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Analytic Model of Hopping Transport in Organic Semiconductors Including Both Energetic Disorder and Polaronic Contributions

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Abstract. We developed an analytical model to describe hopping conductivity and mobility in organic semiconductors including both energetic disorder and polaronic contributions. The model is based on the Marcus jump rates with a Gaussian energetic disorder, and it is premised upon a generalized Effective Medium approach yet avoids shortcoming involved in the effective transport energy or percolation concepts. The carrier concentration dependence becomes considerably weaker when the polaron energy increases relative to the disorder energy, indicating the absence of universality that is at variance with recent publications.

Keywords: organic semiconductors, hopping transport, energetic disorder, polaron.
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INTRODUCTION

Hopping transport of charge-carriers and neutral excitons in disordered organic materials can in principle be controlled by both disorder and polaron effects depending on their relative weight. In conventional disordered organic semiconductors charge-carrier transport is dominated by disorder, while polaron controlled transport prevails in some systems for triplet excitons. The Gaussian disorder model (GDM) [1] has been the most widely used formalism to describe charge-carrier mobility in amorphous organic materials. A prominent further advancement was accounting for the partial density of states (DOS) filling at a large carrier concentration to describe the carrier concentration effect on the charge-carrier mobility [2, 3]. The latter is now conventionally applied to describe charge-carrier mobility in organic field-effect transistors (OFET) and light emitting diodes (OLEDs). Disorder models are conventionally based on a Miller-Abrahams jump rate and thus they neglect any polaron effects. In principle, polaron formation can be incorporated in the disorder formalism by using a polaron jump rate model. It was suggested that the activation energy of the charge transport in a system with superimposed disorder and polaron effects can heuristically be parameterized by splitting the activation energy into a disorder and a polaron term.

Recently Cottaar et al. [4] compared Marcus and Miller-Abraham hopping mobilities calculated using a percolation-type theory and found that carrier concentration dependence of the mobility is invariant with the strength of polaron effects. This contradicts to the previous EMA calculations [5] that predicted a mobility dependence to be much weaker for large polaron binding energies as compared to that for small polaron binding energies.

In the present paper we develop a unified model based on Gaussian disorder using Miller-Abrahams and Marcus jump rates to bridge a gap between disorder-controlled and polaron-controlled transport descriptions. The model will be compared against results from Monte-Carlo simulations. We show that thermally activated hopping transport can indeed be decoupled into a disorder and a polaron contribution. But there is no universality regarding the trade-off between disorder and polaron effects. The present article is an abridged version of Ref.[6].

THEORETICAL FORMALISM

Within the EMA approach the disordered organic medium with localized states for charge carriers is replaced by an effective ordered cubic 3D lattice with spacing $a = N^{-1/3}$ equal to the average distance between localized states, where N is the density of the localized states. We consider that energy ε of the localized states is randomly distributed and their DOS can be described by a Gaussian function $g(\varepsilon) = \left(N/\sigma\sqrt{2\pi}\right)\exp\left[-(1/2)(\varepsilon/\sigma)^2\right]$, where σ is the width of the DOS. For the carrier concentration n the Fermi energy level ε_F is determined from the transcendental equation $n = \int_{-\infty}^{\infty} d\varepsilon\, g(\varepsilon) f(\varepsilon, \varepsilon_F)$, where $f(\varepsilon, \varepsilon_F)$ is given by the Fermi-Dirac statistics $f(\varepsilon, \varepsilon_F) = \{1 + \exp[(\varepsilon - \varepsilon_F)/k_B T]\}^{-1}$.

In the present work, we will apply both the Miller-Abrahams (MA) and Marcus jump rate models to describe an elementary hopping transition between two individual sites. For the MA hopping the jump rate W_{ij} for bare charge-carrier between starting (ε_i) and target (ε_j) states is given as [7]

$$W_{ij} = W_1 \exp\left[-\frac{\left|\varepsilon_j - \varepsilon_i\right| + \left(\varepsilon_j - \varepsilon_i\right)}{2k_B T}\right], \qquad W_1 = \nu_0 \exp\left(-2\frac{a}{b}\right), \tag{1}$$

where ν_0 is the attempt-to-escape frequency and b is a carrier localization radius. On the other hand, the Marcus hopping model [8] is applied to account for polaron formation and W_{ij} has the form

$$W_{ij} = W_2 \exp\left[-\frac{\varepsilon_j - \varepsilon_i}{2k_B T} - \frac{\left(\varepsilon_j - \varepsilon_i\right)^2}{16 E_a k_B T}\right], \qquad W_2 = W_0 \exp\left(-\frac{E_a}{k_B T}\right), \tag{2}$$

where E_a is the is the small polaron activation energy, $W_0 = \left(J_0^2/\hbar\right)\sqrt{\pi/4E_a k_B T}\,\exp(-2a/b)$, J_0 is prefactor in the transfer integral. Note that E_a is related to the reorganization energy λ by $E_a = \lambda/4$.

In the present work, we proceed from calculation of conductivity using an EMA method suggested earlier by Kirkpatrick [9] where the effective conductivity σ_e is determined as

$$\left\langle \frac{\sigma_{12} - \sigma_e}{\sigma_{12} + (d-1)\sigma_e} \right\rangle = 0. \tag{3}$$

Here $\sigma_{12} = G_{12}/a$ is conductivity in two-site cluster approximation, d is dimensionality of the hopping transport system, G_{12} is a two-site conductance and angular brackets $\langle ... \rangle$ denote the configuration averaging. In general, configuration averaging of some value Q is performed by solving a double integral $\langle Q \rangle = \int_{-\infty}^{\infty} d\varepsilon_1 \int_{-\infty}^{\infty} d\varepsilon_2 P(\varepsilon_1) P(\varepsilon_2) Q$, where $P(\varepsilon_1)$ and $P(\varepsilon_2)$ denote certain distribution functions for ε_1 and ε_2, respectively, as detailed below.

The conductance G_{12} can be determined for the MA rate according to [4] as

$$G_{12} = G_1 \frac{\exp\left(-\dfrac{|\varepsilon_1 - \varepsilon_2|}{2k_B T}\right)}{4\cosh\left(\dfrac{\varepsilon_1 - \varepsilon_F}{2k_B T}\right)\cosh\left(\dfrac{\varepsilon_2 - \varepsilon_F}{2k_B T}\right)}, \qquad G_1 = \frac{e^2 W_1}{k_B T} \qquad (4)$$

and for the Marcus rate as

$$G_{12} = G_2 \frac{\exp\left[-\dfrac{(\varepsilon_1 - \varepsilon_2)^2}{16 E_a k_B T}\right]}{4\cosh\left(\dfrac{\varepsilon_1 - \varepsilon_F}{2k_B T}\right)\cosh\left(\dfrac{\varepsilon_2 - \varepsilon_F}{2k_B T}\right)}, \qquad G_2 = \frac{e^2 W_2}{k_B T}. \qquad (5)$$

To calculate the effective conductivity σ_e one has to perform a configuration averaging in Eq. 3. It should be pointed out that the appropriate averaging method turns out to be crucial for an adequate description of kinetic characteristics. An elementary method of configuration averaging would be to separately average over starting site ε_1 and target site ε_2 energies using the product of Gaussian functions $P(\varepsilon_1)P(\varepsilon_2) = g(\varepsilon_1)g(\varepsilon_2)$. Hereafter we shall refer to this averaging method in abbreviation as "averaging-B". However, in reality, a charge-carrier jump occurs from an occupied hopping site with energy ε_1 to an empty site with energy ε_2, and vice versa. Therefore, it is more appropriate to average over the occupied density-of-states (ODOS) distribution for starting site energies and over the unoccupied density-of-states (UDOS) distributions for the target site energies. Therefore, we must choose $P(\varepsilon_1)P(\varepsilon_2) = g(\varepsilon_1)g(\varepsilon_2)f(\varepsilon_1, \varepsilon_F)[1 - f(\varepsilon_2, \varepsilon_F)]$. Let us call this "ODOS-UDOS" averaging method as "averaging-A" for short. We will apply first the averaging A method. Then from Eq. (3) we obtain

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dt_1 dt_2 \frac{\exp\left[-\dfrac{1}{2}(t_1^2 + t_2^2)\right]}{\Phi_A(t_1, t_2, x_F)} \frac{\dfrac{x}{4}\dfrac{\exp\left(-\dfrac{x}{2}|t_1 - t_2|\right)}{\varphi(t_1, t_2, x_F)} - X_e}{\dfrac{x}{4}\dfrac{\exp\left(-\dfrac{x}{2}|t_1 - t_2|\right)}{\varphi(t_1, t_2, x_F)} + (d-1)X_e} = 0, \qquad (6)$$

where $\Phi_A(t_1, t_2, x_F) = \{1 + \exp[x(t_1 - x_F)]\}\{1 + \exp[-x(t_2 - x_F)]\}$. Using the Marcus rate for the hopping conductance it becomes

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dt_1 dt_2 \frac{\exp\left[-\dfrac{1}{2}(t_1^2 + t_2^2)\right]}{\Phi_A(t_1, t_2, x_F)} \frac{\dfrac{x}{4}\dfrac{\exp\left[-\dfrac{x(t_1 - t_2)^2}{16 x_a}\right]}{\varphi(t_1, t_2, x_F)} - Y_e}{\dfrac{x}{4}\dfrac{\exp\left[-\dfrac{x(t_1 - t_2)^2}{16 x_a}\right]}{\varphi(t_1, t_2, x_F)} + (d-1)Y_e} = 0. \qquad (7)$$

Here $X_e = \sigma_e/\sigma_1$, $\quad \sigma_1 = e^2 W_1/a\sigma$, $\quad Y_e = \sigma_e/\sigma_2$, $\quad \sigma_2 = e^2 W_2/a\sigma$, $\quad x = \sigma/k_B T$, $\quad x_a = E_a/\sigma$, $x_F = \varepsilon_F/\sigma$, $x_F = \varepsilon_F/\sigma$, $\varphi(t_1, t_2, x_F) = \cosh[(x/2)(t_1 - x_F)]\cosh[(x/2)(t_2 - x_F)]$. The effective mobility

μ_e and effective diffusivity D_e can be obtained as $\mu_e = \sigma_e/en$ and $D_e = \mu_e k_B T/e$.

In the limiting case of very low carrier concentration we have [2]: $\varepsilon_F = -(1/2)(\sigma^2/k_B T) - k_B T \ln(N/n)$. In this case from Eqs. (6) and (7), one obtains the equations for the effective diffusivity D_e for the MA and Marcus rates, consequently, in the forms

$$\int\limits_{-\infty}^{\infty}\int\limits_{-\infty}^{\infty} dt_1 dt_2 \frac{\exp\left(-\frac{t_1^2 + t_2^2}{2}\right)}{\phi_A(t_1)} \frac{\exp\left[-\frac{x}{2}|t_1 - t_2| - \frac{x}{2}(t_1 + t_2) - \frac{1}{2}x^2\right] - M_e}{\exp\left[-\frac{x}{2}|t_1 - t_2| - \frac{x}{2}(t_1 + t_2) - \frac{1}{2}x^2\right] + (d-1)M_e} = 0, \qquad (8)$$

$$\int\limits_{-\infty}^{\infty}\int\limits_{-\infty}^{\infty} dt_1 dt_2 \frac{\exp\left(-\frac{t_1^2 + t_2^2}{2}\right)}{\phi_A(t_1)} \frac{\exp\left[-xx_a - \frac{x}{16x_a}(t_1 - t_2)^2 - \frac{x}{2}(t_1 + t_2) - \frac{1}{2}x^2\right] - N_e}{\exp\left[-xx_a - \frac{x}{16x_a}(t_1 - t_2)^2 - \frac{x}{2}(t_1 + t_2) - \frac{1}{2}x^2\right] + (d-1)N_e} = 0, \quad (9)$$

where $\phi_A(t_1) = \exp\left[(2t_1 x + x^2)/2\right]$, $M_e = D_e/D_1$, $N_e = D_e/D_2$, $D_1 = a^2 W_1$ and $D_2 = a^2 W_0$. Note, that Fermi level does not enter in Eqs.(8) and (9), in contrast to Eqs. (6) and (7) derived for the conductivity in case of high carrier concentration. We should recall that Eqs.(8) and (9) can be used for calculating the effective diffusivity D_e of both charge-carriers and triplet excitations.

As pointed out above, there could also be another averaging method – *averaging B*. Using this method one obtains the equations similar to Eqs. (6) and (7); however, instead of $\Phi_A(t_1, t_2, x_F)$ we have $\Phi_B \equiv 1$. At vanishing carrier concentration one obtains the equations similar to Eqs. (8) and (9); however, instead of $\phi_A(t_1)$ we have $\phi_B \equiv 1$. As it will be shown below, this averaging *B* method lead to results obtained in [4] in which the Marcus rate has been used.

RESULTS OF CALCULATIONS

Temperature dependences of the diffusion coefficient D_e/D_1 in 3D system calculated for the MA rates by Eq.(8) in the low carrier concentration limit using both *averaging methods A and B* are $D_e = D_1 \exp(-0.43x^2)$ and $D_e = D_1 \exp(-0.53x^2)$, respectively.

Temperature dependences of the diffusion coefficient $D_e/[D_2 \exp(-E_a/k_B T)]$ in 3D system calculated for the Marcus rate model by Eq. (9) in the low carrier concentration limit using both *averaging methods A and B* consequently are $\ln\{D_e/[D_2 \exp(-E_a/k_B T)]\} \cong -C_1 x^2$ and $\ln\{D_e/[D_2 \exp(-E_a/k_B T)]\} \cong -C_2 x^2$. Parameters C_1 and C_2 depend on σ/E_a. Fig. 1 shows the dependences of C_1 and C_2 on σ/E_a, derived in the framework of *averaging A and B* methods, respectively. In addition we show parameter C, obtained by the Monte Carlo simulations for triplet excitons and by the percolation-based scaling theory from [4] (squares with green connecting line). Short dotted lines 1 and 2 shows results from Refs. [10] and [11], respectively.

Fig. 2 presents the carrier-concentration dependences of the Marcus hopping mobility $\mu_e/\mu_2 = (N/n)Y_e \exp(-xx_a)$ calculated for different temperatures by Eq.(7) using the *averaging A* method both at large $E_a/\sigma = 3$ ratio (dashed curves) and for a small $E_a/\sigma = 0.5$ ratio (solid curves).
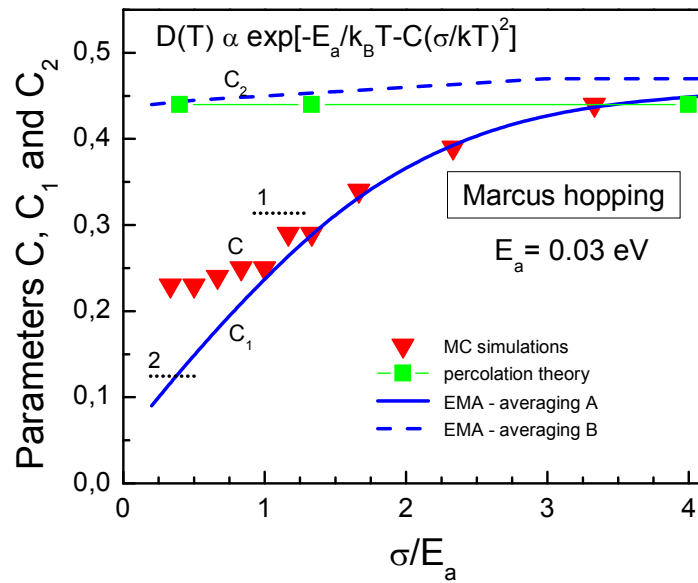
FIGURE 1. Parameters C, C_1 and C_2 vs. σ/E_a obtained for Marcus hopping in 3D system by Monte-Carlo simulations (triangles), derived by the present EMA theory adopting both configuration *averaging A and B* for $E_a = 30$ meV (solid and dashed blue curves, respectively) and by the percolation-based scaling theory from [4] (squares with green connecting line). Short dotted lines 1 and 2 shows results from [10] and [11], respectively.
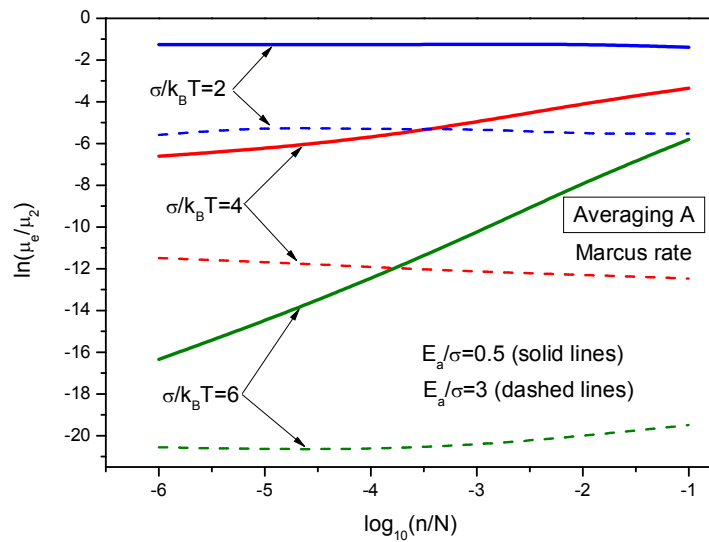

FIGURE 2. The charge-carrier mobility $\mu_e/\mu_2 = (N/n)Y_e \exp(-xx_a)$ vs. carrier concentration n/N calculated for the Marcus rate by Eq. (7) using *averaging A* for different temperatures at $E_a/\sigma = 0.5$ (solid curves) and $E_a/\sigma = 3$ (dashed curves).

The calculations clearly show that the effective charge-carrier mobility depends very weakly on the carrier concentration even at low temperatures in the case when polaron effects dominate over the energy disorder effects ($E_a > \sigma$), while this dependence appears to be strong, especially at low temperatures, when the polaron activation energy is relatively small ($E_a < \sigma$). For the MA rate the dependences of the effective mobility μ_e on charge-carrier concentration are found to be virtually similar for both *averaging A and B* methods, as in [4].

CONCLUSIONS

A key result of the present analytical calculations is that the C-parameter, which weights the relative contribution of disorder and polaron effects as represented by σ/E_a ratio, is not a constant but significantly decreases with decreasing σ/E_a, i.e. with increasing polaron formation energy in the same disordered system. This agrees with previous studies where C =0.31 and 1/8 (cf. Fig. 1, short dotted lines) was obtained in [10] and [11], respectively. These analytical calculations are in agreement with Monte-Carlo simulations data we obtained in the framework of the Marcus jump rate model.

It is, however, at variance with results reported in [4] where the authors applied a percolation-based theory and EMA calculations based on the same Kirkpatrik's method [9] for calculation of the charge-carrier mobility and found the C-parameter independent on the σ/E_a ratio. The latter result was also reproduced by our EMA calculations using the *averaging B* method which we therefore regard as inappropriate in the case of Marcus hopping. Further, the present EMA calculations based on the averaging A method demonstrated that the carrier concentration dependence of the charge carrier mobility $\mu(n/N)$ is not universal as claimed in Ref. [4] but also depends on σ/E_a ratio.

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