Simulation of Carrier Injection and Propagation in Molecularly Disordered Systems

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Abstract— **Simulated charge flows in semiconductor devices based on undoped amorphous Zinc Phthalocyanine films are presented. A three-dimensional Monte Carlo simulator has been implemented to study the transport of electrons in randomized organic media under varying physical conditions which would lead to experimentally untractable demands. In this work the effect of molecular disorder on carrier injection and propagation is investigated. The numeric effects of different morphologic phases on a system's electric characteristics are estimated.**

I. Introduction

Organic opto-electronic devices are assemblies of about 100 nm thin functional layers exhibiting a certain degree of molecular disorder. The most preeminent transport property of these films is the confined motion of carriers and their corresponding lattice-distortions giving rise to a set of activated transport regimes ranging from incoherent phonon-assisted tunneling to bandlike small polaron transport. The dispersive nature of these regimes is caused by the loss of long range order but not related to the system's chemistry. However, the interaction of the different charge-transfer mechanisms with specific properties of branched π and π^* systems is one of the most interesting open questions in the modeling of organic devices, since it can be utilized to govern the sample's electrical characteristics. Kinetic Monte Carlo simulations (KMC) are intended to fill the gap between ensemble Monte Carlo (MC) and molecular-dynamics (MD) simulations. The MD method models the dynamics directly, but for large systems or complex energy landscapes the time-scale is limited to nano- or picoseconds. On the other hand, the phase-space traversal of classical MC techniques does not describe how the system relaxes towards equilibrium. KMC uses an importance sampling criterion associating a time-scale with each step. In this way the simulation of the system's static observables can be enriched by a kinetic description of its dynamics in terms of rates.

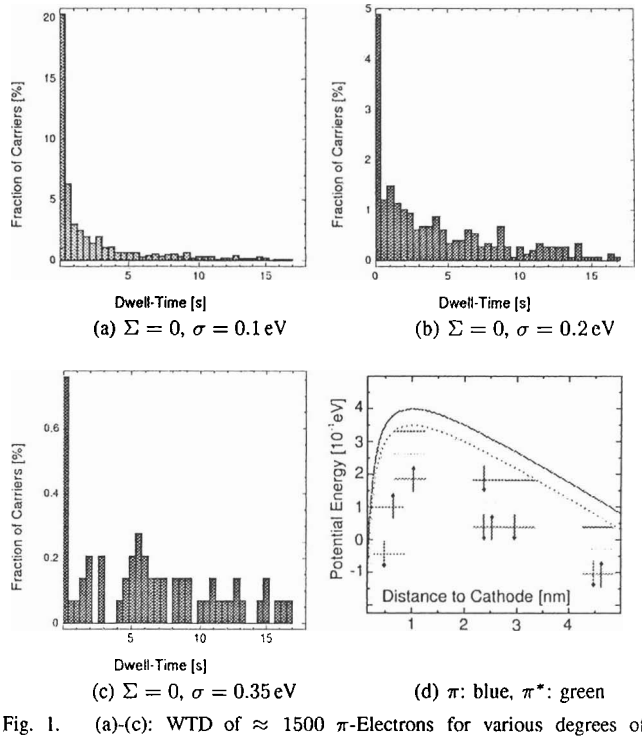
II. Physical Assumptions

The simulator describes a driven, hence non-equilibrium electron gas whose energetic disorder is modeled in analogy to [1] by splitting the molecular energy spectra into a Gaussian density of states (DOS). For amorphous and polycrystalline Zinc Phthalocyanine (ZnPc) we neglected carrier propagation via extended wave-functions and approximated the bulk by a static set of localized orbitals, being charged and discharged by instantaneous electron hops. Diffusive or band-like carrier motion during release and capture was disregarded, hence the electron-gases' velocity distribution was effectively zeroed. So the only non-vanishing contribution to the duration of a carrier exchange was the dwell time the trapped electron had to wait till it was released by a sufficiently energetic phonon. The resulting retardation is the source of dispersive behavior. By triggering the system's time evolution by the electron with the presently shortest waiting time the implicit assumption was made that no two electrons may be displaced simultaneously.

III. The Simulation

A. Simulation of the Carrier Dynamics

According to [2] MC simulations ruled by master equations and thus by transition rates obeying the principle of detailed balance (PDB), can be related to Poisson-like processes if the following three criteria are met: (i) the transition probabilities reflect a dynamical hierarchy ranking the occurence of processes, (ii) the time increments upon successful events are formulated correctly in term of the microscopic kinetics, and (iii) the events must be effectively independent from each other. All three criteria are met for the Abrahams-Miller rate (AM), which approximates the phonon absorption probability



(a) $\Sigma = 0$, $\sigma = 0.1\,\mathrm{eV}$ (b) $\Sigma = 0$, $\sigma = 0.2\,\mathrm{eV}$

(c) $\Sigma = 0$, $\sigma = 0.35\,\mathrm{eV}$ (d) π: blue, π^*: green

Fig. 1. (a)-(c): WTD of $\approx$ 1500 π-Electrons for various degrees of energetic disorder. (c) illustrates the implementation of the molecules as particle resevoirs and the DOS's course at the contact interface.

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by the Boltzmann statistics and assign 1 to their emission.

$$\nu_{ij} = \nu_0 \exp\left[-2\gamma a \frac{\Delta R_{ij}}{a}\right] \times \begin{cases} \exp -\frac{\epsilon_i - \epsilon_j}{k_B T} & \epsilon_j > \epsilon_i \\ 1 & \epsilon_j < \epsilon_i \end{cases}$$

Here, ν_0 denotes the attempt-to-escape frequency, γ describes the wave-function's spatial decay, a is the average lattice constant, ϵ_i and ϵ_j are the site-energies, and ΔR_{ij} is their distance. The AM-rate obeys the PDB, thus driving the system ergodically towards its state of least free energy. The bulk's static disorder is casted into the carrier waiting time distribution (WTD) which establishes a dynamical hierarchy of the processes based on their respective time-scale. The expectation value of the dwell time at a site i is

$$\langle \tau^i \rangle = \left(\sum_{j \neq i} \nu_{ij}\right)^{-1}.$$

The resulting long-tailed WTD (Fig.1 (a)-(c)) accounts for the fact that there are much faster and much slower events than average. The accuracy of $\langle \tau^i \rangle$ is limited by the rate theory used and by the approximation of the rate constants by independent Poisson processes. The AM-rate represents a zero-order approximation for the non-equilibrium dynamics since it neglects multiphonon-processes and therefore the appearance of intermediate states. Consequently, the stochastic delay assigned to an exothermic event is neither assumed to be reduced by an applied electric field nor to be inversely proportional to the transition's heat effect. After each transition the time was incremented by the expired dwell-time, leading to a semi-Markovian dynamics of non-equidistant time steps.

B. Simulation of the Bulk

Transport units are the ZnPc-monomers' π and π^* orbitals. Holes correspond to empty orbitals. Electrons obey Pauli's exclusion principle and are isoenergetic on the same monomer. Hops between monomers may only be described by the AM-rate, if their molecular spectra are unconjugated, hence too different for band-like electron delocalization. The π electrons were not assumed to contribute to space charge, since their Coulomb fields are screened by the nuclear positive counter-charges. A molecule with completely filled π orbitals therefore has been considered as electric neutral. The repulsion between electrons has been simplified to a short-range repulsion on partially populated levels. Inspired by [6] electron injection and ejection at the contacts has been modeled as AM-driven jumps between the contacts's Fermi level and the bulk. The injection barriers was assumed to be lowered by the image force potential (Fig.1 (d)).

Au/ZnPc/Au devices were simulated in-situ at 300 K. The film thickness was set to 30 nm and γ was set to the value extracted by [5] for the amorphous phase, i.e. $\gamma = 1.5 \times 10^{10}\,\mathrm{m}^{-1}$. In accordance with [4], ν_0 was set to $\nu_0 = 1.0 \times 10^{12}\,\mathrm{s}^{-1}$. The contacts' distance from the bulk and a were set to $a = 1.227\,\mathrm{nm}$.

C. Results

The current depends on the distribution of the carriers' start energies. The simulations were thus started with electrons

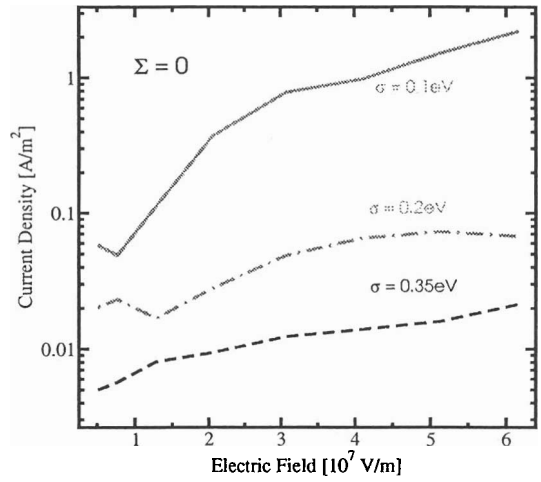

Fig. 2. The current densities field-dependence in systems with weakly, moderately and strongly disordered Homo- and Lumo-bands respectively.

hopping from the contact Fermi-level into a void bulk. After charging of the interface up to a certain space-charge, bulk transport gained in importance since further injections were hampered. After some time the dynamics perpetuated injection as well as ejection and propagation events quite stationaryly. The results can be summarized as follows:

- KMC simulations of spin-$\frac{1}{2}$ particles in a non-empty DOS can be successfully applied to the seamless simulation of interface and bulk-effects.
- The current decreases for enhanced disorder, i.e. spread σ of the DOS. Fig. 2 shows the results for spatially ordered systems, where the spread Σ of γ was set to $\Sigma = 0$.
- For $\sigma = 0.2\,\mathrm{eV}$ the saturating current indicates barrier-overcompensation with increasing field. But the activation energies should increase compared to $\sigma = 0.1\,\mathrm{eV}$. Field-induced traps are absent because of $\Sigma = 0$. So this underestimation is probably due to a inadequacy in the injection model, as explained below.
- A comparison with the data of [3] shows that the presented simulations have to be augmented by additional assumptions like an interface dipole-layer.

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