Hopping transport of interacting carriers in disordered organic materials

Sergey V. Novikov
A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Moscow 119991, Russia

Computer simulation of the hopping charge transport in disordered organic materials has been carried out explicitly taking into account charge-charge interactions. This approach provides a possibility to take into account dynamic correlations that are neglected by more traditional approaches like mean field theory. It was found that the effect of interaction is no less significant than the usually considered effect of filling of deep states by non-interacting carriers. It was found too that carrier mobility generally increases with the increase of carrier density, but the effect of interaction is opposite for two models of disordered organic materials: for the non-correlated random distribution of energies with Gaussian DOS mobility decreases with the increase of the interaction strength, while for the model with long range correlated disorder mobility increases with the increase of interaction strength.

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INTRODUCTION

Hopping transport in disordered organic materials has been extensively studied for the case of low density of carriers, but our understanding of charge transport for the case of high carrier density is not adequate; theoretical studies of the effect of carrier density are scarce. High density of carriers could affect drift mobility \( \mu \) in opposite ways. Small fraction of carriers could occupy deep states, thus providing a possibility for remaining carriers to avoid trapping and acquire much higher mobility. At the same time, charge-charge interactions could provide an additional energetic disorder in the material. This is indeed the case for the simplest model where all charges except one are immovable. In this case, the greater is the density of static charges (i.e. energetic disorder), the smaller is the mobility.

Usually, in theoretical studies the mean field approximation has been used and charge-charge interaction has been totally neglected. This means that these studies dealt only with the effect of filling of deep states: it is assumed that the effects of interaction could be later effectively included via the mobility dependence on the mean local electric field \( \langle \vec{E}_{\text{loc}} \rangle \), which in turn is connected to the mean local charge density \( \rho \) by the Poisson equation

\[
\text{div} \langle \vec{E}_{\text{loc}} \rangle = \frac{4\pi}{\varepsilon} \rho, \quad (1)
\]

where \( \varepsilon \) is a dielectric constant of the material. This line of reasoning totally neglects dynamic correlations. In addition, quite frequently true quasi-equilibrium mobility is formed by the averaging over large domains of the disordered material (see, for example, Ref. [2]). In this situation the very conception of a local (but uniform in space) mobility is invalid. For this reason in this paper we describe a direct dynamic simulation of hopping monopolar transport of interacting carriers.

MODEL

General description

For the model of interacting carriers the total site energy of a carrier is a sum of a static random contribution due to the static intrinsic energetic disorder and fluctuating contribution due to the interaction with all other hopping charges. Tremendous difficulty of the simulation is a necessity to recalculate site energies and hopping probabilities after every hop. In addition, if we consider moderate or high density of charge carriers, then they affect the distribution of average electric field, which in turn leads to the non-uniform average charge density. In this situation we cannot use in simulations a finite basic sample with periodic boundary conditions. The length of the basic sample across the device must be equal to the thickness of the transport layer. This inevitably means that we have to include charge injection in our simulation and analysis of the simulation data becomes much more complicated.

For these reasons we undertook simulation for the simplified model of a transport layer: we assumed that a static compensating charge of the opposite sign is uniformly distributed in the transport layer, with the density being equal to the average density of carriers. In this model the mean local electric field and carrier density are uniform in space and \( \langle \vec{E}_{\text{loc}} \rangle \) is equal to the applied field \( \vec{E} \). Hence, simulation for the moderate basic sample with periodic boundary conditions could be carried out. This particular model is a variant of the "jelly model", very popular for a study of effects of charge-charge interactions in metals.

In order to minimize the necessary runtime even more we performed simulations for rather high temperature \( kT/\sigma = 0.3 \) (here \( \sigma^2 \) is a variance of static intrinsic disorder; typically, in organics \( \sigma \simeq 0.05 - 0.1 \) eV [4]) and took into account only hops to nearest neighbors of
every site (we considered a simple cubic lattice). Site energies and hopping probabilities have been recalculated only for nearest neighbors of sites occupied with carriers. This assumption seems to be very good approximation for disordered organics where \( \alpha a \approx 5 - 10 \) \( ^3 \), here \( a \approx 1 \) nm is a distance between nearest neighbors (lattice scale in a lattice model of a material) and \( \alpha \) is an inverse localization radius of a wave function of a transport site. Miller-Abrahams (MA) hopping rate \( ^6 \) has been used for all simulations. In the calculation of electrostatic site energies a well-established Ewald approach has been used \( ^6 \).

Simulations for two models of a disordered organic material have been carried out: the Gaussian Disorder Model (GDM) where the static intrinsic energetic disorder in the material is represented by a spatially uncorrelated distribution of random energies with the Gaussian DOS \( ^3 \) and the model of dipolar glass (DG) where site energies are strongly correlated \( ^8 \). The later model is better suited to describe organic materials because contributions of static electrostatic sources (of dipolar or quadrupolar nature) to site energies are inevitably strongly spatially correlated due to the long range nature of electrostatic interaction in organic materials \( ^8, 10 \).

Majority of simulations have been performed for the basic sample of a simple cubic lattice with the size \( L = 40a \). Several checks have been made to test an accuracy of the simulation by using the basic sample with size \( L = 80a \). Even for the DG model and rather weak field \( eaE/\sigma \approx 0.1 \) (these are the situations where mobility is very sensitive to the size of a sample) a good agreement has been found with the case \( L = 40a \).

Simulation for a particular set of relevant parameters was started with some arbitrary distribution of carriers and carried out until a stationary state with constant mean carrier velocity has been reached. We have checked that the particular initial distribution of carriers affects only details of the relaxation process but not the value of the asymptotic velocity.

**Waiting time simulation**

General features of the simulation procedure are very similar to those described in Refs. \( ^3, 8 \), apart from the modification of the waiting time calculation. For the only carrier a waiting time \( \tau \) before the next hop is calculated as

\[
\tau = -\frac{1}{\Gamma} \log \gamma,
\]

where \( \gamma \) is a random number with the uniform distribution in \([0,1]\) and \( \Gamma \) is the total hopping rate for the site where carrier is located at the moment \( ^3 \). For many interacting carriers this procedure has to be modified because for any particular carrier, waiting for a hop, the total hopping rate now depends on time, reflecting hopping of other carriers.

A necessary modification could be introduced in the following way. At the start, independent \( \gamma_n \) have been generated for all carriers, and the set of \( \tau_n \) has been calculated using Eq. \( (2) \), as well as the set of initial residuals \( R_n = -\log \gamma_n \). Then the carrier with smallest waiting time \( \tau_{\min} \) made a hop, its new position has been found by the usual way \( ^3 \), and the time counter was advanced by \( \tau_{\min} \). For this carrier a new random number \( \gamma_{\text{new}} \) was generated. For all other carriers new residuals

\[
R_{\text{new}}^n = R_n - \Gamma_n \tau_{\min}
\]

have been calculated and stored (for the hopped carrier a new residual is just \( R_{\text{new}}^n = -\log \gamma_{\text{new}} \)). Then all site energies and hopping rates have been recalculated, the new set of waiting times have been calculated

\[
\tau_{\text{new}}^n = \frac{R_{\text{new}}^n}{\Gamma_{\text{new}}^n}
\]

and the whole procedure has been repeated.

**DANGERS OF MEAN FIELD APPROXIMATION**

To illustrate possible dangers of the mean field approximation we provide results of the transport simulation for the simplest case of no intrinsic static disorder (carriers, hopping in the empty lattice). In this case the mean field solution for the carrier occupation fraction at every site is just a constant equal to the average occupation fraction \( p \). For the MA hopping rate an average carrier velocity for the case of simple cubic lattice and hopping to nearest neighbors only is

\[
v_{\text{MF}} = v_0 [1 - \exp (-\epsilon aE/kT)] (1 - p), \quad v_0 = a\Gamma_0
\]

where two terms in brackets represent contributions of forward and backward hops, factor \( 1 - p \) takes into account occupation of the final site, and \( \Gamma_0 \) is a hopping frequency. Remarkable property of Eq. \( (5) \) is its independence on the interaction strength. Indeed, in our model in the absence of static intrinsic disorder an average total charge density is exactly zero everywhere, thus all interactions enter into consideration only because of dynamic correlations. Results of the simulation are shown in Fig. \( ^{14} \). For strong interaction deviation with Eq. \( (5) \) is significant. Note also, that for \( \epsilon/ea^2E = 0 \) agreement between Eq. \( (5) \) and simulation data is excellent due to the small average occupation fraction \( p \ll 1 \) used in simulation; here dynamic correlations are not important.
FIG. 1: Temperature dependence of the mean carrier velocity $v$ for the MA hopping rate in the case of no intrinsic disorder (dynamic simulation, points). Upper solid line is the mean field result. Numbers near the curves show effective charge-charge interaction parameter $e/eaE$. Average occupation fraction is $p = 0.047$.

RESULTS OF DYNAMIC SIMULATION

General effect of interaction

We found that in our model for not very high occupation fractions $p \leq 0.1$ carrier drift mobility increases with $p$, exactly as in the case of non-interacting carriers. Yet modification provided by the interaction is still significant (see Fig. 2). There is a striking difference between the effects of interaction (i.e., carrier-carrier repulsion) on the mobility in the DG model and GDM. In the DG model repulsion between carriers makes mobility even greater than in the case of no interaction, while for the GDM the opposite situation takes place. This difference is not surprising. Indeed, in the DG charge transport is significantly affected by carrier trapping in deep and broad valleys of the energy landscape (good qualitative description is provided in Ref. [11]). If a carrier is trapped by a valley, then the whole valley with many sites having low energies becomes blocked for other carriers because of repulsion. Thus, filling of the deep states is much more effective in correlated landscape if carrier repulsion is taken into account. This is the reason for the increase of carrier mobility in DG. No such effect takes place for the GDM, and here, evidently, the effect of charge-induced energetic disorder is responsible for the decrease of mobility in comparison to non-interacting case.

This particular result disagrees with the result of a recent paper by Zhou et al [12]. They found that in the GDM carrier interaction enhances mobility in comparison to the case of no interaction if $\sigma/kT \gg 1$. This is opposite to our findings. Quite probably, the disagreement stems from the under-relaxation of the initial (random) carrier configuration used in Ref. [12]; the relaxation process is pretty slow for interacting carriers if $\sigma/kT \gg 1$. We cannot make more detailed comparison because typical relaxation times are not provided in Ref. [12] (in fact, even the strength of carrier repulsion is not provided). Our data indicates, for example, that for $\sigma/kT = 4$ relaxation is not completely over even for $t/t_0 = 1 \times 10^5$ (see Fig. 3); at that time carrier has already travelled in the field direction the distance of $\approx 4 \times 10^3a$.

Remarkable feature of Fig. 3 is a universality of the late relaxation stage. Very early relaxation is different for the initial random distribution and minimal energy distribution (where every carrier was placed at the site where the total energy, provided by the intrinsic disorder and all previously added carriers, has a minimum), but after $t/t_0 \approx 10$ relaxation curves merge into a single curve.

Mobility field dependence

It is very well known that the GDM and DG model provide very different dependences of the mobility on ap-
plied electric field in the case of low carrier density. In the GDM log \( \mu \propto E \) and in DG log \( \mu \propto \sqrt{E} \) [8]. These dependences remains valid for moderate \( p \) too (see Fig. 4).

Significant difference between models could be found in the dependence of the slope of \( \mu(E) \) on \( p \). General tendency for the DG model is that transformation of the mobility curve with the increase of \( p \) roughly resembles the corresponding transformation of the curve with the increase of \( T \) (see, for example, Fig. 1 in Ref. [13]): with the increase of \( p \) mobility becomes greater and the slope of the mobility field dependence becomes smaller. This is not the case for the GDM: here only mobility curve moves upward but the slope remains approximately constant.

This difference could be easily understood. Field dependence of \( \mu \) in the GDM is governed by the carrier escape from deep states to the nearest transport sites usually having much higher energy and could be described by the shift \( \Delta U = eER \) of positions of transport levels in applied field \( E \)

\[
\log \mu \propto \frac{eER}{kT},
\]  

where \( R \approx a \) is a typical distance between transport sites. Random charge distribution provides a smooth random energy landscape superimposed on the intrinsic disorder, but typical additional variation of energy at the scale \( a \) is negligible for small \( p \). Hence, estimation (6) remains valid and the slope of the mobility curve does not depend on \( p \).

Situation in the DG model is quite different. Here mobility field dependence is governed by the carrier escape from wide valleys, and the size of critical valleys, capable of keeping a carrier for the longest time, depends on

FIG. 3: Relaxation of the mean carrier velocity in the GDM for \( \sigma/kT = 4 \), \( eaE/\sigma = 1 \), and \( p = 0.0625 \) (squares). Empty squares show relaxation for random initial locations, while filled squares show relaxation for the case, when initial locations have been taken at the minimal energy positions. Circles shoe the relaxation for higher temperature \( \sigma/kT = 3.33 \).

FIG. 4: Mobility field dependence for \( U_C = 5 \), \( kT/\sigma = 0.3 \), and different values of \( p \): 0.0016, 0.008, 0.016, and 0.032, from the bottom curve upward, correspondingly. Figure (a) shows simulation data for the DG model, and the figure (b) shows data for the GDM, correspondingly. Here \( \mu_0 = ea^2\Gamma_0/\sigma \). If \( a = 1 \) nm and \( \sigma = 0.1 \) eV, then \( eaE \approx 1 \) for \( E = 1 \times 10^6 \) V/cm.
of deep states by non-interacting carriers has been taken into account, while the second one is much more close to the real situation. Evidently, when we consider the effect of carrier density on the mobility, then the effect of charge-charge interactions is no less important than the trivial filling of deep states.

**HOW TO COMPARE WITH EXPERIMENT?**

One can suggest that carrier transport in organic field-effect transistors (OFETs) should be a natural choice for comparison of the simulation results with experiment [13, 14]. Estimation of the carrier density in OFETs show that the density as high as $3 \times 10^{19} \text{cm}^{-3}$ could be achieved [10], that for $a \approx 1 \text{nm}$ corresponds to $p \approx 0.03$. Experimental data for the particular OFET should be compared with the TOF data for a sandwich device having transport layer of the same material; in this way we could measure transport characteristics (e.g., $\sigma$), relevant for the intrinsic disorder in the material. Quite frequently, OFETs demonstrate mobilities much higher that the mobilities measured in TOF experiments, and usually mobility increases with the increase of $p$ [14]. This fact is in general agreement with the model studied in this paper.

However, careful analysis reveals much more complicated situation. Indeed, in many aspects OFETs are very far away from the model, considered in the current study. First of all, in OFETs transport occurs in a thin layer, close to the gate insulator. Quite probably, especially in polymer devices, structure of this layer differs from the structure of the same material in the bulk (polymer chains could be arranged in a special way at the gate insulator surface). This arrangement could provide more ordered structure with less degree of energetic disorder, thus mobility should be enhanced near the interface, but accumulation of surface defects and impurities at the interface could lead to the decrease of the mobility. Next, there is a clear indication that the roughness of the organic semiconductor/dielectric interface affects carrier mobility [14]. At last, the very nature of a gate dielectric (specifically, its polarity) affects carrier mobility in OFETs, because a random orientation of polar groups in the vicinity of a transport layer induces an additional energetic disorder in semiconductor [18, 19]. In short, there are a lot of reasons to believe that transport properties of OFETs are too complicated to be directly compared with the results of this study. We can only state that a significant increase of the carrier mobility with the increase of carrier density in carefully manufactured OFETs does not contradict the results of our study.
CONCLUSION

In conclusion, it was found that charge-charge interaction significantly affects the carrier drift mobility and this effect could not be described by the mobility dependence on average electric field in the model of non-interacting carriers. Effect of the charge-charge interaction is no less important for the true description of the carrier mobility dependence on carrier density than the previously considered effect of simple filling of deep states.

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