Effective-medium theory of hopping charge-carrier transport in weakly disordered organic solids

I. I. Fishchuk*
Institute for Nuclear Research, National Academy of Sciences of Ukraine, Prospect Nauky 47, 03680 Kyiv, Ukraine

D. Hertel and H. Bässler
Institute of Physical, Nuclear and Macromolecular Chemistry and Material Science Center, Philipps-Universität Marburg, Hans-Meerwein-Strasse, D-35032 Marburg, Germany

A. K. Kadashchuk
Institute of Physics, National Academy of Sciences of Ukraine, Prospect Nauky 46, 03028 Kyiv, Ukraine
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An effective-medium theory describing the temperature and electric-field dependence of the drift charge-carrier mobility for the nondispersive transport regime in weakly disordered organic systems is elaborated. Only the energetic disorder effects are taken into consideration, and polaronic effects are neglected. Both the exact (*approach I*) and approximate (*approach II*) Miller-Abrahams expressions were used to describe the carrier jump rates. In previous studies mainly approach II, which ignores phonon emission, was used. We show that only approach I provides correct results for temperature and electric-field dependences of mobility in solids with particularly low energetic disorder. Further, we show that in the case of a small degree of disorder, σ/k_BT, the temperature and field dependences of the charge mobility are much weaker than for larger disorder. Theoretical predictions are in quantitative agreement with the experimental observation in a π-conjugated polymer with weak energetic disorder.

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I. INTRODUCTION

Charge-carrier transport phenomena in disordered organic solids are both of great technological and fundamental interest due to the widespread use of these materials in electrophotographic receptors, electroluminescent and photovoltaic devices, etc.[1–3] It is generally accepted that charge transport occurs due to hopping, therefore mobilities of these materials are generally very low, and strongly field and temperature dependent.[2,3] In the past decade, experimental results on a wide range of doped polymers and main chain and pendant group polymers, as well as vapor-deposited molecular glasses, were successfully described by a formalism based on disorder, due to Bässler.[3,4]

The present study was inspired by recent observations of abnormally weak temperature and electric-field dependences of hole mobility in some π-conjugated polymers as methyl-substituted ladder-type poly(paraphenylene) (MeLPPP),[5,6] which still have no plausible theoretical justification. Due to its rigid structure MeLPPP is a polymer with strongly reduced disorder, as proven by a weak inhomogeneous broadening of the vibronic absorption transitions. A Gaussian fit of the low-energy tail yields a variance of $\sim$0.0335 eV.[6,7] It is believed that charge transport in MeLPPP is controlled by energetic disorder, and the weak temperature dependence of the mobility proves that polaronic effects are unimportant. However, the observed dependence is at variance with the conventional version of the disorder model. It was found that in the range of 393–150 K the mobility decreases by a factor of only 3, and the low-temperature asymptote in the Arrhenius plot yields an activation energy of only 0.022 eV, i.e., less than the variance of the distribution of singlet states.[6] It is worth noting that such dependence seems not to be a unique feature for MeLPPP only; a somewhat similar very weak temperature dependence of the mobility was reported earlier for σ-conjugated aliphatic-substituted polysilylenes and polygermylenes.[8,9] Moreover, it was found[10,11] that the hole mobility in poly(9,9-dioctylfluorene) (PFO) shows an extremely weak electric-field dependence over a broad field range at room temperature, indicating a low degree of energetic disorder in this polymer as well. Obviously, more theoretical work is necessary to explain this puzzle.

In the present work we developed a theory of charge transport using an effective-medium approach (EMA) based on the original form of the Miller-Abrahams type of jump rates. It does, indeed, predict a much weaker temperature and electric-field dependence of the mobility at a low degree of energetic disorder than previously developed disorder models based on simple activated jump rates. Our approach allows a description of experimental data on charge-carrier transport in weakly disordered organic solids. It confirms that the EMA is, indeed, an appropriate analytical method for studying the drift mobility in such systems.

The present paper is organized in the following way. In Sec. II the Miller-Abrahams formalism is outlined, and in Sec. III calculations of the temperature dependence of carrier drift mobility and a Gaussian distribution of the density-of-states (DOS) are presented. The theory is applied to an analysis of the temperature dependence of charge carrier mobility obtained on MeLPPP. Section IV presents calculations of the electric-field dependence of the drift mobility, which was used to interpret the experimental field dependence of mobility in MeLPPP and PFO polymers.

II. MILLER-ABRAHAMS FORMALISM

It is generally accepted that charge-carrier hopping between localized states proceeds via absorption or emission of

a phonon. The Miller-Abrahams (MA) formalism[12] has been used extensively to interpret hopping transport in disordered solids. The key point of the MA model is an expression to describe an intersite jump rate W_{ij} for a charge carrier between sites i and j in the single-phonon approximation. It assumes a weak overlap of the electronic wave function between neighbor hopping sites i and j with energy ε_i and ε_j at the intersite distance $r_{ij}=|\mathbf{r}_{ij}|$, so that $|\varepsilon_j-\varepsilon_i|\gg 2I_{ij}$, where $I_{ij}=I_0\exp(-r_{ij}/b)$ is the integral of overlapping, any b is the localization radius of a charge carrier. In the case of absorption ($\varepsilon_j>\varepsilon_i$) and emission ($\varepsilon_j<\varepsilon_i$) of a phonon, respectively, W_{ij}, can be expressed as[12,13]

$$W_{ij}=Ae^{-2(r_{ij}/b)}\frac{\varepsilon_j-\varepsilon_i}{\hbar}N(\varepsilon_j-\varepsilon_i), \tag{1}$$

$$W_{ij}=Ae^{-2(r_{ij}/b)}\frac{\varepsilon_i-\varepsilon_j}{\hbar}[N(\varepsilon_i-\varepsilon_j)+1], \tag{2}$$

where A is a dimensionless constant and $N(\varepsilon)=[\exp(\varepsilon/k_BT)-1]^{-1}$. Equations (1) and (2) are the principal results of the original paper by Miller and Abrahams[12] to determine jump rates.

Let us substitute $N(\varepsilon_j-\varepsilon_i)$ and $N(\varepsilon_i-\varepsilon_j)+1$ in Eqs. (1) and (2), by equivalent expressions:

$$N(\varepsilon_j-\varepsilon_i)=\frac{1}{2}\frac{e^{-(\varepsilon_j-\varepsilon_i)/2k_BT}}{\sinh\left(\dfrac{\varepsilon_j-\varepsilon_i}{2k_BT}\right)} \tag{3}$$

and

$$N(\varepsilon_i-\varepsilon_j)+1=\frac{1}{2}\frac{e^{(\varepsilon_i-\varepsilon_j)/2k_BT}}{\sinh\left(\dfrac{\varepsilon_i-\varepsilon_j}{2k_BT}\right)}. \tag{4}$$

For uncorrelated site energies and arbitrary spacing $\varepsilon_j-\varepsilon_i$ Eqs. (1) and (2) can be combined with Eqs. (3) and (4) and yield

$$W_{ij}=Ae^{-2(r_{ij}/b)}\frac{k_BT}{\hbar}\frac{\dfrac{|\varepsilon_j-\varepsilon_i|}{2k_BT}}{\sinh\left(\dfrac{|\varepsilon_j-\varepsilon_i|}{2k_BT}\right)}e^{-(\varepsilon_j-\varepsilon_i)/2k_BT}. \tag{5}$$

In our subsequent treatment Eq. (5) will be used, which, by the way, is identical to the MA result.

First, let us consider the situation when $|\varepsilon_j-\varepsilon_i|\gg 2k_BT$. In this case we can simplify Eq. (5) to the form

$$W_{ij}=\nu_0 e^{-2(r_{ij}/b)}e^{-[|\varepsilon_j-\varepsilon_i|+(\varepsilon_j-\varepsilon_i)]/2k_BT}, \tag{6}$$

where $\nu_0=A\overline{|\varepsilon_j-\varepsilon_i|}/\hbar$. Here $\overline{|\varepsilon_j-\varepsilon_i|}$ is the average energy spacing of sites i and j. One can easily see that

$$W_{ij}=\nu_0 e^{-2(r_{ij}/b)}\begin{cases} e^{-(\varepsilon_j-\varepsilon_i)/k_BT}, & \varepsilon_j>\varepsilon_i \\ 1, & \varepsilon_j<\varepsilon_i \end{cases}. \tag{7}$$

It should be mentioned that only expressions (6) or (7) for the intersite jump rates have been commonly used in analytical theories[4] as well as in computer simulations of charge-carrier transport in disordered organic systems in the framework of the MA formalism.

Hereafter we will refer all results obtained by using Eq. (5) as *approach I*, and results obtained from Eqs. (6) or (7) as the (approximate) as *approach II*; we are considering a nondispersive charge carrier only, i.e., moderately high temperatures and weak disorder.

III. TEMPERATURE DEPENDENCE OF THE DRIFT MOBILITY

We start our consideration with the temperature dependence of charge-carrier drift mobility. The appropriate two-site cluster EMA theory for disordered systems was developed previously[14] and the following two self-consistent equations have been obtained:

$$\left\langle \frac{W_{12}-W_e}{\dfrac{W_{12}+W_{21}}{2}+2W_e}\right\rangle=0, \quad \left\langle \frac{W_{21}-W_e}{\dfrac{W_{12}+W_{21}}{2}+2W_e}\right\rangle=0, \tag{8}$$

where W_e is the effective jump rate. The angular brackets denote configuration averaging. To perform calculations using of Eqs. (8), one first needs to choose certain forms of W_{12} and W_{21}, and then carry out the configuration averaging. If the averaging is done correctly, then for zero electric field one must obtain the same value of W_e from both equations. As shown in Ref. 14 we have to average over the energy of the starting state and the target state in the asymptotic occupational density of states (ODOS) and the DOS, respectively.

Let us start with approach I. In this case,

$$W_{12}=W_1\frac{\dfrac{|\varepsilon_2-\varepsilon_1|}{2k_BT}}{\sinh\left(\dfrac{|\varepsilon_2-\varepsilon_1|}{2k_BT}\right)}e^{-(\varepsilon_2-\varepsilon_1)/2k_BT}, \tag{9}$$

$$W_{21}=W_1\frac{\dfrac{|\varepsilon_1-\varepsilon_2|}{2k_BT}}{\sinh\left(\dfrac{|\varepsilon_1-\varepsilon_2|}{2k_BT}\right)}e^{-(\varepsilon_1-\varepsilon_2)/2k_BT}, \tag{10}$$

where $W_1=A(k_BT/\hbar)\exp(-2a/b)$. ε_1 and ε_2 in Eq. (9) are the energy of the starting and target state, respectively, and the reverse in Eq. (10). Positional disorder has been discarded, i.e., $r_{12}=a$, where a is cubic lattice spacing. Then, assuming $X_e=W_e/W_1$, from the first of Eqs. (8) one obtains

$$X_e=\frac{\left\langle \dfrac{e^{-(\varepsilon_2-\varepsilon_1)/2k_BT}}{\cosh\left(\dfrac{|\varepsilon_2-\varepsilon_1|}{2k_BT}\right)}\right\rangle}{\left\langle \dfrac{\tanh\left(\dfrac{|\varepsilon_2-\varepsilon_1|}{2k_BT}\right)}{\dfrac{|\varepsilon_2-\varepsilon_1|}{2k_BT}}\right\rangle}, \tag{11}$$

It will turn out that for $\sigma/k_BT>1, X_e \ll 1$ is valid.

The density-of-states distributions are assumed to be Gaussians with variance σ,

$$P(\varepsilon_1)=\frac{1}{\sigma\sqrt{2\pi}}e^{-(1/2)[(\varepsilon_1-\varepsilon_0)/\sigma]^2}, \quad P(\varepsilon_2)$$

$$=\frac{1}{\sigma\sqrt{2\pi}}e^{-(1/2)(\varepsilon_2/\sigma)^2}, \tag{12}$$

where $\varepsilon_0=-\sigma^2/k_BT$.[15] After substituting Eq. (12) into Eq. (11) and performing the configuration averaging neglecting correlation effects, one obtains

$$X_e=\frac{i_0}{i_1}, \tag{13}$$

where

$$i_0=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt_1\int_{-\infty}^{\infty}dt_2\varphi_0(t_1,t_2)e^{-(t_2-t_1)(x/2)}, \tag{14}$$

$$i_1=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt_1\int_{-\infty}^{\infty}dt_2\frac{\varphi_0(t_1,t_2)}{\varphi_1(t_1,t_2)}. \tag{15}$$

Here

$$\varphi_0(t_1,t_2)=\frac{e^{-(1/2)[(t_1+x)^2+t_2^2]}}{\cosh\left(\left|t_2-t_1\right|\frac{x}{2}\right)}, \tag{16}$$

$$\varphi_1(t_1,t_2)=\frac{\left|t_2-t_1\right|\frac{x}{2}}{\sinh\left(\left|t_2-t_1\right|\frac{x}{2}\right)}, \tag{17}$$

where $x=\sigma/k_BT$. Assuming the validity of Einstein's law relating the drift charge-carrier mobility μ_e to the effective diffusivity $D_e=a^2W_e$ for a disordered organic system, $\mu_e=ea^2W_e/k_BT=\mu_1X_e$ and $\mu_1=A(ea^2/\hbar)\exp(-2a/b)$ is obtained, where μ_1 is a temperature-independent parameter.

Let us consider approach II. In this case,

$$W_{12}=W_2e^{-[|\varepsilon_2-\varepsilon_1|+(\varepsilon_2-\varepsilon_1)]/2k_BT}, \tag{18}$$

$$W_{21}=W_2e^{-[|\varepsilon_1-\varepsilon_2|+(\varepsilon_1-\varepsilon_2)]/2k_BT}, \tag{19}$$

where $W_2=\nu_0\exp(-2a/b)$. Then, the first of Eqs. (8) yields

$$Y_e=\frac{\left\langle\frac{e^{-(\varepsilon_2-\varepsilon_1)/2k_BT}}{\cosh\left(\frac{|\varepsilon_2-\varepsilon_1|}{2k_BT}\right)}\right\rangle}{\left\langle\frac{e^{(|\varepsilon_2-\varepsilon_1|/2k_BT}}{\cosh\left(\frac{|\varepsilon_2-\varepsilon_1|}{2k_BT}\right)}\right\rangle}, \tag{20}$$

where $Y_e=W_e/W_2$, assuming $Y_e\ll 1$. Substituting Eq. (12) into Eq. (20) and performing the configuration averaging in approach I, one obtains

$$Y_e=\frac{i_0}{i_2}, \tag{21}$$

where i_0 is determined by Eq. (14), and i_2 by

$$i_2=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt_1\int_{-\infty}^{\infty}dt_2\frac{\varphi_0(t_1,t_2)}{\varphi_2(t_1,t_2)}, \tag{22}$$

where

$$\varphi_2(t_1,t_2)=e^{-|t_2-t_1|(x/2)}. \tag{23}$$

If we take into account that $\cosh(|t_2-t_1|x/2)\exp(-|t_2-t_1|x/2)\cong 1$, we obtain the approximate expression $Y_e=\langle W_{12}\rangle/W_2$ (see Ref. 14),

$$Y_e=\frac{1}{\sqrt{\pi}}\int_{-\infty}^{\infty}dt\,e^{-t^2}\left[1+\mathrm{erf}\left(t-\frac{1}{\sqrt{2}}x\right)\right], \tag{24}$$

where $\mathrm{erf}(y)=(2/\sqrt{\pi})\int_0^y dt\exp(-t^2)$ is the error function. In this case the effective drift mobility becomes $\mu_e=\mu_0Y_e$, where $\mu_0=(ea^2\nu_0/k_BT)\exp(-2a/b)$ is a temperature-dependent parameter.[2]

The results for X_e and Y_e obtained in the framework of approaches I and II, respectively, are valid for small values of σ/k_BT only, i.e. when the two-site cluster approach is adequate. Earlier the authors of Refs. 16 and 15 developed an EMA theory using approach II, in which contributions from clusters containing more than two sites (closed-loop contribution) was considered. This enabled the authors of Refs. 16 and 15 to extend the applicability range of the EMA-results toward larger values of σ/k_BT. As a result the expression $\mu_e=\mu_0\exp[-(2\sigma/3k_BT)^2]$ was derived, in good agreement with data from computer simulations,[4] again done within the framework of approach II.

Here we suggest a simple method that allows us to calculate μ_e within the framework of the present EMA calculation for large values of σ/k_BT. In this case, charge-carrier transport can occur only via thermal excitation of a carrier to the effective transport energy level ε_p. The concept of the effective transport energy level was applied earlier[17–19] to describe hopping transport in disordered media. In the present paper the ε_p level within the Gaussian-shaped DOS [cf. function $P(\varepsilon_2)$ in Eq. (12)] was calculated from the equation

$$\int_{-\infty}^{\varepsilon_p}P(\varepsilon_2)d\varepsilon_2=p_c, \tag{25}$$

where p_c is the site percolation threshold. For a three-dimensional hopping system $p_c=0.312$.[20] From Eq. (25), $\varepsilon_p\cong-\sigma/2$ is obtained. Adopting this concept and using the Gaussian ODOS distribution for the starting and target states, Eqs. (11) and (20) will be used to calculate μ_e for both approaches. After averaging, the results read

$$X_e = \frac{i_0'}{i_1'}, \tag{26}$$

$$Y_e = \frac{i_0'}{i_1''}, \tag{27}$$

where

$$i_0' = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \varphi(t) \frac{e^{t(x/2)}}{\cosh\left(t\frac{x}{2}\right)} dt,$$

$$i_1' = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \varphi(t) \frac{\tanh\left(t\frac{x}{2}\right)}{t\frac{x}{2}} dt, \tag{28}$$

$$i_1'' = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \varphi(t) \frac{e^{|t|(x/2)}}{\cosh\left(t\frac{x}{2}\right)} dt, \quad \varphi(t) = e^{-(1/2)(t-c+x)^2}. \tag{29}$$

Here $c = -\varepsilon_p/\sigma = 1/2$.

If for i_0' and i_1'', one uses the simplification $\cosh(tx/2) \cong \exp(|t|x/2)$, then Y_e reads

$$Y_e = \frac{1}{2}\left\{ e^{-(1/2)(x-c)^2 + (1/2)c^2}\left[1 - \mathrm{erf}\left(\frac{c}{\sqrt{2}}\right)\right] + \left[1 - \mathrm{erf}\left(\frac{x-c}{\sqrt{2}}\right)\right]\right\}. \tag{30}$$

Using the expression for Y_e under the condition of $x \gg 1$, one obtains

$$\mu_e = \tfrac{1}{2}\mu_0 e^{-[(\sqrt{2}/2)(\sigma/k_BT)]^2}. \tag{31}$$

Figure 1 presents the dependences $\ln(\mu_e/\mu_1) = \ln(X_e)$ and $\ln(\mu_e/\mu_0) = \ln(Y_e)$ versus $(\sigma/k_BT)^2$ (curves 1 and 2, respectively), calculated via Eqs. (26) and (27), respectively. For large values of σ/k_BT, curve 1 can be approximated by $\mu_e \cong \mu_1 \exp[-(3\sigma/5k_BT)^2]$ and curve 2 by $\mu_e \cong \mu_0 \exp[-(2\sigma/3k_BT)^2]$. Interestingly, a similar coefficient of $\frac{3}{5}$ was recently obtained for the temperature dependence of the zero-field mobility using a computer simulation of charge transport using a correlated disorder model.[21] Curves 3 and 4 in Fig. 1 are calculated by Eqs. (13) and (21) for small values of σ/k_BT. As one can see, curve 3 gives the weakest temperature dependence, and could be approximated by the expression $\mu_e \cong \mu_1 \exp[-(4\sigma/9k_BT)^2]$, which can be used for estimation of the parameter σ from the temperature dependence of mobility in weakly disordered organic solids. Note that curves 1 and 3 intersect at $x_1 = \sigma/k_BT_1 = 1.87$ (labeled *A*) and curves 2 and 4 at $x_2 = \sigma/k_BT_2 = 2.54$ (labeled *B*). These intersection points can be considered as a demarcation between regions of weak and strong disorder. It follows that the more exact approach I predicts a somewhat weaker temperature dependence of μ_e than approach II. This should be taken into consideration when σ is estimated by comparing the experimental temperature dependence of μ_e with theory.

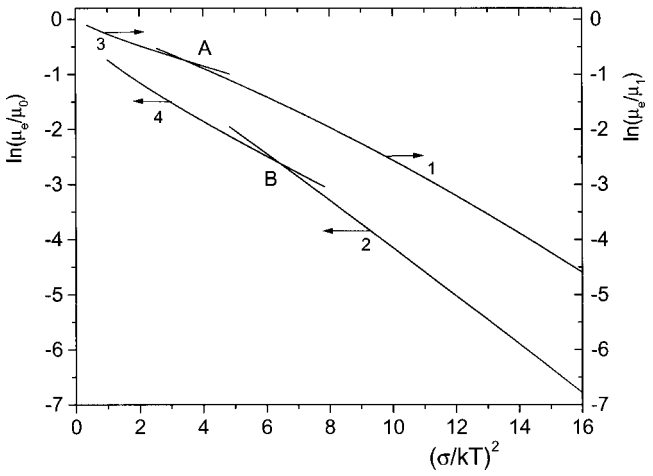

FIG. 1. Temperature dependence of the effective charge-carrier drift mobility $\ln(\mu_e/\mu_1)$ calculated in the framework of the exact approach I (curves 1 and 3) and $\ln(\mu_e/\mu_0)$ calculated within the approximated approach II (curves 2 and 4) for a broad range of σ/k_BT values. Curves 1 and 2 were calculated by taking into account the existence of the effective transport energy level in the case of large σ/k_BT values. The intersection points *A* and *B* define the transition from a weak to strong energetic disorder.

It is worth noting that one should distinguish two situations when calculating the dependence of μ_e on σ/k_BT in the framework of approach II, i.e., (i) changing σ while the temperature T is kept constant, and (ii) changing T while σ is constant. In the former case we have $\ln(\mu_e/\mu_0) = \ln(Y_e)$ (Fig. 1, curve 4) and in the latter case $-\ln(\mu_e/\mu_2) = \ln(xY_e)$, where $\mu_2 = (ea^2\nu_0/\sigma)\exp(-2a/b)$ is a temperature-independent parameter. As one can show, at small values of σ/k_BT there is a considerable discrepancy between those dependences. Such a discrepancy is absent in the framework of approach I, since parameter μ_1 does not depend upon σ or T. This circumstance should be taken into consideration when one performs a computer simulation of charge transport in the framework of approach II. Consequently, the suggested approach I should preferably be used for studying the temperature dependence of charge mobility μ_e.

Figure 2 shows the temperature dependence of the charge-carrier mobility $\mu(T)$ (symbols), measured by the conventional time-of-flight technique at relatively low electric fields in a π-conjugated polymer with reduced energetic disorder, MeLPPP.[6] Within the temperature range $150 < T < 393$ K, equivalent to $1.0 < \sigma/k_BT < 2.6$, the data can be fitted reasonably well by Eq. (13) employing approach I, and assuming $\sigma = 0.0335$ eV and $\mu_1 = 1.4 \times 10^{-3}$ cm^2/V s as fitting parameters. Note that a similar σ value was also obtained by the Gaussian fit of the low-energy portion of absorption spectrum of MeLPPP.[6,7]

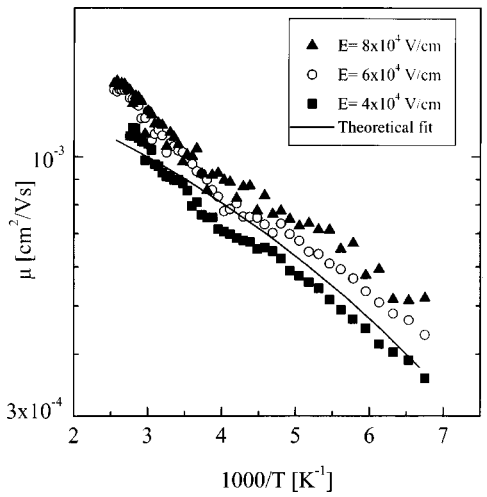

FIG. 2. Experimental temperature dependence of the hole mobility in ladder-type methyl-substituted poly(paraphenylene) (MeLPPP) measured at different electric fields (symbols) (Ref. 6). The solid line is theoretical fit by Eq. (13) within the framework of approach I. The parameters used for the calculation are $\sigma = 0.0335$ eV and $\mu_1 = 1.4 \times 10^{-3}$ cm^2/V s.

IV. ELECTRIC-FIELD DEPENDENCE OF THE DRIFT MOBILITY

Next we shall consider the electric-field dependence of the charge-carrier drift mobility in the nondispersive transport regime calculated in the framework of approaches I and II. For this aim one should generalize the set of equations (8) to the case of arbitrary electric fields. Here we will use the procedure developed by Parris and Bookout,[22] where the full self-consistency was performed by the EMA to calculate kinetic characteristics of a disordered system for arbitrary electric fields. In our case full self-consistency under the electric field **E** directed along the $0X$ axis leads to the set of equations

$$\left\langle \frac{W_{12}^{+} - W_e^{+}}{Q} \right\rangle = 0, \quad \left\langle \frac{W_{21}^{-} - W_e^{-}}{Q} \right\rangle = 0, \tag{32}$$

$$\left\langle \frac{W_{12} - W_e}{\dfrac{W_{12} + W_{21}}{2} + \left(\dfrac{1}{M} - 1 \right) W_e} \right\rangle = 0, \tag{33}$$

where

$$Q = W_e + \left(\frac{W_{12}^{+} + W_{21}^{-}}{2} - \frac{W_e^{+} + W_e^{-}}{2} \right) M_1 + \left(\frac{W_{12}^{+} - W_{21}^{-}}{2} - \frac{W_e^{+} - W_e^{-}}{2} \right) M_2, \tag{34}$$

$$M = \frac{1}{(2\pi)^3} \int d\Omega_{\mathbf{k}} (1 - \cos k_y) \frac{F_1}{F_2}, \tag{35}$$

$$M_1 = \frac{1}{(2\pi)^3} \int d\Omega_{\mathbf{k}} (1 - \cos k_x) \frac{F_1}{F_2},$$

$$M_2 = \frac{\delta}{(2\pi)^3} \int d\Omega_{\mathbf{k}} \sin^2 k_x \frac{1}{F_2}, \tag{36}$$

$$F_1 = \eta (1 - \cos k_x) + (1 - \cos k_y) + (1 - \cos k_z),$$

$$F_2 = F_1^2 + \delta^2 \sin^2 k_x, \tag{37}$$

$$\eta = \frac{W_e^{+} + W_e^{-}}{2 W_e}, \quad \delta = \frac{W_e^{+} - W_e^{-}}{2 W_e}. \tag{38}$$

The sets of equations (32) and (33) allow one to calculate three effective parameters, namely W_e^{+}, W_e^{-}, and W_e, which describe the effective drift velocity along, oppositely, and normal to the electric-field direction, respectively. In the case of $E \to 0$ one obtains the set of equations (8). Calculation of the effective values of W_e^{+}, W_e^{-}, and W_e for arbitrary values of E using Eqs. (32) and (33) is a complicated task, and therefore we shall restrict our consideration to the ranges of relatively weak and strong electric fields where the effective values can be calculated.

For a range of relatively weak electric fields where the following is valid, i.e., $M_2 \ll M_1$ and $2W_e \leqslant W_e^{+} + W_e^{-} \ll W_{12}^{+} + W_{21}^{-}$, Eqs. (32) yield the effective values W_e^{+} and W_e^{-}:

$$W_e^{+} = \frac{\left\langle \dfrac{W_{12}^{+}}{W_{12}^{+} + W_{21}^{-}} \right\rangle}{\left\langle \dfrac{1}{W_{12}^{+} + W_{21}^{-}} \right\rangle}, \quad W_e^{-} = \frac{\left\langle \dfrac{W_{21}^{-}}{W_{12}^{+} + W_{21}^{-}} \right\rangle}{\left\langle \dfrac{1}{W_{12}^{+} + W_{21}^{-}} \right\rangle}. \tag{39}$$

For strong electric fields where $W_e^{+} \geqslant W_e^{-}$ we have $\eta = \delta = W_e^{+}/2W_e \geqslant 1$ and $M_1 = M_2 = 1/2\eta$. Then the effective values W_e^{+} and W_e^{-} read

$$W_e^{+} = \frac{1}{\left\langle \dfrac{1}{W_{12}^{+}} \right\rangle}, \quad W_e^{-} = \frac{\left\langle \dfrac{W_{21}^{-}}{W_{12}^{+}} \right\rangle}{\left\langle \dfrac{1}{W_{12}^{+}} \right\rangle}. \tag{40}$$

For further calculations one has to choose explicitly expressions for W_{21}^{-} and W_{12}^{+} as well as to perform the configurational averaging in Eqs. (39) and (40).

We shall first consider charge transport under relatively weak electric field in a weakly energetically disordered organic system using approach I. Replacing $\varepsilon_2 - \varepsilon_1$ by $\varepsilon_2 - \varepsilon_1 - eaE (e > 0)$ in Eqs. (9) and (10), one obtains expressions for W_{21}^{-} and W_{12}^{+}. When performing a configurational averaging one should take into account that in the expression for W_e^{+} the values ε_1 and ε_2 are the energies of the starting and the target state, respectively, and the reverse in the expression for W_e^{-}. Appropriate configurational averaging in Eq. (39) leads to

$$X_e^{\pm}=\frac{i_0^{\pm}}{i_1^{\pm}}, \tag{41}$$

where

$$i_0^{\pm}=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt_1\int_{-\infty}^{\infty}dt_2\varphi_0^{\pm}(t_1,t_2)e^{-(t_2-t_1\mp f)(x/2)}, \tag{42}$$

$$i_1^{\pm}=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt_1\int_{-\infty}^{\infty}dt_2\frac{\varphi_0^{\pm}(t_1,t_2)}{\varphi_1^{\pm}(t_1,t_2)}, \tag{43}$$

and

$$\varphi_0^{\pm}(t_1,t_2)=\frac{e^{-(1/2)[(t_1+x)^2+t_2^2]}}{\cosh\left(|t_2-t_1\mp f|\frac{x}{2}\right)}, \tag{44}$$

$$\varphi_1^{\pm}(t_1,t_2)=\frac{|t_2-t_1\mp f|\frac{x}{2}}{\sinh\left(|t_2-t_1\mp f|\frac{x}{2}\right)}. \tag{45}$$

Here $X_e^{\pm}=W_e^{\pm}/W_1$ and $f=eaE/\sigma$. Having obtained values X_e^{+} and X_e^{-} we can calculate the effective drift mobility μ_e from the following expression:

$$\mu_e=\mu_1\frac{X_e^{+}-X_e^{-}}{xf}. \tag{46}$$

To obtain Eq. (46), a determination of the drift mobility employed in Ref. 22 has been used. In the asymptotic case of a strong electric field ($x\approx 1, f\gg x$) from Eq. (40) one obtains $X_e^{+}=(xf/2)\exp(xf/2)/\sinh(xf/2)$ and $X_e^{-}=(xf/2)\exp(-xf/2)/\sinh(xf/2)$. Thus the inequality $W_e^{+}\gg W_e^{-}$, used above when obtaining Eq. (40), is indeed valid. In this case the charge carrier mobility given by Eq. (46) turns out to be field independent:

$$\mu_e=\mu_1. \tag{47}$$

It should be noted that in such asymptotic cases Eq. (47) can also be obtained from Eqs. (41). Thus expressions (41) for X_e^{+} and X_e^{-} are able to describe the electric-field dependence of the mobility μ_e over a broad field range in solids under the premise of weak energetic disorder.

Figure 3(a) shows the field dependence of hole mobility $\mu(E)$ (symbols) at various temperatures measured in MeLPPP.[6] In combination with Eq. (41), these data can be fitted reasonably well by Eq. (46) in the framework of approach I assuming $\sigma=0.0335$ eV, $T=390$ K, ($x=1.0$), $\mu_1=2.0\times10^{-3}$ cm^2/V s, and $a=1$ nm for an electric field E changing from 4.0×10^4 to 2.5×10^5 V/cm and an equivalent change of f within $0.12<f<0.75$, i.e., $f<x$. Above (see Sec. III, Fig. 2) a slightly different parameter μ_1 was used for fitting the temperature dependence. This is, however, within the range of experimental scattering of μ data [cf. Fig. 3(a)]. When the electric field increases further, i.e., $f\gg x$, the mobility is predicted to reach a constant value described by Eq. (47). For the present case of $x=1.0$, our calculation predicts that μ_e increases by a factor of 1.58, and becomes constant at higher electric fields.

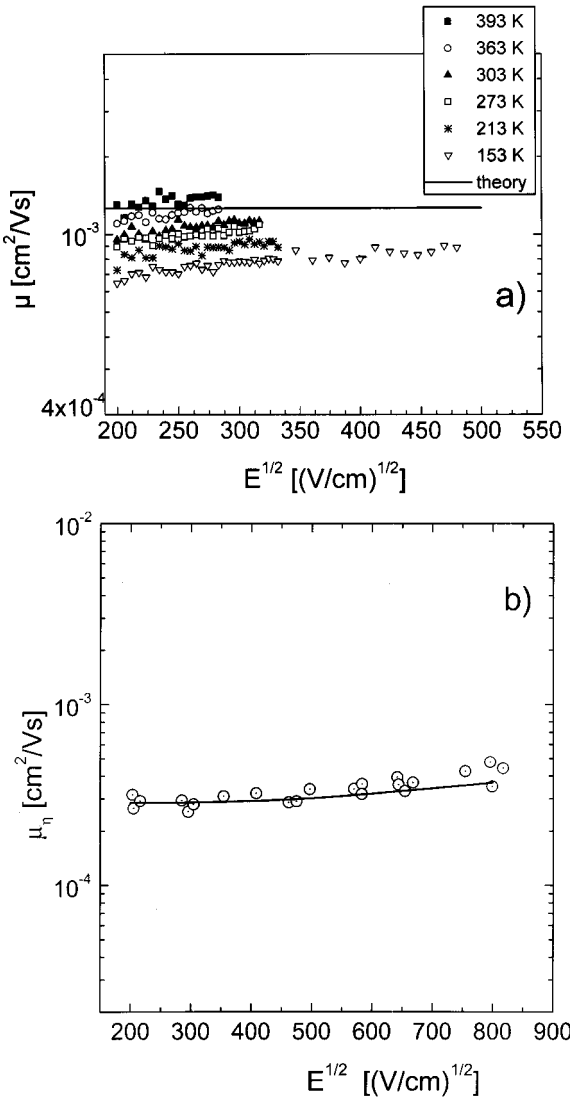

FIG. 3. (a) Electric-field dependence of the hole mobility measured in MeLPPP at different temperatures (symbols) (Ref. 6). The solid line is a theoretical fit by Eq. (46) within the framework of approach I. The parameters used for calculation are $\sigma=0.0335$ eV, $T=390$ K ($x=1.0$), and $\mu_1=2.0\times10^{-3}$ cm^2/V s. (b) Experimental field dependence of the hole mobility measured in PFO measured at room temperature (Refs. 10 and 11). A theoretical fit by Eq. (46), with the parameters $a=3$ nm, $\sigma=0.025$ eV, $T=300$ K ($x=0.97$), and $\mu_1=4.4\times10^{-4}$ cm^2/V s, is given by the solid line.

For comparing the results of our theory with experimental data over a larger field range, we used the data for the charge carrier mobility of poly(9,9-dioctylfluorene) from Refs. 10 and 11. Figure 3(b) gives the field dependence of the hole mobility (circles) measured in PFO at room temperature. As one can see these data also can be fitted well in the framework of approach I [cf. Eqs. (46) and (41)]. Note that in the electric field range employed we have $0.48<f<7.68$, i.e., the cases of both weak and strong fields are covered.

When $x \to 0$ we obtain that $\mu_e \to \mu_1$ over the whole range of electric field, i.e., the drift charge carrier mobility is field independent. This is indeed observed for molecular organic crystals except for low temperatures,[1] where coherence effects become important.

Let us, for the sake of comparison, consider the field dependence of the charge mobility in an organic system with large energetic disorder ($x = \sigma/k_BT \gg 1$) within approach II. Replacing $\varepsilon_2 - \varepsilon_1$ by $\varepsilon_2 - \varepsilon_1 - eaE$ in Eqs. (18) and (19), we obtain expressions for W_{12}^{+} and W_{21}^{-}. First we consider the case of relatively weak fields. Similar to the procedure of obtaining expression (24), here we use the approximate expressions[14] $W_e^{+} = \langle W_{12}^{+} \rangle$ and $W_e^{-} = \langle W_{21}^{-} \rangle$ instead of Eq. (39). Since we consider the case of strong energetic disorder, we can take into consideration that transport occurs only via the effective transport energy level ε_p (see Sec. III). After appropriate configuration averaging, one obtains

$$Y_e^{\pm} = \frac{1}{2}\left\{ e^{-(1/2)(x - c \mp f)^2 + (1/2)(c \pm f)^2}\left[1 - \mathrm{erf}\left(\frac{c \pm f}{\sqrt{2}} \right) \right] + \left[1 - \mathrm{erf}\left(\frac{x - c \mp f}{\sqrt{2}} \right) \right] \right\}, \tag{48}$$

where $Y_e^{\pm} = W_e^{\pm}/W_2$. Using the Y_e^{+} and Y_e^{-} values, one can calculate the effective drift mobility μ_e;

$$\mu_e = \mu_0 \frac{Y_e^{+} - Y_e^{-}}{xf}. \tag{49}$$

When $1/x \ll f \ll x$ (relatively weak electric fields) from Eqs. (48) and (49) one can obtains

$$\mu_e = \mu_3 e^{-[(\sqrt{2}/2)(\sigma/k_BT)]^2 + (\sigma/k_BT)(eaE/\sigma) - (1/2)(eaE/\sigma)^2}, \tag{50}$$

where $\mu_3 = \mu_0/\sqrt{2\pi} x f^2$ is a power function of the electric field.

Now let us consider the case of strong electric fields and large energetic disorder. Using expressions (40) in the asymptotic case when $f \gg x$ (very strong electric fields), one can obtain $Y_e^{+} = 1$ and $Y_e^{-} = \exp(-xf) \ll 1$. This implies the validity of the inequality $W_e^{+} \gg W_e^{-}$, used above. For this case the mobility [Eq. (49)] can be expressed as

$$\mu_e = \mu_0 \frac{k_BT}{eaE}, \tag{51}$$

implying a field-saturated charge carrier velocity rather than mobility. Note that in this asymptotic case Eq. (51) can also be obtained from Eqs. (48). Thus the obtained expressions (48) for Y_e^{+} and Y_e^{-} describe the electric field dependence of the mobility μ_e over a broad field range in organic solids with moderate to large energetic disorder. It should be recalled that intersection points A and B in Fig. 1 define the transition from a weak to strong energetic disorder.

The correlated disorder model recently attracted much attention due to its ability to explain the Poole-Frenkel-type of the field dependence of mobility in the range of relatively weak electric fields.[23] It assumes that in an organic medium site energies are correlated smoothly, e.g., by charge-dipole (charge-quadrupole) interactions. The analytical results were supported by computer simulations.[21,24,25] In order to account for the correlation effects in the present work, we assume that a cluster of energetically correlated neighbor sites is redefined as an effective hopping site. This decreases the effective concentration of effective hopping sites while the mean distance between these sites increases and becomes the correlation length a_c. The new sites are no longer correlated, but distributed in energy according to the Gaussian function of the width σ_d. Therefore one can use the conventional Gaussian disorder model for the rescaled hopping site system, on the premise of strong disorder (approach II). The correlation length a_c can be considered as a characteristic length r_c which depends on the electric field. This is in accordance with the scaling analysis of Ref. 26. In the case of charge-dipole interaction, $r_c = a\sqrt{\sigma_d^2/2eaEk_BT}$.[26] For calculating Y_e^{+} and Y_e^{-} one has to replace σ by σ_d, x by $x_c = \sigma_d/k_BT \gg 1$, and a by $a_c = a\sqrt{(\sigma_d/eaE)(x_c/2)} > a$, i.e., one should replace x and f by x_c and $\sqrt{f_c x_c/2}$ (where $f_c = eaE/\sigma_d$), respectively, in Eqs. (48) and (50). The original Eq. (50) transforms to

$$\mu_e = \mu_3 e^{-[(\sqrt{2}/2)(\sigma_d/k_BT)]^2 + (\sqrt{2}/2)(\sigma_d/k_BT)^{3/2}(eaE/\sigma_d)^{1/2} - (1/4)(eaE/\sigma_d)}, \tag{52}$$

which can be compared to the empirical expression derived from computer simulations:[21,24,25]

$$\mu_e \propto e^{-[0.60(\sigma_d/k_BT)]^2 + 0.78[(\sigma_d/k_BT)^{3/2} - 2](eaE/\sigma_d)^{1/2}}. \tag{53}$$

Note that the two leading terms in the exponent are virtually identical. The third term in the exponent of Eqs. (50) and (52) is able to describe deviations from the straight line in the $\log \mu$ vs $E^{1/2}$ representation observed by computer simulation (cf. Figs. 2 and 3 in Ref. 24) at larger electric field. Similar calculations might also be performed in the case of charge-quadrupole interaction. It is a demonstration that the EMA approach is able to recover the field dependence of the charge-carrier mobility in a quantitative fashion.

V. CONCLUSION

In the present work an analytical EMA approach was developed to describe the temperature and electric-field dependences of the drift mobility of charge carriers in disordered organic systems under the condition of quasi-equilibrium, i.e., nondispersive transport. Spatial disorder was neglected, and a low degree of energetic disorder was taken into account. Polaronic effects were neglected. Two approaches were considered, based upon either the exact expression derived from the Miller-Abrahams formalism for transition rates for single hopping events (approach I), or the simplified expression (approach II) frequently considered as the so-called Miller-Abrahams model, which ignores phonon emission. It turns out that the exact expression gives a notably weaker temperature dependence of the carrier mobility in comparison to the simplified expression in the considered

temperature range. The physical difference between approaches I and II is that the latter is restricted to the condition when $|\varepsilon_1-\varepsilon_2|\gg 2k_BT$ is valid, while the former is valid for the whole range of energies ε_1 and ε_2 when performing the configuration averaging, i.e., the former approach can properly account for charge-carrier jump rates for any energy spacing of neighbor hopping sites. It turns out that only approach I yields the correct jump rate W_{ij} for systems with a reduced degree of energetic disorder ($\sigma/k_BT\approx 1$). Thus one should use expressions $\mu_e\cong\mu_1\exp[-(3\sigma/5k_BT)^2]$ and $\mu_e\cong\mu_1\exp[-(4\sigma/9k_BT)^2]$ in the cases of strong and weak energetic disorder, respectively (cf. curves 1 and 3 in Fig. 1), rather than the conventional expression[15,16] $\mu_e\cong\mu_0\exp[-(2\sigma/3k_BT)^2]$, to extract the parameter of energetic disorder from the temperature dependence of charge carrier mobility.

The results obtained in the framework of our EMA calculations, using both exact and simplified MA expressions for the case of reduced energetic disorder, are in a good quantitative agreement with experimental observation of very weak temperature dependence of charge-carrier mobility in a conjugated polymer (MeLPPP) with exceptionally weak disorder, noting, however, that only the exact MA expression gives a correct result for the charge carrier drift mobility for $\sigma/k_BT<1$.

To study the effect of the electric field on the drift mobility μ_e we have performed the fully self-consistent EMA treatment, which was similar to that earlier reported in Ref. 22. Using approach I we obtained solutions for calculation of the charge mobility for systems with reduced energetic disorder ($\sigma/k_BT\approx 1$). The results are in good agreement with experimental data on MeLPPP (Ref. 6) and PFO (Refs. 10 and 11) (solid curves in Fig. 3). In the case of very strong electric field, i.e., $f\gg\sigma/k_BT$, our theory predicts the saturation of the drift mobility with increasing field, $\mu_e=\mu_1$. Hence the experimentally observed weak increase of $\mu(E)$ in some conjugated polymers within a broad range of E, can be explained.

Finally, we have applied our EMA theory (using approach II) to calculate the charge-carrier mobility under arbitrary electric fields for a disordered system with strong energetic disorder ($\sigma/k_BT\gg 1$) within the framework of both the Gaussian disorder model and the correlated disorder model. The ubiquitous Poole-Frenkel-type $\ln\mu\propto\sqrt{E}$ dependence, observed in both experiment and Monte Carlo simulations, is recovered. In high electric fields ($f\gg x$) $\mu_e=\mu_0k_BT/eaE$ is asymptotically approached.

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*Corresponding author.

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