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Monte Carlo simulation of charge transport in electrically doped organic solids

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Abstract
A model to study the charge transport in electrically doped organic solids via Monte Carlo simulation is proposed. The model includes the finite rate of all possible electron transfers between host and dopant molecules. It is found that for efficiently doped materials, the conductivity increases with dopant concentration, first sublinearly and then superlinearly. The conductivity of electrically doped films is also dependent on the dopant–host energy-level offset: it is high when the ionization of dopants is energetically favourable, but decreases exponentially with increasing energy barrier for dopants to ionize.

1. Introduction
Recently, there has been growing interest in electrical doping of organic molecular solids, as reviewed by Gao and Kahn [1] and by Walzer et al [2]. Efficient electrical doping introduces extra mobile holes (p-type doping) or electrons (n-type doping) in the host material which has few intrinsic carriers when undoped, resulting in greatly enhanced conductivity. Such efficient doping requires the matching of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the dopant and host molecules. So far, both types of doping have been successfully achieved experimentally, although stable n-type doping has met more difficulties [3, 4]. Xue et al have made an interesting study of a molecular donor–acceptor couple and found that either species of the couple can serve as the electrical dopant in the host of the other species [5].

Electrical doping can improve the performance of various organic (opto)electronic devices. High conductivities of doped films have reduced the injection barrier, lowered the operation voltage and improved the power efficiency and the stability of organic light emitting diodes (OLEDs) [6, 7]. Doped films have also improved the efficiency of organic solar cells [8]. There are also explorations of new and interesting applications of electrical doping such as organic p–i–n homojunction structures [9] and linking layers in tandem OLEDs [10, 11].

The energy-level offset between dopants and hosts has a huge effect on the efficiency of electrical doping of organic materials and is therefore an important factor to consider for selecting appropriate materials. However, previous theoretical works on the subject have assumed efficient doping and have not taken the energy-level offset into consideration [12–14]. In this work, we propose a model to study the carrier transport processes in electrically doped organic solids. The effect of the energy-level offset on electrical-doping efficiency is studied by introducing finite rates of charge transfers between dopants and hosts.

2. Simulation model
To simplify the discussion, we just consider n-type doping in this study, and p-type doping is quite similar. For n-type doping, our simulation considers all three possible types of electron transfer processes: (i) the ‘host–host electron transfer’, in which an electron transfers from the LUMO of a host to that of another, (ii) the ‘dopant–host electron transfer’, in which an electron transfers from the LUMO of a dopant to the LUMO of a neighbouring host, or vice versa, and (iii) the ‘dopant-ionized–dopant electron transfer’, which is rare due to...
the small dopant concentration; in such a process an electron transfers from the HOMO of a neutral dopant to the HOMO of a neighbouring dopant cation. For the dopant–host electron transfer process, a so-called ‘forward transfer’ only takes place between a neutral dopant and a neutral host, creating a host anion and a dopant cation; while a so-called ‘backward transfer’ only takes place between a dopant cation and a host anion, eliminating the charges of the two ions. Therefore, the numbers of host anions and dopant cations change with time.

The change in energy due to a forward dopant–host electron transfer is not simply the difference between the dopant HOMO energy $E_{\text{HOMO}}^{\text{dopant}}$ and the host LUMO energy $E_{\text{LUMO}}^{\text{host}}$. Since both the HOMO and LUMO energies are defined for an isolated molecule with respect to the vacuum level, the transfer of an electron between two neighbouring molecules within a dielectric medium will induce a large binding energy $E_b$ due to the Coulomb force between the ionized donor and the acceptor. $E_b$ will facilitate the forward dopant–host electron transfer [13]. Here, we use $\Delta E_{\text{DH}}$ to denote this energy change so that

$$\Delta E_{\text{DH}} = E_{\text{LUMO}}^{\text{host}} - E_{\text{HOMO}}^{\text{dopant}} - E_b. \quad (1)$$

The rates of all the electron transfer processes are assumed to follow the Miller–Abrahams equation [15]. The rate for an electron initially localized on molecule $i$ to transfer to molecule $j$ is

$$v_{i \rightarrow j} = \begin{cases} v_0 \exp(-\Gamma_{ij} r_{ij}) \exp(-\Delta E/kT), & \Delta E > 0, \\ v_0 \exp(-\Gamma_{ij} r_{ij}), & \Delta E \leq 0, \end{cases} \quad (2)$$

where $r_{ij}$ and $\Gamma_{ij}$ are the distance and the coupling coefficient between molecules $i$ and $j$, respectively, and $v_0$ the intrinsic attempt frequency. The change in energy $\Delta E$ due to the transfer contains the following three contributions: (i) the energy difference of the molecular orbitals involved in the transfer for a host–host or dopant–dopant transfer due to the energetic disorder of materials or $\Delta E_{\text{DH}}$ as defined in (1) for a dopant–host transfer (with the material disorder added), (ii) the potential difference due to the applied field $F$ and (iii) the Coulomb potential difference caused by dopant cations and host anions in the material. In this study, we only consider transfers between nearest-neighbouring molecules and assume the same molecular coupling between any pair of molecules so that $\Gamma$ is a constant. Note that, if $j$ is a neutral dopant or a host anion, $v_{ij}$ is set to zero to reflect the site exclusion effect.

Monte Carlo simulation has long been used to study carrier transport in disordered materials [16], but early works have only considered a single carrier in a simulation system, corresponding to the zero-carrier-density limit. In electrically doped organic solids, the densities of mobile carriers and ionized dopants are high and the Coulomb interactions between them must be considered. Therefore, the Monte Carlo algorithm [17] recently extended to include Coulomb interactions between carriers is used in this work. The only modification to the previous algorithm is that the ‘hopping candidates’ are now the aforementioned three types of electron transfer processes with their rates governed by (2).

Simulations are carried out in cubic boxes of $L \times L \times L$ ($L = 51$ in this work) lattice sites with lattice constant $a$ and 3D periodic boundary conditions. Each lattice site represents a host or a dopant. The ratio of the number of dopants to the number of total sites is the doping concentration $c$. A dielectric constant of 4.0, typical for organic materials, is adopted. Meanwhile, we assume the same energetic disorder for both dopants and hosts so that the values of $E_{\text{LUMO}}^{\text{host}}$ for hosts and $E_{\text{LUMO}}^{\text{dopant}}$ for dopants are, respectively, drawn from two Gaussian distributions with the same standard deviation $\sigma_{\text{DOS}}$. An energy offset between the centres of the two distributions is assigned to represent the difference in the macroscopic values of the dopant HOMO and the host LUMO energies. We also assume a constant value for $E_b$. From (1), the two parameters, the energy offset and $E_b$, can be combined together as a single parameter $\Delta E_{\text{DH}}$, which is used to present simulation results below. Since the majority of carriers in real devices employing electrically doped organic layers come from the ionized dopants rather than from injection, each simulation run starts with neutral dopants and hosts without any extra carriers, and all the carriers contributing to current come from the ionization of dopants during the simulation. Due to the changing number of mobile electrons, we calculate the electrical conductivity $\sigma$ of the simulated systems instead of the mobility. After enough time for carriers to relax in energy, $\sigma$ is calculated as $\sigma = \sigma_0 D/FT L^3$, where $F$ is the applied electric field along the $x$ direction of the simulation box, $D$ the summation of the displacements of all mobile electrons along the $x$ direction over a time period of $T$ and $\sigma_0$ a constant that includes all unchanged parameters in our simulations.

### 3. Results and discussion

Figure 1 shows the increase in conductivity $\sigma$ with dopant concentration $c$ in electrically doped organic materials with various energetic disorder. The data were obtained for

![Figure 1: Calculated conductivity (data points) of electrical doped organic solids versus dopant concentration $c$, with various $\sigma_{\text{DOS}}/kT$. The solid lines are a guide for the eye. The dashed lines indicate linear relationships between conductivity and dopant concentration. Parameters used: $e Fa/kT = 0.4$, $\Delta E_{\text{DH}} = 0$.](image-url)
$\Delta E_{DH} = 0$, i.e. there is neither gain nor loss of energy for a dopant-host electron transfer. In such a case, the electrical doping is expected to be efficient. With the dashed lines indicating linear relationships between $c$ and $\sigma$, the simulated results show two stages of the conductivity increase: a sublinear increase followed by a superlinear increase with a transitional $c$ around $10^{-3}$–$10^{-2}$. In real experiments, $c$ is usually limited to a small range and films with $c$ below $10^{-3}$ are hard to fabricate. Therefore, according to figure 1, the conductivity of electrically doped films with dopant concentrations in the range between $10^{-3}$ and 0.1 would increase with dopant concentration in a superlinear or a near-linear fashion. Indeed, this is consistent with reported experiments, such as the superlinear increase shown by figure 6 in [2] and the near-linear increase shown by figure 1 in [3].

As shown in figure 2, the conductivity dependence on $\Delta E_{DH}$ is calculated for doped materials with $c = 0.01$, a typical doping ratio used in experiments. The conductivity shows two distinctive types of asymptotic behaviour: (i) when $\Delta E_{DH} \gg 0$, the conductivity is low and decreases exponentially with increasing $\Delta E_{DH}$, corresponding to inefficient doping; (ii) when $\Delta E_{DH} \ll 0$, the conductivity is high and constant, corresponding to efficient doping. Both types of asymptotic behaviour can be understood by considering the energy that is either required or released when a neutral dopant is ionized. Due to material disorder, the amounts of such energy for different dopant-host pairs are different, and the amounts of such energy involved in the ionization of a dopant with its different neighbouring hosts are also different. Therefore, $\Delta E_{DH}$ as defined by (1) is expected to be proportional to the average of the energy involved in dopant ionization. When $\Delta E_{DH} \gg 0$, the ionization of most neutral dopants requires certain amounts of energy (due to material disorder, the ionization of a very small fraction of dopants would release energy), which could be regarded as thermally activated ionization energy. Since the average of the activation energy is proportional to $\Delta E_{DH}$, the number of ionized dopants, i.e. the number of mobile carriers, in the material decreases exponentially with $\Delta E_{DH}$. If the change in mobility with the number of ionized dopants is much smaller in magnitude than the change in the number of ionized dopants itself (which is expected when the number of mobile carriers is very small when $\Delta E_{DH} \gg 0$), the conductivity will also decrease exponentially with $\Delta E_{DH}$. When $\Delta E_{DH} \ll 0$, the ionization of most neutral dopants releases certain amounts of energy, so that most of the neutral dopants would become ionized. Therefore the number of ionized dopants, i.e. the number of mobile carriers, in the material is large and independent of the value of $\Delta E_{DH}$, and the mobility is high and does not change with $\Delta E_{DH}$. To combine the two asymptotic types of behaviour of conductivity change together, one would expect an equation as

$$\sigma = \frac{\alpha \sigma_0}{1 + \exp \left[ \frac{\Delta E_{DH}}{\alpha} - \frac{\Delta E_0}{\beta} \right]}.$$  

where $\alpha$ and $\beta$ are formulated as dimensionless parameters. Equation (3) gives a good match with the calculated mobilities with the fitting parameters listed in table 1, as shown by the solid line in figure 2, even for $\Delta E_{DH}$ between the two asymptotic regions. Finally the parameter $\Delta E_0$ could be regarded as a switching point so that the electrical doping could be regarded as efficient when $\Delta E_{DH} < \Delta E_0$ and inefficient when $\Delta E_{DH} > \Delta E_0$.

$E_{LUMO}^{{\text{host}}} - E_{HOMO}^{{\text{dopant}}}$ for a particular pair of dopant and host materials is regarded as the energy level mismatch for $n$-type doping, while $E_{LUMO}^{{\text{dopant}}} - E_{HOMO}^{{\text{host}}}$ for $p$-type doping. Usually, a large offset leads to inefficient electrical doping. It would be interesting to know the maximum allowed energy-level mismatch between host and dopant materials for which the doping efficiency does not suffer much, as knowing it could help the selection of materials used for electrical doping. Here we estimate, as an example, the maximum energy-level mismatch allowed for efficient electrical doping, using typical parameters for organic materials. From table 1, $\Delta E_0 = 0.14$ eV for $kT = 0.025$ eV and $\sigma_0/kT = 4$. $E_b$ is about 0.36 eV as estimated from $e^2/4\pi\epsilon_0\epsilon_r a$ [13], where $a = 1$ nm and $\epsilon_r = 4$. Here $\Delta E_{DH} < \Delta E_0$ is regarded as the criterion for efficient doping as explained in the previous paragraph, with (1), the maximum energy-level mismatch allowed for efficient electrical doping is $E_b + \Delta E_0 = 0.5$ eV in this example. Indeed, many reports of efficient electrical doping have shown various degrees of energy-level mismatch, ranging from only 0.04 eV [18] to 0.28 eV [19] and even to 0.56 eV [20]. All these values of mismatch are within the range of our rough estimation.

Table 1. Parameters used in fitting the calculated conductivity shown in figure 2, equation (3).

<table>
<thead>
<tr>
<th>$\sigma_0/kT$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\Delta E_0/\sigma_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>$1.68 \times 10^{-3}$</td>
<td>1.42</td>
<td>1.84</td>
</tr>
<tr>
<td>3</td>
<td>$5.37 \times 10^{-4}$</td>
<td>1.81</td>
<td>1.54</td>
</tr>
<tr>
<td>4</td>
<td>$1.30 \times 10^{-4}$</td>
<td>1.96</td>
<td>1.41</td>
</tr>
</tbody>
</table>
In our simulation, we neglected polaronic effects and considered charge transfers as thermally assisted tunnelling processes, using the Miller–Abrahams instead of the Marcus electron transfer model. Both models are widely used in theoretical studies of charge transport in organic materials. To use the Marcus model, an additional parameter, reorganization energy, has to be introduced. Since the reorganization energy differs greatly in different materials, its introduction would complicate this study. However, our simulation can be easily extended to adopt the Marcus model if the reorganization energies of the electron transfer processes are available.

4. Summary

A model is proposed to study the charge transport in electrically doped organic solids via Monte Carlo simulations. It is found that the conductivity increases with doping concentration, first sublinearly and then superlinearly. The simulations include the finite rates of the host–host, dopant–host and dopant–dopant electron transfer processes so that the dependence of the conductivity on the energy-level offset between dopant and host materials can be studied. This dependence is also found to be described by an empirical equation.

Acknowledgments

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