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Comparison of the time of flight current shapes predicted by hopping and multiple trapping models

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ABSTRACT

We have compared time-of-flight curves predicted by hopping and multiple trapping models with the Gaussian and exponential site/trap energy distributions, fitting Monte-Carlo predictions of the former with numerical calculations of the latter in a wide time domain using logarithmic coordinates $\lg j$–$\lg t$ for the characterization of current shapes and an estimation of transit times. As a prototype hopping theory, we used the Gaussian disorder model while for representing the quasi-band theories we relied on the multiple trapping model, both of these for two types of the site/trap energy distributions. In case of the Gaussian distribution of trap depths, fitting procedure requires adjusting of the two model parameters (an energy distribution parameter σ and a frequency factor ν_0). For an exponential distribution, a one-parameter (ν_0) fitting suffices. The dipolar glass model, unlike the Gaussian disorder model, is basically different from the multiple trapping formalism, but a recently introduced two-layer multiple trapping model seems capable of reproducing TOF current shapes rather well.

1. Introduction

Carrier transport in molecularly doped polymers (MDP) occurs by field-assisted and thermally-activated hopping in a spatially and energetically disordered manifold of the transport sites (dopant molecules) randomly dispersed in a polymer binder. Depending on the electronic properties of these molecules (electron donors or acceptors), an MDP may be a hole or an electron conductor respectively. The main characteristic of the charge transport in MDPs is the carrier mobility experimentally determined by the time of flight (TOF) technique [1,2]. At present, a universally accepted point of view is to treat this phenomenon in terms of the existing hopping theories. Among these three models are most popular. First is the Gaussian disorder model (GDM) proposed by Bässler [3,4], the mainstream tool for processing numerous results on the mobility field and temperature dependence with the aim of finding the model parameters via the dipolar disorder formalism developed by Borsenberger and Bässler [5,6]. The second is a recently emerged dipolar glass model (DGM) [7,8], which seeks to overcome the basic limitation of the GDM, its inability to describe consistently the ubiquitous Poole–Frenkel (PF) type of the mobility field dependence in MDPs [1,2]. There is yet another approach, also emphasizing, like the DGM, the correlation effects, but taking into account the polaronic effects as well, which seems to give a consistent explanation of the field and temperature dependence observed [9].

All of the above hopping theories require time-and labor consuming efforts to perform Monte-Carlo simulations, which greatly hinders their wide application not only in engineering practice but also among scientific community. It is due to this reason that their heuristic counterparts (mainly multiple trapping (MT) model) are still widely used for the simulation of electro-optical devices [10–13].

Although only hopping theories give a true microscopic description of the charge carrier transport in MDPs, much simpler argumentation provided by MT models could be justified by the close analogy between the so-called transport energy in the hopping models and the mobility edge in the quasi-band approach [14,15]. Transport energy, defined as the most probable final energy level of the hopping carrier does not depend on its initial energy if this is situated deep enough and the density of states decreases fast with the depth of the state. This concept suggests that the major exponential contribution to the temperature dependence of the hopping mobility in the steady state could be adequately described by the transport energy serving as an effective activation energy. Though the above approach was sometimes criticized [16] and is certainly not well suited for description of the

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hopping transport in correlated energy landscape [17], it provides a useful heuristic link between MT and hopping models.

The first Monte-Carlo simulations of the GDM [18–20] showed that TOF current shapes closely resemble those predicted by the MT theories for respective trap distributions. Later publications [21,22] confirmed these findings. It was even claimed that both responses might even be identical at low electric fields [23]. In fact, these papers had only shown that transient shapes for both models were similar but no attempt had been made to confirm that mobility field and temperature dependences were identical in a sense that a relation between microscopic parameters of the equivalent models could be established. In this paper, we are going to fill this gap, if only partially.

2. Formulation of the problem

We compare theoretical models using typical set-up of the TOF experiment in which a sheet of carriers is instantly generated in a polymer slab near the illuminated electrode. The surface density of generated charges Σ_0 (cm^{-2}) is much smaller than that residing on the electrodes (small signal regime), so that an electric field F_0 inside the bulk of the polymer is constant and uniform. Due to random motion of individual carriers, the carrier sheet continuously spreads as it drifts to the collecting electrode. An observable quantity in TOF experiment is the current density $j(t)$ in the external circuit. The main characteristics of computer simulations are current shapes and transit times, which we compare for different models. The TOF problem is treated as one-dimensional with the x-axis running along an applied electric field. Charge transport in MDPs occurs as a hopping process, so we use the GDM Monte-Carlo simulation data as a primary source information to be fitted with the MT numerical calculations.

2.1. Hopping models

We considered hopping models with the Gaussian (the GDM) as well an exponential (EDM) site energy distributions. Monte-Carlo simulations of the TOF transients were quite similar to those described previously [3,4]. Parameters of the hopping models refer to a typical polar MDP: polycarbonate doped with 30 wt% *p*-diethylaminobenzaldehyde diphenylhydrazone (30% DEH:PC) [24,25], which is a hole-only conductor.

We assume that transport molecules occupy sites of the simple cubic lattice with the nearest-neighbor distance a = 1.165 nm. The sample thickness is $L = 2 \times 10^4$ a = 23.3 μm. The transfer rate is given by the standard Miller–Abrahams expression [4]. The inverse wave function localization length γ is such that $2\gamma a = 10$. The zero-field mobility μ_0 for the case of no energetic disorder as given by the dipolar disorder formalism is taken to be 0.02 $cm^2/(V\,s)$. There is a well-known relation between this quantity and the frequency ν_{hh} of carrier jumps to the nearest neighbor sites on a cubic lattice (e is an elementary electric charge and k is the Boltzmann constant) [26]

$$\mu_0 = (e/kT)a^2\nu_{hh} \tag{1}$$

In our case, $\nu_{hh} = 3.7 \times 10^{10}\ s^{-1}$. In Monte-Carlo simulations, the quantity $\nu_{hh}^{-1} = 2.7 \times 10^{-11}$ s serves as a normalization time. Site energy distributions are as follows [20]

$$M(E) = \frac{a^{-3}}{\sqrt{2\pi}\sigma}\exp\left(-\frac{E^2}{2\sigma^2}\right) \quad \text{(GDM)} \tag{2}$$

$$M(E) = \frac{a^{-3}}{E_0}\exp\left(-\frac{E}{E_0}\right) \quad \text{(EDM)} \tag{3}$$

where $-\infty \leqslant E \leqslant \infty$ (Eq. (2)) and $0 \leqslant E \leqslant \infty$ (Eq. (3)).

2.2. MT models

Now we would like to briefly discuss the basic physics of this formulation. It is well known that the MT model, based on the quasi-band arguments proposed by A. Rose [27], in its present form is a powerful instrument for describing a plethora of photo- and radiation-induced conductivity results in disordered solids [28] as well as for interpretation of the carrier transport in such systems [29]. Of course, this approach exists only on a phenomenological level.

It is assumed that in a hole-only conductor, photo excited holes appear in a mobile state. Their quantum yield depends on the applied electric field and temperature according to the Onsager theory (see [30]). Subsequent hole migration (drift and diffusion) proceeds in the presence of traps whose depths are statistically distributed in energy. Trapping of the mobile carriers is a first order non-activated process while thermal detrapping obeys the Boltzmann statistics with a frequency factor common to all traps. The bimolecular recombination is of the Langevin type and takes place between mobile holes and the immobile electrons (recombination centers). Direct transitions of holes between traps are forbidden, their migration being possible exclusively via thermal excitation into the valence band.

Following A. Rose, we solve numerically the following set of the coupled differential equations, which are standard for the MT model:

$$\frac{\partial\rho}{\partial t} = \frac{P_0}{\tau_0}\frac{M(E)}{M_0} - \rho\nu_0\exp\left(-\frac{E}{kT}\right), \tag{4}$$

$$P = P_0 + \int_0^{+\infty}\rho dE, \tag{5}$$

$$\partial P/\partial t + \mu_0\partial(FP_0)/\partial x = 0. \tag{6}$$

Eq. (4) is the rate equation describing the gain and loss of holes between the trap manifold and the transport manifold. A corresponding equation for the evolution of holes includes the same gain and loss processes, but also includes drift due to the applied field. We have introduced the combined trap and free population, and broken this equation into two parts, as expressed by (5) and (6).

We assume that a sheet of holes in the conducting states with the planar density Σ_0 is generated near the front electrode at $x = 0$, $P(x,t)$ is the total concentration of carriers, $P_0(x,t)$ is the concentration of mobile holes in transport manifold with the quasi-band mobility μ_0 and the lifetime τ_0, and the density of holes in the trap manifold is given by $\rho(x,E,t)$ (here E is the trap energy). The frequency factor is ν_0. The distribution of trap energies $M(E)$ is given by a half-Gaussian distribution for positive values of the argument with rms σ for the MTg.

$$M(E) = \frac{M_0}{\sigma}\sqrt{\frac{2}{\pi}}\exp\left(-\frac{E^2}{2\sigma^2}\right) \tag{7}$$

and

$$M(E) = \frac{M_0}{E_0}\exp\left(-\frac{E}{E_0}\right) \tag{8}$$

for the MTe (M_0 is the total trap concentration while E_0 is the distribution parameter). In both formulas E is positive (note differences with Eqs. (2) and (3)). In Sections 2.1 and 2.2 we used the same symbols μ_0 and σ (or E_0) as these are meant to be identical. In computations one of the probe values of σ is 0.13 eV while E_0 = 0.05 eV is kept constant. Dispersion parameter for both EDM and MTe is equal to $\alpha = kT/E_0$. Besides, Σ_0 in both MT models is $10^8\ cm^{-2}$.