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Temperature, charge carrier density, and electric field dependence of mobilities in disordered conjugated polymers: simulation results

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Abstract

We present the results of simulation studies of the dependence on temperature, charge carrier density, and electric field of the mobility μ in disordered conjugated polymers. The disorder is modeled by a Gaussian density of states (DOS) with width σ. We base our analysis on an exact numerical solution of the Pauli Master equation. The recently experimentally determined carrier density dependence, ranging from densities typically found in light-emitting diodes (LEDs) up to those found in field-effect transistors (FETs), is fully reproduced. At low temperatures T, we find deviations from the generally accepted $\mu \sim \exp[-\text{const.}(\sigma/kT)^2]$ behavior. Our calculations show that the electric field dependence does not play a prominent role at the driving voltages of polymer devices.

Keywords: computer simulations, conductivity, conjugated polymers

1. Introduction

After the discovery of electroluminescence in the conjugated polymer poly-(p-phenylene vinylene) (PPV) [1] and its derivatives, a lot of attention was paid to the study of the optical and electronic properties of conjugated polymers. Understanding of the charge carrier transport in these polymers is of crucial importance in order to further improve the opto-electronic devices based on these materials. One of the most important parameters in this context is the mobility of the charge carriers. In particular, the dependence of the mobility on temperature and electric field has been addressed in literature. It is by now a well-established fact that the mobility in many disordered organic solids deviates from normal Arrhenius-type behaviour [2], although there are examples where Arrhenius-type behaviour seems to describe the data rather well [3]. Computer simulations modeling hopping in a disordered energy landscape with a Gaussian DOS of width σ gave $\mu \sim \exp[-\text{const.}(\sigma/kT)^2]$, while Poole-Frenkel behavior was found for the electric field dependence [2].

Only recently, attention focused on the dependence of the mobility on charge carrier density [4,5,6]. Recent experiments have shown a strong dependence of the hole mobility on the carrier density in hole-only devices and FETs with conjugated polymers as the active material [4]. Theoretically, the influence of the carrier density and electric field for a Gaussian DOS was studied in a very simplified approach, in which the effect of the electric field on the population of the hopping sites was neglected [6]. In the present study we focus on an exact numerical solution of the Pauli Master equation related to the hopping problem and present results for the dependence of the mobility on the three aforementioned parameters: temperature, carrier density, and electric field.

2. Theory and methodology

The incoherent motion of charge carriers (electrons, holes) for which doubly occupied electronic states are not allowed can be described by the Pauli Master equation

$$\frac{\partial n_i}{\partial t} = -\sum_{j \neq i} \left[W_{ij} n_i (1 - n_j) - W_{ji} n_j (1 - n_i) \right], \qquad [1]$$

where n_i is the occupational density of site i with position vector $\mathbf{R}_i$ and random energy ε_i, in our case drawn from a Gaussian distribution with width σ. W_{ij} is the transition rate for hops from site i to j. For the case of interest, we take W_{ij} as suggested by Miller and Abrahams [7], containing a carrier wave-function overlap factor, and a Boltzmann factor for upward hops in energy:

$$W_{ij} = \nu_0 \exp[-2\alpha |\mathbf{R}_{ij}| - \theta(\varepsilon_{ij}) \beta \varepsilon_{ij}]. \qquad [2]$$

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Here α is the inverse localization radius of the wavefunctions, θ is the stepfunction, ν_0 is an intrinsic rate, and $\varepsilon_{ij}=\varepsilon_j-\varepsilon_i$ includes $q\boldsymbol{E}\cdot\boldsymbol{R}_{ij}$ from the external electric field $\boldsymbol{E}$; q is the particle charge and $\beta=1/kT$. In the above stated form the Master equation is non-linear and difficult to solve directly. Instead, we make use of a very efficient iteration approach that has been developed by Yu *et al.* [8], in which the stationary solution n_i of Eq. 1 is expressed as

$$n_i = \frac{\sum_j W_{ij} n_j}{\sum_k W_{ki}} \left[1 - \frac{\sum_j (W_{ji} - W_{ij}) n_j}{\sum_k W_{ki}} \right]^{-1} . \qquad [3]$$

The approach is to update n_i iteratively from this equation, using already updated values n_j when available. The iteration is stopped when the desired accuracy is reached. In the situations we studied this procedure leads to stable and reliable results.

3. Results and discussion

We perform our simulations on regular arrays with lattice constant a. Most of the simulations are done for 50x50x50 arrays. At the lowest temperatures, where finite size effects are more prominent, 100x100x100 arrays or even 150x150x150 arrays are used. The exponential dependence on $\alpha|\boldsymbol{R}_{ij}|$ in Eq. 2 implies that we can limit the hopping to points in the immediate neighborhood of a point i. We always check that the number of neighboring hopping sites taken into account is enough to ensure converged results. The averaging procedure over different realizations of the disorder is done such that the error bars are smaller than or equal to the symbol size in the figures presented below. The value of the parameter α is taken equal to a typical experimental value, $\alpha\approx10$ [4], and the temperature regime we cover, by varying σ/kT between 2 and 6, includes the typical experimental range $\sigma/kT\approx$4-5 at room temperature [4]. In Fig. 1 we show the results for the mobility as a function of charge carrier density at different temperatures. From Fig. 1 it is clearly observed that for all temperatures the mobility has roughly the same dependence on the charge carrier density. At low carrier density the mobility is practically constant and after a certain carrier density (increasing as a function of temperature) it starts to increase. The density dependence is most pronounced at low temperatures. At $\sigma/kT\approx5$ we see that the mobility increases about three orders in magnitude. The observed density dependence at $\sigma/kT\approx5$ of the mobility is in very good agreement with the experiments of Tanase *et al.* [4]. In that work the high density regime is fitted to the Vissenberg-Matters theory [4,8], assuming an exponential DOS. The present work demonstrates that the mobility can be modeled with a Gaussian DOS all the way from the low-density regime, relevant for LED operation, up to the high-density regime, relevant for FET operation. At high temperatures $\sigma/kT\approx$1-2 the mobility becomes almost density independent and at still higher temperatures (not shown) the mobility even decreases with increasing density. We come back to this issue later.

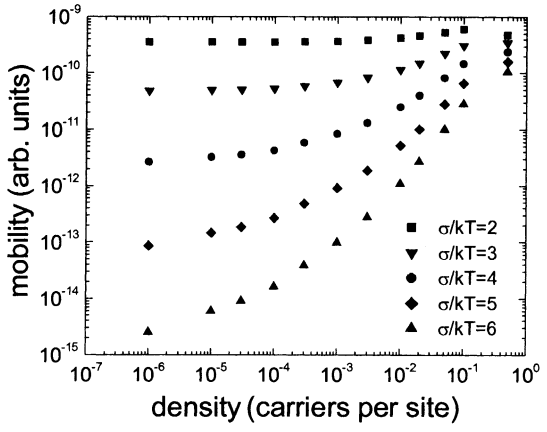

Fig. 1. Mobility vs. charge carrier density at different temperatures, for a disordered hopping system with a Gaussian density of states of width σ.

The mobility in the low-density limit has a strong temperature dependence, which is often discussed in literature [2]. In this limit Fermi statistics goes over into Maxwell-Boltzmann statistics and the mobility becomes density independent. In Fig. 2 we show the temperature dependence of the mobility at a low density of 10^{-5} (LED regime) and a relatively high density of 0.05 (FET regime) carriers per site. At low temperatures we observe that a $\mu\sim\exp[-\text{const.}(\sigma/kT)]$ dependence describes the data better than the $\mu\sim\exp[-\text{const.}(\sigma/kT)^2]$ dependence proposed in [2]. We attribute this to the fact that at low temperatures Fermi-Dirac statistics becomes important, leading to hopping around the Fermi level [5]. At even lower temperatures (not shown) variable-range hopping becomes important leading to a $\mu\sim\exp[-(T_0/T)^{1/4}]$ Mott behavior.

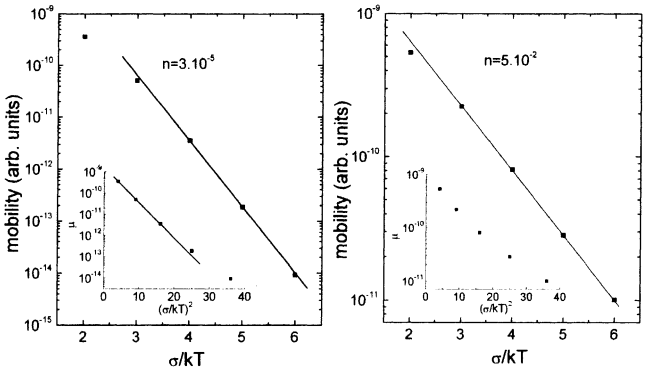

Fig. 2. Mobility vs. σ/kT for a density of 10^{-5} (left) and 0.05 (right) carriers per site. Insets: the same, but plotted vs. $(\sigma/kT)^2$. The straight lines are guides to the eye.

The electric field dependence in conjugated polymers is often modeled by a Poole-Frenkel behavior $\mu\sim\exp[\gamma\sqrt{(qaE/\sigma)}]$. Previously, it was assumed that the hole current in polymer LEDs was dominated by such an