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Role of the reorganization energy for charge transport in disordered organic semiconductors

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While it is commonly accepted that the activation energy of the thermally activated polaron hopping transport in disordered organic semiconductors can be decoupled into a disorder and a polaron contribution, their relative weight is still controversial. This feature is quantified in terms of the so-called C factor in the expression for the effective polaron mobility: $\mu_e \propto \exp[-E_a/k_BT - C(\sigma/k_BT)^2]$, where E_a and σ are the polaron activation energy and the energy width of a Gaussian density of states (DOS), respectively. A key issue is whether the universal scaling relation (implying a constant C factor) regarding the polaron formation energy is really obeyed, as recently claimed in the literature [Seki and Wojcik, J. Chem. Phys. **145**, 034106 (2016)]. In the present work, we reinvestigate this issue on the basis of the Marcus transition rate model using extensive kinetic Monte Carlo simulations as a benchmark tool. We compare the polaron-transport simulation data with results of analytical calculations by the effective medium approximation and multiple trapping and release approaches. The key result of this study is that the C factor for Marcus polaron hopping depends on first the degree of carrier localization, i.e., the coupling between the sites, further whether quasiequilibrium has indeed been reached, and finally the σ/E_a ratio. This implies that there is no universal scaling with respect to the relative contribution of polaron and disorder effect. Finally, we demonstrate that virtually the same values of the disorder parameter σ are determined from available experimental data using the C factors obtained here irrespective of whether the data are interpreted in terms of Marcus or Miller-Abrahams rates. This implies that molecular reorganization contributes only weakly to charge transport, and it justifies the use of the zero-order Miller-Abrahams rate model for evaluating the DOS width from temperature-dependent charge transport measurements regardless of whether or not polaron effects are accounted for.

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I. INTRODUCTION

Charge-carrier transport in amorphous organic semiconductors (AOSs) occurs by noncoherent hopping through the manifold of localized states distributed in space and energy, which is commonly described by a Gaussian density of states (DOS) distribution of energetic width σ. The latter is a measure of the energetic disorder that is generally accepted to be a dominant factor governing the charge transport in AOS films. Although the pertinent energetic disorder can account for a broad variety of experimental observations in AOSs, such as the mobility temperature and electric-field dependences, or the transition from nondispersive to dispersive transport regimes upon lowering temperature [1], in some organic systems polaron formation is sometimes taken into account. This is because an organic molecule or a subunit of a conjugated polymer can undergo structural reorganization upon charging. Depending on the value of the reorganization energy, this could result in a significant polaronic nature of charge transport, and consequently, the observed temperature dependence of the carrier mobility may be governed by the superposition of disorder and polaron effects.

Although a large amount of work was done on the description of charge-carrier transport in AOSs for the last decades, an adequate theoretical description of the polaronic transport in disordered media remains challenging. In particular, there has been a long-standing discussion concerning the expression for the effective polaron mobility μ_e obtained for energetically disordered organic semiconductors when using a Marcus-type intersite hopping rate model. The commonly accepted relation, which was heuristically suggested, splits the activation energy of the zero electric field mobility into a disorder and a polaron term. It reads as follows [2]:

$$\mu_e = \mu_0 \exp\left[-\frac{E_a}{k_BT} - C\left(\frac{\sigma}{k_BT}\right)^2\right]. \quad (1)$$

The argument presumes that transport occurs by hopping in a Gaussian-shaped distribution of energy sites, but each jump

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is associated with an additional constant activation energy, that is, the polaron activation energy E_a, which is equal to a quarter of the total reorganization energy associated with the charge transfer ($E_a = \lambda/4$). The prefactor μ_0 is the infinite temperature mobility. What has been in dispute for decades is the numerical value of the C factor (coefficient) which weights the relative contribution of disorder and polaron effects. In their original paper [2], Bässler *et al.* suggested a long time ago to consider the C factor in Eq. (1) as a constant that is determined entirely by the energetic disorder effects and, consequently, to adopt the same value as that derived before for the charge transport in a polaron free system (i.e., $C = 4/9 \approx 0.44$) within the Miller-Abrahams rate model [1]. Recently, this issue was thoroughly investigated [3–5] by combining Monte Carlo simulation studies and analytical calculations using an effective medium approximation (EMA), and a dependence of the C factor on the σ/E_a ratio was shown. The latter effect has also been confirmed by several different theoretical approaches [6–8].

Nevertheless, recently Seki and Wojcik [9] have questioned the variability of the C factor in Eq. (1) and the existence of a nonlinear dependence of the relative weights of polaron and disorder contributions to the hopping transport on the σ/E_a ratio. They performed both kinetic Monte Carlo (KMC) numerical simulations and EMA calculations considering the nearest-neighbor hopping regime. They used Marcus rates and found that the C factor is virtually independent of E_a. A value of $C \cong 1/2$ was obtained by EMA, while the KMC data revealed slightly different values of $C = 0.42$ and 0.5 for three-dimensional (3D) and two-dimensional (2D) transport systems, respectively. This would imply a universal scaling relation for the polaronic mobility with the polaron formation energy. A similar conclusion was also drawn in Ref. [10] where a very weak σ/E_a dependence of the C factor was reported. It is important to mention that the authors of Ref. [9] actually used a simplified Marcus relation, where the prefactor was assumed to be constant.

In the present paper, we reinvestigate the C factor issue on the basis of Marcus theory for polaron hopping rates by combining kinetic Monte Carlo simulations and two alternative theoretical approaches EMA and a multiple trapping and release (MTR) formalism. We have advanced these methods for considering the hopping transport problem for different rates, and obtained the C factor in the context of Eq. (1). Our work brings additional insights to light on aspects related to *polaronic* hopping transport that have not been considered so far. We demonstrate that the C factor turns out to depend on whether transport has reached equilibration or not, and on the degree of carrier localization. Moreover, it changes with the σ/E_a ratio. Thus, our study is in sharp contrast to the notion of a "universal scaling law" recently published by Seki and Wojcik in Ref. [9], and we clarify that and why there is no universal scaling regarding the polaron formation energy. The present results help to build an understanding on the interplay of disorder and polaronic effects, and their quantitative dependence on different transport parameters.

This paper is organized as follows. First, we describe our kinetic Monte Carlo simulation method (Sec. II) and the theoretical formulation of our EMA and MTR analytic approaches (Sec. III). In Sec. IV we present the results of the KMC simulations and the theoretical calculations of the temperature-dependent diffusivity obtained for Miller-Abrahams (MA) and Marcus hopping rates for the nearest-neighbor hopping regime, and the corresponding C factors are evaluated as a function of the σ/E_a ratio. Subsequently we consider the impact of variable-range hopping. In Sec. V we apply our results to reanalyze available experimental data, and a concluding discussion is given in Sec. VI.

II. MONTE CARLO SIMULATIONS

The thermally activated hopping of excitations in a disordered organic solid is studied using a grid-based kinetic Monte Carlo (KMC) method to monitor the motion of excitations as hopping events. We place a particular emphasis on the dependence of the C factor on the σ/E_a ratio and the degree of excitation localization. The excitation can, in principle, be equally well a charge carrier or a triplet exciton since (i) both move by an exchange mechanism, and (ii) the transfer of a triplet can, to first order, be described as a correlated exchange of two charges. The physical meaning of the excitation depends on the value chosen for the energetic disorder and the reorganization energy. The KMC simulations were done by employing an isotropic three-dimensional (3D) simulation box (50×50×50 lattice sites) with a lattice constant of 1.5 nm. Since energetic disorder is inherent to conventional thin-film organic semiconductors, the lattice sites are assigned a random energy drawn from a Gaussian distribution $g(\varepsilon)$ with a standard deviation σ centered at zero energy, i.e., $\varepsilon_0 = 0$.

$$g(\varepsilon) = \frac{N}{\sigma\sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{\varepsilon - \varepsilon_0}{\sigma}\right)^2\right], \tag{2}$$

where N is the density of localized states. To describe the diffusion of excitations through the disordered medium, both Miller-Abrahams (MA) and Marcus hopping rates have been used. This is done to find out whether the hopping process and thus the value of the C factor is altered by the hopping rate chosen for determining the diffusivity of the excitations. The MA hopping rate between an initial site of energy ε_i and final site of energy ε_j is given by [11]

$$\begin{aligned} W_{ij} &= W_0 \exp\left[-\frac{|\varepsilon_j - \varepsilon_i| + (\varepsilon_j - \varepsilon_i)}{2k_B T}\right], \\ W_0 &= \nu_0 \exp(-2\gamma R_{ij}), \end{aligned} \tag{3}$$

where W_0, the MA rate prefactor, is determined by the hopping distance R_{ij}. The inverse localization radius γ is related to the electronic coupling matrix element between adjacent sites. ν_0 is the attempt to escape frequency usually being close to an intermolecular phonon frequency, k_B is the Boltzmann constant, and T is temperature. The parameter γ is assumed to be isotropic in all directions. The MA formalism does not consider any polaronic effects related to the reorganization energy. These effects can be taken into account by considering a semiclassical Marcus-type hopping rate [12,13]:

$$\begin{aligned} W_{ij} &= W_1 \exp\left[-\frac{E_a}{k_B T} - \frac{\varepsilon_j - \varepsilon_i}{2k_B T} - \frac{(\varepsilon_j - \varepsilon_i)^2}{16 E_a k_B T}\right], \\ W_1 &= (J_{ij}/\hbar)\sqrt{\pi/4E_a k_B T}, \end{aligned} \tag{4}$$

where W_1 denotes the Marcus prefactor that, in contrast to the MA rate, depends on temperature. $J_{ij} = J_0^2 \exp(-2\gamma R_{\rm ij})$ represents the electronic coupling, J_0 is the nearest-neighbor coupling constant, E_a is the small-polaron activation energy related to the reorganization energy λ by $E_a = \lambda/4$.

In conventional Monte Carlo simulations, the initial site energy is typically sampled from the DOS distribution centered at $\varepsilon_0 = 0$. Therefore, an excitation generated at a site with arbitrary energy in the DOS first energetically relaxes toward the tail states. While the energetically downward hops are dominant initially, a quasiequilibrium between the thermally activated upward hops and the downward hops is eventually obtained at later times. Therefore, the diffusivity within a disordered semiconductor is time dependent until the excitation has relaxed to a mean equilibrium energy below the center of the DOS ($\varepsilon_{\rm eq} = -\sigma^2/k_BT$). This time dependence, i.e., the nonequilibrium nature of the simulated diffusivity, affects the resulting transport properties [14,15]. Thus, the diffusion coefficient can critically depend on whether the initial energy is chosen from the DOS (centered at 0 eV) or the occupied DOS (ODOS) distribution centered at the equilibrium energy $\varepsilon_{\rm eq}$ below the DOS center, with the same σ. The analytical theories in the present paper (and, in general) are formulated under the premise of equilibrium transport; in order to provide an adequate comparison with the analytical results, our KMC simulations are thus performed under the conditions that the initial energy of an excitation is sampled from a Gaussian ODOS distribution of width σ centered at $\varepsilon_0 = \varepsilon_{\rm eq} = -\sigma^2/K_BT$. Hereafter we refer to this as the "ODOS approach" to distinguish it from the conventional "DOS approach."

At the beginning of the simulation, $t = 0$, an excitation is generated randomly at one of the lattice sites. In the case that the simulation is intended to start with an excitation in the ODOS, the energy of that lattice site is manually adjusted to be part of the ODOS. At each kinetic step, the excitation can hop to any of the nearest-neighbor sites. For the case of variable-range hopping (VRH) simulations, excitations are also allowed to access non-nearest hopping sites. Every permissible hop is treated as an event and for each event i, the rate W_i is calculated. For the selection of an event, firstly, for each event i the partial sum $S_i = \sum_{\beta=1}^{i} W_\beta$ is calculated. A random number φ is drawn from the interval (0, W_T], with $W_T = \sum_{\beta=1}^{N_E} W_\beta$, N_E being the total number of events (permissible hops). From all possible events, the event i for which $S_{i-1} < \varphi \leqslant S_i$ holds is selected. The selected event is executed for the corresponding excitation and the simulation time (t) is updated by the waiting time, $\tau_w = -\ln(X)/W_T$ where X is a random number between 0 and 1. The simulation stops after 10^5 hops. The initial ($t = 0$) and final (after 10^5 hops) position of the excitation in the lattice are used to determine the values for mean diffusivity, $D = \Delta x^2/t$. Results are obtained by averaging over 5000 simulation trials accounting for different disorder configurations. The simulations do not take the effect of conjugation or correlated disorder into consideration.

III. THEORETICAL FORMULATION

A. Effective medium approximation approach

The effective medium approximation (EMA) is an analytic method that has been often used to describe different aspects of the charge transport properties in disordered semiconducting materials. This approach is conventionally used for the nearest-neighbor hopping transport in a periodic cubic lattice of different spatial dimensionalities from one dimensional (1D) to 3D. 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 the localized states, where N is the density of the localized states. We consider that the energy ε of the localized states is randomly distributed and their DOS can be described by a Gaussian function with width σ, represented by Eq. (2). Such kind of DOS distribution is applicable for both charged and neutral excitations (excitons) in organic disordered solids. Polaron effects arising at sufficiently large electron-phonon coupling and/or high enough temperatures can be accounted for by employing the Marcus rate for nonadiabatic hopping transfer given by Eq. (4). Recently, we suggested a generalized EMA approach [5] which is applicable for an arbitrary polaron activation energy E_a compared to the energetic disorder parameter σ. This approach is based on the following self-consistency equation suggested earlier by Kirkpatrick [16] for the effective conductivity $\sigma_e = G_e/a$ characterizing the whole disordered system,

$$\left\langle \frac{\sigma_{12} - \sigma_e}{\sigma_{12} + (d-1)\sigma_e} \right\rangle = 0, \tag{5}$$

where $\sigma_{12} = G_{12}/a$ is conductivity in two-site cluster approximation, d is the dimensionality of the hopping transport system, G_{12} is two-site conductance, and angular brackets $\langle \cdots \rangle$ denote the configuration averaging. The above-mentioned EMA study, similar to that in the paper by Seki and Wojcik [9], was done using a constant Marcus rate prefactor $W_1 = 1$ in Eq. (4). This approach will be hereafter referred to as a "simplified Marcus" rate approach.

In the present work, we performed EMA calculations of the effective diffusion coefficient by using the full Marcus rate equation, i.e., explicitly taking into account the temperature-dependent prefactor. We focus our consideration here on the low carrier concentration transport regime and the limit of weak electric fields, when $eF\Delta R_{ij} \ll \sigma$. ΔR_{ij} is the hopping distance which, implicitly, depends on the energetic disorder. As demonstrated in Ref. [5], the effective diffusivity is $D_e = a^2 W_e$, where W_e is the effective jump rate between neighboring localized sites. It can be derived within the EMA approach by the following integral equation obtained as a result of configuration averaging in Eq. (5):

$$\int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \exp\left[-\frac{1}{2}\left(t_1^2 + t_2^2\right)^2\right] \frac{x^{1/2}\exp\left[-\frac{x}{16x_a}(t_1 - t_2)^2 - \frac{x}{2}(t_1 + t_2) - \frac{1}{2}x^2\right] - X_e}{x^{1/2}\exp\left[-\frac{x}{16x_a}(t_1 - t_2)^2 - \frac{x}{2}(t_1 + t_2) - \frac{1}{2}x^2\right] + (d-1)X_e} = 0, \tag{6}$$

where $X_e = D_e/D_0$, $D_0 = a^2(J/\hbar)\sqrt{\pi/4E_a\sigma}\exp(-x\,x_a)$, $x = \sigma/k_BT$, and $x_a = E_a/\sigma$. It is worth noting that in the EMA approach we use direct configurational averaging over a DOS distribution, which avoids shortcomings involved in the effective transport energy $\varepsilon_{\text{trans}}$ or percolation concepts. The EMA is in particular a suitable method for studying hopping transport in disordered materials with not very large energetic disorder and it naturally allows accounting for the dimensionality of the system.

B. Multiple trapping and release approach

The multiple trapping and release (MTR) theory was initially developed for the description of trap-controlled transport in inorganic semiconductors with band conduction. Thus, according to the MTR, charge carriers can only be transported via conductive delocalized states lying above the so-called mobility edge ε_c. The carriers interact with localized states (traps) through trapping and thermal release. Despite the fact that all electronic states in conventional organic semiconductors are localized, a relatively simple MTR formalism can still be used to describe the hopping transport. The MTR description is commonly based on the concept of the transport energy $\varepsilon_{\text{trans}}$ playing the role of the mobility edge in the classical MTR model. There are two general approaches to defining the transport energy. The first one considers the transport level $\varepsilon_{\text{trans}}$ as a characteristic energy of the states predominantly contributing to the electric conductivity [17–20]. Due to the energetic disorder, such "conductive states" are actually distributed over a certain energy interval. Another approach (the effective transport energy concept) [18,19,21–26] considers the transport level as a parameter in the mean release rate of carriers from rather deep, mostly populated states. This release rate can be approximated in a form similar to the MTR model:

$$\omega(\varepsilon) = \omega_0 \exp\left(-\frac{\varepsilon_{\text{trans}} - \varepsilon}{k_BT}\right), \tag{7}$$

where ε is the energy of the initial state, and ω_0 is the frequency factor which is different from W_0 in Eq. (3).

It should be noted that there are many reports (see, for instance, [17–21,24,25]) on derivations of the transport energy for nonpolaronic hopping transport in Gaussian DOS, which were formulated for the Miller-Abrahams rate. There have been few applications of the effective transport energy concept to the Marcus rate model, except to its truncated form [22,23]. On the other hand, the transport energy approach does not need to be invoked explicitly to apply the MTR method to the hopping transport. Instead, the problem of defining the transport energy can be circumvented in the event that one can split all the available states into "transporting" states, which provide the principal contribution to the transport and "trapping" states, which delay carriers. The former states can be referred to as conductive states in a similar manner to the classical MTR model, and the latter ones can be considered as traps. This idea was proposed long ago by Schmidlin [27]; however, more work needs to be done on developing a general calculation method to obtain transport parameters with this approach. Below, we present our MTR approach, which makes use of this idea by Schmidlin. Our approach is quite general and is suitable for the description of hopping transport irrespective of a jump rate model. We apply it to the analysis of temperature-dependent carrier diffusivity for both MA and Marcus rates in the limit of small carrier concentration and low electric fields. The gist of our approach lies essentially in reducing the well-known master equation of hopping transport [24,27,28] to the balance equation of the MTR model at arbitrary jump rates (see the Appendix for more details).

In practice, we identify a "conductive" state by the condition that the escape time from this state does not exceed a certain time t_0. Since the carrier release is a stochastic process, the probability that a given state is conductive, is determined by the Poisson distribution as

$$\varphi(\varepsilon) = 1 - \exp[-\omega(\varepsilon)t_0] \approx \omega(\varepsilon)t_0, \;\; \omega(\varepsilon)t_0 \ll 1, \tag{8}$$

provided that the critical time t_0 is rather small relative to a typical hopping time. Note that the approximation (7) is not relevant anymore to Eq. (8) and to the subsequent equations. The trap-controlled diffusivity in the MTR approach can then be expressed as [25,29]

$$D = D_c\frac{p_c}{p} \approx (a^2/t_0)\frac{\int_{-\infty}^{\infty} d\varepsilon g_{\text{ODOS}}(\varepsilon)\varphi(\varepsilon)}{\int_{-\infty}^{\infty} d\varepsilon g_{\text{ODOS}}(\varepsilon)}, \tag{9}$$

where p_c and p are the carrier concentration in "conductive" states and the total concentration, respectively. $D_c \approx a^2/t_0$ is the carrier diffusivity in conductive states, $a \approx N^{-1/3}$ is the mean hopping distance in conductive states, and $g_{\text{ODOS}}(\varepsilon)$ is the ODOS distribution proportional to the product $g(\varepsilon)\exp(-\varepsilon/k_BT)$ under quasiequilibrium conditions. The parameter t_0 cancels in Eq. (9) after combining Eqs. (8) and (9), and therefore the diffusivity is proportional to the mean release rate averaged over the ODOS distribution. The resulting relation reads as

$$D \approx a^2\langle\omega(\varepsilon)\rangle = a^2\frac{\int_{-\infty}^{\infty} d\varepsilon\omega(\varepsilon)g(\varepsilon)\exp(-\varepsilon/k_BT)}{\int_{-\infty}^{\infty} d\varepsilon g(\varepsilon)\exp(-\varepsilon/k_BT)}. \tag{10}$$

Further, to determine the mean release rate $\omega(\varepsilon)$ and to consider the variable-range hopping (VRH) regime, we use the *mean hopping parameter* method suggested by Arkhipov *et al.* [30], which is very similar to the method proposed by Apsley and Hughes [31] for a weak electric field and low carrier concentration limit. The function $\omega(\varepsilon)$ can be expressed as follows:

$$\omega(\varepsilon) = \omega_0 e^{-\langle u\rangle(\varepsilon)}, \quad \langle u\rangle(\varepsilon) = \int_0^{\infty} du\, e^{-n(\varepsilon,u)}, \tag{11}$$

where u is the hopping parameter; $n(\varepsilon, u)$ is the average number of target neighbor sites whose hopping rates are not smaller than a given value of $\omega_0\exp(-u)$. An important modification was done here with respect to the previous works [30,31] in order to preclude multiple carrier jumps within pairs of occasionally close localized states: Hopping neighbors for which return jumps to initially occupied states are more probable than jumps to other states are excluded from $n(\varepsilon, u)$. This also implies including the percolation effects [24,32,33] in a first approximation (see the Appendix for details). If the oscillations of a carrier within pairs of localized states are not excluded, then our MTR approach for the MA rate leads to a similar low-field mobility as obtained in

Ref. [30]. This similarity applies within the accuracy of the prefactor a^2, and using the Einstein relation $\mu = eD/k_BT$. It should be mentioned that results of the calculation with Eq. (11) for the MA rates showed that Eq. (7) can be considered as a good approximation for the release frequency $\omega(\varepsilon)$ when the localized states are rather deep, $\varepsilon < \varepsilon_{\text{trans}}$. Upon applying Eq. (7) and the Einstein relation, Eq. (10) reduces to the well-known result from the transport level method: $\mu \approx (e\omega_0 a^2/kT)\exp\,[-\varepsilon_{\text{trans}}/k_BT - 0.5(\sigma/k_BT)^2]$ [17–21,24,25]. However, using Eq. (7) as an approximation is generally inappropriate in the case of the Marcus rate model.

IV. RESULTS

A. C factor in the limit of purely disorder-controlled transport

To find the value of the C factor, which weighs the polaronic and disorder contributions to the temperature dependence of the mobility [Eq. (1)], we first consider simulations of charge-carrier transport using the kinetic Monte Carlo method. We differentiate between two cases, that is, transport in thermal equilibrium, and transport out of thermal equilibrium. It is well known that, in many experimental situations, e.g., in time of flight (TOF) and transient electroluminescence (TEL) measurements, one observes an initial short, sharp spikelike decay of the signal. This is because immediately after carrier injection or creation somewhere within the DOS, the carrier is usually *not* in thermal equilibrium. Rather, it relaxes energetically through a sequence of energetically downhill jumps until a quasiequilibrium transport is achieved, where thermally activated uphill jumps are in balance with downhill jumps. Experimentally, this is visible as a plateau in the intensity of the transient signal. This implies that the carrier moves between states that are energetically distributed, statistically with the same width (σ) as before, yet centered around an equilibrium energy, $\varepsilon_{\text{eq}} = -\sigma^2/k_BT$, below the center of the full DOS. The energetic distribution of these states is referred to as occupied density of states (ODOS). The relaxation behavior is well reproduced in KMC simulations when a carrier is initially placed at a random site within the full DOS. Following the carrier's trajectory implies following the relaxation process [1,14,15]. Transport in thermal equilibrium is reached and monitored eventually, yet long simulation times may be needed to arrive at this stage. A different situation prevails when the carrier moves under equilibrium conditions. This is the case, for example, in charge extraction by linearly increasing voltage (CELIV) experiments. Here, the carrier moves only within the ODOS. In KMC simulations, this can be realized by imposing the condition that the carrier starts its trajectory on a site within the equilibrium distribution, i.e., within the ODOS. The impact of nonequilibrium transport on the diffusivity is thus eliminated. For our KMC study, we consider both transport under equilibrium and out of equilibrium. The analytical EMA method and the MTR formalism in the present study apply only to the case of equilibrium transport.

Here, we first assess the impact of the two different KMC simulation approaches (DOS vs ODOS) on the temperature dependence of a quasiparticle diffusion coefficient (D) within the premise of the *Miller-Abrahams* rate model, using Eq. (3) for the hopping rate. This implies that we neglect any polaronic disorder, corresponding to the situation of $E_a = 0$ in Eq. (1). We expect $\ln(D)$ to be proportional to $-C(\sigma/k_BT)^2$ from Eq. (1), so that the value of C corresponds to the slope in a $\ln(D)$ vs $(\sigma/k_BT)^2$ plot, as shown in Fig. 1. The results obtained for equilibrium transport are compared against those obtained using the EMA method and the MTR formalism in Fig. 1(a). The simulations were done employing our ODOS-simulation method for a lattice representing an isotropic 3D disordered organic system with different widths of the Gaussian ODOS ($\sigma = 50$, 70, and 100 meV), and considering solely the nearest-neighbor hopping (coordination number $N = 6$). Since all excitations are thermally equilibrated right from the start of the simulation, a perfect linear dependence of $\ln(D)$ vs $(\sigma/k_BT)^2$, depicted by a dotted line, is observed over a broad temperature range irrespective of the energetic disorder. The slope of this dependence yields a C factor of about 0.47. The temperature dependences of the diffusion coefficient calculated by effective medium and MTR theories are presented by solid and dashed lines, respectively, and are vertically translated for clarity of display. They demonstrate almost perfect agreement with the KMC simulation data over

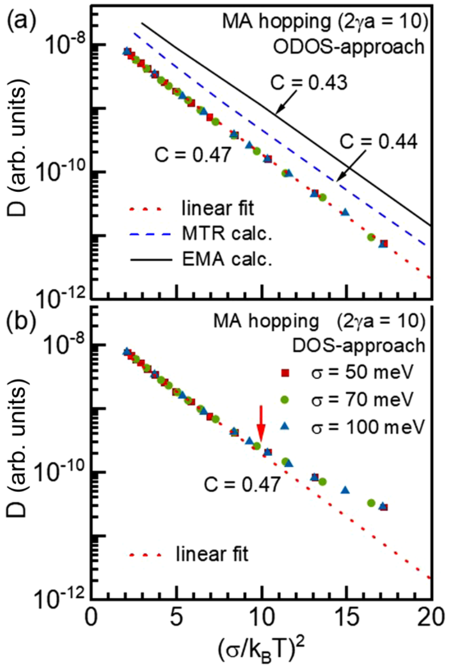

FIG. 1. Kinetic Monte Carlo simulations (symbols) of the diffusion coefficient as a function of disorder-normalized temperature for the *Miller-Abrahams rate* and the nearest-neighbor hopping regime in an isotropic 3D disordered organic system with different energetic disorder values ($\sigma = 50$, 70, and 100 meV, indicated by red squares, green circles, and blue triangles, respectively). The KMC simulations are performed (a) for equilibrium transport, using the ODOS and (b) for nonequilibrium transport, using a conventional DOS as starting distribution. Dotted lines in both figures represent a linear fit to $\ln(D) \propto -C(\sigma/k_BT)^2$. Dashed and solid curves in (a) are the results obtained by MTR and EMA theories, respectively. These calculated curves are shifted vertically relative to each other for clarity. The arrow in (b) depicts the crossover from nondispersive to dispersive transport.

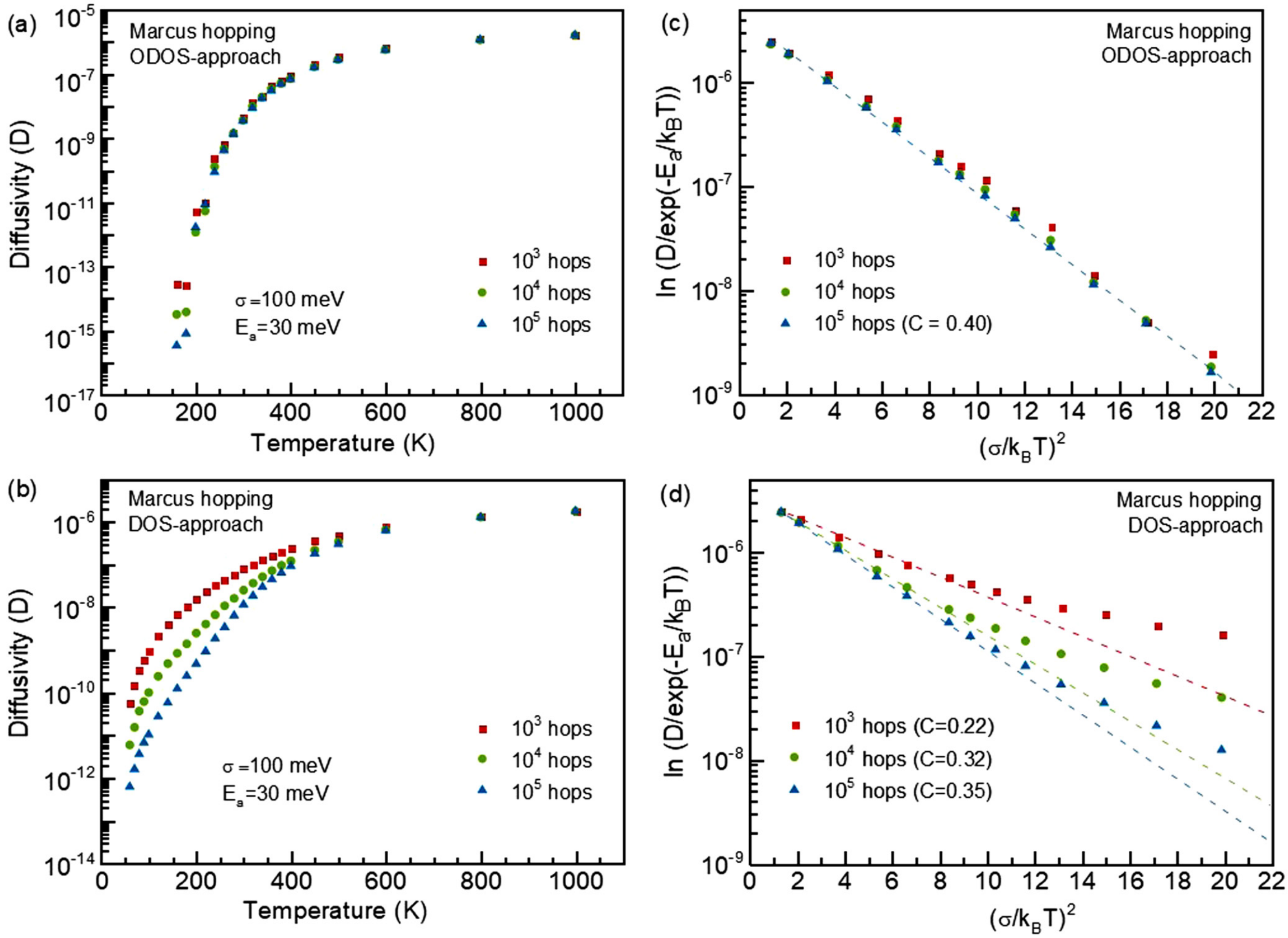

FIG. 2. Temperature dependencies of the diffusion coefficient obtained for the *Marcus rate* by kinetic Monte Carlo simulations (symbols) for the nearest-neighbor hopping in an isotropic 3D disordered organic system at different number of hops during simulations (ranging from 10^3 to 10^5) performed using (a), (c) conventional DOS and (b), (d) equilibrated ODOS-simulation approaches. Simulations are done at $\sigma = 100$ meV and $E_a = 30$ meV. Straight lines in (c), (d) represent the linear fit of the above simulated super-Arrhenius plot (symbols) made in the temperature range where the $\ln[D/\exp(-E_a/k_BT)] \propto (\sigma/k_BT)^2$ law is obeyed.

a broad range of σ/k_BT, yielding virtually the same C factor (0.43–0.44) for the Miller-Abrahams hopping in conjunction with the nearest-neighbor hopping regime. This testifies the reliability of our ODOS-based simulation approach, which can be adequately compared against analytic theories formulated just for the nondispersive transport in disordered organic solids.

Figure 1(b) presents the temperature-dependent diffusivity simulated in the more conventional way, i.e., when the energy of an initial site is sampled from the DOS distribution. The figure demonstrates that the diffusion coefficient obtained by the conventional DOS-simulation approach follows the predicted $\ln(D) \propto -C(\sigma/k_BT)^2$ dependence (depicted by a dotted line) only at relatively low energetic disorder or high temperatures ($\sigma/k_BT \leqslant 3.3$). The dependence progressively deviates from a straight line at larger σ/k_BT values. This is a well expected result indicative of the contribution from the nonequilibrium (dispersive) transport to the simulated diffusivity, which consequently leads to an overestimation of diffusion coefficients at larger σ/k_BT. Hence, the C factor can be derived only from the high-temperature branch of the obtained dependence, where it is 0.47 as in the case of equilibrium transport.

B. *C* factor when a polaronic contribution is considered

Next, we test our equilibrated Monte Carlo simulation approach for the *Marcus rate* model, using Eq. (4) for the hopping rate. This is equivalent to the situation of $E_a \neq 0$, and $\sigma \neq 0$ in Eq. (1). Figures 2(a) and 2(b) show temperature-dependent diffusion coefficients, parametric in the number of hops during simulations, obtained for equilibrium transport (ODOS approach) and nonequilibrium transport (DOS approach), respectively. We used $\sigma = 100$ meV and $E_a = 30$ meV, and hopping is restricted to the nearest-neighbor lattice sites. A general observation is that the diffusivity increases as the temperature increases, and this is accompanied by a decrease in the rate of increment. This is a typical behavior for thermally activated hopping transport [1]. The results for the two simulation approaches differ insofar that for the ODOS approach, representing equilibrium transport, the temperature dependence of diffusivity remains almost identical irrespective of the number of hops after which the diffusion coefficient is evaluated. When plotting $\ln[D/\exp(-E_a/k_BT)]$ vs $(\sigma/k_BT)^2$ such as to readily read off the value of C from the slope in Fig. 2(c), the expected linear dependence (with $C = 0.4$) is obtained irrespective of the number of hops executed by the excitation (with minor deviations at lower number of hops). In contrast, when transport is not in equilibrium, represented by the conventional DOS approach, the temperature dependence of the diffusivity depends on the number of hops executed, and $\ln[D/\exp(-E_a/k_BT)]$ deviates significantly from the linear dependence on $(\sigma/k_BT)^2$, suggesting an overestimation of diffusivity values at lower temperatures [Fig. 2(d)], analogous to the behavior of the diffusivity for the case of MA rates in Fig. 1(b). Moreover, the dependence on the number of hops complicates the determination of the exact C factor even when considering the high-temperature (low σ/k_BT) range since the lower the number of hops, the further away the transport is from equilibrium. Extrapolating the high-temperature regime by linear fits, shown as dashed lines in Fig. 2(d), yields a C factor that increases progressively from $C = 0.22$ (for 10^3 hops) to 0.32 (10^4 hops) and to 0.35 (10^5 hops).

To summarize the results obtained so far, in Sec. IV A we considered the value of C, allowing for only nearest-neighbor hops, for a *purely disorder-controlled* transport for the case of transport both in and out of equilibrium. In thermal equilibrium, the values obtained by three independent approaches, that is, KMC simulation, EMA theory, and the MTR formalism, agree on a value of $C = 0.45 \pm 0.02$. Out of thermal equilibrium, KMC predicts a lower value that depends on the deviation from the equilibrium situation. In Sec. IV B we extended our KMC study to the case of transport in a disordered energy landscape *with consideration of reorganization energy*, exemplarly using $\sigma = 100$ meV and $E_a = 30$ meV ($\frac{\sigma}{E_a} = 3.3$). A value of $C = 0.40$ is approached asymptotically as carriers reach thermal equilibrium. This value is lower than what we obtained for the case when polaronic contributions are neglected. In the next section, we focus on the dependence of the C factor on the relative size of the disorder to the reorganization energy, still restraining our simulations to nearest-neighbor hops.

C. Impact of the reorganization energy on the *C* factor

Having seen that the value of the C factor is modified when a polaronic contribution to the transport is taken into account, we systematically addressed the dependence of the C factor on the magnitude of the polaronic contribution. Figure 3 presents the C factor as a function of the σ/E_a ratio. As before, we used the Marcus-type hopping rate in the presence of disorder, Eq. (4), and allowed only for nearest-neighbor hops. In addition to the results obtained for equilibrium (ODOS) and nonequilibrium (DOS) transport, we show the results from the MTR formalism and the EMA calculations, which treat the equilibrium situation. For comparison, we also include the values obtained with the simplified Marcus expression used previously by Seki and Wojcik [9], where the preexponential factor [W_1 in Eq. (4)] is approximated by a constant ($W_1 = 1$).

For all approaches we obtain the same qualitative result, that is, that the factor C increases with increasing σ/E_a ratio, i.e., with increasing the relative strength of the disorder effect. This is in line with our previous finding [5]. We note that the C factor obtained under inclusion of polaronic effects is always smaller than that obtained using a pure Miller-Abrahams rate ($C \cong 0.44$). Evidently, any contribution from geometric reorganization of the molecule reduces the relative weight of the disorder contribution to transport. However, in the limit of vanishing E_a, exemplified by the data point at $\sigma/E_a = 10$ in Fig. 3, the MA result is recovered asymptotically.

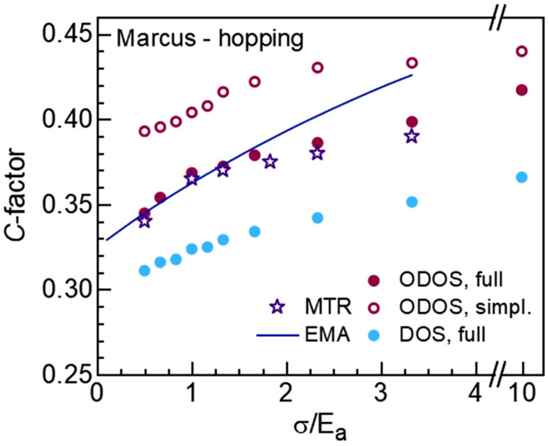

FIG. 3. C factor vs σ/E_a derived from kinetic Monte Carlo simulations of the nearest-neighbor hopping diffusivity $D(T)$ using a Marcus rate in an isotropic 3D system and $2\gamma a = 10$. Also shown are results from analytic MTR and EMA calculations. The KMC simulations marked “DOS, full” refer to the case of nonequilibrated transport; all other data are obtained for transport under equilibrium. For comparison, values obtained using a Marcus-type hopping rate with a constant preexponential factor is also shown (“ODOS, simpl.”)

Regarding the results, we again find a gratifying quantitative agreement between the three different equilibrium nearest-neighbor hopping (NNH) approaches used, that is, the KMC simulation (ODOS), the MTR formalism, and the EMA calculations, as depicted in Fig. 3 by stars and solid line, respectively. As expected, the EMA calculations agree with simulation data only at low to moderate energetic disorder ($\sigma/E_a < 2$), where EMA formalism is more justified. In the present study we used a conventional EMA approach based on a self-consistency equation (5), which is not suitable for a strongly inhomogeneous medium, or in other words, for high disorders. This explains the disagreement between the KMC ODOS simulations and EMA at large σ/E_a values [34]. The agreement between the three different and independent approaches gives confidence in the absolute values obtained for the factor C.

Analogous to the results in the previous sections, calculations carried out using a conventional KMC approach, where the carrier is placed at random in the DOS and then relaxes, yield a reduced value of the factor C as compared to the ODOS approach, i.e., a lower contribution of the disorder to transport, depending on how far from equilibrium the transport takes place. In contrast, an increased value of the factor C is obtained when the Marcus-type hopping rate is simplified by assuming a constant prefactor. We obtain principally the same results as that obtained before for $W_1 = 1$ in the paper by Seki

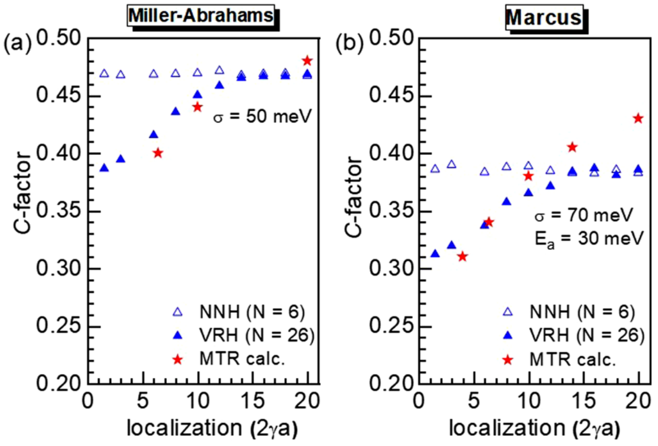

FIG. 4. The C factor as a function of localization derived from kinetic Monte Carlo simulations of hopping diffusivity $D(T)$ in both the nearest-neighbor hopping (empty symbols) and variable-range hopping (filled symbols) regimes using (a) a Miller-Abrahams or (b) a Marcus-type hopping rate. Results of analytic MTR calculations in the VRH regime for MA and Marcus rates are shown by red stars in (a), (b), respectively.

and Wojcik [9]. Evidently, this simplification is a rather coarse approximation that overestimates the C factor.

D. *C* factor in variable-range hopping (VRH) regime

The nearest-neighbor hopping (NNH) considered in the preceding section was modeled assuming just six nearest neighbors of a site i on a cubic 3D lattice ($N = 6$). However, it is well known that hops between the non-nearest-neighboring sites can also contribute to the hopping transport. This is described by variable-range hopping (VRH) [6] which is a more general approach and considers transitions of carriers to further neighbors than the nearest ones. Here VRH was implemented in the KMC simulations by allowing long-distance jumps to as many as $N = 26$ neighbors in total, i.e., up to the third-nearest neighbor. The probabilities of such jumps are determined by the carrier localization parameter ($2\gamma a$). Figure 4 presents the C factor obtained as a function of $2\gamma a$, with larger values implying stronger localization. Simulation results are shown for jumps to the third-nearest neighbor ($N = 26$ sites), thus enabling the VRH regime (filled triangles), and they are compared to those allowing for hopping to next-nearest neighbors ($N = 6$, empty triangles). We only considered the case of equilibrium transport, once for purely disorder-controlled transport, using a Miller-Abrahams type hopping rate [Eq. (3)] and once when including polaronic effects through a Marcus-type hopping rate [Eq. (4)]. Also shown are values obtained using the MTR formalism. For the EMA calculations that we used in the previous section, a distinction between NNH and VRH cannot be implemented explicitly.

As expected, no dependence of the C factor on the localization length was observed for the case of NNH because this regime is preserved at $N = 6$ irrespective of the inverse localization length (γ) value. On the other hand, Figs. 4(a) and 4(b) demonstrate a clear decrease in C factor with decreasing $2\gamma a$ in the VRH regime as found by both the KMC simulations (filled triangles) and the MTR theoretical calculations (stars). At large localization, the values converge to the value of NNH for all the simulations, which is a trivial observation, since at large localization or very poor electronic coupling, the NNH regime becomes dominating. We note the difference between the KMC and the MTR obtained values for C in the limit of large localization. While this is a minor effect for pure disorder-dominated transport, it is significant when polaronic contributions are included. We speculate whether in this case, MTR is less suitable, since the distinction between "transporting" and "trapping" states, on which this formalism is based, becomes blurred [33].

Overall, the results obtained so far have demonstrated that

(i) There is very good agreement between three approaches for the C factor for equilibrium transport. Depending on conditions, values range from 0.30 to 0.47.

(ii) The value of the C factor decreases when transport is out of equilibrium.

(iii) The value of the C factor decreases when reorganization contributes to the transport.

(iv) The value of the C factor decreases when the wave function of the charge or excitation is less localized.

This behavior is not consistent with the notion of a "universal scaling law," at least not in the strict mathematical sense. For practical purposes, one may consider that, in thermal equilibrium, the values for C range around 0.40 ± 0.05. We shall therefore evaluate the impact of this variation in the next section.

V. ANALYSIS OF EXPERIMENTAL DATA

The theoretical and simulation results obtained in the previous sections are utilized here to analyze earlier experimental transport data. A frequently encountered albeit problematic procedure adopted in the community to obtain the polaronic activation energies (E_a) for transport is to analyze the $1/T$ dependence of zero-field mobility using Eq. (1) presuming zero disorder, i.e., Eq. (12a). Similarly, the energetic disorder can be obtained by analyzing the temperature dependence of the zero-field mobility ($1/T^2$ dependence) assuming $C = 0.44$ within a purely disorder-controlled MA formalism, i.e., $E_a = 0$, as established by previous KMC and EMA approaches [1]; see Eq. (12b):

$$\mu(T) = \mu_0 \exp\left[-\left(\frac{E_a}{k_B T}\right)\right], \tag{12a}$$

$$\mu(T) = \mu_0 \exp\left[-0.44\left(\frac{\sigma}{k_B T}\right)^2\right]. \tag{12b}$$

However, this procedure has serious shortcomings, because disorder and reorganization energy are entangled, as reflected in the use of the unified model, Eq. (1).

In this section, we illustrate how much difference can be expected in the σ and E_a values when using different formalisms to fit the data. For this assessment, we analyze the temperature dependence of the zero-field TOF mobility for holes in a series of conjugated alternating phenanthrene indenofluorene copolymers reported by Hoffmann *et al.* [35]. We analyze four copolymers from this paper labeled as

TABLE I. E_a and σ values obtained from fitting with Eq. (12). Also given are E_a values obtained from DFT calculations (from Ref. [35]).

Copolymer	E_a (meV) by Eq. (12a)	σ (meV) by Eq. (12b)	E_a (meV) by DFT
1	178 ± 2	109 ± 2	46
3	235 ± 2	102 ± 2	38
7	329 ± 2	89 ± 2	25
9	397 ± 2	91 ± 2	31

copolymers 1, 3, 7, and 9 (see Sec. 1 of the Supplemental Material [36] or Ref. [35] for chemical structure). For reference, we quote in Table I the values obtained in Ref. [35] from fitting the mobilities of the copolymers with Eq. (12).

As discussed in detail in Ref. [35], it turns out that the σ values obtained from Eq. (12) are consistent with those obtained by other methods, while the E_a values are unrealistically large. Thus, one needs to obtain estimation for E_a by other means, such as density-functional theory (DFT) calculations.

If we wish to assess how the values derived for σ and E_a depend on the C factor used, a straightforward test is therefore to take the DFT-calculated E_a value and subsequently employ Eq. (1) to determine σ for several values of C. Figure 5(a) presents the experimental mobility data reported by Hoffmann *et al.* [35] (symbols) plotted against $1/T^2$ on a semilogarithmic scale. The solid lines are the corresponding fits done using Eq. (1) with $C = 0.40$ and using the DFT-calculated E_a values summarized in Table I. A comparison of the fits to the experimental data with Eq. (1) for $C = 0.35,\ 0.40,$ and 0.44 is shown exemplarily for copolymer 1 in Fig. 5(b). It illustrates that the fits with different approaches coincide perfectly and are almost indistinguishable. Given the limited temperature range from 300 to 350 K for which the mobility was determined, this is expected. The data for copolymers 3, 7, and 9 agree similarly well and are shown in Sec. 2 of the Supplemental Material [36]. The disorder parameters obtained as a result of fittings are summarized in Table II.

We observe that the σ values obtained when using a pure MA approach, Eq. (12b), or a unified approach, i.e., Eq. (1), with different values for C differ by less than 10% from each other. This is within the typical experimental error range (note that the error given refers to the fitting procedure). Our result implies that the consideration of the polaronic contribution to the transport description, and the question of how much weight this should be given, is *not* critical for the determination of the disorder value as long as C ranges around $C = 0.40 \pm 0.05$.

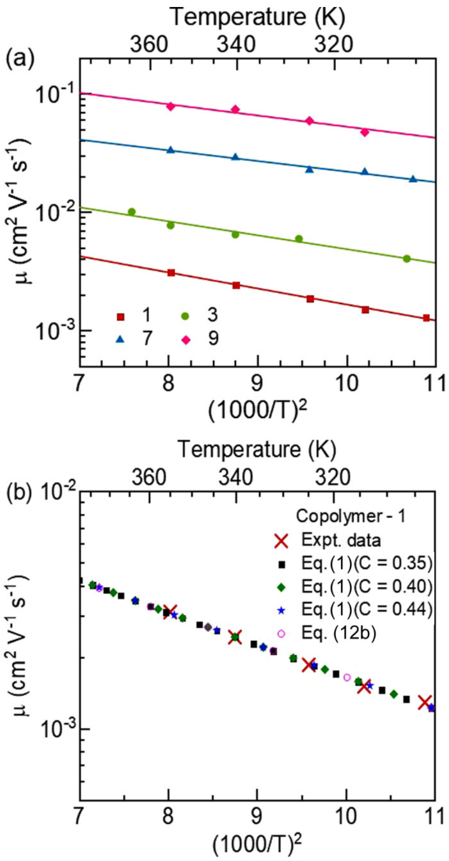

FIG. 5. (a) The temperature dependence of the mobility plotted as μ vs $1/T^2$ on a semilog scale, along with the zero-field TOF mobility for copolymers 1 (red squares), 3 (green circles), 7 (pink triangles), and 9 (blue diamonds) as reported in Ref. [35]. Solid lines represent the fitting results using Eq. (1) with $C = 0.40$ and E_a values presented in Table I. (b) Comparison of the fits done by using Eq. (1) with $C = 0.35,\ 0.40,$ and 0.44, and by using Eq. (12b) (MA rate).

However, a very different result is obtained when the disorder value from the pure MA approach is used in Eq. (1), and E_a is determined parametric in the C factor. Table III summarizes the values obtained. The fits to the experimental data are as good as in Fig. 5. They can be found in Sec. 2 of the Supplemental Material [36] for reference. However, the

TABLE II. The σ values obtained from fitting with Eq. (1), using the DFT-calculated E_a values from Table I.

Copolymer	σ (meV) by Eq. (1), $C = 0.35$	σ (meV) by Eq. (1), $C = 0.40$	σ (meV) by Eq. (1), $C = 0.44$
1	116 ± 2	108 ± 2	103 ± 2
3	108 ± 2	101 ± 2	96 ± 2
7	95 ± 2	89 ± 2	85 ± 2
9	97 ± 2	91 ± 2	86 ± 2

TABLE III. E_a values obtained from fitting with Eq. (1), using σ values from Table I.

Copolymer	E_a (meV) by Eq. (1), $C = 0.35$	E_a (meV) by Eq. (1), $C = 0.40$	E_a (meV) by Eq. (1), $C = 0.44$
1	78 ± 2	35 ± 2	0 ± 2
3	69 ± 2	33 ± 2	0 ± 2
7	50 ± 2	21 ± 2	0 ± 2
9	54 ± 2	24 ± 2	0 ± 2

E_a values span a much wider range, implying that the fitting approach has a huge effect. This demonstrates that the value obtained for E_a depends more strongly on the correct choice of the C factor than the values obtained for σ. It seems that the range of values obtained using Eq. (1) with $C = 0.40 \pm 0.03$ is reasonably realistic (cf. Sec. 3 of the Supplemental Material [36] for detailed discussion), while a full neglect of disorder contributions as in a pure Marcus model, Eq. (12a), results in values that are at variance with other experiments.

VI. DISCUSSION AND CONCLUSIONS

This study illuminates several points regarding the description of charge transport. It clarifies that the relative contribution of polaron and disorder effects to the charge-carrier mobility, as quantified through the value of the C factor, depends on various factors.

One aspect is whether charge transport takes place *in equilibrium or out of equilibrium*: The further away the transport is from equilibrium, the lower is the contribution of disorder, and thus the lower is the C factor. It is straightforward that disorder should play a lesser role when hops occur mostly downward in energy. One may need to bear this in mind when analyzing experimental data where transport is far out of equilibrium, e.g., on very short timescales after carrier generation. Our study, notably Figs. 1 and 2, indicates that this is of relevance to both MA as well as Marcus rates. Correspondingly, it can become important to perform the KMC calculations under equilibrium conditions, e.g., by starting from the ODOS distribution instead of the full DOS, if one wishes to obtain a reliable value that is independent of simulation time or temperature. This is an important insight, as most available KMC simulations are premised on the condition that the initial energy of an excitation is sampled from a DOS distribution.

Another aspect is that the value of the C factor depends on the *ratio between the reorganization energy and the disorder*. This had been noted before by several groups [5,6,22], though there are also disagreeing calculations [9]. The gratifying feature in our work is the quantitative agreement of $C(\sigma, E_a)$ obtained via three independent approaches, that is, KMC simulations, EMA calculations, and the MTR formalism. As discussed above, EMA calculations apply to the range of lower disorder values, while the MTR formalism is more meaningful for the range of higher disorder values where the distinction between conducting and trapping states is maintained. KMC applies over the entire range of disorder values, though for comparison with the EMA and MTR formalism, one needs to ensure that the simulation is conducted for the quasiequilibrium case. In this context, we noticed the importance of using the full Marcus-type hopping rate, i.e., including the temperature-dependent prefactor. The evolution of $C(\sigma, E_a)$ was only rendered consistently between the three approaches when using Eq. (4) with the temperature-dependent prefactor. This may account for the difference to the work by Seki and Wojcik, who assumed a constant Marcus prefactor [9].

A further aspect concerns the dependence of the C factor on the *delocalization of the carrier wave function*. We revealed the effect of the degree of carrier localization in organic semiconductors on the C factor for Marcus polaron hopping. It was found to feature a qualitatively similar trend to that obtained for MA hopping of nonpolaronic carriers (Fig. 4). In both cases the weak carrier localization gives rise to a significantly lower C factor. This is equivalent to the earlier noticed dependence of the C factor on lattice geometry, coordination number, or dimensionality [37–39]. Our study implies a reduced contribution of disorder when more lattice sites are accessible for transport. It is easy to see that disorder should matter less when a particular energy barrier can simply be circumvented by a different pathway, so that increases in dimensionality, coordination number, or accessible neighbor sights all reduce the contribution of disorder. This aspect is easily overlooked, and perhaps not always sufficiently appreciated. For example, in our earlier work [5], we reported a stronger dependence of the C factor on σ/E_a than here. The reason is that in the earlier work, the lattice chosen was not a strictly simple cubic lattice but a slightly orthorhombic one. This was done in order to match the experimental conditions and it resulted in a stronger evolution of $C(\sigma, E_a)$. This dependence on dimensionality and available lattice sites implies that the distribution of chromophores in a film, and in particular, any existence of partial order, will have a significant impact on the appropriate value of the C factor.

Given the variation of the C factor with experimental conditions, one may question what can be learned from an analysis of temperature-dependent mobility data in the framework of Eq. (1). The investigation we performed clearly indicated that such an analysis provides a reasonable basis for the assessment of disorder using a C factor of $C = 0.40 \pm 0.03$. "Reasonable" means here that the values are within 10% of each other and the value obtained from a pure MA approach, and agree with any other information available from experiments [35]. In this way, our work eventually provides a "legitimization" for the use of the simple MA rate model to the description of the charge transport in realistic disordered organic solids. This is a key message of our paper, especially relevant for experimentalists, who routinely use the Gaussian disorder model (GDM) for their data analysis and naturally want to know to what extent this zero-order approach is accurate in determination of the width of the DOS. We emphasize that Eq. (1) with $C = 0.40 \pm 0.03$ is fully applicable only when the carrier transport is in quasiequilibrium. This is when $(\sigma/k_BT)^2 < 10$, i.e., $\sigma/k_BT < 3.3$ as evident from Figs. 1 and 2. Experimentally, these conditions are usually fulfilled for CELIV measurements or for nondispersive TOF measurements where the plateau and the subsequent kink in the current transients are clearly visible. Note that our conclusion about the appropriateness of the MA rate is consistent with the recent finding by de Vries *et al.* in Ref. [40] based on full quantum mechanical treatment; however, in our work the problem was tackled from the standpoint of established hopping-transport theories and computer simulations. As also mentioned by de Vries, the values obtained for the reorganization energy are significantly less reliable. Typical values of the reorganization energy in conventional organic semiconductor have been estimated as $\lambda = 100$–200 meV [40].

Further, we would like to note that, although the impact of carrier equilibration on the C factor was indeed shown before for the case of nonpolaronic transport (MA rates), it has rarely been considered for the polaronic hopping transport given by the Marcus rate. Also, the effect of the degree of carrier localization in organic semiconductors on the C factor was not reported before for the Marcus hopping rate, while it has been demonstrated for the nonpolaronic transport regime. In addition, almost all theoretical efforts in the description of variable-range hopping (VRH) in organic semiconductors were based so far just on the MA rate model and the VRH remains virtually unexplored for the Marcus rate model. Our work resolves the long-standing controversy regarding the C factor and explains why different values were obtained in the literature. We identify differences in the approaches used in the previous works and their specific aspects leading to the contradictory results.

Our initial question on how strongly the reorganization energy contributes to charge transport in disordered organic semiconductors may thus be answered in a brief way as "not much." The polymers of Ref. [35] that we used as experimental example are typical conjugated polymers insofar that their backbones consist of bridged or fused, i.e., rigid, phenyl rings as well as more flexible triphenylamines. They have a disorder parameter around 100 meV and an E_a of less than 50 meV, i.e., a reorganization energy λ of less than 200 meV. These values can be considered as representative. We found that entirely ignoring the polaronic contribution by analyzing the $\mu(T)$ data in terms of the simple Gaussian disorder model overestimates the disorder by roughly 10%. This can be taken as an indication that the polaronic contribution is small.

Finally, in the present paper we made important methodological advancements in both analytical treatment and computer simulations of polaron transport. In particular, we have extended the multiple trapping and release (MTR) theoretical approach to describe the Marcus polaron hopping. An important advantage of the suggested approach is that it allows avoiding the transport energy (TE) concept, as the calculation of the TE for Marcus rates turned out to be very problematic, which is in contrast to MA rates where this concept is conventionally used. Further, we have improved the algorithm of kinetic Monte Carlo simulations (KMC) to consider adequately the equilibrated polaron transport in a Gaussian DOS, which can be ensured under the conditions that the initial energy of an excitation is sampled from a Gaussian occupational DOS (ODOS) distribution shifted by the equilibrium energy below the DOS center. We found that this aspect has a significant impact on the polaron transport, which has normally been overlooked in previous relevant KMC simulation studies.

ACKNOWLEDGMENTS

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APPENDIX: APPLICABILITY OF THE MULTIPLE TRAPPING MODEL TO THE DESCRIPTION OF HOPPING TRANSPORT

We start from the well-known master equation of hopping transport for the occupation probability, f_i, of the ith hopping state [24,28],

$$\partial f_i/\partial t = \sum_{j\neq i}[\nu_{ji} f_j(1-f_i) - \nu_{ij} f_i(1-f_j)], \qquad \text{(A1)}$$

where ν_{ij} is the hopping rate of a carrier from the ith state to the jth state. We assume that the release of carriers from the rather deep states i, the rate of release from which determines the magnitude of diffusivity and mobility, occurs preferably to relatively shallow energy states j having very low occupation probability, $f_j \ll 1$. This contrasts with the mechanism of the Mott-type conductance near the Fermi level, which might typically be realized in the low-temperature limit and is not considered here [25]. The low occupation probability results from low mean occupation time of these states, since most of the jumps per unit time occur via these shallow j states. Particularly, capture of carriers by the deep i states occurs from these "fast" j states. Further, we assume that the population of the "fast" states (of the energies ε_j) can be described by the quasiequilibrium Boltzmann's function, $f_j = f_0\exp[-\varepsilon_j/k_BT]$. At the same time, the deep states of the energies ε_i can be filled with much higher probability $f_i \cong 1$; their population can also be far from a quasiequilibrium distribution if the initial energy distribution of the carriers is not equilibrated as a consequence of a rather small number of the release events from i states. Using the detailed balance principle, $\nu_{ji} = \nu_{ij}\ \exp[(\varepsilon_j - \varepsilon_i)/k_BT]$, and introducing the symbol $\omega_i = \sum_{j\neq i}\nu_{ij}$, one can rewrite the balance equation (A1) as follows:

$$\partial f_i/\partial t = f_0(x,t)\exp[-\varepsilon_i/k_BT](1-f_i)\omega_i - f_i\omega_i, \qquad \text{(A2)}$$

where x is the set of spatial coordinates. One may assume that the prefactor f_0 in Eq. (A2) is j independent, provided that the spatial scale and timescale of variations of this prefactor is much larger than several hopping lengths and several hopping times, respectively.

The magnitude of the release frequency of a carrier from the state i, ω_i, not only depends on its energy, ε_i, but also on other characteristics (such as energies, distances, and orientations) of the surrounding states. It is known from percolation theory that the states, which contribute to the transport predominantly, form a network with some characteristic size r_{c0} (correlation radius of percolation cluster) [32–34]. One can simplify the description of transport, provided that the function f in Eq. (A1) is averaged on the spatial scale of r_{c0} (which is temperature and disorder dependent) and on the respective timescale, t_{c0} (the diffusion time for the distance r_{c0}). One can select the "conductive" states among the "fast" states by relating the prefactor $f_0(x,t)$ and the concentration of carriers (the "mobile" carriers) in these states, $p_c(x,t)$,

$$f_0(x,t) = p_c(x,t)/N_c, \qquad \text{(A3)}$$

where N_c is an effective concentration of "conductive" states. This concentration does not depend on coordinates and time due to quasiequilibrium occupation of conductive states and macroscopic uniformity of the material. The other "fast" states and i states are considered below as traps (the shallower and the deeper fraction, respectively). Then one can rewrite Eq. (A2) in the continual form, introducing the spatially uniform energetic distribution function of traps $g_t(\varepsilon)$, energy-dependent release frequency $\omega(\varepsilon)$ instead of ω_i, the averaged occupation probability $f(\varepsilon, x, t)$, and the distribution of occupied traps $\rho(\varepsilon, x, t) = g_t(\varepsilon) f(\varepsilon, x, t)$. Multiplying Eq. (A2) by $g_t(\varepsilon)$, and using Eq. (A3), one obtains the balance equation of the MTR model [29],

$$\frac{\partial \rho(\varepsilon,x,t)}{\partial t}\frac{1}{c(\varepsilon)} = [g_t(\varepsilon) - \rho(\varepsilon,x,t)]p_c(x,t) - N_C\rho(\varepsilon,x,t)\exp\left(\frac{\varepsilon}{k_BT}\right), \tag{A4}$$

where $c(\varepsilon) = [\omega(\varepsilon)/N_C]\exp(-\varepsilon/k_BT)$ is the capture rate of a carrier on a trap of given energy. A model of hopping rates, ν_{ji}, defines only the shape of the function $\omega(\varepsilon)$, and hence $c(\varepsilon)$, and the value of N_C. One can find the latter value from the equation which follows from Eq. (A3) and the definition of the function, $\varphi(E)$; see Eq. (8),

$$p_c(x,t) = \frac{p_c(x,t)}{N_C}\int_{-\infty}^{\infty} dE\, g(\varepsilon)\varphi(\varepsilon)\exp\left(-\frac{\varepsilon}{k_BT}\right), \tag{A5}$$

eliminating $p_c(x,t)$ from both sides of this equation. Since $\varphi(\varepsilon) \approx \omega(\varepsilon)t_0$, hence $g_t(\varepsilon) \approx g(\varepsilon)$. Provided that $p(x,t) \approx \int_{-\infty}^{\infty} d\varepsilon\, \rho(\varepsilon,x,t)$, under quasiequilibrium Eq. (A4) yields

$$p(x,t) = p_c(x,t)\int_{-\infty}^{\infty} dE\frac{g(\varepsilon)}{N_C}\exp\left(-\frac{\varepsilon}{k_BT}\right). \tag{A6}$$

Equation (10) follows from Eqs. (9), (A5), and (A6).

Thus, one needs to calculate the release frequency $\omega(\varepsilon)$ for defining $c(\varepsilon)$ and N_C in Eq. (A4). In this work, we calculate it from Eq. (11), where

$$n(\varepsilon,u) = \iint_{\Omega(\varepsilon,u)} d\varepsilon' d^3r g(\varepsilon')P(\varepsilon,\varepsilon',u), \tag{A7}$$

where the integration volume $\Omega(\varepsilon,u)$ in the $\varepsilon' - r$ space (r is the distance to a neighbor state and ε' is its energy) is defined by the condition that the hopping rate from the initial state to any state in this volume is not smaller than a given value, $\omega_0\exp(-u)$, where u is the hopping parameter; $P(\varepsilon,\varepsilon',u)$ is the probability that the jump is not followed by returning to the initial state (of the energy ε):

$$P(\varepsilon,\varepsilon',u) = \begin{cases} 0, & n_0(\varepsilon',u') \leqslant 1 \\ 1 - e^{-[n_0(\varepsilon',u')-1]}, & n_0(\varepsilon',u') > 1 \end{cases}, \tag{A8}$$

where $u'(\varepsilon,\varepsilon',u) = u + (\varepsilon - \varepsilon')/k_BT$ is the hopping parameter for the returning jump, and

$$n_0(\varepsilon,u) = \iint_{\Omega(\varepsilon,u)} d\varepsilon' d^3r g(\varepsilon'). \tag{A9}$$

Thus, the neighbor states, for which the initial state is the nearest hopping neighbor (in u space), are not considered. The term $n_0 - 1$ appears in Eq. (A8), because one state (the initial state) definitely persists for the most relevant (i.e., upward in energy) jumps. The integration volume Ω depends on the model of hopping rates (for example, MA or Marcus).

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