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Field dependence of the mobility in organic insulators with a generic Gaussian correlation between the site energies

José A. Freire
Departamento de Física, Universidade Federal do Paraná, 81531-990, Curitiba-PR, Brazil

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We analyze a master equation model for the time-of-flight experiment in an organic material where the internal transport is due to thermally activated hops between localized molecular orbitals. An expression for the transit time of a photocreated carrier across a finite one-dimensional sample is obtained in terms of the orbital energies and the microscopic hopping rates. Two forms of hopping rates commonly used in the literature are considered, the Miller-Abrahams rate and the small-polaron or Marcus rate. The average of the transit time expression with respect to an arbitrary, correlated, Gaussian distribution of molecular orbital energies is obtained exactly for both forms of rates. We use this averaged expression to investigate how different forms of energetic correlations and of hopping rates leave their imprint on the field dependence of the mobility. We find that a Poole-Frenkel field dependence of the mobility at low fields is obtained both with a power-law and with an exponential correlation, moreover, the factor γ in $\mu \sim \exp(\gamma\sqrt{E})$ is obtained and we find that its temperature dependence does not distinguish between the two forms of energetic correlation. The form of the hopping rate only manifests itself in the mobility at fields above a certain critical field whose expression for an arbitrary form of correlation is explicitly obtained.

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I. INTRODUCTION

The mobility of charge carriers in organic materials is a determining factor in the performance of organic devices. Mobility measurements, mainly using the time-of-flight technique, suggested the following mobility with a Poole-Frenkel (PF) field dependence

$$\mu = \mu_0 \exp[-\Theta(T)]\exp[\gamma\sqrt{E}]. \tag{1}$$

In the form proposed by Gill,[1] $\Theta = \Delta_0/kT$ and $\gamma = B(1/kT - 1/kT_0)$.

The modeling of organic insulators has a milestone in the Gaussian disorder model (GDM). This model describes the disordered organic as a set of localized states with energies distributed Gaussianly and with transport between sites ocuring via thermally activated hops. The model rely heavily on Monte Carlo simulations as a computational tool. In the first works with this model[2] it was claimed that the numerical results contained a field dependent mobility in the form $\mu \sim \exp(E/E_0)$. As more experiments were done, all poynting to a PF field dependence in the form of Eq. (1), the numerical results were reinterpreted and a PF field dependence were claimed to be present,[3] although in a very narrow range of fields.

As studies of the GDM later showed, it is necessary to include correlations in the distribution of site energies in order to obtain a mobility with a PF field dependence over the range of fields observed in the experiments. Garstein and Conwell[4] analyzed numerically a three-dimensional (3D) model with short-range correlations, Dunlap and co-workers[5] studied analytically a one-dimensional (1D) model with power-law correlations originated from the interactions of the carriers with randomly oriented dipoles, their findings were later confirmed by a 3D simulation.[6] Yu and co-workers[7] studied analytically a 1D model where the source of energetic correlation were the thermal fluctuations on the molecular geometries, the energetic correlation in this model decays with distance as the Yukawa potential but the authors studied essentially its power-law limit, their findings were confirmed by 3D simulations on the same paper. Finally Parris and co-workers[8] studied the power-law correlations with using a small-polaron rate, both analytically in 1D and numerically in 3D.

The power-law correlations studied in Refs. 5–8 showed that there is a difference in the PF factor γ predicted by the analytical 1D models and by the 3D numerical simulations. In 1D one obtains $\gamma \propto C/(kT)^{3/2}$, whereas the 3D numerical experiments suggest $\gamma \propto C'[1/(kT)^{3/2} - 1/(kT_0)^{3/2}]$, something more similar to the form proposed empirically by Gill,[1] albeit with a different temperature exponent.

Based on these results one may ask whether the power-law correlation is the only alternative to produce a mobility with a PF dependence at low fields. Numerical simulations[4,9] suggested that short range correlations can have a similar effect on the mobility but these studies were not followed by an analytical model that could establish the dependence of the factor γ on the temperature and on the range of the correlations. Our work intends to fill this gap. We analyzed essentially the same 1D model discussed in Refs. 5, 7, and 8, but considered both a Miller-Abrahams hopping rate and a small-polaron rate, together with a general form of Gaussian correlation between the energy sites. Although the analytical result obtained can be used to discuss any form of correlation, here we concentrated on the power-law correlation and on the exponential correlation, the latter being the prototype of short range correlations.

II. THE MASTER EQUATION MODEL

In a time-of-flight (TOF) experiment the material of interest is placed between two electrodes and a light source generates free carriers in the material, electrons in the lowest unoccupied molecular orbital (LUMO) and holes in the highest occupied molecular orbital (HOMO) in the case of an organic material. If the carrier photocreation happens in the vicinity of the cathode we may admit that the holes are readily absorbed and that the electrons are driven by the applied field towards the collecting anode (or vice versa if the field is reversed). It is desirable that the electrodes do not inject carriers into the system so that the measured signal is only due to the photocreated carriers.

The movement of charge inside the material generates a time-dependent current in the external circuit that connects the electrodes. The relation between $I(t)$ and the current density inside the material is

$$I(t) = \frac{A}{L}\int_0^L j(x,t)dx, \tag{2}$$

where A is the electrode cross section and L is the material thickness and uniformity in the direction perpendicular to the field is assumed. From the measured TOF signal one extracts the average transit time τ and obtains the mobility via $\mu = L/(\tau E)$.

The electrons are transported in the disordered organic material by thermally activated hops between localized states corresponding to the LUMO of the organic material (the following applies as well if the carriers being transported are holes in the HOMO). This type of transport is conveniently described using a master equation for the electron population in the LUMO levels. We will restrict ourselves to a 1D chain of sites uniformly spaced with lattice spacing a. The site energy is $u_n = \epsilon_n - e\varphi_n$, where ϵ_n is the molecular orbital energy (HOMO or LUMO) and $\varphi_n = -Ean$ is the electric potential at the nth site. We will treat the effect of the disorder by treating the energies ϵ_n as stochastic variables Gaussianly distributed with zero average and variance σ. This σ is related to the width of the photoemission peaks and is of the order of 100 meV for typical organic materials.[10]

We will restrict ourselves to nearest neighbors hops only. The master equation reads

$$\frac{dP_n}{dt} = w_{n+1,n}P_{n+1} + w_{n-1,n}P_{n-1} - (w_{n,n+1} + w_{n,n-1})P_n. \tag{3}$$

We will discuss two forms of hopping rate commonly found in the literature. The Miller-Abrahams (MA) rate[11] for the hop from a site of energy u_i to a site of energy u_j is

$$w_{i,j}^{\mathrm{MA}} = \omega_0 \min\{1, \exp[(u_i - u_j)/kT]\}. \tag{4}$$

The Marcus or small-polaron (SP) rate[12] is

$$w_{i,j}^{\mathrm{SP}} = \omega_0 \exp[-(u_i - u_j - E_p)^2/4kTE_p], \tag{5}$$

here E_p is the reorganization energy and we are ignoring the temperature and reorganization energy dependence of the prefactor ω_0. Both rates respect detailed balance, $w_{i,j} = w_{j,i}\exp[(u_i - u_j)/kT]$.

We will consider a chain of N sites and will assume that the electrodes do not inject carriers into the material. We take the injection rates as zero, $w_{0,1} = w_{N+1,N} = 0$, and the absorption rates as constants, $w_{1,0} = \omega_c$ (cathode) and $w_{N,N+1} = \omega_a$ (anode).

We have a closed system of ordinary differential equations

$$\frac{d\mathbf{P}}{dt} = \mathsf{M}\cdot\mathbf{P}, \tag{6}$$

where $\mathbf{P} = (P_1, \ldots, P_N)$ and the tridiagonal matrix M contains the hopping rates. The solution is $\mathbf{P}(t) = \exp[\mathsf{M}t]\cdot\mathbf{P}(0)$. We chose as initial condition a carrier in the first site, $P_n(0) = \delta_{n,1}$. The fraction of electrons that reaches the anode is given by $\kappa = \int_0^\infty \omega_a P_N\, dt$, and the probability of arrival between t and $t+dt$ can be written as $(\omega_a/\kappa)P_N\, dt$.

Using the exact expression for $P_N(t)$ and exploiting the fact that all eigenvalues of the matrix M are negative, we obtain

$$\kappa = -\omega_a(\mathsf{M}^{-1})_{N1}, \tag{7}$$

for the fraction of electrons that arrive at the anode, and

$$\tau = \frac{\omega_a}{\kappa}\int_0^\infty tP_N(t)dt = -\frac{(\mathsf{M}^{-2})_{N1}}{(\mathsf{M}^{-1})_{N1}}, \tag{8}$$

for their average transit time.

In Ref. 13 an exact expression for the matrix elements $(\mathsf{M}^{-1})_{N1}$ and $(\mathsf{M}^{-2})_{N1}$ was obtained in terms of the forward hopping rates and the site energies. From this reference we find the fraction of electrons that make it to the anode as

$$\kappa = \left(1 + \omega_c\sum_{k=1}^{N}\frac{\exp[\beta_{k,1}]}{\nu_k}\right)^{-1}, \tag{9}$$

and the average arrival time as

$$\tau = \frac{\sum_{k=1}^{N}\left(\sum_{n=k}^{N}\frac{\exp[\beta_{n,k}]}{\nu_n}\right)\left(1 + \omega_c\sum_{m=1}^{k-1}\frac{\exp[\beta_{m,1}]}{\nu_m}\right)}{1 + \omega_c\sum_{k=1}^{N}\frac{\exp[\beta_{k,1}]}{\nu_k}}. \tag{10}$$

We use the shorthand notation $\beta_{n,k}$ for $(u_n - u_k)/kT$ and ν_k for $w_{k,k+1}$. The above expression only assumed detailed balance, the energy dependence of the ν_k as well as the distribution of the site energies can be arbitrary.

III. ENERGETIC AVERAGE

The physical transit time is computed by taking an average of Eq. (10) over the distribution of molecular orbital energies $\{\epsilon_1, \ldots, \epsilon_N\}$. When the cathode does not absorb charge, $\omega_c = 0$, all carriers arrive at the anode, $\kappa = 1$, and the energetic average of τ can be done analytically for both rates (4) and (5) and for an arbitrary Gaussian distribution of site energies. We will discuss this case below recalling that in Ref. 13 it was shown that the boundary condition at the electrodes become unimportant at high fields, $eEa > kT$.

In this case Eq. (10) becomes

$$\tau = \sum_{k=1}^{N} \sum_{n=k}^{N} \frac{\exp[\beta_{n,k}]}{\nu_n}. \tag{11}$$

The corresponding expression used in Ref. 5 was

$$\tau_{\mathrm{Dun}} = \sum_{k=1}^{N} \sum_{n=0}^{N-1} \frac{\exp[\beta_{k+n,k}]}{\nu_{k+n}}, \tag{12}$$

where we used our notation and did not assume a particular form for the forward hopping rate. This expression involves sites beyond the last site because it was derived by Derrida[14] for a *periodic* one-dimensional system. In this case the ensemble average appears naturally if one identifies

$$\frac{1}{N}\sum_{k=1}^{N} \frac{\exp[\beta_{k+n,k}]}{\nu_{k+n}} = \left\langle \frac{\exp[\beta_{k+n,k}]}{\nu_{k+n}} \right\rangle = f_n. \tag{13}$$

In our approach, based on Eq. (11), the ensemble average is introduced in addition and implies that the arrival time so computed corresponds to a time-of-flight measurement made on a sample where hops between chains aligned with the field direction is forbidden. When we take the ensemble average of Eq. (11), and assume translational invariance of the averages, we obtain

$$\langle \tau \rangle = \sum_{n=0}^{N-1} (N-n) f_n, \tag{14}$$

that should be compared with $N\sum_{n=0}^{N-1} f_n$ of Ref. 5. In the limit of large N the two expressions coincide. Note, however, that the derivation of $\langle \tau \rangle$ based on Eq. (10) is valid even for a finite system.

We assume that the probability distribution function for the molecular orbital energies is

$$P(\boldsymbol{\epsilon}) = \frac{1}{\sqrt{(2\pi)^N |\mathsf{G}|}} e^{-(1/2)\boldsymbol{\epsilon}\cdot \mathsf{G}^{-1}\cdot \boldsymbol{\epsilon}^T}, \tag{15}$$

where $\boldsymbol{\epsilon} = (\epsilon_1, \ldots, \epsilon_N)$ and $|\mathsf{G}|$ is the determinant of the matrix G. The matrix G contains the information about the correlations since $G_{ij} = \langle \epsilon_i \epsilon_j \rangle$. The average molecular orbital energy can be taken as zero since (11) only contains energy differences. Assuming only translational invariance, $G_{ij} = G_{|i-j|}$, one can compute analytically the energetic average of (11) with this distribution both in the case of the MA hopping rate as in the case of the SP rate, see details in the Appendix.

The energetic average of (11) with the Miller-Abrahams hopping rate (4) gives, in the general case ($N \gg 1$),

$$\omega_0 \langle \tau \rangle_{\mathrm{MA}} = N \sum_{k=0}^{N} e^{-k\Delta} A_k, \tag{16}$$

where

$$A_k = \frac{e^{g_0 - g_k}}{2}\left\{1 + \mathrm{erf}\left(\frac{\Delta + g_0 - g_1 - g_k + g_{k+1}}{2\sqrt{g_0 - g_1}}\right)\right\} + \frac{e^{g_0 - g_{k+1} - \Delta}}{2}\,\mathrm{erfc}\left(\frac{\Delta - g_0 + g_1 - g_k + g_{k+1}}{2\sqrt{g_0 - g_1}}\right), \tag{17}$$

and where we have defined a dimensionless field, $\Delta = eEa/kT$, and a dimensionless correlation function, $g_k = G_k/(kT)^2$. erf and erfc are the usual error and complementary error functions.

The corresponding expression for the small-polaron hopping rate (5) is

$$\omega_0 \langle \tau \rangle_{\mathrm{SP}} = N \sum_{k=0}^{N} e^{-k\Delta} B_k, \tag{18}$$

where

$$B_k = \sqrt{\frac{\varepsilon_p}{\varepsilon_p - g_0 + g_1}} \exp\left[\frac{\varepsilon_p - 2\Delta + 3g_0 + g_1 - 2g_k - 2g_{k+1}}{4} + \frac{(\Delta - g_k + g_{k+1})^2}{4(\varepsilon_p - g_0 + g_1)}\right], \tag{19}$$

and $\varepsilon_p = E_p/kT$ is the dimensionless relaxation energy.

Both expressions can be used with an arbitrary Gaussian distribution of molecular orbital energies. The mobility can be obtained from the average transit time using $\mu = Na/\langle \tau \rangle E$. These expressions are the central result of this paper and will be used below to investigate how the form of the hopping rate and of the energy correlation manifest themselves in the field and temperature dependence of the mobility.

Of importance in the discussion that follows is the high-field limit of the average arrival time, when the sums in (16) and (18) can be approximated by just the first term. One finds for the MA hopping rate that

$$\mu_{\mathrm{MA}} \to \frac{\mu_0}{\Delta}, \quad \Delta > g_0 - g_1, \tag{20}$$

and for the SP hopping rate that

$$\mu_{\mathrm{SP}} \to \frac{\mu_0}{\Delta}\sqrt{\frac{\varepsilon_p - g_0 + g_1}{\varepsilon_p}} \exp\left[-\frac{(\Delta - \varepsilon_p)^2}{4(\varepsilon_p - g_0 + g_1)}\right], \quad \Delta > 1 + \frac{g_0 - g_2}{2}, \tag{21}$$

where $\mu_0 = ea^2\omega_0/kT$ is our natural unit of mobility, and where, in the SP case, we assumed $\varepsilon_p \gg g_0$. Notice that the domain of validity of these asymptotic expressions define a critical field where the transport start to be dominated by the actual form of the hopping rate. Below this critical field the disorder and the energetic correlation determine the mobility in a manner almost independent of the hopping rate, see below.

IV. ENERGETIC CORRELATION

We begin discussing the role of the energetic correlation with the uncorrelated case, where $g_k = s^2 \delta_{k,0}$ ($s = \sigma/kT$). This

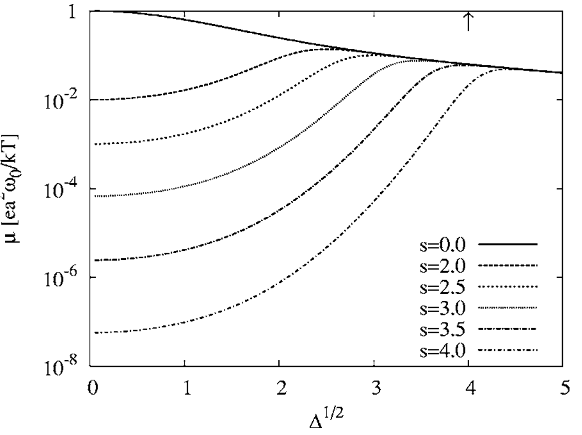

FIG. 1. Field dependence of the mobility, in the uncorrelated case, with the MA rate and for various disorder parameters. The curves change their field dependence to $1/\Delta$ when $\Delta > s^2$. Compare with Fig. 5 of Ref. 15 obtained with a 3D Monte Carlo simulation. The arrow signals the position of the crossover field in the case of $s=4$, $\Delta_c=16$.

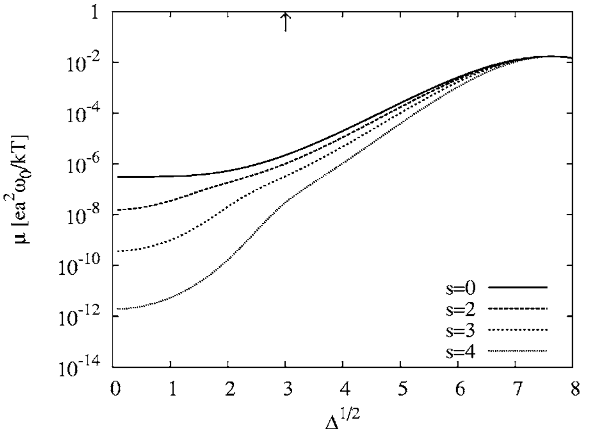

FIG. 2. Field dependence of the mobility, in the uncorrelated case, with the SP rate ($\varepsilon_p=60$) and for various disorder parameters. For fields $\Delta > 1+s^2/2$, in the asymptotic domain, an approximate $e^{\gamma\sqrt{\Delta}}$ field dependence is observed. The arrow signals the position of the crossover field in the case of $s=4$, $\Delta_c=9$.

single-site variance σ is of the order of 100 meV in disordered organic materials as pointed out above. In this case the sums in (16) and (18) can be done exactly. We find for the Miller-Abrahams hopping rate

$$\omega_0\langle\tau\rangle_{\mathrm{MA}} = \frac{N}{2}\left\{1 + \mathrm{erf}\left(\frac{\Delta}{2s}\right) + e^{s^2-\Delta}\,\mathrm{erfc}\left(\frac{\Delta-2s^2}{2s}\right) + \left(\frac{e^{s^2}}{e^{\Delta}-1}\right) \times\left[1 + \mathrm{erf}\left(\frac{\Delta+s^2}{2s}\right) + e^{-\Delta}\,\mathrm{erfc}\left(\frac{\Delta-s^2}{2s}\right)\right]\right\}, \quad (22)$$

and for the small-polaron hopping rate we find

$$\omega_0\langle\tau\rangle_{\mathrm{SP}} = N\sqrt{\frac{\varepsilon_p}{\varepsilon_p-s^2}}\left\{\exp\left[\frac{(\varepsilon_p-\Delta)^2}{4(\varepsilon_p-s^2)}\right] + \left(\frac{1}{e^{\Delta}-1}\right)\exp\left[\frac{\varepsilon_p-2\Delta+3s^2}{4} + \frac{\Delta^2}{4(\varepsilon_p-s^2)}\right]\right\}. \quad (23)$$

The critical field in the uncorrelated case is $\Delta_c=s^2$ for the MA rate and $\Delta_c=1+s^2/2$ for the SP rate. In Figs. 1 and 2 we show the mobility versus the square-root of the dimensionless field $\Delta=eEa/kT$ for both rates in the uncorrelated case. It is evident from the figures that: (i) the analytical result (22) reproduces very well the 3D Monte-Carlo results of Ref. 15. (ii) The MA rate produces a mobility with a PF field dependence over a very narrow range of fields, besides having a nonobserved $1/\Delta$ decaying behavior at high fields, $\Delta > s^2$. (iii) The SP rate at high-fields, $\Delta > 1+s^2/2$, have a mobility in the form $\Delta^{-1}e^{-(\Delta-\varepsilon_p)^2/4(\varepsilon_p-s^2)}$, which produces a field dependence closely resembling the PF behavior for $\Delta < \varepsilon_p$. The higher the value of the relaxation energy ε_p and the smaller the disorder parameter s, the wider the field range of this approximate PF behavior. For $kT=25$ meV (room temperature), $\sigma=100$ meV, $E_p=1$ eV, and for a lattice spacing of $a=10$ Å this corresponds to 2×10^6 V/cm$<E<10^7$ V/cm. This range of fields does not correspond to the experimental observations that show a PF field dependence starting at fields as low as 8×10^3 V/cm.[16]

Now we discuss two important cases of energetic correlation: the power-law decaying correlation, $G_0=\sigma^2$, $G_k=r\sigma^2/|k|^{\alpha}$, $(k\neq0)$; and the exponentially decaying correlation, $G_k=\sigma^2e^{-|k|/\xi}$, ξ being the correlation length in units of the lattice parameter.

Depending on the exponent α in the power-law case, the parameter r (assumed positive) must fall within a certain range to ensure that all eigenvalues of the G matrix are positive in the $N\to\infty$ limit. For instance, if $\alpha=1$ one must have $0\leqslant r<0.72$. In the exponential case any value of the correlation length ξ can be used.

The power-law case is important since, as it was shown in Refs. 4 and 5, the electrostatic interaction of the electrons with randomly oriented dipoles in the organic material can give rise to a correlation in the molecular orbital energies decaying as a power law, with an exponent $\alpha=1$. In the charge-dipole model of Ref. 5 the parameter r appeared in the form of the ratio between the typical molecular size and the lattice parameter. The exponentially decaying correlation has not yet, to our knowledge, been explicitly investigated. However, the relevance of short range correlations and their possible physical origin have been discussed in Refs. 4 and 9. Another form of correlation that combines the exponential form and the power-law form (with unit exponent) was discussed in Ref. 7.

The mobility in the high-field limit is given by Eqs. (20) and (21). To obtain the mobility in the low-field limit we could follow the strategy of Ref. 5 and ignore in Eq. (11) nearest neighbor energy differences, this amounts to replacing ν_n by ω_0 in the MA case, and by $\omega_0e^{-\varepsilon_p/4}$ in the SP case. In fact we shall use an even better approximation, that was implicitly used in Ref. 8, that consists in replacing ν_n by $\langle\nu_n\rangle_{\Delta=0}$. Furthermore we convert the sums in Eqs. (16) and (18) into integrals which, for both forms of correlations, are then evaluated in the saddle-point approximation. We find for the power-law correlation with exponent $\alpha=1$,

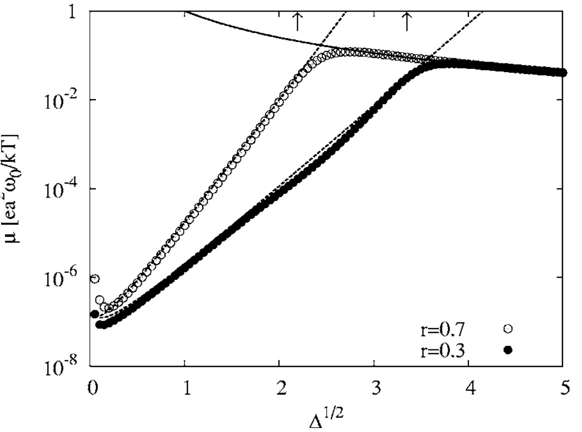

FIG. 3. Field dependence of the mobility with the MA rate and with an energy correlation decaying as a power-law with exponent $\alpha=1$ and $s=4$. The parameter r is the ratio G_1/G_0 and must be smaller than 0.72 as explained in the text. The dashed lines correspond to the low-field approximation of Eq. (24) and the solid line corresponds to the high-field limit $1/\Delta$. The two arrows mark the predicted location of the critical fields, $\Delta_c=s^2(1-r)$.

$$\mu_{\text{pow}} \to \frac{\mu_0 f}{(\pi^2 r s^2 \Delta)^{1/4}} \exp[-s^2 + 2\sqrt{rs^2}\sqrt{\Delta}]. \tag{24}$$

For a general exponent α the argument in the exponential involves $(rs^2)^{1/(1+\alpha)}\Delta^{\alpha/(1+\alpha)}$. As for the exponential correlation we obtain

$$\mu_{\text{exp}} \to \frac{\mu_0 f}{(2\pi\xi\Delta)^{1/2}} \exp[-s^2 + \xi\Delta - \xi\Delta\ln(\xi\Delta/s^2)]. \tag{25}$$

In the low-field limit the only signature of the actual form of the hopping rate is in the overall factor f, the average nearest neighbor hopping rate at zero field in units of ω_0. We find

$$f_{\text{MA}} = \tfrac{1}{2}[1 + \exp(g_0 - g_1)\text{erfc}(\sqrt{g_0 - g_1})], \tag{26}$$

$$f_{\text{SP}} = \sqrt{\frac{\varepsilon_p}{\varepsilon_p + g_0 - g_1}} \exp\left[-\frac{\varepsilon_p^2}{4(\varepsilon_p + g_0 - g_1)}\right]. \tag{27}$$

The disorder and the energetic correlation completely determine the temperature and field dependence of the mobility in the low-field limit.

To access the validity of these approximate expressions we compare them with a numerical evaluation of the $N \to \infty$ limit of the sums in Eqs. (16) and (18) in the following.

In Fig. 3 we show the case of the MA hopping rate and a power-law decaying energy correlation, with exponent $\alpha=1$. The disorder is fixed by the parameter $s=\sigma/kT=4$. One observes that the approximate expression in Eq. (24), using the f_{MA} of Eq. (26), does capture the mobility field dependence at low fields. It is also evident from the figure that the critical field that separates the low and high-field regimes is given with reasonable accuracy by $\Delta_c=g_0-g_1=s^2(1-r)$.

In Fig. 4 we show the case of the MA rate and an exponentially decaying energy correlation. Like in Fig. 3 we fixed the disorder parameter at $s=4$. One observes that the approximate expression in Eq. (25), also using the f_{MA} of Eq. (26), does capture the mobility field dependence at low fields. The position of the critical field is also correctly given by $\Delta_c=g_0-g_1=s^2(1-e^{-1/\xi})$.

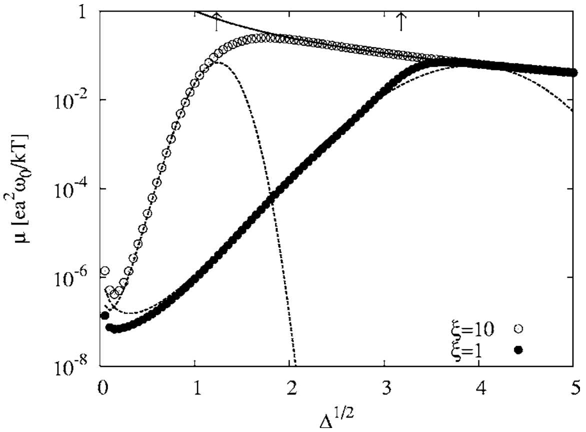

FIG. 4. Field dependence of the mobility with the MA rate and with an energy correlation decaying exponentially. The dashed lines correspond to Eq. (25) and the solid line corresponds to $1/\Delta$. The two arrows mark the predicted location of the critical fields, $\Delta_c=s^2(1-e^{-1/\xi})$.

In Fig. 5 we show the case of the SP hopping rate. One observes that, both in the case of the power-law correlation as in the case of the exponential correlation, the low-field limit of the mobility is well captured by the expressions in Eqs. (24) and (25), using the factor f_{SP} of Eq. (27). In the high field limit one has the expression in Eq. (21) which also contains an apparent PF dependence. The position of the critical field, in the SP case, is given by $\Delta_c=1+(g_0-g_2)/2$. This field is indicated by arrows in the figure.

Of relevance in a comparison with experiments is the temperature dependence of the factor γ in the PF field dependence, $\mu \sim e^{\gamma\sqrt{E}}$. The approximate expression of Eq. (24)

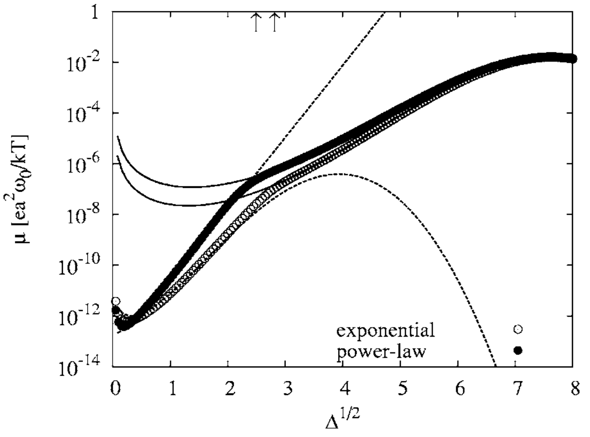

FIG. 5. Field dependence of the mobility with the SP rate for both forms of energetic correlation and with $s=4$. In the power-law correlation we took $\alpha=1$ and $r=0.7$, in the exponential correlation we took $\xi=1$. The dashed lines correspond to Eqs. (24) and (25), whereas the solid lines correspond to the high-field limit of the SP rate, Eq. (21). The two arrows mark the predicted location of the critical fields, $\Delta_c=1+(s^2/2)(1-r/2)$ in the power-law case, and $\Delta_c=1+(s^2/2)(1-e^{-2/\xi})$ in the exponential case.

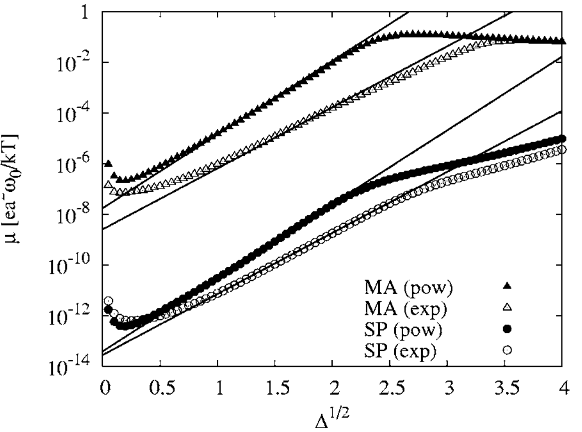

FIG. 6. Field dependence of the mobility for both forms of energetic correlation and both forms of hopping rate. The disorder parameter was taken to be $s=4$. In the power-law correlation we took $\alpha=1$ and $r=0.7$, in the exponential correlation we took $\xi=1$. The solid lines correspond to a PF fitting using the parameter γ of Eqs. (28) and (29).

implies that in the presence of a power-law decaying correlation

$$\gamma_{\text{pow}} = 2\sqrt{r\sigma^2 ea/(kT)^3}, \tag{28}$$

a result already known from Ref. 5. The approximate expression (25) does not have an exact PF field dependence but only an approximate one. The argument of the exponential, $F(\Delta)=\xi\Delta-\xi\Delta\log(\xi\Delta/s^2)$, can be approximated by $(s^2/4)\times(1+\log 4)+s\log 4(\sqrt{\xi\Delta}-s/2)$ in the low field region. Therefore, in the presence of an exponential correlation one has

$$\gamma_{\text{exp}} = (\log 4)\sqrt{\xi\sigma^2 ea/(kT)^3}. \tag{29}$$

Both factors γ contain the same $T^{-3/2}$ dependence. In Fig. 6 we illustrate how well the field dependence of the mobility can be represented by a pure PF dependence using the factors γ of Eqs. (28) and (29). In the figure we reproduce the low field region of some of the curves shown in Figs. 3–5 together with the PF fit. The fit ignores the field dependence of the prefactors in Eqs. (24) and (25). The range of fields where the relative error, $|\mu-\mu_{\text{fit}}|/\mu$, is within 10% is somewhat limited for the MA rate: $0.86<\Delta<1.88$ for the power-law correlation and $2.56<\Delta<4.24$ for the exponential correlation, and quite large for the SP rate: $0.46<\Delta<4.24$ for the power-law case and $0.86<\Delta<6.30$ for the exponential correlation. Interestingly enough the exponential correlation has a wider range of pure PF dependence than the power-law correlation, for both rates. With regard to the precision with which the PF dependence can be inferred from a time-of-flight measurement of the mobility see Ref. 17.

It is evident that the PF field dependence can be obtained either with a power-law correlation or with an exponential correlation and that the temperature dependence of the factor γ does not distinguish between the two forms of correlation. The field dependence of the mobility would distinguish between the two forms of hopping rates only at fields $\Delta>s^2$, see Fig. 6. For $a=10$ Å, $\sigma=100$ meV and at room temperature one has to have $E>4\times10^6$ V/cm. To push this field to lower values requires more ordered samples, higher temperatures and larger average hopping distances.

These results are based on an analytical solution of a 1D model for the organic material. What gives us confidence that these results are still valid in a 3D version of our model are: (i) the results of the simulations of Ref. 6 that validated the 1D results of Ref. 5, whose analysis were on the same line as ours but restricted to a symmetric hopping rate and a power-law correlation, (ii) the 3D simulation of Ref. 8 on a system with SP hopping rate and power-law correlation that validated the 1D model of the same reference and (iii) the earliest simulation of a correlated system, Ref. 4, that treated a system with MA hopping rate and with short range correlations, not exponential though. In this work it was qualitatively found that the factor γ increases with the range of correlations but, since the work was not accompanied by an analytical 1D model, the dependence of the PF factor γ on the temperature and on the correlation length, that we established to be in the form of Eq. (29) when the correlation decays exponentially, was not obtained.

In fact, the mobility in 3D for the MA hopping rate and power-law correlation was shown[6] to depend on temperature and field as $\exp[-(3s/5)^2+0.78(s-2/\sqrt{s})\sqrt{r\Delta}]$, compare with Eq. (24). This indicates that the γ factor is smaller in 3D in comparison to the 1D result for the same amount of disorder. The same type of effect was seen in the case of the Marcus rate, see Ref. 8.

V. CONCLUSION

The main results of this work are: (i) the exact expression for the average transit time in a one-dimensional model of a time-of-flight experiment performed on an organic insulator, Eq. (10), (ii) the exact average of its simplified version with a general, correlated, Gaussian distribution of site energies for both the Miller-Abrahams, Eqs. (16) and (17), and the small-polaron hopping rates, Eqs. (18) and (19), (iii) the expression for the critical fields, that mark the transition from the disorder dominated to the hopping rate dominated mobility, in the MA and SP cases, showing the influence of the correlation, Eqs. (20) and (21), and (iv) the expression of the PF factor γ in the case of an exponential correlation, Eq. (29).

We used the general expressions of the average arrival time to compare two forms of energy correlation: the power-law, that had already been discussed along these lines in Refs. 5 and 8, and the exponentially decaying correlation, not yet discussed in the literature although being the prototype for short range correlations of any kind. We found that the mobility contains a PF field dependence at low fields in both cases. In the power-law case one must have an exponent exactly equal to one whereas in the exponential case the correlation length has to be of the order of the lattice spacing in order for the field range of PF behavior to be significant. We found the explicit temperature and correlation length dependence of the factor γ in the exponential case, Eq. (29), and verified that it has the same temperature dependence as the factor γ in the power-law case with unit exponent.

With regard to the form of the hopping rate, its mark on the field dependence of the mobility only shows up at fields above $\sigma^2/(eakT)$, in fact the precise expression for the critical fields for both rates and for an arbitrary correlation was obtained, see Eqs. (20) and (21). At low fields the only characteristic that distinguishes SP rate from MA rate is the factor $\exp(-E_p/4kT)$ that makes the mobility of the former case smaller than the latter case, assuming the same prefactor ω_0 in both rates. For further discussions on this point see Ref. 8. To our knowledge the measurement of the mobility has not yet provided a clear indication of the underlying hopping mechanism in the organic.

With regard to developments of the present work we need: (i) a 3D simulation with an exponential correlation to verify if the factor γ predicted in Eq. (29) keeps its form. Based on the 3D simulations of the power-law case,[6] that confirmed factor γ found in the 1D analytical model,[5] we suspect that the same will happen for the exponential correlation, (ii) to verify how the off-diagonal disorder, that adds a random prefactor in the hopping rate proportional to the exponential of the overlap integral of the molecular orbitals,[3] modifies our results and (iii) to check if the positional disorder, that makes the electrostatic energy of the molecular orbitals to depend on the random location of the various molecules, has an influence on the mobility field dependence, in this regard see Ref. 18.

APPENDIX: CORRELATED ENERGY DISTRIBUTION

To establish the notation used in the text we list bellow some formulas for a set of N Gaussianly distributed correlated stochastic variables, $\boldsymbol{\epsilon}=(\epsilon_1,\ldots,\epsilon_N)$.

First the full distribution function

$$P(\boldsymbol{\epsilon})=\frac{1}{\sqrt{(2\pi)^N|\mathsf{G}|}}e^{-(1/2)\boldsymbol{\epsilon}\cdot\mathsf{G}^{-1}\cdot\boldsymbol{\epsilon}^T}, \tag{A1}$$

where $|\mathsf{G}|$ is the determinant of the matrix G.

This distribution is normalized and the following averages can be readily obtained

$$\langle\epsilon_i\rangle=0, \tag{A2}$$

$$\langle\epsilon_i\epsilon_j\rangle=\mathsf{G}_{ij}, \tag{A3}$$

$$\langle e^{\mathbf{c}\cdot\boldsymbol{\epsilon}}\rangle=e^{(1/2)\mathbf{c}\cdot\mathsf{G}\cdot\mathbf{c}}, \tag{A4}$$

where $\mathbf{c}$ is a constant vector (independent of $\boldsymbol{\epsilon}$).

The reduced distribution functions, obtained by integrating (A1) over a subset of $\{\epsilon_1,\ldots,\epsilon_N\}$, are also Gaussian. We define the following submatrices of the G matrix

$$\mathsf{g}(i)=G_{ii},\quad \mathsf{g}(i,j)=\begin{bmatrix} G_{ii} & G_{ij}\\ G_{ji} & G_{jj}\end{bmatrix},\ \text{etc.} \tag{A5}$$

The n-reduced distribution function is

$$p(\epsilon_i,\ldots,\epsilon_k)=\frac{1}{\sqrt{(2\pi)^n|\mathsf{g}(i,\ldots,k)|}}e^{-(1/2)\boldsymbol{\epsilon}\cdot\mathsf{g}(i,\ldots,k)^{-1}\cdot\boldsymbol{\epsilon}}, \tag{A6}$$

where $\boldsymbol{\epsilon}=(\epsilon_i,\ldots,\epsilon_k)$ is an n vector. In particular, the one-reduced distribution is

$$p(\epsilon_i)=\frac{1}{\sqrt{2\pi|G_{ii}|}}e^{-(1/2)\epsilon_i^2/G_{ii}}. \tag{A7}$$

In the text we assumed spacial uniformity so that the pair-correlation G_{ij} only depends on $|i-j|$. We therefore defined $G_{|i-j|}=G_{ij}$. Equations (17) and (19) are averages involving at most three Gaussian variables

$$\int\int\int d\epsilon_k d\epsilon_n d\epsilon_{n+1}\frac{\exp[(\epsilon_n-\epsilon_k-(n-k)eEa)/kT]}{\nu_n}\times p(\epsilon_k,\epsilon_n,\epsilon_{n+1}), \tag{A8}$$

and can be explicitly evaluated both for the MA rate, $\nu_n=\omega_0\min\{1,\exp[(\epsilon_n-\epsilon_{n+1}+eEa)/kT]\}$ and for the SP rate, $\nu_n=\omega_0\exp[-(\epsilon_n-\epsilon_{n+1}+eEa-E_p)^2/4kTE_p]$.

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