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Transient space-charge-perturbed currents in organic materials: A Monte Carlo study

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ABSTRACT

The transient current holds rich information about carrier transport and is used to derive charge mobility in the time-of-flight (TOF) measurement. Because carriers have finite charge, all transient currents are space-charge-perturbed (SCP). Previous theories of transient SCP currents are derived by neglecting diffusion and assuming a constant mobility, which is unfit for organic materials because of the hopping behavior of carriers. Due to the lack of knowledge, we do not fully understand the results from TOF experiments, which hinders the understanding of the charge transport mechanisms. Here, we perform Monte Carlo simulations of multi-particle carrier movement to study the transient SCP currents in organic materials. Coulomb interactions are calculated, and it is assumed that multiple carriers cannot occupy the same site simultaneously. Our results show that space-charge perturbation has two opposite effects on charge transport. In most cases, the net result is slower carrier movement, which suggests that TOF measurements under SCP conditions underestimate the charge mobility of organic materials.

1. Introduction

Charge mobility is crucial to the performance of organic electronic devices [1–4]. Mobility measurement is therefore one important way to assess organic semiconductors. The standard method to do this is the time-of-flight (TOF) experiment, in which the mobility is extracted from the transient current [5,6]. Although the TOF measurement has been widely conducted, the transient current in organic materials is not fully understood.

The charge carriers will cause electric potentials which will perturb the current, meaning all transient currents are space-charge-perturbed (SCP). Ideally, if the space-charge perturbation can be neglected, the current is said to be space-charge-free (SCF) [7]. Most previous theories on the transient current are limited to the SCF case, which does not exist in reality [8–11]. Under the assumption of no diffusion and a constant mobility, Papadakis analyzed the SCP currents in 1967. The results suggest that the SCP current has a cusp, which appears at an earlier time as the current density increases [12,13]. This analysis, however, is unfit for organic materials because of the hopping process of carriers. Unfortunately, the theoretical analysis has been little advanced since then. Due to the lack of proper theories, the transient SCP currents in organic materials, which are obtained from the TOF experiments, cannot be fully understood [14,15]. This makes it difficult to further reveal the charge transport mechanisms.

There is also a disadvantage of studying the charge transport process by the TOF experiment. The injected current density is limited in the range of 10^{-2} CV (where C is the capacitance of the device and V is the applied voltage) in the conventional TOF measurement to avoid space-charge perturbation [5]. This makes it difficult to perform measurements at low electric fields or for materials with impurity.

Because of the weak coupling between molecules and the frequently present disorder, charge transport in

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organic materials is quite different from that in inorganic ones. It is considered that charges are strongly localized and hop between adjacent sites. The energy distribution of the sites is often described as Gaussian [16]. These properties make the derivation of accurate analytical expression impossible. Monte Carlo (MC) method, on the other hand, proves to be a very useful way to understand the charge transport process in organic materials over the years [17–22]. One achievement using MC simulations is the Gaussian disorder model, which is perhaps by far the most successful theory of charge transport in amorphous organic materials [23]. Due to computer efficiencies, early MC simulations of transient currents are of one-particle movement and space-charge perturbation could not be taken into account. In this paper, we perform MC simulations of multi-particle carrier evolution in a TOF device configuration, which enables us to study the transient SCP current and charge transport under this situation. We found that the effect of space-charge perturbation on carrier transport is complicated, depending on the SCP degree and the energetic disorder parameter. Generally, charge mobilities extracted from SCP currents in the TOF experiment are slightly underestimated for organic materials.

2. Theoretical details

In the TOF measurement, the sample is sandwiched between two electrodes, one of which is transparent. A short pulse of laser is used to generate a thin sheet of carriers near this electrode. Under the influence of an external electric field, the carriers will drift to the other electrode. The transient current in the circuit is recorded by an oscilloscope. In the absence of deep traps, if the carriers do not diffuse and all have the same drifting velocity, they will reach the other electrode at the same time. In this case, the transient current remains constant and disappears at the carrier transit time τ. However, the actual photocurrents of organic materials exhibit a large extent of anomaly, depending on their physical properties and the experimental conditions [8,22]. Practically, τ is usually determined from the intersection of the asymptotes to the plateau and trailing edge of the transient current [5]. Charge mobility μ is calculated as:

$$\mu = d/\tau E \tag{1}$$

where d is the film thickness and E is the electric field.

In organic materials, the carriers are considered to be largely localized. The charge transport process can be viewed as successive hops between adjacent molecules [16]. In the case of weak electron-phonon coupling, the phonon assisted hopping rate v_{ij} from site i to j can be described using the Miller–Abrahams model [24]:

$$v_{ij} = v_0 \exp\left(-2\gamma|R_{ij}|\right)\begin{cases} \exp(-\frac{\varepsilon_j-\varepsilon_i}{k_BT}) & \varepsilon_j > \varepsilon_i \\ 1 & \varepsilon_j \leqslant \varepsilon_i \end{cases}$$

where v_0 is the phonon vibration frequency, γ is the inverse localization radius, R_{ij} is the distance from site i to j, k_B is the Boltzmann constant, T is the temperature and ε_i and ε_j are the energy levels of the respective sites.

Our system of interest consists of $n_x \times n_y \times n_z$ sites, where n_z is 1000. The site distance a is set to 1.6 nm and $2\gamma a$ equals 10 [23,25]. Periodic boundary conditions are applied in x and y directions. Electric field is applied along z direction. Layers $z = 1$ and $z = n_z$ are set as electrodes. At time 0, a fixed number of carriers are generated at layer $z = 2$. No injection of carriers from electrodes are allowed. The carriers are assumed to be electrons, but the conclusions also apply to hole transport. The site energy distribution is considered to be in Gaussian form [23]:

$$g(\varepsilon) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{\varepsilon^2}{2\sigma^2}\right)$$

where σ is the standard deviation. The energetic disorder parameter is expressed as $\hat{\sigma} = \sigma/k_BT$.

Only hops between adjacent sites are considered in our simulations and a maximum hopping distance of $\sqrt[3]{a}$ is allowed. The carrier dwell time t_i on site i and the hopping direction k are calculated using the following equations [18,26,27]:

$$t_i = -\frac{\ln(\xi_1)}{\sum_j v_{ij}}$$

$$\frac{\sum_{j=1}^{k-1} v_{ij}}{\sum_j v_{ij}} < \xi_2 \leqslant \frac{\sum_{j=1}^{k} v_{ij}}{\sum_j v_{ij}}$$

where ξ_1 and ξ_2 are random numbers uniformly distributed between 0 and 1.

The multi-particle carrier movement is implemented by performing one hop of one carrier every step [28]. Each carrier has its own local time. The hopping carrier is chosen that its movement causes the smallest advancement of the global time. After each step, dwell times of all carriers are recalculated. This process is repeated until all carriers have reached the other electrode.

In our simulation, carriers interact with each other in two ways. One is that two carriers cannot occupy the same site. This is done by set the hopping rate at the blocked direction to zero. The other is Coulomb interaction between charge carriers. Since carriers drift in z direction and periodic boundary conditions are applied in x and y directions, Coulomb interactions can be taken into account in a layer averaged way. The electric potential difference from site i to j caused by carriers is written as:

$$\Delta\varphi_{ij,layer} = \sum_l \Delta\varphi_{ij,l} = -\sum_l \frac{\rho_l(|d_{j,l}| - |d_{i,l}|)}{2\varepsilon_0\varepsilon_r}$$

where ρ_l is the charge density of layer l, $d_{i,l}$ and $d_{j,l}$ are the distances from site i or j to layer l, ε_0 is the vacuum permittivity and ε_r is the relative permittivity and is set to 4, a value commonly found in organic materials [27].

The TOF simulation is considered to be in current mode, which satisfies the relationship: $RC \ll \tau$ [29]. Here, R is the resistance in the circuit. Under this situation, the electric potential difference between the electrodes $\Delta\varphi$ always equals the applied voltage V: $\Delta\varphi \equiv V$. $\Delta\varphi$ consists of two parts: $\Delta\varphi \equiv \Delta\varphi_e + \Delta\varphi_c$. Here, $\Delta\varphi_e$ and $\Delta\varphi_c$ represent the