Analysis of the carrier transport in molecularly doped polymers using the multiple trapping model with the Gaussian trap distribution

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1. Introduction

Modern optoelectronic devices such as light-emitting diodes [1], field-effect transistors [2] and solar cells [3] using organic semiconductors require profound understanding of the charge carrier transport for their efficient operation similar to that already achieved in the electrophotographic technology [4,5]. In a recently published review [6], the problem of the charge carrier transport in organic semiconductors has been discussed in detail. It shows that the Gaussian disorder model (GDM) based on a hopping transport of charge carriers still remains a powerful instrument for describing charge motion in disordered organic substances (small molecule glasses, molecularly doped polymers, polymers with charge-transporting molecules residing in the main chain or as pendant groups) [7,8].

As most device-operation oriented calculations refer to steady-state conditions [1–3], they mostly rely on the well-known empirical expressions for carrier mobilities at different fields and temperatures derived from computer (mainly Monte-Carlo) simulations based on the GDM for a model disordered organic semiconductor [4,8].

Experimental studies of the charge carrier transport employ the famous time of flight (TOF) technique, which allows not only to measure the carrier mobility but to study the non-equilibrium phase of the transport process by observing TOF current transients on a wide time scale following a δ-pulse excitation. Based on the optical TOF technique, these transients have been shown to consist of an initial spike transforming into a flat or slightly sloping plateau followed by an anomalously long tail (when plotted in linear j – t coordinates) and seemingly agree with the GDM predictions [4].

To supplement the model Monte-Carlo simulations, we developed a numerical program for a quasi-band analog of the GDM, the so-called multiple trapping model with the Gaussian trap distribution (MTMg) [9,10]. Both approaches give close results as far as TOF shapes are concerned. One of the factors, which stimulated this theoretical effort, is the much-changed situation in the carrier transport after we introduced an electron gun to perform TOF measurements in the widest dynamic range realizing all three modifications of the TOF experiment [11]. These are the conventional TOF method with the surface generation, the TOF-2 technique with the bulk generation and a TOF-1a variant in which the width of the generation zone varies in a controlled manner.

It has been revealed that the carrier transport in a typical polar MDP is non-equilibrium despite the fact that TOF curves feature a flat plateau [9–11]. Also, it was shown that cusps (rising plateaus), traditionally disregarded by investigators [4], reflected some internal property of a MDP sample. To explain the whole plethora of experimental observations previously viewed as contradictory [13,14].
An exponential trap distribution with a rather large dispersion parameter (close to 0.8) describes a dispersive carrier transport. Then, TOF-2 curves, obviously unaffected by the surface layer (bulk excitation), should have a non-Gaussian form in accordance with experiment. Transient curves produced by 3 keV electrons (maximum range about 0.3 μm) feature pronounced cusps as carriers exit generation zone in the defective layer and enter the bulk where their mobility is several times higher. As electron energy increases, the fraction of carriers generated in the bulk increases leading to the formation of the progressively weaker cusps. At some electron energy a perfectly flat plateau appears as a result of fine tuning of two currents, one being due to carriers generated in the surface layer, the other arising from bulk generated carriers. At still higher energies, the plateau begins to slope, until finally, the bulk excitation makes the current form featureless when viewed in linear coordinates. It is important to stress that in all cases, whatever the form of the plateau (flat one included), the tail stays anomalously broad, reflecting dispersive rather than the Gaussian carrier transport. The two-layer model is capable of semi-quantitatively describing the whole sequence of the current shape changes [12]. Surely, the above model captures truthfully the physics of the flat plateau formation arising from an intricate interplay of carriers emerging from the surface layer and the bulk.

In the present paper we compute TOF current transients for a homogeneous polymer using MTMg for several values of the disorder energy σ, an electric field and temperature. Then we introduce a two-layer model based on the MTMg aiming to explain TOF-1a results using model parameters for a typical MDP.

2. Homogeneous polymer

In our computations we rely on reported values of the GDM parameters extracted using the dipolar disorder formalism of Borssenberger and Bässler [8,15]. These are the total disorder energy σ, the mobility of carriers μ0, extrapolated to zero electric field (via Poole–Frenkel functional dependence) for temperature T → ∞ and the mean distance r between dopant molecules calculated using the lattice gas model (ρ = Nl0.8, where Nl is the dopant concentration).

The simple relationship between μ0 and σ [16] (notations are standard)

\[ μ_0 = \frac{e}{kT} b^2 v_{th} \] (1)

allows one to define frequency v_{th} which may be related to the zero-field frequency factor \( v_0 \) of the model (\( v_0 = 6v_{th} \) [9]). MTMg parameters σ and μ0 are taken to be the same as given above. The last parameter of the model, the lifetime of the quasi-free carriers τ0 is found from the relationship \( v_0 τ_0 = 3.0 \) [9]. The situation with a finite electric field is discussed later.

Parameter values chosen for numerical simulations are as follows: \( μ_0 = 0.01 \text{ cm}^2/\text{V s} \), σ = 0.13 eV and \( v_{th} = 10^3 \text{ cm}^2/\text{s} \) and are close to those for polycarbonate doped with 30 wt.% of aromatic hydrazone DEH [30%DEH-PC] [9,17]. In addition, the sample thickness L is 20 μm, the electric field \( E = 20 \text{ V/μm} \), temperature 290 K (\( kT = 0.025 \text{ eV} \)) and the planar density of the generated carriers \( 10^3 \text{ cm}^2 \) (a small signal regime). When these change, it is clearly stated.

We start our analysis by investigating effects of the total disorder σ (Fig. 1). Current curves coincide at early times (≤ 10 fs), then they start to diverge, their decay generally following an algebraic law \( j \propto t^{-β} \). The exponent \( β = -\frac{d \ln j}{d \ln t} \) depends on time and progressively diminishes until a kink occurs signaling carrier transit across the sample. Two tangents (dotted straight lines) on a \( \ln j - \ln t \) plot just preceding and following the kink intersect at the transit time \( t_1 \) (shown on the figure for curve 3). The procedure to find \( t_1 \) is illustrated for curve 3.

\( β_1 \) (before) and \( β_2 \) (after the transit) are useful characteristics of the carrier transport. Values of these parameters are summarized in Table 1. We see that as σ rises \( t_0 \) and \( β_1 \) both increase (especially strongly the first one) but \( β_2 \) systematically decreases.

It is known that MTMg predicts mobility equilibration at long times. Dashed straight lines on the figure show the equilibrium currents in a semi-infinite sample. Also, note that TOF curves 2 and 3 are similar to dispersive transients if viewed at times bracketing the time of flight \( 10^{-2} t_0 \leq t \leq 10^2 t_0 \) but the famous criterion of the Scher–Montroll theory [18] or the MTM [11] (\( β_1 + β_2 = 2.0 \)) fails.

Fig. 2 gives the above curves in a linear \( j \sim t \) representation in a normalized form. Traditionally found two times of flight \( t_0 \) and \( t_{1/2} \) (shown for curve 2) and the relative tail width \( W = t_{1/2}/t_0 \) are also included in Table 1. While for curves 1 and 2 this procedure is rather straightforward, finding this data for the last curve is hardly possible. Still, according to the traditional classification only two first curves may be qualified as non-dispersive (in a sense that they can be readily processed in linear coordinates) whereas the last one should definitely be regarded as a dispersive one. Note that the point with coordinates \((1, 1)\) on the figure corresponds to the intersection of the two tangents mentioned above.

Unlike curves 2 and 3, which are non-equilibrium, curve 1 (see Figs. 1 and 2) is unique as it is characterized by a flat plateau. This feature is certainly due to the low value of σ. Experiment fully corroborates this conclusion: TAPC glass (σ = 0.067 eV) and TAPC doped polystyrene at high loadings (σ ≤ 0.075 eV) [19,20] exhibit flat plateaus with times of flight in the microsecond range in full accord with our computations.

It is known that the GDM (and even more so the MTMg) is incapable of explaining consistently the origin of the Poole–Frenkel effect. Yet, in our analysis of \( 30%\text{DEH-PC} \), an electric field and temperature. Then we introduce a two-layer model based on the MTMg aiming to explain TOF-1a results using model parameters for a typical MDP.

Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>σ, eV</th>
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<tbody>
<tr>
<td>0.07</td>
<td>0.10</td>
</tr>
<tr>
<td>β1</td>
<td>0.03</td>
</tr>
<tr>
<td>β2</td>
<td>9.7</td>
</tr>
<tr>
<td>t0 (ms)</td>
<td>5.60 × 10^{-3}</td>
</tr>
<tr>
<td>t0 (ms)</td>
<td>6.10 × 10^{-3}</td>
</tr>
<tr>
<td>t1/2 (ms)</td>
<td>6.30 × 10^{-3}</td>
</tr>
<tr>
<td>W</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Fig. 1. Computed TOF transients (solid curves) in logarithmic coordinates. Parameters σ equals 0.07 (1), 0.1 (2) and 0.13 eV (3). Dashed straight lines refer to a semi-infinite sample and belong to the corresponding solid curve. The procedure to find \( t_0 \) is illustrated for curve 3.
(PF) effect. Instead, the dipolar disorder formalism introduces it in a prescribed manner contrary to the dipolar glass model, which explains this effect self-consistently [21,22]. It is not clear, which of the MTMg parameters fits best to account for the PF effect, if only in a prescribed manner. It seems to be the frequency factor $k_{PF}$ only in a prescribed manner. It explains this effect self-consistently [21,22]. It is not clear, which of the MTMg parameters fits best to account for the PF effect, if only in a prescribed manner. It seems to be the frequency factor $k_{PF}$ only in a prescribed manner. It explains this effect self-consistently [21,22].

According to the MTMg analysis [25], the equilibrium mobility $\mu$ in our case is equal to $8 \times 10^{-6}$ cm$^2$/V s and does not depend on the electric field. We equate it with the zero-field mobility $\mu(0)$ and use it as a standard in evaluating PF effect represented by the ratio $\mu/\mu(0)$ where $\mu$ stands for the mobility found using computed times of flight given in Table 2.

There are some problems with estimating data points for $F=0$ for all curves except a theoretical one. Direct numerical computations for very small electric fields ($\leq 0.01$ V/µm) are difficult to perform and besides, one has to take into account the presence of an ordinary diffusion (neglected so far). It is quite fair to assume that all zero-field mobilities are very close to $\mu(0)$.

It is seen that curves on Fig. 4 fall into two groups, one relating to PF effect (1–4) and the other (5–7) describing data for field independent frequency factor. In the first group, data based on $t_{1/2}$ best reproduces the PF theoretical dependence, followed by $t_0$ and $t_{10}$. But still, data scatter is not that conspicuous. We see that even for $v_0 = const$ the ratio $\mu/\mu(0)$ increases as the field rises, this fact being in line with the carrier transport becoming more and more dispersive. For completeness, we indicate the maximum values of this ratio at 200 V/µm: 508 (group 1) and 3.42 (group 2), respectively.

To judge the influence of the field on the current shape, we plotted normalized curves from Fig. 3 in linear coordinates as well (Fig. 5). Again, calculations include the case of no PF effect. The following observations should be noted.

At low fields (less than 20 V/µm) the PF effect is of almost no importance as far as the transient shape is concerned although the current shape itself changes dramatically (compare curves 6, 5, and 4). In the absence of PF effect the transient shape changes continuously in the whole field range (as already reported in [9]), while PF curves practically do not change in the field range 20–200 V/µm, their transient shape acquiring an almost universal character. This behavior is reminiscent of the famous universality law found experimentally [18] and explained by the SM theory [18] or the MTM [26]. A weak universality found in the present work appears on $j-t$ plots and only in the time interval embracing the time of flight.

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**Fig. 2.** The same transients as on Fig. 1 but in the linear normalized coordinates. The procedure to find $t_0$ and $t_{1/2}$ is shown for curve 2.

**Fig. 3.** Computed TOF transients (solid curves) in logarithmic coordinates with (1, 3, 5) and without (2, 4, 6) taking into account PF effect (see Table 2). Electric field 200 V/cm (1, 2), 20 V/cm (3, 4) and 2 V/µm (5, 6). Dashed straight lines refer to a semi-infinite sample and belong to the corresponding solid curve.

**Fig. 4.** Mobility ratio $\mu/\mu(0)$ as a function of the square root of the electric field. Theoretical curve 1 and the computed mobilities based on $t_{1/2}$ (2, 7), $t_0$ (3, 6) and $t_0$ (4, 5). PF effect taken into account (1–4) and neglected (5–7). The symbols are computed data points.
Table 2
Computed slopes and times of flight for three values of the electric field with and without account of the prescribed PF effect (see text).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Field, V/μm</th>
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<tbody>
<tr>
<td></td>
<td>2</td>
</tr>
<tr>
<td>PF factor</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2</td>
</tr>
<tr>
<td>β₁</td>
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</tr>
<tr>
<td></td>
<td>0.12</td>
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<tr>
<td>t₀ (ms)</td>
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<tr>
<td></td>
<td>0.77</td>
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<td></td>
<td></td>
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<tr>
<td>t₁/₅ (ms)</td>
<td>15.4</td>
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<tr>
<td></td>
<td>1.18</td>
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<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>0.37</td>
</tr>
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Fig. 5. Transients 2–6 from Fig. 3 presented in the linear normalized coordinates. j₀ is the current density at the time of flight.

Fig. 6. Computed TOF transients (solid curves) in logarithmic coordinates referring to σ equal to 0.07 (1–3) and 0.1 eV (4–6) for temperatures 350 (1, 4), 290 (2, 5) and 250 K (3, 6). Dashed straight lines refer to a semi-infinite sample and belong to the corresponding solid curve.

At last, we performed numerical calculations of the mobility temperature dependence. Computed curves are presented in Fig. 6 for two values of σ (0.07 and 0.1 eV) and three temperatures (250, 290 and 350 K) with dashed straight lines referring again to a semi-infinite sample. Here we plot numerical data only for the case of V₀ = const intending to explore mainly the effects of a non-equilibrium transport. The plots on Fig. 7 represent the temperature dependence of the transit times as a function of 1/T².

Analytic formula [25] predicts that with a good approximation \( \bar{\mu}^{-1} \propto \exp \left( \frac{\sigma^2}{kT} \right) \) which is slightly different from the famous GDM expression \( \bar{\mu}^{-1} \propto \exp \left( \frac{4kT}{\sigma^2} \right) \) [7,8]. Our main interest is to check whether the general dependence \( \bar{\mu}^{-1} \propto 1/T^2 \) holds. One notes that for \( \sigma = 0.07 \text{ eV} \) even the theoretical curve shows some curvature but data points are very close to each other and to the theoretical curve. In the case of \( \sigma = 0.1 \text{ eV} \) the theoretical curve becomes straight but computed times of flight increasingly deviate from the theoretical dependence as temperature falls. As in the case of the PF effect, the least deviating data points belong to t₁/₅ with those of t₀ deviating most. As a result, effective values of \( \sigma \) found from processing data for t₁/₅, t₀ and t₀ are 0.084, 0.080 and 0.074 eV respectively compared to theoretical value 0.1 eV. We see that the effect of the non-equilibrium transport in this case is quite perceptible but for \( \sigma = 0.07 \text{ eV} \) it is hardly seen.

3. Non-homogeneous polymer: two-layer model

Recently, we have shown that according to the GDM numerous examples of the flat plateaus on experimental TOF curves should not even appear [9]. In a similar situation, involving the weakly dispersive transport (\( \sigma \approx 0.85 \)) one had to apply the two-layer multiple trapping model for universal current transients to describe successfully the experimental results obtained by a TOF-1a technique in 30%DEH:PC [12]. Let us try the same approach for the MTMg.

MTMg parameters describing the carrier transport reported in [11,12] have been slightly corrected to better fit the existing data cited in [24] so that \( \sigma = 0.128 \text{ eV}, \ V₀ = 1.25 \times 10^{11} \text{ s}^{-1}, \ \mu₀ = 0.01 \text{ cm}^2/\text{V s}, \ t₀ = 2.4 \times 10^{-11} \text{ s} \). A defective layer 1 μm thick with inferior transport characteristics compared to the bulk has been introduced into the model (the sample thickness 13.8 μm, the electric field 20 V/μm).

Unlike [12], we propose to explain the origin of the surface defective layer as arising from the sublimation of the dopant molecules through the free surface exposed to air during coating/drying procedure. In electron-beam experiments reported in [11,12] it is this free side of the samples that invariably faced the beam. As a result, a thin depletion layer with a reduced concentration of the dopant has been controlling TOF transients. Due to an exponential concentration dependence, the carrier mobility in the depletion layer will be lower than in the bulk. Thus, there is no need to
invoke any extrinsic traps. Also, it is only natural to expect that the Gaussian trap distribution should be the same in both parts of the sample with \( \sigma = 0.128 \text{ eV} \). Lowering \( \mu_0 \) by a factor of six and applying Eqs. 1 and 2, we specify MTMg parameters for the depletion layer. Besides, the problem of an energetic set-off between the discreet transport level and the center of the trap distribution inherent in the approach adopted in [12] is automatically eliminated.

Computation results show (Figs. 8 and 9) that increasing the thickness of an irradiation zone (assumed rectangular like in its physical origin comes from the dipolar energy landscape, which happens to be spatially closely correlated [21–23]). The net effect of the spatial energy correlation consists in that the thermally activated release of holes trapped by critical traps whose radius becomes effectively controlled by the applied electric field [22]. It seems sound to suggest that exactly the frequency factor \( v_0 \) should be ascribed the specified field dependence, if only in a prescribed manner at this stage.

Thus, the proposed two-layer MTMg seems to be capable of describing the non-equilibrium bulk carrier transport under uniform excitation (TOF-2 experiment) and explain the appearance of a flat plateau with anomalously broad tail at some intermediate electron energy (TOF-1a experiment), which generally should not be identified with the equilibration of the carrier transport. Even more, the new model is capable of accommodating both the non-Arrhenius mobility temperature dependence as well as its Poole-Frenkel field dependence. As an analytical model, it is amenable to accurate numerical calculations, which are not as time consuming as the Monte-Carlo simulations.

At the request of Referee, we now compare our calculations with the relevant Monte-Carlo simulations reported in [29,30] for a homogeneous system. It should be noted that those simulations
referred to a model organic semiconductor $\rho = 0.6$ nm like in polyvinylcarbazole) for a range of $\sigma$ (in particular, $\sigma/kT$) and studied the non-dispersive to dispersive transition. Unfortunately, simulation results were presented in arbitrary units only. Therefore, we could not draw any quantitative comparisons. Still, some qualitative comparisons are worth mentioning. Comparing Fig. 1 in our work and in [29] shows that $\beta_4$ rises with increasing $\sigma$ quite similarly in both cases. Addressing Fig. 7 in [29], we see that curves presented on both linear and logarithmic plots resemble very closely our curve 3 on Figs. 1 and 2 ($\beta_4$ equals 0.27 and 0.26 eV respectively). The similarity increases even more if $t$-coordinate on our Fig. 2 is properly compressed. Thus, our numerical calculations qualitatively agree with the model Monte-Carlo simulations reported in [29,30].

5. Summary

We have shown that MTMg can successfully predict current shapes provided that GDM parameters are determined within the dipolar disorder formalism. Computations prove that the carrier transport is surely non-equilibrium for MDPs with $\sigma \geq 0.09$ at room temperature. The flat plateaus on TOF transients originate from the surface layer interference. For $\sigma \leq 0.075$ eV the theory predicts transport equilibration at typical experimental conditions ($T \geq 250$ K). All three times of flight ($t_1$, $t_2$, and $t_0$) are quite representative as far as the field and temperature dependence of the mobility is concerned, the second one being of universal application.

It is important that the proposed MTMg reproduces quite truthfully both the non-Arrhenius temperature mobility dependence as well as its ubiquitous PF field dependence. The first property is a direct consequence of the model parameter $\sigma$ combining the van-der-Waals and the dipolar disorder energies. While the second one arises from the PF type field dependence of the model frequency factor prescribed by the dipolar glass model [21–23].

A two-layer extension of MTMg along the lines of the two-layer MTM recently suggested in [12] describes adequately TOF-1a results including flat plateau formation for the non-equilibrium carrier transport.

References