Monte-Carlo study of drift mobility in ultrathin organic layers: Miller-Abrahams and Marcus models

Ya. V. Burdakov and V.R. Nikitenko
National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Moscow, 115409, Russia
E-mail: vladronik@yandex.ru

Abstract. It is shown by the means of Monte-Carlo modeling that the drift mobility decreases considerably along with the increasing of the layer thickness from 10 to 100 nm, if the hopping rates are calculated in the framework of the Marcus model, according to approximately the same low, as in the case of the Miller-Abrahams model. The diffusion current can contribute approximately the same contribution, as an energetic relaxation of the generated non-equilibrium charge carriers, for the case of moderate disorder.

1. Introduction
The investigation of non-stationary transport of charge carriers in very thin (less than 100 nm) layers of organic materials is important both from the fundamental viewpoint (the investigation of peculiarities of energy distribution of hopping centers and morphology of the thin layers) and for applications, because just the layers of this thickness are applicable in light-emitting diodes, photovoltaic cells and other basic elements of organic electronics. In the several works it was shown, that the drift mobility decreases along with increasing of the film thickness, if the thickness is rather small, even for the case of quasi-equilibrium initial generation of charge carriers [3-5]. Calculations were performed in the framework of Miller-Abrahams (MA) model. However, the Marcus model [6], which accounts for the polaronic effect, is often used for the analyses of hopping transport in organic materials, in parallel with the MA model. The temperature and field dependence of both the “true” and drift mobility is well investigated in the framework of the MA model, both experimentally [7] and theoretically – by the means of numerical [7] and analytic [8,9] methods, while analytic description of mobility in Marcus model is less developed [10].

In this work, the drift mobility in ultrathin organic layers is investigated by the means of Monte Carlo simulation for the different dimensionality, generation conditions and boundary conditions. The comparison of the results from both the models is carried out. The simulations yield considerable decreasing of the drift mobility along with decreasing of the thickness \( L \) from 10 to 100 nanometers from both the models. The method for the determination of the quasi-equilibrium mobility from the analyses of the obtained thickness dependence of the drift mobility is proposed, and the analysis of the reasons of the decreasing of the drift mobility is carried out.

2. The method of simulations.
The model of MC simulations, that is similar to the work [4], is used here. The model is based on the well-known Gaussian disorder model [7]. The localized states (hopping centers) form a simple cubic lattice with the lattice constant \( a \). Energies of the centers are distributed as a Gaussian function with the variance \( \sigma \). At variance with the works [3,4], both MA and Marcus models were used for the description of the hopping rates from a state \( i \) to the state \( j \), \( \nu_{ij} \). In the MA model,

\[
\nu_{ij} = v_0 \exp \left( -2\gamma r - \frac{(\Delta \epsilon_{ij} + |\Delta \epsilon_{ij}|)}{kT} \right),
\]

while in Marcus model

\[
\nu_{ij} = v_0 \exp \left( -2\gamma r - \frac{(\epsilon_j - \epsilon_i + E_F)^2}{4E_F kT} \right),
\]
where \( r \) is the distance between the states \( i \) and \( j \), \( \gamma \) is the inverse localization radius of the wave function, \( E_r \) is the reorganization energy, \( v_0 \) is the frequency factor, \( T \) is the absolute temperature and \( k \) is the Boltzmann’s constant. In these simulations the value \( 2\gamma a = 10 \) is assumed.

Both three- and two-dimensional (molecular monolayer) structures were investigated (3D and 2D systems, respectively). Various boundary conditions were also considered. In the first variant, the layer is sandwiched between two electrodes, an electron generates next to the left electrode and it cannot penetrate across the interface. When the electron achieve the right electrode (in the direction of the electric force), the procedure is finished. This variant refers below as (0:0). In the second variant, both the boundaries of the layer are considered as virtual ones, i.e. the layer is a part of a prolonged media, hence a carrier can perform the same random walk outside the layer. The simulation finished in this case, then the electron crosses the right boundary at the last time. The longitude of the zone outside the layer, in which the random walk is possible, taken as \( 30a \) (it is enough to provide free walk of a carrier at all values of the field strength under consideration. This variant refers below as (30:30). A carrier is provided to move much longer in the transversal directions, than the longitudinal thickness of the layer.

In parallel, we consider different variants of an initial energy distribution of charge carriers. The initial energy distribution of generated carriers is the same as the Gaussian distribution of hopping centers, (referred as Notquas). The initial occupation probability is a Boltzmann’s function of an energy of a center (referred below as Quas), hence the initial energy distribution of carriers is shifted down by the value of \( \sigma^2/kT \). One can investigate an influence of the energetic relaxation and conventional diffusion on the drift mobility, comparing results of the models Notquas, Quas and (0:0), (30:30), respectively.

The mean inverse of the transit time, \( \langle 1/\tau_r \rangle \), defines from the series of simulations (the typical number is 3000 at a given set of parameters). Then the drift mobility calculates as the mean drift velocity, divided by the electric field strength, \( F \): \( \mu_{dr} = (L/F)(1/\tau_r) \), where \( L=Na \).

3. Results and discussion

The figure 1a shows, that the drift mobility varies smaller with changes of the dimensionality and reorganization energy at smaller values of the layer thickness, than at larger ones.

![Figure 1](image1.png)

Figure 1 (a) The comparison of the thickness dependences of the drift mobility at various values of dimensionality (the solid curves – 3D, the dashed curves – 2D) from the MA and Marcus models for the case of weak field, \( eFa/kT=0.1 \). (b) The same for the case of 2D conductivity by the use of Marcus model at two values of the field strength \( F \), \( eFa/kT=0.1 \) and \( eFa/kT=1 \). \( \mu_0 = (e/kT)v_0 \exp(-2\gamma a) \). The calculations performed in the variant Quas (0:0).

The drift mobility decreases and approaches to the infinite-medium value faster in 3D case, than in the 2D case, probably due to preferable possibility to avoid deep trapping. Figure 1b shows that the thickness dependence of the drift mobility is more pronounced, if the field is weaker.

Figure 2a shows, that the mobility from the Marcus model approaches to the respective results of the MA model along with decreasing of reorganization energy, \( E_r \) (providing that \( ErkT>1 \)). The calculations performed under this condition. However, the drift mobility, being normalized by the value \( \mu_0 \exp(-Er/4kT) \), tends to saturate at high values of \( E_r \), see the figure 2b.
Figure 2 (a) The comparison of the thickness dependences of drift mobility from MA model and from Marcus model, parametric in reorganization energy, $E_r$, ($E_r/kT=2;4;8;16$), $eFa/kT=0.4$. (b) The same, but the mobility from Marcus model is normalized by the value $\mu_0\exp(-E_r/4kT)$. Calculations performed in the variant Quas (0:0).

Figure 3a demonstrates that the mobility is smaller and more proximal to the quasi-equilibrium under the condition (30:30), than (0:0). It is not surprising, because the number of hops is larger in the letter case, than in the former. The transition from non-equilibrium to the quasi-equilibrium generation makes the thickness dependence weaker, but not eliminates it totally, see the fig. 3b.

Figure 3 (a) The comparison of the drift mobility from MA and Marcus models, parametric in reorganization energy ($E_r/kT=2$ and 16), for the case of quasi-equilibrium initial generation, at various boundary conditions, $eFa/kT=0.4$ (a); (b) the drift mobility from the Marcus model, $E_r/kT=8$, at various conditions of initial generation and boundary conditions.

Calculations of this work confirms for the case of Marcus model the decreasing of drift mobility along with increasing thickness, if values of the thicknesses are rather small,

$$\mu = \mu_0 \left[1 + \left(\frac{L}{L_0}\right)^{\beta}\right],$$

as it was founded earlier for the case of MA model [3,4].

The power low exponent $\beta$ has the values close to unity. Accounting for the precision of calculations, we cannot find a systematic dependence of the value of $\beta$ on the reorganization energy. Rather, it depends on the field strength and on the disorder parameter, $\sigma/kT$, in the same manner, as it was reported previously [3,4]. For example, $\beta = 0.9 \pm 0.15$ at $\sigma/kT = 3$ and $eFa/kT = 0.4$ from the model (0:0) Quas. The MA model yields $\beta = 1.16$. Apparently, the exponent from the Marcus model is smaller to some extent, than for the case of MA model. The reduction of the exponent $\beta$ is more considerable under the change of the initial and boundary conditions: $1.7 \pm 0.05$ from (0:0) Notquas, $1.1 \pm 0.1$ from the (30:30) Notquas, $0.9 \pm 0.15$ from the (0:0) Quas, and $0.75 \pm 0.1$ from the (30:30) Quas model, i.e. along
with approaching to the quasi-equilibrium limit. It is important, that one can define the infinite-thickness limit (i.e. the quasi-equilibrium, “true” value of mobility, $\mu_\infty$, by the use of eq. (3). This procedure yields to the results, which are in a good agreement with the known values [7,8], for the case of the MA model [11], and one has a large economy of computing resource in comparison with the direct calculations in a rather thick layer.

$$\mu(x) \propto \frac{1}{N}$$

**Figure 4** The same as in the figure 3, but the mobility is normalized in order to illustrate the eq. (3)

It is instructive to analyze the difference of results from the models with different initial and boundary conditions, see the figure 3. Obviously, the drift mobility is more proximal to the quasi-equilibrium limit for the case of the initial quasi-equilibrium generation, than for the case of non-equilibrium generation, but the thickness dependence remains considerable in the latter case. The contribution of diffusion current in the thin (about 10 nm) films seems to be the most important reason, rather than the lack of trapping to the deep states, due to the small value of disorder. This contribution is less pronounced, if carriers have a possibility to walk outside the region $0 < x < L$.

4. Conclusions
This paper shows that the Marcus model results in approximately the same power law of decreasing of the drift mobility along with the increasing of the thickness of the thin films, as the MA model. Meanwhile, the drift mobility has a weaker dependence on the reorganization energy, than the quasi-equilibrium (the “true”) mobility. The diffusion current should be included in the analytic modeling for the case of ultrathin (about 10 nm), in order to have a quantitative description of the transient current.

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