2}{2\sigma_\mathrm{h}^2}\right) + \exp\left(-\frac{(\epsilon + Eea)^2}{2\sigma_\mathrm{h}^2}\right) + 4\exp\left(-\frac{\epsilon^2}{2\sigma_\mathrm{h}^2}\right)\right\}. \tag{15}$$

The enhanced host carrier density leads, via equation (12), to an enhanced mobility. From a more elaborate analysis, within which the occupation probability of field-displaced host and guest states is calculated in a more explicit way from host-to-guest and guest-to-host Miller–Abrahams hopping rates, it follows that the approach given above provides an excellent approximation up to intermediate-size fields ($Eea < \sigma$) [34]. The mobility resulting from the above approach is plotted in figure 4 (dashed–dotted curves). We observe that this leads to a very good agreement, especially for a carrier concentration of 10^{-5}, where the model is expected to work best. We note that in the ME calculations not only nearest-neighbor hops are taken into account, but also hops to 124 sites in a cube around a central site. It would not be very difficult to include further hops in the model. However, because of the rather small value of the wavefunction localization length, $\alpha^{-1} = 0.1 \times a$, the changes would be very small. We also note that field-induced detrapping has been studied by several authors and that the importance of the effect depends strongly on the precise shape of the DOS. For example, for the case of a pure system with an exponential DOS, hopping beyond the nearest neighbor can be relevant, as shown by Marianer and Shklovskii [33].

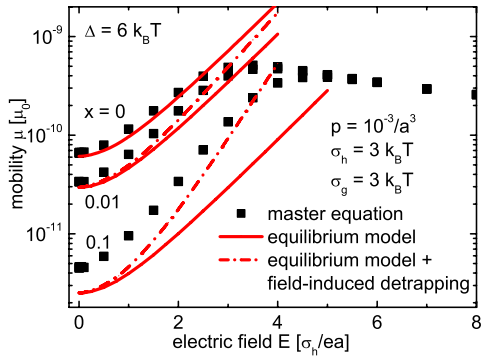

Figure 5. Dependence of the mobility on the electric field E for a host–guest system with a carrier density of $p = 10^{-3}/a^3$, with a host and guest DOS of width $\sigma_\mathrm{h} = \sigma_\mathrm{g} = 3k_\mathrm{B}T$, and a trap depth $\Delta = 6k_\mathrm{B}T$, at three different guest concentrations. Squares: master-equation results. Solid lines: 'equilibrium model'. Dashed–dotted lines: 'equilibrium model' with field-induced detrapping. For the guest concentrations of 0.01 and 0.1 the parameters are the same as for the two points indicated by the arrows in the inset of figure 2.

The field dependence displayed in figure 4 for the lowest carrier concentration, 10^{-5}, may be compared with the results obtained from the EMT prediction given by Fischchuk *et al* for essentially the same material parameters but for a vanishing carrier density ([17], curve 3 in figure 10(b)). Contrary to this EMT prediction, we do not find a transition from a $\log(\mu) \propto \sqrt{E}$ to a $\log(\mu) \propto E$ shape of the field dependence of the mobility with increasing field. Moreover, in contrast to the EMT prediction, which does not saturate, our mobility saturates and decays then as $1/E$, as explained above.

In figure 5 we depict the electric-field dependence of the mobility for the same parameter values as in the inset of figure 2 for three different guest concentrations: $x = 0$ (pure host system), 0.01 and 0.1. These last two values are indicated by the arrows in the inset of figure 2. The figure contains the results obtained with the ME approach, the 'equilibrium model', and the equilibrium model with field-induced detrapping. In agreement with general trends observed in experimental studies [21] the field dependence is seen to increase strongly with increasing guest concentration. The 'equilibrium model' with field-induced detrapping correctly

describes this trend. For the highest guest concentration considered, $x = 0.1$, the regime is entered where guest-to-guest hopping starts to contribute to the transport (see figure 1(c)). Obviously, the 'equilibrium model' starts to fail here. Firstly, it already underestimates the mobility at zero field. Secondly, it is no longer possible to give a simple description of the field dependence.

We note that OLED research is presently focusing on thin dye-doped emissive layers of a few times 10 nm sandwiched in between electron-and hole-transporting layers [35]. Since such devices are operated at biases of a few volts and since this voltage almost completely drops over the emissive layer, a relatively large field of the order of 10^8 V m^{-1} is present in this layer. With a typical value $\sigma = 0.1$ eV for the width of the disorder such field strength corresponds to a value $eEa/\sigma \approx 1$ (taking 1 nm for a). At such a field strength the field dependence of the mobility is very important (see figures 4 and 5). Therefore, we expect very useful applications of our model to such devices.

4. Summary and conclusions

We have investigated the hopping transport in host–guest systems with a bimodal Gaussian density of states using a master-equation approach and (at small electric fields) a percolation model. The master-equation approach used is thus the most sophisticated theoretical approach applied to these systems. We have focused on material parameters which are typical for OLEDs, and on transport at relatively high temperatures in the nearest-neighbor hopping regime. The main conclusions are:

(i) At all guest concentrations, the low-field mobility can be described equally well with a numerical percolation model as with the (for large trap depths less stable) master-equation approach.

(ii) For small guest concentrations, in the trap-limited hopping regime, the small-field mobility can be described very well within an 'equilibrium model', in which the number of carriers thermally activated from guest to host sites is evaluated and in which these activated carriers are assumed to move in the undisturbed density of states of the host.

(iii) For intermediate guest concentrations, in the mixed cross-over regime in between trap-limited transport and guest-to-guest transport at which the mobility attains a minimum, the mobility is significantly larger than predicted from effective-medium theory. In section 3.1, this has been argued to have much significance for the modeling of high-performance OLEDs.

(iv) For high electric fields, the 'equilibrium model' fails because it does not take the field-induced detrapping of carriers into account. A simple model (section 3.2) has been proposed for including this effect. It leads to a much stronger dependence of the mobility on the electric field in host–guest systems as compared to pure host systems, in agreement with experiments.

We envisage that the approach introduced in this paper for including field-induced detrapping might also be applicable to transport in related systems, such as systems with a Gaussian host DOS and an exponential trap DOS. Recently, Mandoc *et al* [36] successfully used such a model DOS for analyzing electron transport in poly-phenylene-vinylene (PPV) organic semiconductors. The same 'equilibrium model' described by equation (10) was used for calculating the mobility, but field-induced detrapping was not taken into account. It would be interesting to investigate the possible role of that effect.

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