Carrier heating in disordered organic semiconductors

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We propose a semi-implicit model for hopping transport in disordered media with application to organic semiconductors. The results show excellent agreement with both Monte Carlo and standard master-equation calculations. In organic LEDs the applied field would result in heating of the charge carrier population by up to 100 °C above the lattice temperature and is more effective at lower temperatures. We show that the voltage dependence of the mobility in space charge limited LEDs is largely due to carrier heating and not to the previously considered charge density or barrier lowering effects. At the end we look into the effect of accounting for the soft nature of organic materials via the inclusion of polaronic rate (binding energy) and we find that carrier heating is suppressed at polaron binding energies above 0.1 eV.

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INTRODUCTION

The issue of charge transport in disordered organic semiconductors has been studied for a few decades[1–9] by now. The evolution of organic LEDs and organic FETs has triggered attempts to provide a single physical picture[8–12] through the use of implicit models. In the paper by Roichman *et al.*[8] it was shown that while the MMA model can reproduce organic FET related mobility data[13] it could not self-consistently describe the injection and transport[14] in organic LEDs. On the other hand it has been suggested[15] that percolation theory in the form developed by Vissenberg *et al.* in the context of FETs (Ref. 16) can be applied also to LEDs which, if true, leads to the inevitable conclusion that the mobility in organic LEDs is electric field independent. In this paper we reexamine the role of the electric field using a model that can account also for carrier heating effects. We also use this new formalism to study the effect of polaron binding energy on the carrier temperature under high electric fields.

The transport of charge carriers in amorphous organic semiconductors is modeled as hopping transport between localized states assuming specific energetic and spatial distribution functions. This physical framework has been studied for many years using different types of model formulations[1–8] which differ mainly by the method used to average microscopic details to obtain a macroscopic property, as mobility. The Monte Carlo approach (MC),[2,17] promoted by Bassler *et al.*, is a numerical experiment performed on a finite grid of localized sites. The averaging here is done by drawing different grids (sites values) and performing the calculation again until the differences between distinct draws become statistically insignificant. In the master equation (ME) approach[5] the averaging itself is done in a very similar manner although the basic approach of following occupation probability instead of particles makes the actual calculation different to the MC one. These two types of numerical experiments are often considered as a reference for examining other models where the averaging procedure used is not explicit (as in percolation,[3,7] effective transport energy,[6] mean medium approximation[8] (MMA), and more). It has been suggested that under certain conditions the implicit models may be too crude of an approximation. Specifically we would be interested in the MMA approach as it can handle a range of charge densities and the barrier lowering effect of the electric field.[8,13] A first hint, related to the carrier heating phenomena,[18–20] as to what might be missing in the implicit models approach we found in the paper by Ambegaokar *et al.*[3] which explicitly states that the requirement for current conservation (continuity) perturbs the charge energy distribution with respect to standard Fermi distribution. The other flaw that may arise is when the averaging is done assuming the sites are uniformly distributed in space (instead of being on a discrete grid) thus leading to a loss of the exponential dependence of the intersite hopping rate on the site density[21] which in some cases can be corrected for by adding exponential prefactor containing minimal intersite distance divided by mean hoping distance.[22] In this contribution we emphasize the energy redistribution of charge carriers population under the influence of an applied electric field. This shift of the distribution, which is absent in all the above-mentioned implicit models, affects the electric field dependence of the transport and is the central point of this paper.

THE ESME MODEL

The energy-space master equation like approach (ESME) that we introduce calculates the population probability of a site having a given energy. The validity of this model is limited to variables that would be determined by averaging over large ("infinite") samples. Two such variables are the charge carriers' mobility and their energy distribution. Unlike the standard master equation approach the sites here are "counted" according to their energy and not their spatial location.[23] Since sites of different energies are located at different positions in the sample we can apply the current continuity requirement in energy space. The formalism itself is constructed in a manner similar to the standard (spatial) master equation formalism and uses a small size three-dimension (3D) discrete grid for the solution process.

As in any master equation approach, the unknown is the population of the individual sites throughout the system. In

our formalism the physical sites are counted via their energy only and hence the quantity that needs to be solved for is the energy distribution of the occupation probability, $n(\varepsilon)$, for a given electric field and charge concentration. To find $n(\varepsilon)$ we solve the system of nonlinear rate equations describing population density, $N(E)$, flow between submanifolds of different energies. The occupation probability, $n(\varepsilon)$, would then be found using $n(E)=N(E)/g(E)$ where $g(E)$ is the number density of sites at energy E. Thus the ESME rate equation is written as

$$\frac{dN(E)}{dt} = -N(E)\int_{-\infty}^{+\infty} dE'\left[g(E')\left(1-\frac{N(E')}{g(E')}\right)\times\sum_{\vec{r}}\nu(E,E',\vec{F}\vec{r})\right] + \ldots + g(E)\left(1-\frac{N(E)}{g(E)}\right)\times\int_{-\infty}^{+\infty} dE'\left[N(E')\sum_{\vec{r}}\nu(E',E,\vec{F}\vec{r})\right]. \quad (1)$$

The first term in the equation describes jumps out from sites of a given energy E and the second term describes the jumps from sites at any other energy into sites at energy E. The terms $N(E)$ and $[g(E)-N(E)]$ account for the density of filled and empty states, respectively. The sum over $\vec{r}$ takes into account that in the physical sample the transfer of charge population between different energies involves hopping in real space. Thus $\vec{r}$ defines all possible hopping vectors which are dictated by the morphology of the sample. $\hat{F}$ is a unit vector in the direction of electric field $\vec{F}$ and ν is the hopping rate between sites separated by distance $|\vec{r}|$. To retain the dependence on the actual site density the sum of rates is carried out over a discrete (3D) grid. Note that under steady state $(d/dt=0)$ this equation set dictates that the flow into the energy band between E and $E+dE$ is equal to the flow out of this band thus the current continuity or charge conservation conditions are implemented by the ESME formalism.

To account for a finite charge density the system should be solved for a given total charge density (N_{tot}) and hence we add the requirement

$$\int_{-\infty}^{+\infty} dEN(E) = N_{tot} = \text{const}. \quad (2)$$

For the actual calculation to be performed we need to define all possible $\vec{r}$ and to do so we create a grid and position the initial site at its center. The potential final sites are all the other points on the grid thus creating a well defined set of vectors $\vec{r}$. To be able to compare some of our calculations to those carried out by others we first use a hopping rate that its energy dependence is due to a Boltzmann factor only (this rate is commonly called Miller-Abrahams rate[24] although it appears in early paper by Anderson and others)

$$\nu(E,E',\vec{F}\vec{r}) = \nu_0 \exp(-\gamma|\vec{r}|)\times\begin{cases} e^{(E-\vec{F}\cdot\vec{r}-E\prime/k_BT)}, & \left(\dfrac{E-\vec{F}\cdot\vec{r}-E\prime}{k_BT}\right)<0 \\ 1, & \text{else}. \end{cases}$$

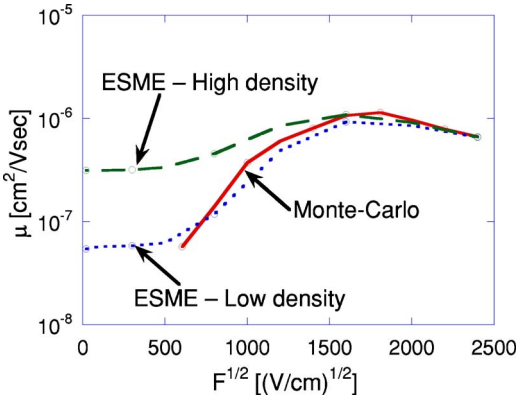

FIG. 1. (Color online) Comparison of ESME to MC simulation of Goldie (Ref. 17) for the following parameters: $a=0.8$ nm, $\gamma=10/\text{a}$, $T=300$ K, $\sigma=4$ kT, $\nu_0=10^{12}$ sec^{-1}. The dotted line was calculated for the low density limit and the dashed line for a relative filling of the DOS being 7×10^{-3}.

Equations (1) and (2) form a nonlinear set of equations which are readily solved using conventional software packages. To test if the ESME approach is relevant to practical physical scenarios we refer to MC and ME calculations performed by others. First we compare the mobility value and its dependence on electric field to those produced by the MC simulations presented in Ref. 17. The choice of this specific reference was determined by the necessity to find all numerical parameters of the system under simulation including ν_0—jump-attempt frequency. Unfortunately this important parameter is usually omitted in the vast majority of the papers. Since such Monte Carlo simulations are generally done for single carrier at a time they represent the low charge density limit of the system. In Fig. 1 we present the mobility values extracted from Ref. 17 (solid line) along with the ESME calculations performed for the low density limit (dotted line) and for a charge density that fills 7×10^{-3} of the total DOS (dashed line). We note the excellent agreement in absolute values as well as in the functional form.

In the Introduction we emphasized that in the implicit models the missing phenomena is that of charge redistribution in energy under applied electric field. The data in suggests that this is now rectified but we believe that a more direct proof is required. To provide this proof we compare the charge energy distribution predicted by the ESME model to the averaged data produced using master equation approach as described in the paper by Saxena and Bishop. Again, the ESME calculations were done for the same (as in Ref. 5) charge concentration, field strength and Gaussian density of states function width parameter. As Fig. 2 shows there is an eminent agreement between our calculation and the results of the named authors. As expected, at low fields charge carrier distribution follows the Fermi-Dirac function at the lattice temperature. But at high fields significant deviation from this Fermi-Dirac function is observed.

CARRIER HEATING

After establishing the good agreement between the ESME model and the averaged data produced by Monte Carlo (MC)

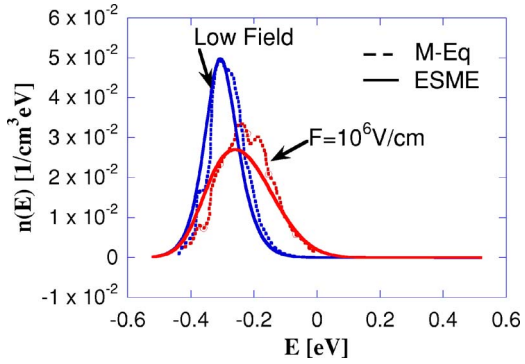

FIG. 2. (Color online) Comparison of ESME with Yu-Saxena-Bishop Master equation results (Ref. 5). The calculation was performed for the following parameters: $a=1$ nm, $\gamma=10/a$, $T=300$ K, $\sigma=4.3$ kT, $n=6.9\times10^{-3}$. Field strengths are 0.5×10^5 and 1×10^6 V/cm, respectively.

(Ref. 17) and master equation (ME) (Ref. 5) approaches we look into the charge redistribution in energy under applied electric field. It has been suggested by Shklovskii *et al.*[18,19] that the effect of application of electric field to amorphous semiconductors can be described as a rise in the effective temperature of the charge carriers. Using the ESME model we found that the redistribution of the charge carrier population can be rather well described by Fermi-Dirac distribution at some elevated temperature T_{eff} (see inset to Fig. 3). Namely, the effective temperature T_{eff} and the Fermi level E_f are sufficient set of parameters allowing to numerically approximate the obtained curves. By using different material parameters we observed that the fitting parameters T_{eff} and E_f depend on the field strength (normalized by the distance between sites) and the phononic temperature of the media. However, in agreement with the general prediction in Ref. 18, T_{eff} and E_f are independent of the charge carrier concentration and the disorder parameter, be it σ for Gaussian disorder or E_0 for exponential DOS. The effective temperature dependence on the applied electric field for a fixed lattice (phonon) temperature is shown in Fig 3. The circles denote the carrier temperature in exponential DOS and the squares for Gaussian DOS. The solid lines are fits using the dependence suggested in Ref. 19, $(T_{eff}/T_L)^2=1+[0.37Fa/(kT/q)]^2$. We note that the original paper[18] predicted the factor to be 0.5 and our fit results in 0.37 ± 0.02. As we show below the amount of heating depends on the exact description of the transport. We emphasize that this carrier-heating effect is distinct from the joule heating effect that is dependent on the thermal circuit[25] of a given device.

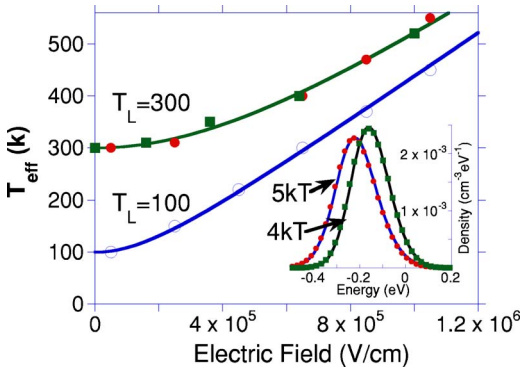

FIG. 3. (Color online) Effective temperature of the carrier population in Gaussian (squares) and exponential (circle) DOS as a function of applied electric field ($a=1$ nm). The solid line is the heuristic formula: $(T_{eff}/T_L)^2=1+[0.37Fa/(kT/q)]^2$ after Ref. 19. Higher curves were calculated for lattice temperature of 300 K and the lower for 100 K. The inset shows the calculated charge distribution for a total density of 5%, applied field of 10^6 V/cm and disorder parameter $\sigma=4$ kT (square symbols) and $\sigma=5$ kT (round symbols). The full lines are the fit to a Fermi-Dirac distribution resulting in effective temperature of 620 k ($E_f=-0.234$ eV) and 610 k ($E_f=-0.265$ eV) for $\sigma=4$ kT and $\sigma=5$ kT, respectively.

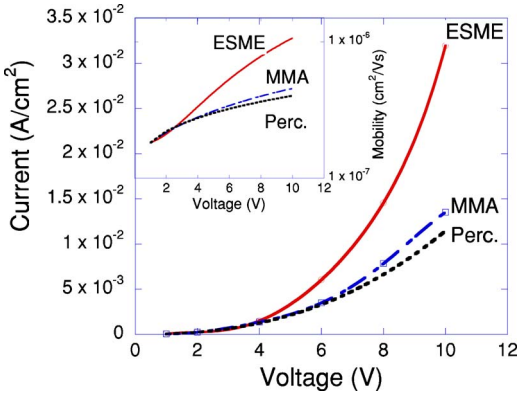

FIG. 4. (Color online) Calculated space charge limited current for a percolation model (Perc), MMA model, and ESME model. The inset shows the mobility as a function of applied voltage that was derived using the above models. (The mobility derived by the percolation model was multiplied by a factor of ~10 to make the mobility at 1 V identical between all three models.) Note the importance of the carrier heating that is present only in the ESME model. In all three models we used $a=1$ nm, $\gamma=a/10$, $T=300$ K, $\sigma=4$ kT, $\nu_0=10^{12}$ sec^{-1}.

To quantify the effect of the electric field on the operation of organic LEDs we compare three models: (1) percolation model[15] where the mobility has only charge density dependence. (2) The MMA model[8] that accounts for charge density as well as barrier lowering under applied field. (3) ESME that accounts for charge density, barrier lowering under applied field, and carrier heating. To do so we calculated the space charge limited current (SCLC) which is typical of OLED devices. For this calculation we first found the field and density dependent mobility (μ) using[8] $E=V/d$ and $P=\frac{3}{2}\left(\frac{\varepsilon V}{qd^2}\right)$. Next, we used the well known expression[26] $J_{SCL}=\frac{9}{8}\varepsilon\mu\frac{V^2}{d^3}$. Figure 4 shows the SCLC as a function of voltage and calculated for $d=100$ nm and $\sigma=4$ kT ($T=300$ k). The difference between the percolation and MMA model is very small at these charge densities implying that the barrier lowering by the electric field is not a significant factor at these densities.[8] Above 4 V the current predicted by the ESME is significantly larger compared to that of the MMA showing that the carrier heating is the most significant factor under such operating conditions. The inset shows, on a semilogarithmic scale, the mobility that was calculated as a function of voltage. In this bias range the charge density (P) is on the order of $10^{16}-10^{17}$ cm^{-3} where the methods neglecting carrier heating predict low voltage dependence.

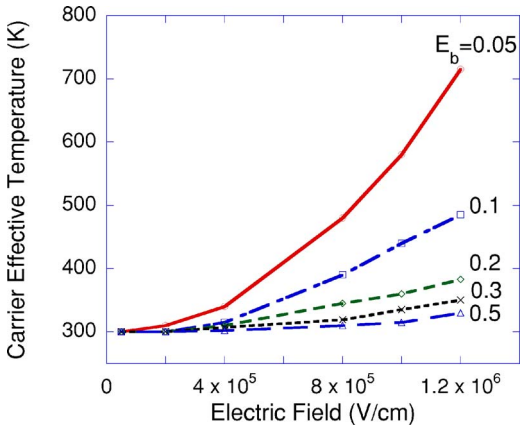

FIG. 5. (Color online) Effective carrier temperature for lattice temperature (T_L) of 300 K and varying polaron binding energies.

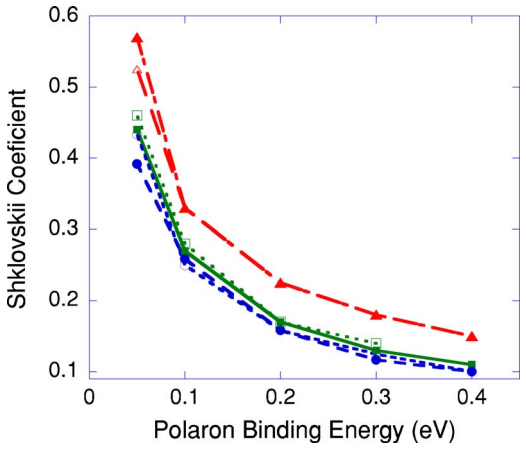

FIG. 6. (Color online) The fitted Shklovskii coefficient for the electric field induced carrier temperature rise. The difference between different values of σ (130 meV—empty symbols and 90 meV—filled symbols) is negligible but we find an increase as the lattice temperature is raised from 250 k (circles), to 300 k (squares), and to 450 k (triangles).

CARRIER HEATING IN SOFT MATERIALS

Thanks to an insightful comment, we take our model outside the most common scope used by Monte Carlo or master equation methods. Since the material we are interested in is soft (organic) the formation of polarons is something that needs to be considered and the effect of the polaron binding energy should be computed. The rate that we use can be found in book by Mott[1] or in Marcus theory[27,28]

$$\nu(E,E',\vec{F}\vec{r}) = \nu_0 \exp(-\gamma|\vec{r}|)\exp\left(-\frac{E_b}{2kT}\right)\exp\left(\frac{E-\vec{F}\cdot\vec{r}-E'}{2k_BT} - \frac{(E-\vec{F}\cdot\vec{r}-E')^2}{8kTE_b}\right).$$

Here all the symbols are as before and E_b is the polaron binding energy. We performed computer simulation of effective heating for wide range of polaronic binding energy, Gaussian density of states width (σ) and temperatures relevant for conducting polymers. In the simulation we found that the effective heating is practically independent on the density of states width parameter σ, but is strongly dependent on the polaronic binding energy E_b as shown in Fig. 5. As previously the effective temperature approximately obey the scaling law suggested by Shklovskii[18,19] however, the coefficient of field-temperature proportionality depends on the value of the binding energy which seems to suppress the heating effect. Figure 6 shows the fitted Shklovskii coefficients as a function of the polaron binding energy and for three lattice temperatures. We note that introducing the polaronic effect make the Shklovskii coefficients dependent on the polaron binding energy.

DISCUSSION

We have presented a semi-implicit energy space master equation model and used it to examine the charge transport in disordered organic films. We started by using the most common, now days, framework that uses the Boltzmann factor dependence and neglects any possible polaron binding energy. The results of the ESME model compare well with the averaged data produced by the explicit Monte Carlo and master equation approaches that have the carrier heating built into them. The ESME describes well the electric field induced charge density redistribution in energy and consequently predicts well the charge density and electric field dependence of the mobility. This implies that if one is interested in a macroscopically averaged value as the charge mobility there is no need to be concerned with fine morphological features that would create local dead ends or bottlenecks. Although this may sound surprising at first, it is in good agreement with the prediction by Scher and Montroll[4] that in cases where local dead ends or bottlenecks play an important role the mobility is an ill defined concept.

The calculation shows that in OLEDs the carrier population may be significantly heated by up to 100 °C above the device temperature making the transport parameters highly

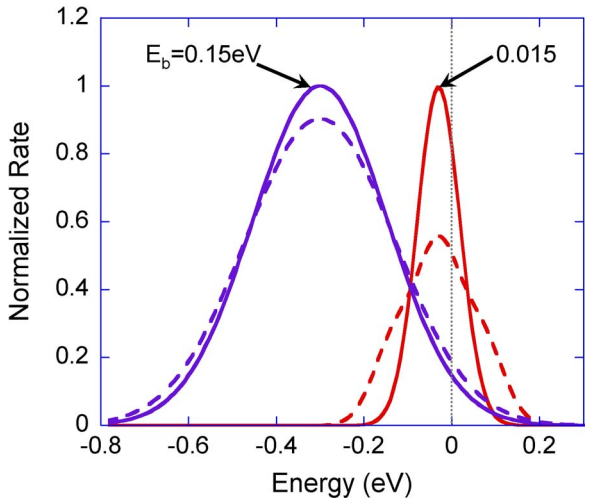

FIG. 7. (Color online) The normalized polaronic hopping rates for binding energies of 0.015 eV and 0.15 eV. The solid line is at zero applied electric field and the dashed for 10^6 V/cm.

electric field dependent. This implies that percolation type models which are valid at the low field limit are not best suited for describing OLEDs. By comparing three different models we could show that for SCLC LEDs the voltage dependence of the mobility is not due to charge density or barrier lowering effects but is rather dominated by the electric field induced carrier heating, which up to now was included only in the fully explicit models (MC or ME).

Accounting for polaron binding energy, as suggested, turned out to be an important issue. To gain an intuitive understanding why the nature of the hopping rate may make a difference we plot in Fig. 7 the normalized hopping rates as a function of the energy required to reach the near neighbors (negative means hopping down in energy) for two binding energies (0.15 eV and 0.015 eV; $T=300$ k). The solid line is for zero electric field and the dashed line is for an electric field of 10^6 V/cm. We note that as the polaron binding energy goes up the polaronic rate favors hopping to very low energies and the probability of hopping to higher energies (i.e., heating) is suppressed. Applying an electric field broadens the probability by an amount proportional to the electric field. Therefore, the narrow distribution of the low binding energy rate is much more affected by the field. Our results suggest that the role of the polaron binding energy indictating the transport is much more than just activation energy.

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