PHYSICAL REVIEW B **74**, 115204 (2006)

Calculating charge-carrier mobilities in disordered semiconducting polymers: Mean field and beyond

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(Received 14 April 2006; published 19 September 2006)

We model charge transport in disordered semiconducting polymers by hopping of charges on a regular cubic lattice of sites. A large on-site Coulomb repulsion prohibits double occupancy of the sites. Disorder is introduced by taking random site energies from a Gaussian distribution. Recently, it was demonstrated that this model leads to a dependence of the charge-carrier mobilities on the density of charge carriers that is in agreement with experimental observations. The model is conveniently solved within a mean-field approximation, in which the correlation between the occupational probabilities of different sites is neglected. This approximation becomes exact in the limit of vanishing charge-carrier densities, but needs to be checked at high densities. We perform this check by dividing the lattice in pairs of neighboring sites and taking into account the correlation between the sites within each pair explicitly. This pair approximation is expected to account for the most important corrections to the mean-field approximation. We study the effects of varying temperature, charge-carrier density, and electric field. We demonstrate that in the parameter regime relevant for semiconducting polymers used in practical devices the corrections to the mobilities calculated from the mean-field approximation will not exceed a few percent, so that this approximation can be safely used.

DOI: 10.1103/PhysRevB.74.115204 PACS number(s): 72.20.Ee, 72.80.Le, 73.61.Ph

I. INTRODUCTION

Conjugated semiconducting polymers are investigated intensively for their use in areas as diverse as light-emitting diodes,[1,2] photovoltaic cells,[3–5] and transistors.[6] Understanding the charge transport in these polymers is essential for further progress in these areas. The central quantity in this transport is the charge-carrier mobility μ, which quantifies how easily charge carriers move when an electric field is applied. In particular, it is crucial to understand how μ depends on the various parameters of the system.

Theoretically, the electrical conduction in these disordered polymers has been described by hopping of charge carriers from one localized state at a specific site to another. Most often, the disorder is introduced by assuming that the energy of these localized states is a random variable. In the context of polymer light-emitting diodes this randomness is usually taken to be Gaussian, with a standard deviation σ that is typically 0.1–0.2 eV. Early research of this so-called Gaussian disorder model (GDM) has focused on the dependence of μ on the temperature T and the electric field E. In particular, the ground-breaking work of Bässler and co-workers in this area should be mentioned.[7,8] Their Monte Carlo simulations for the GDM showed a non-Arrhenius dependence $\mu \propto \exp[-(T_0/T)^2]$ on temperature and a Poole-Frenkel $\mu \propto \exp[\gamma\sqrt{E}]$ dependence on electric field, in a limited field range. The concept of correlated disorder was introduced,[9] leading to the correlated disorder model (CDM), which can explain Poole-Frenkel behavior in a broad range of field strengths. As physical explanations for this correlated disorder charge-dipole interactions[10,11] and thermal fluctuations in molecular geometries[12] were suggested.

In polymer field-effect transistors, where the number of carriers per site can become of the order of a few percent, it was demonstrated that there is an important dependence of the mobility on the charge-carrier density.[13] Recent experimental work has pointed out that in polymer diodes there is also a strong dependence of the mobility on the charge-carrier density.[14–16] At first sight this is surprising, since in these diodes the charge-carrier density is only of the order of 10^{-4}–10^{-5} per site at typical operating conditions. A dependence on charge-carrier density at such low densities can be rationalized from the fact that in a Gaussian density of states (DOS) the number of energetically low-lying states that is thermally accessible is only a small fraction of the total amount of states, so that state-filling effects caused by the Fermi-Dirac statistics are still important. Evaluation of this dependence can be done numerically[17,18] or semianalytically.[20] Very recently, we showed that by using a space-charge limited model with the numerically determined dependence of the mobility on the charge-carrier density and the electric field for the GDM, it is possible to obtain excellent fits for the current-voltage characteristics of hole-only diodes with PPV-type polymers as the active layer.[18] The main conclusion of that work is that the previously assumed dependence of the mobility on the electric field is actually, for a large part, a dependence on the charge-carrier density. In order to explain the current-voltage characteristics of these polymers, it is therefore not necessary to assume correlation in the disorder, as in the CDM.

In the approach followed in Ref. 18 the mobility is determined by solving the master equation for the mean-field occupational probabilities of the sites. In this approximation correlations between occupational probabilities of different sites are neglected. The approximation becomes exact in the limit of vanishing charge-carrier density. It is not *a priori* clear, however, that it is justified at finite densities. Hence it also not *a priori* clear whether the charge-carrier density dependence obtained with this approximation is correct. We want to emphasize that throughout the years the mean-field approximation has been the standard approach in literature to calculate the conductance of disordered systems for the case that state-filling effects are important, starting from the early work of Miller and Abrahams [19] up to more recent work.[12,13,17] Therefore the question of the validity of the mean-field approximation has a very broad scope.

In the present paper we explain in detail how we obtain the master equation for the occupational probabilities in the mean-field approximation and how this equation is solved. Moreover, we go beyond the mean-field approximation by dividing the lattice of sites into neighboring pairs of sites, treating correlations between the two sites of each pair explicitly. Since correlations between neighboring sites are expected to be the most important ones, this treatment is a good check of the validity of the mean-field approximation.

II. THEORY

We model the polymer as a set of sites i ($i=1,\ldots N$) with a total number M of charge carriers of equal sign. Hopping of charge carriers between sites i and j is supposed to be a Markovian process occurring with a rate $W_{i,j}$, to be specified later on. We assume that, due to the strong on-site Coulomb interaction, double occupancy of a site does not occur, but we neglect the Coulomb interaction between carriers at different sites. The state of the system is fully described by specifying the occupation η_i of all sites: $\eta_i=1$ (occupied) or $\eta_i=0$ (unoccupied). Let $P(\{\eta\})$ be the probability that the system is in the state with occupations $\{\eta\}=(\eta_1,\eta_2,\ldots,\eta_N)$. In a stationary situation, the time derivative of $P(\{\eta\})$ should be zero, leading to the balance equation

$$\frac{dP(\{\eta\})}{dt}=\sum_{i,j,i\neq j}[-W_{i,j}\eta_i(1-\eta_j)P(\{\eta\})+W_{j,i}\eta_j(1-\eta_i)P(\{\eta\}_{i\leftrightarrow j})]=0, \tag{1}$$

where $\{\eta\}_{i\leftrightarrow j}$ is the state in which the occupations of the sites i and j are interchanged. The first term between the square brackets in Eq. (1) is related to transitions from the state $\{\eta\}$ to all other states (loss) and the second term to transitions from all other states to the state $\{\eta\}$ (gain). If every state of the system can be reached from every other state, Eq. (1) can in principle be solved for the probabilities $P(\{\eta\})$, from which the properties of the system, such as the charge-carrier mobility, can be calculated. In practice, this is impossible for the system sizes we would like to consider, since the number of states is $\binom{M}{N}$, which is a stunningly large number for the system sizes and number of charges we would like to consider, preventing the evaluation of the exact solution of Eq. (1).

In the mean-field approximation, all correlations between occupational probabilities of the sites are neglected, leading to a factorization of the probability $P(\{\eta\})\approx P(\eta_1)P(\eta_2)\cdots P(\eta_N)$. Inserting this approximation into Eq. (1) and summing over all η_k except for $k=i$ we obtain the balance equations for $P(\eta_i=1)$ and $P(\eta_i=0)$. Writing $P(\eta_i=1)=p_i$, the balance equation for $P(\eta_i=1)$ becomes the familiar master equation for the occupational probabilities p_i:

$$\sum_{j\neq i}[-W_{i,j}p_i(1-p_j)+W_{j,i}p_j(1-p_i)]=0. \tag{2}$$

The balance equation for $P(\eta_i=0)$ follows automatically from this equation and the fact that $P(\eta_i=0)=1-p_i$. From Eq. (2) and the requirement that $\Sigma_i p_i=M$ the occupational probabilities p_i can be determined. The number of probabilities to be determined is N and solving Eq. (2) is therefore quite feasible, even for rather large systems.

The mean-field approximation can be systematically improved by dividing the system in clusters of sites, taking into account correlations between occupational probabilities within each cluster, but neglecting correlations between clusters. The simplest improvement is the division of the system into pairs of sites and approximating $P(\{\eta\})\approx P(\eta_1,\eta_2)P(\eta_3,\eta_4)\cdots P(\eta_{N-1},\eta_N)$ (assuming N to be even). We will label the pairs with I or J ($I,J=1,\ldots N/2$) and the members of each pair with σ or τ ($\sigma,\tau=1,2$), leading to an alternative labeling $I\sigma,J\sigma,I\tau,J\tau$ of the sites besides i,j.

It is convenient to introduce the abbreviations

$$p_I^{(0)}=P(\eta_{I1}=0,\eta_{I2}=0),$$

$$p_I^{(1)}=P(\eta_{I1}=1,\eta_{I2}=0),$$

$$p_I^{(2)}=P(\eta_{I1}=0,\eta_{I2}=1),$$

$$p_I^{(12)}=P(\eta_{I1}=1,\eta_{I2}=1),$$

$$p_{I\sigma}=p_i=p_I^{(\sigma)}+p_I^{(12)}, \tag{3}$$

corresponding to the probabilities within pair I for no occupation of site 1 or 2, occupation of only site 1, occupation of only site 2, occupation of both sites 1 and 2, and the occupation of site σ, respectively. Inserting the above pair factorization into Eq. (1), summing over all η_k for $k\notin I$, and using the abbreviations Eq. (3), we obtain the balance equations for the probabilities $p_I^{(0)}$, $p_I^{(1)}$, and $p_I^{(2)}$ in what we will call the pair approximation. We find for these balance equations, respectively,

$$\sum_{j\notin I,\sigma}[-W_{j,I\sigma}p_jp_I^{(0)}+W_{I\sigma,j}(1-p_j)p_I^{(\sigma)}]=0,$$

$$-\left\{\sum_{j\notin I}[W_{I1,j}(1-p_j)+W_{j,I2}p_j]+W_{I1,I2}\right\}p_I^{(1)}$$

$$+\sum_{j\notin I}[W_{j,I1}p_jp_I^{(0)}+W_{I2,j}(1-p_j)p_I^{(12)}]+W_{I2,I1}p_I^{(2)}=0,$$

$$-\left\{\sum_{j\notin I}[W_{I2,j}(1-p_j)+W_{j,I1}p_j]+W_{I2,I1}\right\}p_I^{(2)}$$

$$+\sum_{j\notin I}[W_{j,I2}p_jp_I^{(0)}$$

$$+ W_{I1,j}(1-p_j)p_I^{(12)}] + W_{I1,I2}p_I^{(1)} = 0. \tag{4}$$

In addition we have

$$p_I^{(0)} + p_I^{(1)} + p_I^{(2)} + p_I^{(12)} = 1, \tag{5}$$

and

$$\sum_I [p_I^{(1)} + p_I^{(2)} + 2p_I^{(12)}] = M. \tag{6}$$

From Eqs. (4)–(6) the probabilities $p_I^{(0)}$, $p_I^{(1)}$, $p_I^{(2)}$, and $p_I^{(12)}$ can be determined. Note that the balance equation for $p_I^{(12)}$ automatically follows from Eqs. (4) and (5).

We will now specify our system further. We use a regular cubic lattice of sites with lattice constant a. The position of site i is given by $\mathbf{R}_i$ and its energy, which is drawn randomly from a Gaussian distribution with standard deviation σ, by ε_i. We consider hopping as a thermally assisted tunneling process with coupling to a system of acoustical phonons, leading to transition rates of the form[19]

$$W_{i,j} = \begin{cases} \nu_0 \exp(-2\alpha R_{i,j} - \beta\varepsilon_{i,j}), & \varepsilon_{i,j} \geq 0, \\ \nu_0 \exp(-2\alpha R_{i,j}), & \varepsilon_{i,j} < 0, \end{cases} \tag{7}$$

where $\beta \equiv 1/k_B T$, ν_0 is an intrinsic rate, $\mathbf{R}_{i,j} \equiv \mathbf{R}_j - \mathbf{R}_i$ is the distance between sites i and j, $\varepsilon_{i,j} \equiv \varepsilon_j - \varepsilon_i - eER_{i,j,x}$, E is the strength of an electric field applied in the x direction, e is the charge of the carriers, and α is the inverse localization length of the localized wave functions under consideration. Because we will only allow hopping within a limited spatial range that is much smaller than the system size, we can use periodic boundary conditions, with a "circular" electric field in the x direction.

For the solution of the master equation (2) for the occupational probabilities p_i in the mean-field approximation we follow an iteration procedure similar to that suggested by Yu *et al.*[12] We rewrite Eq. (2) in the form

$$p_i = \frac{\sum_{j \neq i} W_{j,i} p_j}{\sum_{j \neq i} [W_{i,j}(1-p_j) + W_{j,i} p_j]}. \tag{8}$$

Note that p_i does not occur on the right-hand side of this equation. Therefore we can use this equation in an iteration scheme. Following Ref. 12, we use implicit iteration, meaning that updated values for p_j are used in Eq. (8) if they have already been calculated. Otherwise the p_j obtained in the previous iteration cycle are used. As starting probabilities, we take the Fermi-Dirac probability $p_{i,0} = \{\exp[(\varepsilon_i - \mu^c)/k_B T] + 1\}^{-1}$, where the chemical potential μ^c is chosen such that the charge-carrier density $p = \Sigma_i p_i / Na^3 = M/Na^3$ has a specified value.

A problem with the iteration scheme based upon Eq. (8) is that it does not conserve the charge-carrier density. We solve this problem in the following way. After each iteration, we calculate a local chemical potential μ_i^c defined by the relation $p_i = \{\exp[(\varepsilon_i - \mu_i^c)/k_B T] + 1\}^{-1}$. If the charge-carrier density has changed by a relative error greater than a specified value (typically 10^{-4}) we shift all μ_i^c by a constant such that for the p_i recalculated from this relation the charge-carrier density is conserved.

Because of the implicit iteration, the specific way in which we sweep through the lattice could influence the convergence. We found that a systematic sweep through the lattice, updating lattice sites with either the x, y, or z coordinate as the fastest running variable, almost always leads to a satisfactory convergence.

Once the occupational probabilities p_i are found, the mobility μ can be calculated from

$$\mu = \frac{\sum_{i,j,i \neq j} W_{i,j} p_i (1-p_j) R_{i,j,x}}{pNEa^3}. \tag{9}$$

In the iteration scheme we check for the convergence of μ. For the results presented in the next section a relative error of 10% in μ is tolerated. In the comparison with the mobilities calculated in the pair approximation, however, we continue iterating until a relative error smaller than 10^{-5} is obtained.

In solving the balance equation (4) in the pair approximation we follow the same philosophy as above. We rewrite Eqs. (4) and (5) as

$$p_I^{(0)} = \frac{\sum_{j \notin I,\sigma} W_{I\sigma,j}(1-p_j) p_I^{(\sigma)}}{\sum_{j \notin I,\sigma} W_{j,I\sigma} p_j},$$

$$p_I^{(1)} = \frac{\sum_{j \notin I} [W_{j,I1} p_j p_I^{(0)} + W_{I2,j}(1-p_j) p_I^{(12)}] + W_{I2,I1} p_I^{(2)}}{\sum_{j \notin I} [W_{I1,j}(1-p_j) + W_{j,I2} p_j] + W_{I1,I2}},$$

$$p_I^{(2)} = \frac{\sum_{j \notin I} [W_{j,I2} p_j p_I^{(0)} + W_{I1,j}(1-p_j) p_I^{(12)}] + W_{I1,I2} p_I^{(1)}}{\sum_{j \notin I} [W_{I2,j}(1-p_j) + W_{j,I1} p_j] + W_{I2,I1}},$$

$$p_I^{(12)} = 1 - p_I^{(0)} - p_I^{(1)} - p_I^{(2)}, \tag{10}$$

and use the same principle of implicit iteration. As starting values, we use the mean-field results: $p_{I,0}^{(0)} = (1-p_{I1})(1-p_{I2})$, $p_{I,0}^{(1)} = p_{I1}(1-p_{I2})$, $p_{I,0}^{(2)} = (1-p_{I1})p_{I2}$, and $p_{I,0}^{(12)} = p_{I1}p_{I2}$. In the pair approximation the mobility can be calculated from

$$\mu = \frac{\sum_{I,J,I \neq J;\sigma,\tau} W_{I\sigma,J\tau} p_{I\sigma}(1-p_{J\tau}) R_{I\sigma,J\tau,x} + \sum_I (W_{I1,I2} p_I^{(1)} - W_{I2,I1} p_I^{(2)}) R_{I1,I2,x}}{pNEa^3}. \tag{11}$$

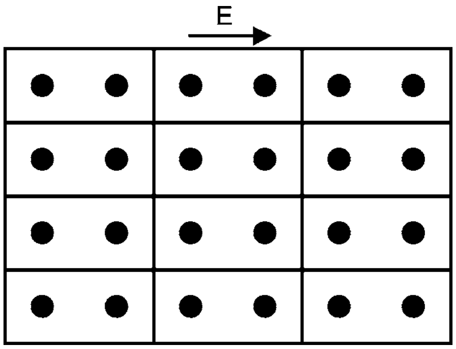

FIG. 1. Division of the lattice into pairs of sites oriented parallel to the electric field. Only a part of a plane of the cubic lattice is shown.

We choose to divide the lattice into nearest-neighbor pairs oriented parallel to the electric field; see Fig. 1. We also performed calculations for pairs oriented perpendicular to the electric field, but the results for the mobility obtained with this choice differed less from the mean-field mobilities than the results obtained with the parallel choice. Only the results for the parallel choice will be discussed in the next section. Although the iteration scheme used for the pair approximation does not conserve the charge-carrier density either, it turned out not to be necessary to correct for this.

For the inverse localization length α of the localized wave functions we have taken $\alpha=10/a$, a typical value for the polymers to which we have applied our mean-field results.[14,18] For this value of α it is sufficient to take into account hopping to nearest neighbors (distance a), next-nearest neighbors ($\sqrt{2}a$), and next-next-nearest neighbors ($\sqrt{3}a$) for the parameter range studied in the next section. Our experience is that the effect of changing α is mainly a change of a prefactor in the mobility. For a more detailed discussion of the role of α we refer to Ref. 20.

For large enough system sizes, the determined mobility would not depend on the specific disorder configuration. Often, we cannot reach such large system sizes. For those cases, reliable results for the mobility can be obtained by averaging over a number of disorder configurations. For the results obtained within the mean-field approximation we average until we have determined the mobility to a relative accuracy of 10%, which typically requires an average over 10–50 disorder configurations. We make sure that our system sizes are large enough such that finite-site effects in the final results for the mobility are negligible. Our mean-field calculations are typically done for system sizes of $100\times100\times100$ sites. For calculations at the lowest densities and the highest values of σ/k_BT we used $150\times150\times150$ sites. The calculations in the pair approximation, which are computationally much more demanding, are typically done for system sizes of $20\times20\times20$, leading to limitations regarding the temperature range for which these calculations could be done. The final accuracies in the results for the mean-field mobilities presented in the next section are smaller than the symbol sizes. For the calculations performed within the pair approximation we present the differences in the mobilities with those obtained in the mean-field approximation. We find that the mobilities obtained in the pair approximation are always *smaller* than the mean-field mobilities. This is to be expected, since correlations will effectively reduce the available space for a charge carrier, and hence its mobility.

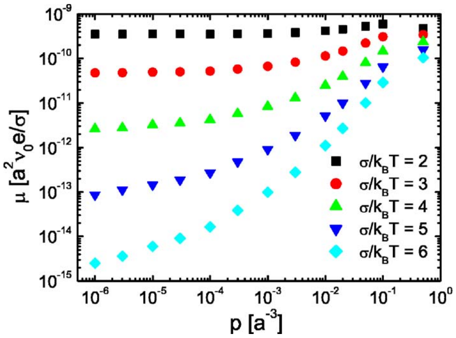

FIG. 2. (Color online) Dependence of the mean-field mobility on the charge-carrier density p at an electric field $E=10^{-3}\sigma/ea$, for different values of σ/k_BT.

III. RESULTS AND DISCUSSION

In Fig. 2 we display the results for the mobility as a function of the charge-carrier density p for various values of σ/k_BT at a small electric field (in the linear regime of the field dependence). As we have shown recently,[18] the dependence of the mobility on the charge-carrier density can be quite well fitted to results obtained from a semianalytical percolation approach.[20]

In Figs. 3 and 4 we display the results for the mobility as a function of the electric field at a low carrier density, $p=10^{-5}/a^3$, typical for the operation regime of polymer light-emitting diodes, and a high carrier density, $p=0.05/a^3$, typical for the operation regime of polymer field-effect transistors. For not too high electric fields we have found that the dependence of the mobility on the electric field can be incorporated in a field- and temperature-dependent prefactor that does not depend on the charge-carrier density.[18]

Previously, the dependence of the mobility on the charge-carrier density and electric field was studied in a so-called

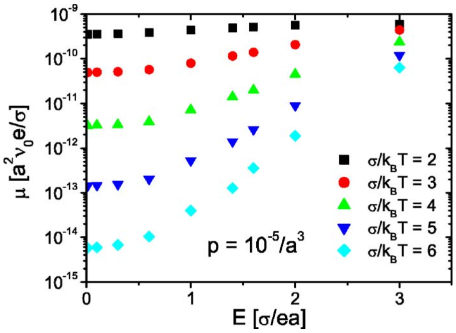

FIG. 3. (Color online) Dependence of the mean-field mobility on the electric field E at a low charge-carrier density $p=10^{-5}/a^3$, for different values of σ/k_BT.

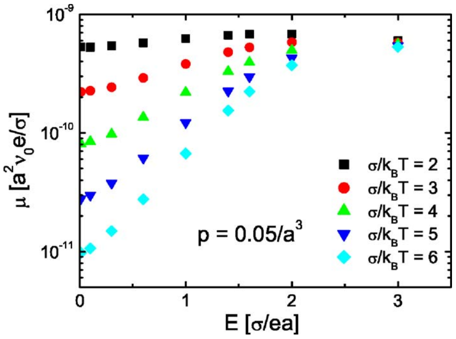

FIG. 4. (Color online) Dependence of the mean-field mobility on the electric field E at a high charge-carrier density $p=0.05/a^3$, for different values of σ/k_BT.

mean-medium approximation (MMA),[17] in which the current between two sites is obtained by averaging the transition rate between the sites over the Gaussian energy distribution of both sites. We have checked that the current obtained in this way can be several orders of magnitude too high at low temperatures. The reason is that this approximation does not account for the percolative nature of the conduction mechanism, which is an essential ingredient. This percolative nature leads to an intricate spatial structure of the electrochemical potential and the current.[21] Nevertheless, the qualitative dependencies of the mobility on charge-carrier density and electric field obtained within the MMA are similar to those shown here.

In Figs. 5–7 we display the relative difference between the mobility calculated within the pair approximation and within the mean-field approximation, for varying inverse temperature, charge-carrier density, and electric field. As expected, the correction to the mean-field approximation becomes larger for increasing charge-carrier density; see Fig. 6. The correction also increases with decreasing temperature; see Fig. 5. This can also be rationalized, since at decreasing temperature the number of thermally accessible sites decreases, so that correlations become more important. The correction to the mean-field mobility decreases with increasing electric field; see Fig. 7. This is due to the fact that at high electric fields the volume accessible for the charge carriers increases because energetic barriers can more easily be overcome, so that correlations become less important.

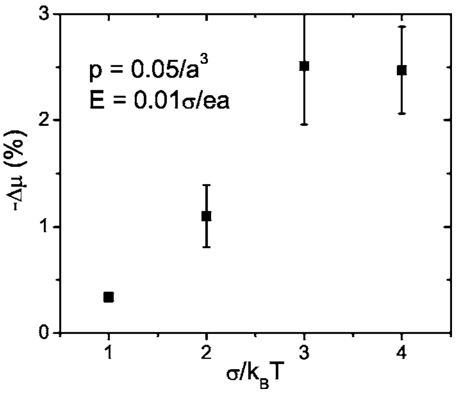

FIG. 5. Difference between the mobility calculated within the pair approximation and the mean-field approximation for varying inverse temperature, at a high charge-carrier density $p=0.05/a^3$ and a small electric field $E=0.01\sigma/ea$. The error bar is indicated.

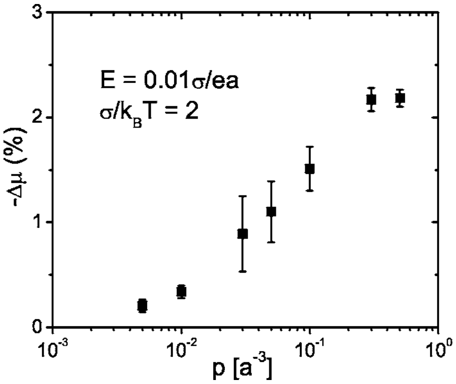

FIG. 6. Difference between the mobility calculated within the pair approximation and the mean-field approximation for varying charge-carrier density, for $\sigma/k_BT=2$ and a small electric field $E=0.01\sigma/ea$.

Due to the numerical restrictions, in particular restrictions on the system sizes, it is hard to access with the pair approximation the important range of values $\sigma/k_BT=4-6$ ($\sigma\approx 0.1-0.15$ eV at room temperature) corresponding to polymers of practical interest.[18] Nevertheless, it is clear from the trends in Figs. 5–7 that the corrections will probably not exceed a few percent in this range. The largest corrections are to be expected for polymer field-effect transistors,[6] for which the charge-carrier density is high and the electric field in the channel direction low. However, even for this situation we expect that using the mean-field approximation is safe, certainly in view of the fact that knowledge about the quantitative value of the mobility to within an order of magnitude is often sufficient.

Concluding, we have discussed how the mobility for hopping on a regular cubic lattice within a Gaussian disorder model can be numerically determined within the mean-field approximation. Moreover, we have demonstrated how we can go beyond the mean-field approximation by dividing the

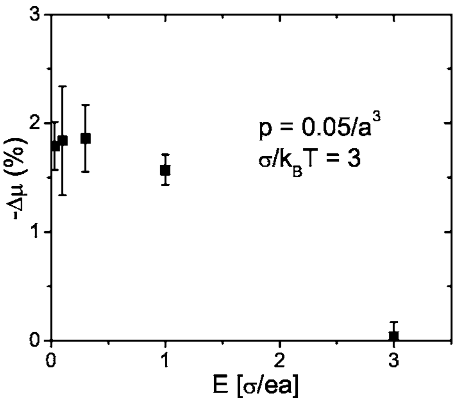

FIG. 7. Difference between the mobility calculated within the pair approximation and the mean-field approximation for varying electric field, for $\sigma/k_BT=3$ and a high charge-carrier density $p=0.05/a^3$.

lattice in nearest-neighbor pairs of sites and treating the correlation between the sites of the pair explicitly. The results for the mobility calculated within this pair approximation are only a few percent smaller than those calculated within the mean-field approximation. Since the correlations between nearest-neighbor pairs are the most dominant ones, we can conclude that the use of the mean-field approximation is justified. Hence our results demonstrate the validity of the approach followed in our earlier work,[18] which emphasizes the importance of the dependence of the charge-carrier mobility on charge-carrier density. We repeat that in that and in the present work the *disorder* was assumed to be uncorrelated. We are presently investigating whether we can also describe the experimental current-voltage characteristics in Ref. 18 with the dependence of the charge-carrier mobility on the charge-carrier density and the electric field following from the correlated disorder model. If successful, this could reconcile our findings with the broadly accepted Poole-Frenkel behavior of the electric-field dependence of the mobility.

ACKNOWLEDGMENTS

We would like to thank F.H.J. Redig, W.F. Pasveer, R. Coehoorn, and M.A.J. Michels for many stimulating discussions. The computations in this work were made possible by support from NCF (Dutch National Computer Facilities).

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