Drift mobility in thin organic layers: joint Monte-Carlo and analytic modeling

V R Nikitenko, V M Sukharev, N A Sannikova
National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Moscow, Russia
E-mail: VMSukharev@mephi.ru

Abstract. Hopping transport of charge carriers in thin (up to 100 nm) organic layers, which are suitable for organic light-emitting diodes and solar cells, is modeled in the framework of Gaussian disorder model. Monte-Carlo simulations yield considerable decrease of drift mobility with thickness of the layer, which is in good agreement with the developed analytic model.

1. Introduction

Organic electronics devices (light-emitting diodes, photovoltaic elements, etc.) consist of thin (in the range of 10 - 100 nm) active layers. Predictive modelling of operation of such devices unavoidably needs correct characterization of charge transport in thin organic layers. Charge transport, being of hopping nature, can be described in the framework of Gaussian disorder model (GDM) [1]. Values of mobility, which have been obtained from experiments for thicker layers (> 1 micrometre), are often used for modelling the light-emitting diodes. However, one has to expect, that mobility is size dependent on a spatial scale of tens and even hundreds nanometers (irrespective to non-equilibrium or quasi-equilibrium regime of charge generation), in accordance with recent Monte-Carlo (MC) simulations [2,3]. The reason is that percolation paths, which are interrupted in thick films, determine conductivity in thin disordered films, providing that a thickness L is less or comparable with a scale of percolation network [4]. In other words, a carrier, passing through a thin film, has small probability to meet rather deep states, which control mobility. In this work this statement is supported by joint MC and analytic modeling.

2. Monte-Carlo procedure and analytic model.

In MC simulations, we use a conventional model, where hopping centres (localized states) are located at sites of simple cubic lattice with a lattice constant $a_0$. Number of sites along any transversal direction exceeds 10 times a number of sites along the electric field direction. Energies of sites are distributed randomly according to Gaussian distribution $g(E)$ with the variance $\sigma$:

$$g(E) = \left(\frac{1}{\sqrt{2\pi\sigma^2}}\right) \exp\left[-\frac{E^2}{2\sigma^2}\right].$$

(1)

Probability of hopping from site $i$ to site $j$ is $P_{ij} = \frac{v_j}{v_i}$, $v_i = \sum v_{il} (i \neq l)$. Due to exponential decreasing of hopping rate with increasing of distance $r$, we take into account only those sites whose distance from point $i$ is less than $3a_0$ along any direction.
The final state \(i\) is determined on each step \(i\) by the condition, that a random number \(0 \leq x_i \leq 1\) is between \(P_{ij-1}\) and \(P_{ij}\) \((P_{i0} = 0)\). Waiting time before jump, \(t_i = y_i/v_i\), is defined by another random number \(y_i\), according to exponential distribution \(P_{ii} = \exp(-v_i t)\). Hopping rates are determined by usual Miller-Abraham’s expression:

\[
v_{ij} = \omega_0 \exp \left[ -2\gamma r_{ij} - \left( \Delta E_{ij} + \Delta E_{ji} \right)/2kT \right],
\]

where \(\omega_0\) is a frequency factor, \(\gamma\) is inverse localization radius, \(r_{ij}\) is a distance between sites \(i\) and \(j\), \(\Delta E_{ij} = E_i - E_j - eF(r_{ij}\cos \theta)\), \(T\) is absolute temperature, \(k\) is Boltzmann constant, and \(\theta\) is angle of directions of electric field, \(F\), and of a jump, \(r_{ij}\). The value \(2\gamma a_0 = 10\) is assumed. Quasi-equilibrium initial distribution is considered in order to omit effects of dispersive transport, \(\exp(-E/kT)\). An event (i.e. random walk of a carrier across the volume) starts with an electron being born in the \(l\)-th layer, where the number \(l\) satisfies to the condition: \(leFa_0 >> 1\), hence visit of a carrier to the left boundary is improbable. It allows analysing the mobility, depending on the medium properties, without the influence of the electrode (dummy injecting electrode). If the electron appears in the nearest to right electrode layer, event is over. Drift mobility is calculated from the average drift velocity, i.e. from an average (over 10000 events) inverse transit time \(t_{tr}\),

\[
\mu = (L/F)(1/t_{tr}).
\]

The basic idea of the analytic model is the following: probability to meet a rather deep state (releasing from this state determines drift mobility) decreases along with the number of states \(N_0\), visited by a carrier. Average (over the ensemble of drifting carriers) value \(<N_0>\), obviously, decreases along with decreasing of film thickness or with increasing of field strength \(F\). One can expect increase of probability to meet a deep state of a given energy, hence decrease of drift mobility, along with increasing of layer thickness. The simplest approach to quantify this dependence of mobility is to “cut off” deep energies from the Gaussian density of states (DOS) \((1)\), hence to introduce an effective DOS \(g_{eff}(E)\):

\[
g_{eff}(E) = g(E)\eta(E-E_\ast),
\]

where \(\eta(E-E_\ast)\) is the step function. The average number \(<N>\) of carrier’s captures by states with energies \(E < E_\ast\), is less than unity, consequently such capture is improbable:

\[
<N> = <N_0>\varphi(E_\ast) = 1,
\]

where \(\varphi(E_\ast)\) is a probability of a carrier to be captured after the hop to a state of energy \(E < E_\ast\). Obviously, the value of \(<N_0>\) increases along with the layer thickness \(L\) at a given field strength, while \(\varphi(E_\ast)\) decreases along with decreasing of the energy \(E_\ast\), hence this energy decreases along with increasing \(L\). The magnitude of mobility is determined by the states of energies around \(-\sigma^2/kT\) [1]. Consequently, mobility approaches to its infinite-medium limit under the condition \(E_\ast(L) < -\sigma^2/kT\).

The model for calculations of mobility rests upon transport level concept [5], which has been modified recently [6], introducing a disorder-dependent percolation factor \(B>1\) on the base of MC simulations of a random walk of a carrier around deep initial state. The concept of transport level (or transport energy) is known to be a useful approximation for analytic modeling, because it can greatly simplify the description of hopping transport by its reduction to the formalism of multiple trapping model. Real and formal (effective) transport levels, \(E_{trans}\) and \(E_{tr}\), and typical hopping distance, \(a\), are defined by the following equations [6]:

\[
\frac{4\pi}{3} N_0 \int_{E_{trans}}^{E_\ast} dE' g(E') \left[ (E_{tra} - E')/2\gamma kT \right]^2 = B/2,
\]

\[
\frac{4\pi}{3} N_0 \int_{E_{tr}}^{E_\ast} dE' g(E') \left[ (E_{tra} - E')/2\gamma kT \right]^3 = B,
\]

\[
\frac{4\pi}{3} N_0 \int_{E_{tra}}^{E_\ast} dE' g(E') \left[ (E_{tra} - E')/2\gamma kT \right]^3 = B.
\]
where \( N_t \) is a spatial density of localized states. Integration in Eq. (7) performs over \( E-r \) region around deep initial state of energy \( E \to -\infty \), which includes \( B>1 \) neighbour states with transition rate \( \nu \equiv \omega_0 \exp\left[-\left(E_u - E\right)/kT\right] \). Eq. (6) means that upward and downward jumps from a state of energy \( E_{trans} \) occur with equal probabilities. Percolation factor \( B \) was determined from MC simulations [6]:

\[
B = 2.2 + 0.2(\sigma / kT -1.5), \quad \sqrt{2} \leq \sigma / kT \leq 4.
\]

Mobility is calculated in analogy with multiple trapping model [6],

\[
\mu = \mu_c v_0 r_0 \int_{E_{trans}}^{E_{trans}} \frac{dE_g}{E_0} \exp\left[\left(E_{trans} - E\right)/kT\right],
\]

by the use of effective density of states, \( g_{\text{eff}}(E) \), see Eq. (4). In Eq. (9) \( \mu_c = \omega_0 \exp\left(-2\gamma a\right)(e/kT)a^2/6 \) is the characteristic mobility in "conducting" states (near transport level), \( v_0 r_0 \approx kT/\sigma \) [6]. The energy \( E_0 \) is defined by Eq. (5), where the probability \( \phi(E) \) is also defined on the base of transport level. Transport level does not depend on \( E_0 \), as long as \( E_0<<E_{trans} \), due to sharp decreasing of \( g(E) \), \( E \to -\infty \).

**Results and discussion**

Figure 1 shows, that the analytical model yields good agreement with MC simulations, up to field strength \( F = 5 \times 10^5 \) V/cm. Mobility is normalized by the value \( \mu_0 = \omega_0 \exp\left(-2\gamma a\right)(e/kT)a^2 \). Mobility decreases with increasing thickness as a power law [2], approaching to the infinite-media limit \( \mu_\infty \),

\[
\mu = \mu_\infty \left[1+\left(L/L_0\right)^{-\beta}\right], \quad L \geq 20 \text{ nm}.
\]

Values of constants \( \mu_\infty \), \( L_0 \) and \( \beta \) are defined by fitting of MC-data to Eq. (11). The power-law exponent \( \beta \) increases slightly along with increasing of disorder and decreases along with increasing of field strength. It increases from 1.0 to 1.3 and from 0.6 to 1.0 along with the increase of \( \sigma/kT \) from 3 to 5 at \( F = 1 \times 10^4 \) and \( F = 5 \times 10^5 \) V/cm, respectively.

![Figure 1](image.png)

**Figure 1.** Dependence of mobility on layer thickness, a) \( F = 1 \times 10^4 \) V/cm, b) \( F = 5 \times 10^5 \) V/cm. Solid lines – analytical modelling, see Eqs. (5)-(10), points – MC results, Eq. (3). \( T=295K \).

Remarkably, the analytic model is able to fit MC data for mobility in thin films for a broad range of disorder parameter \( \sigma/kT \) and electric field strength, by the use the same disorder-dependent (but field-
independent) percolation factor $B$, see Eq. (9), which has been used successfully [6] in modeling of low-field mobility in infinite media. One has to consider, however, field dependence of transport level to achieve quantitative accuracy at high-field and high-disorder limit.

Figure 2 shows considerable impact of film thickness on disorder dependence of drift mobility. Temperature dependence in thick (> 1 micrometer) films, referred here as infinite media, describes ubiquitously as follows [1]:

$$
\mu_\infty(T) \propto \exp\left[-A(F)K_BT^2 \right], \quad A(F) = C_\infty - \sqrt{F/F_\infty},
$$

(12)

where $C_\infty \approx 0.44$ and $F_\infty \approx 1.2 \cdot 10^7 \text{ V/cm}$ at $2\gamma_o = 10$. Figure 2 shows progressive deviations from the law (11) with increasing disorder and decreasing $L$. Fit of the low-disorder pattern by eq. (3), see dashed lines in the Figure 2, yields considerable decrease of the value of $A$ along with the decrease of thickness, namely $A = 0.37, 0.33, 0.31$ and $0.27$ at $L = \infty, 100, 50$ and $20$ nm, respectively. The first value of $A$ is in excellent agreement with Eq. (11) at $F = 1 \cdot 10^5 \text{ V/cm}$.

Figure 2. Temperature dependences of drift mobility: $L=20$ nm (squares), 50 nm (circles), 100 nm (up triangles), infinity (down triangles), see $\mu_\infty$ in Eq. (11). Solid lines – interpolation of MC data, dashed line – low-disorder fit in accord with Eq. (12). $F=1\cdot10^5 \text{ V/cm}, T=295$K.

Size dependence of mobility in thin organic layers has to be accounted for predictive modeling of charge transport in organic light-emitting diodes. As a first approximation, one can use thickness-dependent spatially-uniform mobility, see Eq. (11).

The work was supported by Russian Ministry of Education and Science in the frames of Competitiveness Growth Program of National Research Nuclear University MEPhI, Agreement 02.A03.21.0005.

References
[1] Bässler H, 1993 Phys. Stat. Sol. (b). 175 15
[2] Korolev N A, Nikitenko V R, and Ivanov D V 2011 Semiconductors 45 230
[3] S Raj Mohan, Manoranjan P Singh, M P Joshi 2010 Organic Electronics 11 1642
[4] Shklovskii B I and Efros A L 1984 Electronic Properties of Doped Semiconductors (Heidelberg: Springer)
[5] Arkhipov V I, Emelianova E V and Adriaenssens G I 2001 Phys. Rev. B 64 125125
[6] Nikitenko V R, Strikhanov M N 2014 J. Appl. Phys. 115 073704