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Carrier-density and field-dependent charge-carrier mobility in organic semiconductors with correlated Gaussian disorder

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ABSTRACT

Recently, it has been demonstrated that for organic semiconductors with a Gaussian density of states (DOS) and with on-site energies that are spatially uncorrelated the hopping mobility of charge-carriers can be strongly carrier-density-dependent (extended Gaussian disorder model, EGDM). In the literature, it has been argued that for some materials, the on-site energies are actually spatially correlated. In this paper, we develop a full description of the mobility in a correlated Gaussian DOS (extended correlated disorder model, ECDM), using a master-equation method. We show that the mobility is less strongly carrier-density-dependent than in the EGDM, but that the field dependence is more pronounced. The field dependence is found to be described by a Poole-Frenkel factor, as has been deduced from empirical analyses of experimental data, but only in a limited field range. As an example of an application, we present a comparison between analyses of the current–voltage–temperature $J(V,T)$ characteristics of a poly-phenylene-vinylene (PPV) based hole-only device using the EGDM and the ECDM. For both cases, excellent fits can be obtained, but with the EGDM a more realistic value of the intersite distance is found than in the case of the ECDM. We view this as an indication that site-energy correlations do not play an important role in PPV.

1. Introduction

The interest in electronic devices based on disordered semiconducting organic materials is rapidly increasing. Important applications are organic light-emitting diodes (OLEDs) [1,2] organic field-effect transistors [3], and organic photo-voltaic devices [4]. It is of crucial importance to understand the charge-carrier transport in these materials in order to design and synthesize appropriate materials and to improve the efficiency and lifetime of devices. Many investigations have addressed the mobility μ of charge-carriers in these materials, since this is one of the important parameters controlling the performance of devices.

Charge transport in polymers and organic small-molecule materials occurs by thermally assisted tunneling – hopping – between localized molecular states. In several studies, the dependence of μ on temperature T and electric-field E, due to this hopping process, has been investigated [5–10]. Bässler and co-workers introduced a model with an uncorrelated Gaussian distribution of the random energies of hopping sites, which became known as the "Gaussian disorder model" (GDM). They found a temperature dependence of the mobility of the form $\mu \propto \exp[-(T_0/T)^2]$ and a Poole-Frenkel behavior $\mu \propto \exp[\gamma\sqrt{E}]$ for the electric-field dependence in a rather limited range of electric-fields [5,6]. Gartstein and Conwell argued that in order to obtain a Poole-Frenkel behavior in a broad range of electric-fields, as observed in time-of-flight mobility measurements, it is necessary to assume correlation

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between the site energies, leading to what is now known as the "correlated disorder model" (CDM) [7]. Indeed, their simulations, which assume static fluctuations of the site energies due to the interaction of a charge-carrier with permanent and induced dipoles, show that the concept of correlation between the energies of spatially close sites leads to an extended range of validity of the Poole-Frenkel law [7]. Dunlap et al. developed a one-dimensional analytical model with correlations caused by randomly oriented dipoles, which yields a Poole-Frenkel E dependence of μ in agreement with time-of-flight measurements of molecularly doped polymers [8]. An extension of this model to three dimensions was developed by Novikov et al. [9]. Apart from dipoles, long-range thermal fluctuations in the molecular geometries of a polymer were suggested as a possible cause for correlation in the disorder [10]. Recently, it has also been suggested that the Poole-Frenkel dependence on the electric-field is caused by carrier heating [11]. In an early study the assumption of a Poole-Frenkel field dependence of the hole mobility appeared to lead to a good description of the current–voltage $J(V)$ characteristics of hole-only devices of PPV(poly-phenylene vinylene)-based polymers [12].

In organic field-effect transistors, where the carrier-density is relatively high (up to on average 0.01–0.1 carriers per site), a dependence of the mobility on the charge-carrier-density p was taken into account in the modeling [13]. In sandwich-type hole-only devices containing, e.g., PPV-based or polyfluorene-based polymers used in OLEDs, the carrier-densities are typically much smaller, *viz.* 10^{-5}–10^{-4} carriers per site, except in a thin region near the anode interface. Nevertheless, it was concluded during the last few years that it is also for such devices and in OLEDs important to take the dependence of μ on p into account [14–16]. By changing the thickness of the polymer layer it was demonstrated that by only assuming a dependence of μ on E of the Poole-Frenkel type it is not possible to fit the $J(V)$ characteristics of hole-only devices with different thicknesses without changing the fit parameters, but that a consistent set of fits can be obtained by assuming a dependence of μ on p [15,16]. Several theoretical and computational approaches were employed to describe this carrier-density dependence of the mobility [10,17–19]. From a numerical solution of the master-equation within the GDM for the occupation probabilities of an array of hopping sites Pasveer et al. obtained a dependence of μ on T, E, and p that was shown to lead to excellent agreement of calculated and measured $J(V,T)$ characteristics of hole-only devices of PPV-based polymers [18]. We call this the "extended" Gaussian disorder model (EGDM), in order to indicate that the carrier-density dependence of the mobility is taken into account. It was found that only at high voltages and low temperatures the dependence of μ on E plays a role.

Pasveer and co-workers concluded that it is not necessary to assume correlations in the site energies in order to obtain for the PPV-based hole-only devices studied agreement with measured $J(V)$ characteristics. However, this does not yet proof that the site energies are uncorrelated, as it has not yet been established whether the experiments performed are sufficiently sensitive to the occurrence of correlations. In this paper, we first provide the required theoretical basis for addressing this question, *viz.* by deriving from master-equation calculations and percolation theory (Section 2) a full description of the temperature, electric-field and carrier-density dependence of the mobility (Section 3). To be definite, we will consider correlated disorder as caused by random dipoles, since this is the most commonly accepted model. We show that the carrier-density dependence of the mobility is weaker than in the EGDM, but that the field dependence is stronger. As an application of our results, we re-analyse in Section 4 the $J(V)$ characteristics of the PPV-based hole-only devices studied already in Ref. [18] within this extended version of the CDM ("ECDM"), by making use of a drift–diffusion device model. For the device considered, a very good description of the $J(V)$ characteristics can also be obtained within the ECDM, but with a much smaller intersite distance than obtained within the description using the EGDM. In Section 5 a summary and conclusions are given.

2. Methods

As in Ref. [18], we determine the charge-carrier mobility μ of carriers on an array of hopping sites, representing a disordered semiconducting organic material, by considering the master-equation for the mean-field occupation probabilities of these sites:

$$\sum_{j\neq i}[W_{ij}p_i(1-p_j)-W_{ji}p_j(1-p_i)]=0. \tag{1}$$

Here p_i is the time-averaged probability that site i is occupied by a charge-carrier and W_{ij} is the transition rate for hopping from site i to j. The factors $1-p_i$ account for the fact that only one carrier can occupy a site, due to the high Coulomb penalty for the presence of two or more carriers at the same site. We assume hopping of carriers from site to site as a thermally assisted tunneling process and coupling to a system of acoustical phonons, leading to the Miller–Abrahams transition rates [20]:

$$W_{i,j}=\begin{cases} \nu_0\exp[-2\alpha R_{ij}-\beta(\varepsilon_j-\varepsilon_i)] & \varepsilon_j\geqslant\varepsilon_i,\\ \nu_0\exp[-2\alpha R_{ij}] & \varepsilon_j<\varepsilon_i,\end{cases} \tag{2}$$

where $\beta\equiv 1/k_BT$, with k_B the Boltzmann constant; ν_0 is an intrinsic rate, $R_{ij}\equiv|\mathbf{R}_j-\mathrm{R_i}|$, with $\mathbf{R}_i$ and $\mathbf{R}_j$ the site positions; α is the inverse localization length of the localized wave functions under consideration and ε_i is the on-site energy of site i. The energy differences in Eq. (2) are supposed to contain a contribution $-eER_{ij,x}$ due to an electric-field E applied in the x direction, where e is the charge of the carriers.

As in Ref. [18] we solve Eq. (1) by an iteration procedure comparable to the one proposed by Yu et al. [10], starting from the zero-field Fermi–Dirac distribution. We take a regular cubic lattice of sites with lattice constant a and periodic boundary conditions. For the inverse localization length we take the same value as in Ref. [18]: $\alpha=10/a$. The effect of changing α is predominantly a change of the prefactor of the mobility, which is not a matter of concern here, and a slight change in the temperature dependence of the mobility. We refer to Ref. [19] for a more detailed dis-