Effect of electric field on diffusion in disordered materials. I. One-dimensional hopping transport

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An exact analytical theory is developed for calculating the diffusion coefficient of charge carriers in strongly anisotropic disordered solids with one-dimensional hopping transport mode for any dependence of the hopping rates on space and energy. So far, such a theory existed only for calculating the carrier mobility. The dependence of the diffusion coefficient on the electric field evidences a linear, nonanalytic behavior at low fields for all considered models of disorder. The mobility, on the contrary, demonstrates a parabolic, analytic field dependence for a random-barrier model, being linear, nonanalytic for a random-energy model. For both models, the Einstein relation between the diffusion coefficient and mobility is proven to be violated at any finite electric field. The question on whether these nonanalytic field dependences of the transport coefficients and the concomitant violation of the Einstein's formula are due to the dimensionality of space or due to the considered models of disorder is resolved in the following paper [A. V. Nenashev, F. Jansson, S. D. Baranovskii, R. Österbacka, A. V. Dvurechenskii, and F. Gebhard, Phys. Rev. B **81**, 115204 (2010)], where analytical calculations and computer simulations are carried out for two- and three-dimensional systems.

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I. INTRODUCTION

Charge carrier transport in disordered materials—inorganic, organic, and biological systems—has been in the focus of intensive experimental and theoretical studies for several decades due to various current and potential applications of such materials in modern electronic devices (see, for instance, Ref. 1 and references therein). An essential part of the research is dedicated to studying the mobility of the charge carriers, μ, and their diffusion coefficient, D, as the decisive transport coefficients responsible for the performance of most devices. Among other features, the relation between these two transport coefficients is the subject of intensive research, since this relation (called the "Einstein relation") often provides significant information on the underlying transport mechanism.[1] In numerous experimental studies on organic disordered materials, essential deviations from the conventional form

$$\mu = \frac{e}{kT} D \tag{1}$$

of this relation have been recognized.[2–8] In Eq. (1), e is the elementary charge, T is temperature, and k is the Boltzmann constant. Einstein derived this relation between μ and D for the case of thermal equilibrium in a nondegenerate system of charge carriers. Deviations from Eq. (1) were predicted theoretically for nonequilibrium transport at low temperatures[9–11] and also for equilibrium transport in degenerate systems if the density of states (DOS), which can be used by the charge carriers, strongly depends on energy, for instance, exponentially[12] or according to a Gaussian distribution.[13] Usually, the former DOS is assumed for inorganic amorphous semiconductors, while the latter one is assumed for disordered organic materials, such as molecularly doped and conjugated polymers.[14–19] In this paper and in the following one (Ref. 20), we derive general equations for calculating the diffusion coefficient and the mobility of charge carriers and apply them to systems with the Gaussian DOS, since most of the experimental evidences for the violation of Eq. (1) have been reported for organic disordered materials. The DOS is taken as

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

where N is the spatial concentration of conducting states and σ is the energy scale of the DOS distribution.

Remarkably, experiments on disordered organic materials evidence that at relatively low electric fields, at which the carrier mobility μ is field independent and hence the carrier transport can be treated as Ohmic one (low-field regime), the diffusion coefficient D of charge carriers and concomitantly the relation between μ and D become essentially dependent on the magnitude of the applied electric field F.[2,4–6] Our aim in this paper and in the following one[20] is to provide an analytical theory for the field-dependent diffusion coefficient and mobility of charge carriers. The theory will be checked by computer simulations.

Charge transport in disordered organic materials is dominated by incoherent hopping of electrons and holes via localized states randomly distributed in space, with the DOS described by Eq. (2).[14–19] The transition rate between an occupied state i and an empty state j, separated by the distance r_{ij}, is described by the Miller-Abrahams expression[21]

$$\Gamma_{ij} = \nu_0 e^{-2r_{ij}/a} \begin{cases} e^{-\Delta\varepsilon_{ij}/kT}, & \Delta\varepsilon_{ij} > 0 \\ 1, & \Delta\varepsilon_{ij} \le 0, \end{cases} \tag{3}$$

where ν_0 is the attempt-to-escape frequency. The energy difference between the sites is

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$$\Delta\varepsilon_{ij} = \varepsilon_j - \varepsilon_i - Fe(x_j - x_i), \tag{4}$$

where the electric field F is assumed to be directed along the x direction. The localization length of the charge carriers in the states contributing to hopping transport is a. We assume the latter quantity to be independent of energy and we will neglect correlations between the energies of the localized states, following the Gaussian-disorder-model of Bässler.[17–19]

The challenging problem arises of how to describe theoretically the field-dependent diffusion of charge carriers in the hopping regime within the Gaussian DOS. This very problem was addressed in the numerical simulations by Richert *et al.*[22] Using a Monte Carlo algorithm with a randomly distributed parameter a (the so-called off-diagonal disorder), it was shown that the diffusion coefficient for hopping transport in the Gaussian DOS depends essentially on the field strength at such low electric fields that the mobility of charge carriers remains field independent.[22] This result was interpreted in analytical calculations by Bouchaud and Georges,[23] who considered a hopping process in a one-dimensional (1D) system of equidistant localized states with transition rates essentially different from those given by Eq. (3). In the calculations of Bouchaud and Georges,[23] the transition rates between the neighboring sites were taken as

$$\Gamma_{i,i\pm1} = \Gamma_0 \exp\left[\frac{\Delta_{i\pm1,i} \pm eFd}{2kT}\right], \tag{5}$$

with $\Delta_{i,i+1}=\Delta_{i+1,i}$ distributed according to $g(\Delta_{ij})$ given by Eq. (2). We will call this model the random-barrier model (RBM) in contrast to the model described by Eqs. (2) and (3), which we call the random-energy model (REM). Bouchaud and Georges[23] suggested for the field-dependent part of the diffusion coefficient in the RBM the expression $D(F)-D(0) \propto F \exp[3\sigma^2/8(kT)^2]$, which they claimed to be precisely the dependence found in Ref. 22. Later, the authors of Ref. 22 studied the quantity $D(F)-D(0)$ by computer simulations in more details[24] and found a quadratic dependence of $D(F)-D(0)$ on F at low fields and no turnover to a linear field dependence as suggested by Bouchaud and Georges.[23] The question arises then on whether this discrepancy in the field dependences of the diffusion constant between the computer simulations[24] and analytical calculations[23] is due to different models [RBM (Ref. 23) against REM (Ref. 24)] or it is due to different dimensionalities considered in these two approaches [1D in analytical calculations[23] against three dimensions (3D) in computer simulations[24]]. The only way to answer this question is to obtain exact results for the REM in 1D and to compare them to the results for the RBM in 1D on one hand and to the results for the REM in 3D on the other hand. This task demands developing a new analytical method for calculating drift and diffusion in 1D systems for the hopping transport mode. In Sec. II, we present such method. We also present in Sec. III the exact result for the field-dependent diffusion in the RBM, which differs from the one given by Bouchaud and Georges.[23] Section IV is devoted to analytical results on the field-dependent diffusion coefficient and mobility in the REM in the 1D case. The exact results for both RBM and REM give a linear field dependence of the diffusion coefficient at low fields. In Sec. V, we present the results obtained by computer simulations in 1D systems. Concluding remarks are gathered in Sec. VI.

The following paper[20] is devoted to diffusion in 3D systems. The results in the 3D case clearly demonstrate a quadratic field dependence of the diffusion coefficient at low fields. One should then conclude that the discrepancy between the linear[23] and the quadratic[24] field dependences of the diffusion constant reported in the literature is due to the different space dimensionalities considered in the two approaches. One should note that the differences between 1D systems and 3D systems with respect to the field-dependent diffusion coefficient have been reported in the literature, albeit for systems with essential correlations between energies and spatial positions of localized states involved into the hopping transport. Relying essentially on such correlations, Parris *et al.*[25] obtained an exact result for the field-dependent diffusion coefficient in 1D systems, which was not confirmed in computer simulations carried out on 3D correlated systems.[26] Our study leads to a similar conclusion for the Gaussian-disorder model without space-energy correlations. This study was necessary, since the theory from Ref. 25 cannot be applied to the case of uncorrelated disorder.

II. ANALYTICAL METHOD

This section is devoted to one-dimensional hopping in the presence of an electric field. The considered system consists of a chain of sites separated by a constant distance d. Each site is either empty or occupied by a carrier. We consider the limit of small carrier concentration, therefore the probability for the ith site to be occupied, p_i, is small for each i. The time evolution of probabilities p_i is described by equation

$$\frac{\partial p_i}{\partial t} = \Gamma_{i-1,i}p_{i-1} + \Gamma_{i+1,i}p_{i+1} - (\Gamma_{i,i-1} + \Gamma_{i,i+1})p_i, \tag{6}$$

where Γ_{ij} is the rate of transition from site i to site j. Transition rates Γ_{ij} are assumed to be time independent, to be nonzero only for nearest neighbors ($\Gamma_{ij} \neq 0 \Leftrightarrow |i-j|=1$), and to obey the principle of detailed balance

$$\frac{\Gamma_{i,i+1}}{\Gamma_{i+1,i}} = \exp\frac{\varepsilon_i - \varepsilon_{i+1} + eFd}{kT}, \tag{7}$$

where ε_i is the energy of a carrier on the ith site *without* the electric field and F is the electric field strength.

Our aim is to obtain analytical expressions for diffusion coefficients with transition rates Γ_{ij} chosen according to either RBM or REM. A similar problem was considered by Derrida[27] who obtained exact results for diffusion coefficient in *finite* systems with arbitrarily chosen transition rates. But, in the limit of an *infinite* system, his expression [Eq. (47) of Ref. 27] contains an uncertainty of type "$\infty-\infty$" and resolving this uncertainty is a nontrivial task. Derrida considered an infinite system only for the case if Γ_{ij} are random *independent* variables, except that only Γ_{ij} and Γ_{ji} may be correlated. This condition is fulfilled for the RBM, but not for the REM, in which Γ_{ij} and Γ_{jk} are correlated due to the common

site j. Therefore Derrida's approach can hardly be generalized to for the REM. Here we propose another analytical approach for evaluating the diffusion coefficient in the infinite disordered one-dimensional systems. Derrida's method uses a definition of the diffusion coefficient D related to random walks

$$D = \frac{1}{2}\lim_{t\to\infty}\frac{d}{dt}(\langle x^2(t)\rangle - \langle x(t)\rangle^2), \tag{8}$$

where $x(t)$ is the position of the particle at time t. On the contrary, our method is based on the macroscopic definition of D as the ratio of the diffusion current j_D and the long-scale gradient of the concentration n of particles

$$D = -\frac{j_D(x)}{dn(x)/dx}. \tag{9}$$

We believe that both methods give the same results, though our method has an advantage of providing an *explicit* expression for D in the general case of the *infinite* one-dimensional system [see Eqs. (27), (29), and (38) below]. This expression can be straightforwardly applied to the particular cases of the RBM and REM.

We start by considering the continuous-medium approximation. This approximation deals with the carrier concentration $n(x,t)$ averaged upon a sufficiently large spatial scale. The time evolution of this concentration obeys the Fokker-Planck equation

$$\frac{\partial n}{\partial t} = -v\frac{\partial n}{\partial x} + D\frac{\partial^2 n}{\partial x^2}, \tag{10}$$

provided that n varies in space sufficiently slowly (that is, the characteristic scale of spatial variation is large as compared to the scale of averaging). Here, v is the drift velocity and D is the diffusion coefficient. Let us consider the initial concentration $n(x,0)$ in the form

$$n(x,0) = n_0 \exp(\eta x), \tag{11}$$

with an infinitely small factor η. The solution of Eq. (10) with the initial condition (11) reads

$$n(x,t) = n_0 \exp(\eta x - \lambda t), \tag{12}$$

where

$$\lambda = v\eta - D\eta^2. \tag{13}$$

Since both λ and η are infinitely small, one can resolve Eq. (13) with respect to η in the following way:

$$\eta = \frac{1}{v}\lambda + \frac{D}{v^3}\lambda^2 + O(\lambda^3). \tag{14}$$

We will use Eq. (14) for calculating the drift velocity v and the diffusion coefficient D. For this aim, we need a *microscopic* definition of the coefficients λ and η expressed in terms of occupation probabilities p_i rather than in terms of the concentration n.

To obtain an exponential time dependence of the concentration, $n \sim \exp(-\lambda t)$, we can simply postulate that each probability p_i depends on time in the same way, $p_i \sim \exp(-\lambda t)$. Therefore, $\partial p_i/\partial t = -\lambda p_i$ and Eq. (6) can be written as

$$-\lambda p_i = \Gamma_{i-1,i}p_{i-1} + \Gamma_{i+1,i}p_{i+1} - (\Gamma_{i,i-1} + \Gamma_{i,i+1})p_i. \tag{15}$$

This is the way of introducing λ on a microscopic scale.

For the *spatial* dependence of probabilities, one cannot expect an analogous form, $p_i \sim \exp(\eta d i)$, if the system has spatial disorder, i.e., no translation symmetry. Instead, we expect that

$$p_i = p_0 C_i \exp(\eta d i), \tag{16}$$

where the coefficients C_i does not exponentially grow or decay when i tends to infinity. Consequently,

$$\log\frac{p_i}{p_0} = \eta d i + O(1), \tag{17}$$

which gives

$$\eta = \lim_{i\to\pm\infty}\frac{1}{di}\log\frac{p_i}{p_0} \tag{18}$$

or, equivalently,

$$\eta = \frac{1}{d}\left\langle \log\frac{p_{i+1}}{p_i}\right\rangle, \tag{19}$$

where angle brackets denote averaging over the site number i.

Equation (19) can serve as the microscopic definition of η. However, it is more convenient for our aim to define η in another way

$$\eta = \frac{1}{d}\left\langle \log\frac{j_{i,i+1}}{j_{i-1,i}}\right\rangle, \tag{20}$$

where $j_{i,i+1}$ is the flow of carriers from site i to site $i+1$,

$$j_{i,i+1} = \Gamma_{i,i+1}p_i - \Gamma_{i+1,i}p_{i+1}. \tag{21}$$

It is easy to show that Eqs. (19) and (20) give equal values of η. Indeed, in a macroscopic consideration, the flow of particles $j(x,t)$ is connected to the concentration $n(x,t)$ as

$$j = vn - D\,\partial n/\partial x. \tag{22}$$

Therefore, if $n \sim \exp(\eta x)$, then $j \sim \exp(\eta x)$. Going to a microscopic picture, one can get Eq. (19) from $n \sim \exp(\eta x)$ and Eq. (20) from $j \sim \exp(\eta x)$. Consequently, the value of η should be the same in all these equations.

Let us now obtain v and D from Eq. (20). For this purpose, we rewrite Eq. (15) taking into account Eq. (21),

$$-\lambda p_i = j_{i-1,i} - j_{i,i+1}, \tag{23}$$

which gives

$$\frac{j_{i,i+1}}{j_{i-1,i}} = 1 + \lambda\frac{p_i}{j_{i-1,i}}. \tag{24}$$

The ratio $p_i/j_{i-1,i}$ is a function of λ since the probability p_i and the carrier flow $j_{i-1,i}$ are defined by a λ-dependent equation (15). We expand this ratio in a Taylor series

$$\frac{p_i}{j_{i-1,i}} = a_i + \lambda b_i + O(\lambda^2). \tag{25}$$

(Our coefficients a_i are the same as Derrida's r_n in Ref. 27.) Substitution of Eqs. (24) and (25) into Eq. (20) gives

$$\eta = \frac{1}{d}\left\langle \log\left(1 + \lambda \frac{p_i}{j_{i-1,i}}\right)\right\rangle$$

$$= \frac{1}{d}\langle \log[1 + \lambda a_i + \lambda^2 b_i + O(\lambda^3)]\rangle$$

$$= \frac{\lambda}{d}\langle a_i\rangle + \frac{\lambda^2}{d}(\langle b_i\rangle - \langle a_i^2\rangle/2) + O(\lambda^3). \tag{26}$$

Comparing the latter equation to Eq. (14), one obtains v and D,

$$v = \frac{d}{\langle a_i\rangle}, \quad D = d^2 \frac{\langle b_i\rangle - \langle a_i^2\rangle/2}{\langle a_i\rangle^3}. \tag{27}$$

The expression for v coincides with that obtained by Derrida [Eq. (63) of Ref. 27], whereas the expression for D is a new result.

In the rest of this section, we obtain explicit expressions for the quantities a_i and b_i. The mean values $\langle a_i\rangle$, $\langle a_i^2\rangle$, and $\langle b_i\rangle$ will be evaluated in Sec. III for the RBM and in Sec. IV for the REM leading to the analytical expressions for the diffusion coefficient D in the RBM and in the REM.

In order to find the coefficients a_i, we set λ to zero in Eq. (25). As it is seen from Eq. (23), the carrier flow $j_{i,i+1}$ does not depend on i in the case of $\lambda=0$. Dividing Eq. (21) by the carrier flow, one obtains a set of equations for coefficients a_i,

$$\forall i \quad \Gamma_{i,i+1}a_i - \Gamma_{i+1,i}a_{i+1} = 1. \tag{28}$$

The solution of Eq. (28) can be presented as an infinite series

$$a_i = \frac{1}{\Gamma_{i,i+1}} + \frac{\Gamma_{i+1,i}}{\Gamma_{i,i+1}\Gamma_{i+1,i+2}} + \frac{\Gamma_{i+1,i}\Gamma_{i+2,i+1}}{\Gamma_{i,i+1}\Gamma_{i+1,i+2}\Gamma_{i+2,i+3}} + \cdots, \tag{29}$$

which can be checked directly by substituting Eq. (29) into Eq. (28). To prove the convergence of the series (29), let us rewrite it using the condition of detailed balance, Eq. (7),

$$a_i = \Gamma_{i,i+1}^{-1} + B^{-1}\exp\left(\frac{\varepsilon_{i+1} - \varepsilon_i}{kT}\right)\Gamma_{i+1,i+2}^{-1}$$

$$+ B^{-2}\exp\left(\frac{\varepsilon_{i+2} - \varepsilon_i}{kT}\right)\Gamma_{i+2,i+3}^{-1} + \cdots, \tag{30}$$

where $B=\exp(eFd/kT)$. For any physically reasonable system, the quantities $\exp[(\varepsilon_{i+k}-\varepsilon_i)/kT]\Gamma_{i+k,i+k+1}^{-1}$ can be regarded as having an upper boundary. Denoting this boundary as C, we get an upper estimate for a_i,

$$a_i < C + B^{-1}C + B^{-2}C + \cdots = \frac{C}{1 - B^{-1}}, \tag{31}$$

which proves convergence of the series (29) under the condition $B>1$, i.e., $eF>0$.

In order to obtain b_i, we need a set of equations connecting b_i to b_{i+1} in analogy with Eq. (28) that connects a_i to a_{i+1}. We will derive the necessary equations using Eqs. (21) and (24) and the Taylor expansion (25). Let us first divide Eq. (21) by $j_{i,i+1}$ and slightly rearrange it

$$\Gamma_{i,i+1}\frac{j_{i-1,i}}{j_{i,i+1}}\frac{p_i}{j_{i-1,i}} - \Gamma_{i+1,i}\frac{p_{i+1}}{j_{i,i+1}} = 1. \tag{32}$$

Let us now use the expansion (25) for quantities $p_i/j_{i-1,i}$,

$$\Gamma_{i,i+1}\frac{j_{i-1,i}}{j_{i,i+1}}(a_i + \lambda b_i) - \Gamma_{i+1,i}(a_{i+1} + \lambda b_{i+1}) = 1 + O(\lambda^2). \tag{33}$$

The latter equation contains the ratio $j_{i-1,i}/j_{i,i+1}$. We derive this ratio from Eq. (24) using also the expansion (25),

$$\frac{j_{i-1,i}}{j_{i,i+1}} = \frac{1}{1 + \lambda p_i/j_{i-1,i}} = \frac{1}{1 + \lambda a_i + O(\lambda^2)} = 1 - \lambda a_i + O(\lambda^2). \tag{34}$$

Finally, let us substitute Eq. (34) into Eq. (33),

$$\Gamma_{i,i+1}(1 - \lambda a_i)(a_i + \lambda b_i) - \Gamma_{i+1,i}(a_{i+1} + \lambda b_{i+1}) = 1 + O(\lambda^2), \tag{35}$$

and collect separately terms which do not contain λ and those proportional to λ. The former terms lead to Eq. (28), while the latter ones give the equation

$$\Gamma_{i,i+1}(\lambda b_i - \lambda a_i^2) - \Gamma_{i+1,i}\lambda b_{i+1} = 0. \tag{36}$$

Equation (36) provides a desired set of equations for coefficients b_i,

$$\forall \ i \quad \Gamma_{i,i+1}b_i - \Gamma_{i+1,i}b_{i+1} = \Gamma_{i,i+1}a_i^2. \tag{37}$$

The solution of Eq. (37) can be found as an infinite series

$$b_i = a_i^2 + \frac{\Gamma_{i+1,i}}{\Gamma_{i,i+1}}a_{i+1}^2 + \frac{\Gamma_{i+1,i}\Gamma_{i+2,i+1}}{\Gamma_{i,i+1}\Gamma_{i+1,i+2}}a_{i+2}^2 + \cdots \tag{38}$$

that can be checked by substitution into Eq. (37). Like Eq. (29), the series (38) converges provided the product eF is positive. To prove it, we substitute the condition of detailed balance, Eq. (7), into this series

$$b_i = a_i^2 + B^{-1}\exp\left(\frac{\varepsilon_{i+1} - \varepsilon_i}{kT}\right)a_{i+1}^2 + B^{-2}\exp\left(\frac{\varepsilon_{i+2} - \varepsilon_i}{kT}\right)a_{i+2}^2$$

$$+ \cdots. \tag{39}$$

In any real system, we find an upper limit for the quantities $\exp[(\varepsilon_{i+k}-\varepsilon_i)/kT]a_{i+k}^2$. Setting this limit equal to $\tilde{C}$, we obtain an upper estimate for b_i,

$$b_i < \tilde{C} + B^{-1}\tilde{C} + B^{-2}\tilde{C} + \cdots = \frac{\tilde{C}}{1 - B^{-1}}. \tag{40}$$

Therefore, the series (38) converges if $B>1$, i.e., if $eF>0$.

As a result, we have obtained an analytical expression (27) for the diffusion coefficient D in a one-dimensional hopping system. For coefficients a_i and b_i that contribute into Eq. (27), we have found series representations (29) and (38) in the case $eF>0$. It is easy to write down analogous series for a_i and b_i in the opposite case, $eF<0$.

III. RANDOM-BARRIER MODEL: EXACT RESULTS

Let us now apply Eqs. (27), (29), and (38) to the random-barrier model described by Eqs. (2) and (5). In this model, any two transition rates Γ_{ij} and Γ_{kl} are statistically independent if (ij) and (kl) are different pairs of sites. The rates $\Gamma_{i,i+1}$ and $\Gamma_{i+1,i}$, related to the same pair, are connected to each other. As a result, all statistical properties of the random-barrier model are defined by mean values $\langle \Gamma_{i,i+1}^m \Gamma_{i+1,i}^n \rangle$ with different m's and n's. We introduce the following notations for these mean values:

$$m_1 = \langle \Gamma_{i+1,i}/\Gamma_{i,i+1} \rangle,$$

$$m_2 = \langle \Gamma_{i+1,i}^2/\Gamma_{i,i+1}^2 \rangle,$$

$$m_3 = \langle 1/\Gamma_{i,i+1} \rangle,$$

$$m_4 = \langle 1/\Gamma_{i,i+1}^2 \rangle,$$

$$m_5 = \langle \Gamma_{i+1,i}/\Gamma_{i,i+1}^2 \rangle. \tag{41}$$

In order to obtain the drift velocity v and the diffusion coefficient D from Eq. (27), one should calculate the mean values $\langle a_i \rangle$, $\langle a_i^2 \rangle$, and $\langle b_i \rangle$. We start with calculating $\langle a_i \rangle$. Let us denote successive terms in the expansion (29) as $a^{(0)}, a^{(1)}, a^{(2)}, \ldots$ Then,

$$\langle a^{(0)} \rangle = \left\langle \frac{1}{\Gamma_{i,i+1}} \right\rangle = m_3,$$

$$\langle a^{(1)} \rangle = \left\langle \frac{\Gamma_{i+1,i}}{\Gamma_{i,i+1}} \right\rangle \left\langle \frac{1}{\Gamma_{i+1,i+2}} \right\rangle = m_1 m_3,$$

$$\langle a^{(2)} \rangle = \left\langle \frac{\Gamma_{i+1,i}}{\Gamma_{i,i+1}} \right\rangle \left\langle \frac{\Gamma_{i+2,i+1}}{\Gamma_{i+1,i+2}} \right\rangle \left\langle \frac{1}{\Gamma_{i+2,i+3}} \right\rangle = m_1^2 m_3,$$

$$\ldots$$

$$\langle a^{(k)} \rangle = m_1^k m_3. \tag{42}$$

Consequently,

$$\langle a_i \rangle = \langle a^{(0)} \rangle + \langle a^{(1)} \rangle + \langle a^{(2)} \rangle + \cdots = m_3(1 + m_1 + m_1^2 + \cdots)$$
$$= m_3/(1 - m_1). \tag{43}$$

The mean value $\langle a_i^2 \rangle$ can be represented as a sum of values $\langle a^{(k)} a^{(l)} \rangle$ over all pairs k, l,

$$\langle a_i^2 \rangle = \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} \langle a^{(k)} a^{(l)} \rangle. \tag{44}$$

It is easy to check that

$$\langle a^{(k)} a^{(l)} \rangle = \begin{cases} m_1^{l-k-1} m_2^k m_3 m_5, & \text{if } k < l \\ m_2^k m_4, & \text{if } k = l \\ m_1^{k-l-1} m_2^l m_3 m_5, & \text{if } k > l. \end{cases} \tag{45}$$

Then, presenting Eq. (44) in the form

$$\langle a_i^2 \rangle = \sum_{k=0}^{\infty} \langle (a^{(k)})^2 \rangle + 2 \sum_{k<l} \langle a^{(k)} a^{(l)} \rangle, \tag{46}$$

using Eq. (45), and introducing the notation $p = l - k - 1$, we obtain

$$\langle a_i^2 \rangle = \sum_{k=0}^{\infty} m_2^k m_4 + 2 \sum_{k=0}^{\infty} \sum_{l=k+1}^{\infty} m_1^{l-k-1} m_2^k m_3 m_5$$
$$= \frac{m_4}{1 - m_2} + 2 m_3 m_5 \sum_{k=0}^{\infty} m_2^k \sum_{p=0}^{\infty} m_1^p$$
$$= \frac{m_4}{1 - m_2} + \frac{2 m_3 m_5}{(1 - m_1)(1 - m_2)}. \tag{47}$$

In an analogous way, we denote successive terms of the series (38) as $b^{(0)}, b^{(1)}, b^{(2)}, \ldots$. The mean values of these quantities are

$$\langle b^{(0)} \rangle = \langle a_i^2 \rangle,$$

$$\langle b^{(1)} \rangle = \left\langle \frac{\Gamma_{i+1,i}}{\Gamma_{i,i+1}} a_{i+1}^2 \right\rangle = m_1 \langle a_i^2 \rangle,$$

$$\langle b^{(2)} \rangle = \left\langle \frac{\Gamma_{i+1,i} \Gamma_{i+2,i+1}}{\Gamma_{i,i+1} \Gamma_{i+1,i+2}} a_{i+2}^2 \right\rangle = m_1^2 \langle a_i^2 \rangle,$$

$$\ldots$$

$$\langle b^{(k)} \rangle = m_1^k \langle a_i^2 \rangle. \tag{48}$$

Therefore,

$$\langle b_i \rangle = \langle b^{(0)} \rangle + \langle b^{(1)} \rangle + \langle b^{(2)} \rangle + \cdots = \langle a_i^2 \rangle (1 + m_1 + m_1^2 + \cdots)$$
$$= \langle a_i^2 \rangle / (1 - m_1). \tag{49}$$

Finally, we substitute Eqs. (43), (47), and (49) for the mean values $\langle a_i \rangle$, $\langle a_i^2 \rangle$, and $\langle b_i \rangle$ into Eq. (27). This gives

$$v = d \frac{1 - m_1}{m_3}, \tag{50}$$

$$D = d^2 \frac{1 - m_1^2}{2 m_3^3 (1 - m_2)} [m_4 (1 - m_1) + 2 m_3 m_5]. \tag{51}$$

Equations (50) and (51) are not new results—they were obtained in Ref. 27 [Eqs. (67) and Eq. (70), respectively]. Their derivation in the frame of our method clearly demonstrates that both methods (Derrida's and ours) are consistent. In the rest of this section, we will apply these equations to the case of Gaussian distribution of barrier heights.

For the transition rates defined by Eqs. (2) and (5), the mean values $m_1 \ldots m_5$ are easy to evaluate. Setting Γ_0 equal to unity for the sake of simplicity, we obtain

$$m_1 = \exp\left(-\frac{eFd}{kT}\right),$$

$$m_2 = \exp\left(-\frac{2eFd}{kT}\right),$$

$$m_3 = \exp\left(\frac{\sigma^2}{8(kT)^2} - \frac{eFd}{2kT}\right),$$

$$m_4 = \exp\left(\frac{\sigma^2}{2(kT)^2} - \frac{eFd}{kT}\right),$$

$$m_5 = \exp\left(\frac{\sigma^2}{8(kT)^2} - \frac{3eFd}{2kT}\right). \tag{52}$$

From Eq. (50), one obtains the result for the drift velocity v,

$$v = 2d \exp\left(-\frac{\sigma^2}{8(kT)^2}\right)\sinh\left(\frac{eFd}{2kT}\right). \tag{53}$$

Note that we derived the latter equation only for the case $eF>0$. However, it is easy to show that Eq. (53) is valid for any direction of the electric field. Indeed, the right-hand side of the equation is an odd function of the electric field F. The left-hand side (drift velocity) should also be odd because the system is symmetrical with respect to a left-to-right mirror reflection ($x \to -x$, $F \to -F$, $v \to -v$). Therefore, if Eq. (53) is satisfied for positive electric fields, it remains valid for negative fields and vice versa.

An expression for the diffusion coefficient D as a function of F can be obtained by substituting the mean values (52) into Eq. (51). Strictly speaking, this procedure is valid for D only in the case $eF>0$. One can however generalize this expression for any sign of the electric field using the fact that (for symmetry reasons) D is an even function of F. One simply should replace eF by its absolute value $|eF|$ in all expressions. The result reads

$$D = d^2 \exp\left(-\frac{\sigma^2}{8(kT)^2} - \frac{|eF|d}{2kT}\right) + d^2 \exp\left(\frac{\sigma^2}{8(kT)^2}\right)\sinh\left(\frac{|eF|d}{2kT}\right). \tag{54}$$

Equation (54) was obtained for *nonzero* electric fields. However, one can check that it holds also for $F=0$. This equation clearly shows that in case of absence of disorder, $\sigma=0$, the diffusion coefficient has an analytic dependence on the electric field. It is the presence of disorder that converts this dependence into a nonanalytic one.

Equation (54) differs from the expression given by Bouchaud and Georges,[23] $D(F)-D(0) \propto F \exp[3\sigma^2/8(kT)^2]$, though it is linear in F to first order. Equation (54) is plotted in Fig. 2 together with numerical results obtained in Sec. V.

IV. RANDOM-ENERGY MODEL: EXACT RESULTS

The random-energy model in one dimension implies the following definition of transition rates:

$$\Gamma_{i,i\pm1} = \Gamma_0 \exp\left(-\frac{\Delta\varepsilon_{i,i\pm1} + |\Delta\varepsilon_{i,i\pm1}|}{2kT}\right), \tag{55}$$

where $\Delta\varepsilon_{i,i\pm1}=\varepsilon_{i\pm1}-\varepsilon_i \mp eFd$ is the difference between the energies of a charge carrier on the final site and on the initial site, respectively, for each jump. For simplicity, we set the constant $\Gamma_0 \equiv \nu_0 \exp(-2d/a)$ to unity.

For the REM, one can use the same way of calculating the velocity and the diffusion constant as for the RBM. The REM contains more correlations between transition rates that the RBM, which leads to more complicated calculations of the mean values $\langle a_i \rangle$, $\langle a_i^2 \rangle$, and $\langle b_i \rangle$. In the REM, each rate Γ_{ij} depends on the energies ε_i and ε_j, which are independent random variables. Therefore, the rates Γ_{ij} and Γ_{kl} are correlated if the pairs of sites (ij) and (kl) have at least one site in common.

We will see below that the drift velocity v and the diffusion coefficient D depend on 11 quantities $m_1 \ldots m_{11}$ related to the statistics of site energies and transition rates

$$m_1 = \langle e^{-\varepsilon_i/kT} \rangle,$$

$$m_2 = \langle e^{-2\varepsilon_i/kT} \rangle,$$

$$m_3 = \langle \Gamma_{i,i+1}^{-1} \rangle,$$

$$m_4 = \langle e^{\varepsilon_i/kT} \Gamma_{i,i+1}^{-1} \rangle,$$

$$m_5 = \langle e^{-\varepsilon_i/kT} \Gamma_{i,i+1}^{-1} \rangle,$$

$$m_6 = \langle \Gamma_{i,i+1}^{-2} \rangle,$$

$$m_7 = \langle e^{\varepsilon_i/kT} \Gamma_{i,i+1}^{-2} \rangle,$$

$$m_8 = \langle e^{2\varepsilon_i/kT} \Gamma_{i,i+1}^{-2} \rangle,$$

$$m_9 = \langle e^{(\varepsilon_{i+1}-\varepsilon_i)/kT} \Gamma_{i,i+1}^{-1} \Gamma_{i+1,i+2}^{-1} \rangle,$$

$$m_{10} = \langle e^{\varepsilon_{i+1}/kT} \Gamma_{i,i+1}^{-1} \Gamma_{i+1,i+2}^{-1} \rangle,$$

$$m_{11} = \langle e^{(\varepsilon_{i+1}+\varepsilon_i)/kT} \Gamma_{i,i+1}^{-1} \Gamma_{i+1,i+2}^{-1} \rangle. \tag{56}$$

In the following, we proceed for the REM along the same steps as for the RBM in the previous section.

A. Calculation of $\langle a_i \rangle$

Let us denote successive terms of the expansion (30) as $a^{(0)}$, $a^{(1)}$, $a^{(2)}$, and so on. Then $\langle a_i \rangle = \langle a^{(0)} \rangle + \langle a^{(1)} \rangle + \langle a^{(2)} \rangle + \ldots$. The latter quantities can be easily expressed via m_1, m_3, and m_4,

$$\langle a^{(0)} \rangle = \langle \Gamma_{i,i+1}^{-1} \rangle = m_3,$$

$$\langle a^{(1)} \rangle = B^{-1} \langle e^{-\varepsilon_i/kT} \rangle \langle e^{\varepsilon_{i+1}/kT} \Gamma_{i+1,i+2}^{-1} \rangle = B^{-1} m_1 m_4,$$

$$\langle a^{(2)}\rangle = B^{-2}\langle e^{-\varepsilon_i/kT}\rangle\langle e^{\varepsilon_{i+2}/kT}\Gamma^{-1}_{i+2,i+3}\rangle = B^{-2}m_1m_4, \quad (57)$$

and, generally, $\langle a^{(k)}\rangle = B^{-k}m_1m_4$ for any $k>0$. Then,

$$\langle a_i\rangle = m_3 + (B^{-1}+B^{-2}+\cdots)m_1m_4 = m_3 + \frac{m_1m_4}{B-1}. \quad (58)$$

B. Calculation of $\langle a_i^2\rangle$

According to Eq. (44), the calculation of $\langle a_i^2\rangle$ is reduced calculating the mean values $\langle a^{(k)}a^{(l)}\rangle$ for all integer $k\geq 0$ and $l\geq 0$. Thus one can reduce the mean values $\langle a^{(k)}a^{(l)}\rangle$ to

$$\langle a^{(k)}a^{(l)}\rangle = \begin{cases} m_6, & \text{if } k=l=0 \\ B^{-1}m_9, & \text{if } k=0,\ l=1 \\ B^{-l}m_4m_5, & \text{if } k=0,\ l>1 \\ B^{-2k}m_2m_8, & \text{if } k>0,\ l=k \\ B^{-2k-1}m_2m_{11}, & \text{if } k>0,\ l=k+1 \\ B^{-k-l}m_2m_4^2, & \text{if } k>0,\ l>k+1. \end{cases} \quad (59)$$

The next step is the estimate of the infinite series (44). It is convenient to rearrange the summation in Eq. (44), separating terms corresponding to different lines of Eq. (59)

$$\langle a_i^2\rangle = \langle (a^{(0)})^2\rangle + \sum_{k=1}^{\infty}\langle (a^{(k)})^2\rangle + 2\langle a^{(0)}a^{(1)}\rangle + 2\sum_{l=2}^{\infty}\langle a^{(0)}a^{(l)}\rangle + 2\sum_{k=1}^{\infty}\langle a^{(k)}a^{(k+1)}\rangle + 2\sum_{k=1}^{\infty}\sum_{p=2}^{\infty}\langle a^{(k)}a^{(k+p)}\rangle, \quad (60)$$

where $p=l-k$. Substituting Eq. (59) into this expansion, one gets

$$\langle a_i^2\rangle = m_6 + m_2m_8\sum_{k=1}^{\infty}B^{-2k} + 2B^{-1}m_9 + 2m_4m_5\sum_{l=2}^{\infty}B^{-l} + 2m_2m_{11}\sum_{k=1}^{\infty}B^{-2k-1} + 2m_2m_4^2\sum_{k=1}^{\infty}B^{-2k}\sum_{p=2}^{\infty}B^{-p}. \quad (61)$$

Finally, one can sum up the geometric series. The result reads

$$\langle a_i^2\rangle = m_6 + \frac{2m_9}{B} + \frac{2m_4m_5}{B(B-1)} + m_2\frac{Bm_8+2m_{11}}{B(B^2-1)} + \frac{2m_2m_4^2}{B(B-1)(B^2-1)}. \quad (62)$$

C. Calculation of $\langle b_i\rangle$

In an analogous way, $\langle b_i\rangle$ can be expressed as a sum $\langle b^{(0)}\rangle+\langle b^{(1)}\rangle+\langle b^{(2)}\rangle+\cdots$, where $b^{(0)},b^{(1)},\ldots,b^{(i)},\ldots$ are the terms of the expansion (39). Keeping in mind that, according to Eq. (29), the values $a_{i+1},a_{i+2},\ldots$ do not depend on ε_i, one can express the mean values $b^{(k)}$ as follows:

$$\langle b^{(0)}\rangle = \langle a_i^2\rangle,$$

$$\langle b^{(1)}\rangle = B^{-1}\langle e^{-\varepsilon_i/kT}\rangle\langle e^{\varepsilon_{i+1}/kT}a_{i+1}^2\rangle = B^{-1}m_1M, \quad (63)$$

$$\langle b^{(2)}\rangle = B^{-2}\langle e^{-\varepsilon_i/kT}\rangle\langle e^{\varepsilon_{i+2}/kT}a_{i+2}^2\rangle = B^{-2}m_1M, \quad (64)$$

and so on for larger i, where $M=\langle e^{\varepsilon_i/kT}a_i^2\rangle$. Thus,

$$\langle b_i\rangle = \langle a_i^2\rangle + (B^{-1}+B^{-2}+\cdots)m_1M \quad (65)$$

or

$$\langle b_i\rangle = \langle a_i^2\rangle + \frac{m_1}{B-1}M. \quad (66)$$

In order to find M, one can expand it in series analogous to Eq. (44),

$$M \equiv \langle e^{\varepsilon_i/kT}a_i^2\rangle = \sum_{k=0}^{\infty}\sum_{l=0}^{\infty}\langle e^{\varepsilon_i/kT}a^{(k)}a^{(l)}\rangle, \quad (67)$$

and express each term of the expansion via

$$\langle e^{\varepsilon_i/kT}a^{(k)}a^{(l)}\rangle = \begin{cases} m_7, & \text{if } k=l=0 \\ B^{-1}m_{10}, & \text{if } k=0,\ l=1 \\ B^{-l}m_4m_3, & \text{if } k=0,\ l>1 \\ B^{-2k}m_1m_8, & \text{if } k>0,\ l=k \\ B^{-2k-1}m_1m_{11}, & \text{if } k>0,\ l=k+1 \\ B^{-k-l}m_1m_4^2, & \text{if } k>0,\ l>k+1. \end{cases} \quad (68)$$

The following steps are the same as the ones leading from Eq. (59) to Eq. (62). Instead of proceeding in this way, one can recognize that Eq. (59) transforms to Eq. (68) by the following replacements:

$$m_6\to m_7, \quad m_9\to m_{10}, \quad m_5\to m_3, \quad m_2\to m_1.$$

Applying the same replacements to Eq. (62), we obtain the result for M,

$$M = m_7 + \frac{2m_{10}}{B} + \frac{2m_3m_4}{B(B-1)} + m_1\frac{Bm_8+2m_{11}}{B(B^2-1)} + \frac{2m_1m_4^2}{B(B-1)(B^2-1)}. \quad (69)$$

Substituting Eqs. (62) and (69) into Eq. (66), one obtains the expression for $\langle b_i\rangle$ in terms of the values $m_1\ldots m_{11}$.

D. Drift velocity and diffusion coefficient

Combining Eqs. (27), (58), (62), (66), and (69) leads to

$$v = \frac{d}{m_3 + m_1m_4/(B-1)}, \quad (70)$$

$$D = \frac{v^3}{2d}\left[m_6 + \frac{2m_9}{B} + \frac{2m_4m_5}{B(B-1)} + m_2\frac{Bm_8+2m_{11}}{B(B^2-1)} + \frac{2m_2m_4^2}{B(B-1)(B^2-1)} + \frac{2m_1}{B-1}\left(m_7 + \frac{2m_{10}}{B} + \frac{2m_3m_4}{B(B-1)} + m_1\frac{Bm_8+2m_{11}}{B(B^2-1)} + \frac{2m_1m_4^2}{B(B-1)(B^2-1)}\right)\right], \quad (71)$$

where $B=\exp(eFd/kT)$. Note that we derived these equations for the case $eF>0$. One can easily generalize the equations for the case $eF<0$, keeping in mind that v is an odd function of F and D is an even function.

Equation (70) was obtained previously by Cordes *et al.*[28] using Derrida's method,[27] while Eq. (71) is a new result. Equations (70) and (71) are general for the case of the REM—their derivation is not restricted by a special choice of the density of states or by the choice of the relation between the transition rates Γ_{ij} and the site energies $\varepsilon_i, \varepsilon_j$. We used only four assumptions: (i) all sites are arranged in the line with constant distance d between them; (ii) there are only transitions between nearest neighbors; (iii) transition rates "forth" and "back" ($\Gamma_{i,i+1}$ and $\Gamma_{i+1,i}$) obey the principle of detailed balance, Eq. (7); (iv) energies of different sites are independent random variables having the same distribution function.

E. Gaussian density of states

We will now evaluate the quantities $m_1 \ldots m_{11}$ assuming a Gaussian density of states, Eq. (2), and the Miller-Abrahams transition rates, Eq. (55). This evaluation is straightforward, for example,

$$m_1 = N_0^{-1}\int e^{-\varepsilon/kT} g(\varepsilon)d\varepsilon = \frac{1}{\sqrt{2\pi}\sigma}\int \exp\left(-\frac{\varepsilon}{kT}-\frac{\varepsilon^2}{2\sigma^2}\right)d\varepsilon = \exp\left(\frac{\sigma^2}{2(kT)^2}\right),$$

$$m_3 = N_0^{-2}\int\int \Gamma_{12}^{-1} g(\varepsilon_1)g(\varepsilon_2)d\varepsilon_1 d\varepsilon_2 = \frac{1}{2\pi\sigma^2}\int\int \exp\left(\frac{\varepsilon_2-\varepsilon_1-eFd+|\varepsilon_2-\varepsilon_1-eFd|}{2kT} - \frac{\varepsilon_1^2+\varepsilon_2^2}{2\sigma^2}\right)d\varepsilon_1 d\varepsilon_2.$$

The latter integral can be evaluated by substitution $u=\varepsilon_1+\varepsilon_2$, $v=\varepsilon_1-\varepsilon_2$, and the result is

$$m_3 = \frac{1}{2}\mathrm{erfc}\left(-\frac{eFd}{2\sigma}\right)+\frac{1}{2}\exp\left(\frac{\sigma^2}{(kT)^2}-\frac{eFd}{kT}\right)\mathrm{erfc}\left(\frac{eFd}{2\sigma}-\frac{\sigma}{kT}\right), \tag{72}$$

where erfc is the complementary error function, $\mathrm{erfc}(x)=2\pi^{-1/2}\int_x^\infty e^{-t^2}dt=1-\mathrm{erf}(x)$.

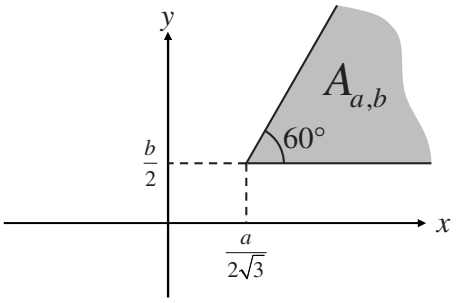

FIG. 1. Integration area for the definition of the function $\mathcal{F}(a,b)$.

The values $m_9 \ldots m_{11}$ are triple integrals. They cannot be expressed in elementary functions, but they can be reduced (by a substitution $u=\varepsilon_1+\varepsilon_2+\varepsilon_3$, $v=\varepsilon_1-\varepsilon_2$, $w=\varepsilon_1+\varepsilon_2-2\varepsilon_3$) to a function $\mathcal{F}(a,b)$ defined as

$$\mathcal{F}(a,b) = \frac{1}{\pi}\int\int_{A_{a,b}} e^{-(x^2+y^2)}dxdy, \tag{73}$$

where the area of integration $A_{a,b}$ is shown in Fig. 1.

The results are collected in Table I. These results obtained for Miller-Abrahams hopping rates, Eq. (55), look rather complicated for analytical estimates. Below in Sec. V, we use these expressions from Table I for numerical calculations and present the results for the Miller-Abrahams hopping rates, Eq. (55). Here we will proceed with analytical calculations based on slightly modified expressions for the hopping rates, which allow straightforward analytical estimates. We suggest using, instead of Eq. (55), the following "modified Miller-Abrahams rates:"

$$\Gamma_{i,i\pm1} = \Gamma_0\left[1+\exp\left(\frac{\Delta\varepsilon_{i,i\pm1}}{kT}\right)\right]^{-1}, \tag{74}$$

where the constant Γ_0 will be set equal to unity for the sake of simplicity. The difference between Eqs. (55) and (74) becomes negligible when $|\Delta\varepsilon_{i,i\pm1}| \gg kT$. Therefore, for $\sigma \gg kT$, we expect a good agreement between results obtained with these two kinds of hopping rates.

Results for the modified Miller-Abrahams rates are also shown in Table I. Substituting them into Eqs. (70) and (71), one can get the explicit expressions for the drift velocity and the diffusion coefficient[30]

$$|v| = d\frac{B-1}{2A+B-1}, \tag{75}$$

$$D = d^2\frac{4A^4(B-1)^2+16A^3(B-1)+16A^2+2A(3B+1)(B^2-1)+(B-1)^3(B+1)}{2(B+1)(2A+B-1)^3}, \tag{76}$$

where $A=\exp(\sigma^2/(kT)^2)$ and $B=\exp(|eF|d/kT)$.

TABLE I. The values of $m_1 \ldots m_{11}$ for the random-energy model with Gaussian density of states. "MA" refers to using Miller-Abrahams hopping rates, Eq. (55), and "modified MA" to hopping rates defined by Eq. (74). Other notations: $A=\exp(\sigma^2/(kT)^2)$, $B=\exp(eFd/kT)$, $\alpha=\sigma/kT$, and $\beta=eFd/\sigma$; erfc is the complementary error function. The function $\mathcal{F}(a,b)$ is defined by Eq. (73).

Notation	Definition	Value (MA)	Value (modified MA)
m_1	$\langle e^{-\varepsilon_i/kT}\rangle$	$\sqrt{A}$	$\sqrt{A}$
m_2	$\langle e^{-2\varepsilon_i/kT}\rangle$	A^2	A^2
m_3	$\langle \Gamma_{i,i+1}^{-1}\rangle$	$\frac{1}{2}[\mathrm{erfc}(-\frac{\beta}{2})+AB^{-1}\,\mathrm{erfc}(\frac{\beta}{2}-\alpha)]$	$1+AB^{-1}$
m_4	$\langle e^{\varepsilon_i/kT}\Gamma_{i,i+1}^{-1}\rangle$	$\frac{1}{2}\sqrt{A}[\mathrm{erfc}(-\frac{\beta}{2}-\frac{\alpha}{2})+B^{-1}\,\mathrm{erfc}(\frac{\beta}{2}-\frac{\alpha}{2})]$	$\sqrt{A}(1+B^{-1})$
m_5	$\langle e^{-\varepsilon_i/kT}\Gamma_{i,i+1}^{-1}\rangle$	$\frac{1}{2}\sqrt{A}[\mathrm{erfc}(-\frac{\beta}{2}+\frac{\alpha}{2})+A^2B^{-1}\,\mathrm{erfc}(\frac{\beta}{2}-\frac{3\alpha}{2})]$	$\sqrt{A}(1+A^2B^{-1})$
m_6	$\langle \Gamma_{i,i+1}^{-2}\rangle$	$\frac{1}{2}[\mathrm{erfc}(-\frac{\beta}{2})+A^4B^{-2}\,\mathrm{erfc}(\frac{\beta}{2}-2\alpha)]$	$1+2AB^{-1}+A^4B^{-2}$
m_7	$\langle e^{\varepsilon_i/kT}\Gamma_{i,i+1}^{-2}\rangle$	$\frac{1}{2}\sqrt{A}[\mathrm{erfc}(-\frac{\beta}{2}-\frac{\alpha}{2})+A^2B^{-2}\,\mathrm{erfc}(\frac{\beta}{2}-\frac{3\alpha}{2})]$	$\sqrt{A}(1+2B^{-1}+A^2B^{-2})$
m_8	$\langle e^{2\varepsilon_i/kT}\Gamma_{i,i+1}^{-2}\rangle$	$\frac{1}{2}A^2[\mathrm{erfc}(-\frac{\beta}{2}-\alpha)+B^{-2}\,\mathrm{erfc}(\frac{\beta}{2}-\alpha)]$	$A^2(1+B^{-2})+2AB^{-1}$
m_9	$\langle e^{(\varepsilon_{i+1}-\varepsilon_i)/kT}\Gamma_{i,i+1}^{-1}\Gamma_{i+1,i+2}^{-1}\rangle$	$A\mathcal{F}(-3\beta,2\alpha-\beta)+A^3B^{-2}\mathcal{F}(3\beta-3\alpha,\beta-3\alpha)$ $+AB^{-1}\left[\frac{1}{2}\mathrm{erfc}\left(\frac{\alpha-\beta}{2}\right)-\mathcal{F}(3\alpha-3\beta,\alpha-\beta)\right]$ $+A^4B^{-1}\left[\frac{1}{2}\mathrm{erfc}\left(\frac{\beta}{2}-2\alpha\right)-\mathcal{F}(3\beta,\beta-4\alpha)\right]$	$A[1+A^2B^{-2}+(1+A^3)B^{-1}]$
m_{10}	$\langle e^{\varepsilon_{i+1}/kT}\Gamma_{i,i+1}^{-1}\Gamma_{i+1,i+2}^{-1}\rangle$	$\sqrt{A}\mathcal{F}(-\alpha-3\beta,\alpha-\beta)+A^{3/2}B^{-2}\mathcal{F}(3\beta-2\alpha,\beta-2\alpha)$ $+\sqrt{A}B^{-1}\left[\frac{1}{2}\mathrm{erfc}\left(-\frac{\beta}{2}\right)-\mathcal{F}(2\alpha-3\beta,-\beta)\right]$ $+A^{5/2}B^{-1}\left[\frac{1}{2}\mathrm{erfc}\left(\frac{\beta}{2}-\frac{3\alpha}{2}\right)-\mathcal{F}(\alpha+3\beta,\beta-3\alpha)\right]$	$\sqrt{A}[1+AB^{-2}+(1+A^2)B^{-1}]$
m_{11}	$\langle e^{(\varepsilon_{i+1}+\varepsilon_i)/kT}\Gamma_{i,i+1}^{-1}\Gamma_{i+1,i+2}^{-1}\rangle$	$A\mathcal{F}(-2\alpha-3\beta,-\beta)+AB^{-2}\mathcal{F}(3\beta-\alpha,\beta-\alpha)$ $+AB^{-1}\left[\frac{1}{2}\mathrm{erfc}\left(\frac{-\alpha-\beta}{2}\right)-\mathcal{F}(\alpha-3\beta,-\alpha-\beta)\right]$ $+A^2B^{-1}\left[\frac{1}{2}\mathrm{erfc}\left(\frac{\beta}{2}-\alpha\right)-\mathcal{F}(2\alpha+3\beta,\beta-2\alpha)\right]$	$A[1+B^{-2}+(1+A)B^{-1}]$

Now we will consider the mobility $\mu(F)=v(F)/F$ and the diffusion coefficient $D(F)$ in the limit of small field. We restrict ourselves to the case of modified Miller-Abrahams rates. For $F=0$, one can obtain from Eqs. (75) and (76)

$$D(0)=\mu(0)\frac{kT}{e}=\frac{d^2}{2}\exp[-(\sigma/kT)^2]. \tag{77}$$

For small temperatures, $kT\ll\sigma$, the mobility and the diffusion coefficient can be approximated by simple expressions

$$\mu(F)\approx\frac{ed^2}{2AkT}+\frac{|Fe|ed^3}{4A(kT)^2}+\frac{F^2e^3d^4}{12A(kT)^3}, \tag{78}$$

$$D(F)\approx\frac{d^2}{2A}+\frac{|Fe|d^3}{2kT}+\frac{F^2e^2d^4A}{8(kT)^2}+\frac{|Fe|^3d^5A}{16(kT)^3}. \tag{79}$$

These approximations are valid for sufficiently small fields, $|eFd|<kT$.

From the latter approximated expressions, it is obvious that there is a cusp at $F=0$ for both $\mu(F)$ and $D(F)$. The dependence $D(F)$ demonstrates a linear behavior for very small fields ($|eFd|\ll kT/A$), when the first two terms in Eq. (79) are dominating, and a parabolic behavior for intermediate fields ($kT/A\ll|eFd|\ll kT$), when the third term is dominating.

V. NUMERICAL RESULTS

In order to verify the analytical results obtained above, we perform numerical calculations for a one-dimensional chain of N hopping sites using the equations that give the drift velocity v and the diffusion coefficient D as a function of all the hopping rates $\Gamma_{i\pm1,i}$ in the chain[27]

$$D=\frac{1}{\left(\sum_{n=1}^{N}r_n\right)^2}\left(v\sum_{n=1}^{N}u_n\sum_{i=1}^{N}ir_{n+i}+N\sum_{n=1}^{N}\Gamma_{n,n+1}u_nr_n\right)-v\frac{N+2}{2}, \tag{80}$$

$$v=\frac{N}{\sum_{n=1}^{N}r_n}\left[1-\prod_{n=1}^{N}\left(\frac{\Gamma_{n+1,n}}{\Gamma_{n,n+1}}\right)\right], \tag{81}$$

$$r_n=\frac{1}{\Gamma_{n,n+1}}\left[1+\sum_{i=1}^{N-1}\prod_{j=1}^{i}\left(\frac{\Gamma_{n+j,n+j-1}}{\Gamma_{n+j,n+j+1}}\right)\right], \tag{82}$$

$$u_n = \frac{1}{\Gamma_{n,n+1}}\left[1 + \sum_{i=1}^{N-1}\prod_{j=1}^{i}\left(\frac{\Gamma_{n-j+1,n-j}}{\Gamma_{n-j,n-j+1}}\right)\right]. \quad (83)$$

In this section, we follow Ref. 27 and set the distance d between sites equal to unity for the sake of simplicity.

For both the RBM and the REM, the diffusion coefficient was obtained for different temperatures and fields, by generating several chains with random jump rates (according to the respective model), evaluating Eq. (80) for each chain and averaging the results. Long chains (10^7 and 10^8 sites) were needed to obtain a good agreement between different realizations of the chains.

For chains of this length, a direct evaluation of Eqs. (80)–(83) is not practical. Below, the equations are rewritten in a form that can be evaluated in $O(N)$ steps using recursion relations. Define

$$g_n = \frac{\Gamma_{n,n-1}}{\Gamma_{n,n+1}} \quad \text{and} \quad h_n = \frac{\Gamma_{n+1,n}}{\Gamma_{n,n+1}} \quad (84)$$

and further

$$G_n = 1 + \sum_{i=1}^{N-1}\prod_{j=1}^{i} g_{n+j}, \quad (85)$$

$$H_n = 1 + \sum_{i=1}^{N-1}\prod_{j=1}^{i} h_{n-j}, \quad (86)$$

so that $r_n = G_n/\Gamma_{n,n+1}$ and $u_n = H_n/\Gamma_{n,n+1}$. All G_n and H_n, and thus r_n and u_n can now be calculated efficiently from

$$G_{n-1} = g_n G_n - G + 1, \quad (87)$$

$$H_{n+1} = h_n H_n - H + 1, \quad (88)$$

where $G = H = g_1 g_2 \ldots g_N = h_1 h_2 \ldots h_N$. For the first term in the brackets in Eq. (80), define $S_n = \Sigma_{i=1}^{N} i r_{n+i}$ and $S = \Sigma_{i=1}^{N} r_n$. Now

$$S_{n+1} = S_n - S + N r_{n+1}. \quad (89)$$

These relations are numerically stable if $G < 1$, which is satisfied if the average drift is to the right (toward larger site indices). The diffusion coefficient is now given by

$$D = \frac{1}{S^2}\left(v\sum_{n=1}^{N}\frac{H_n S_n}{\Gamma_{n,n+1}} + N\sum_{n=1}^{N}\frac{G_n H_n}{\Gamma_{n,n+1}}\right) - v\frac{N+2}{2}. \quad (90)$$

It seems tempting to write Eq. (87) in the form

$$G_n = (G_{n-1} + G - 1)/g_n,$$

so that all equations could be evaluated starting from $n=1$, but this form is too susceptible to numerical errors to be usable in practice. Thus one has to evaluate all G_n with Eq. (87) starting from G_N and store them in a table. S_n and H_n do not need to be stored since they can be evaluated while performing the sum in Eq. (90) starting from $n=1$.

With this method of evaluation, numerical results for the diffusion coefficient were obtained. The results are shown in Fig. 2 for the RBM, together with the analytical results, and in Fig. 3 for the REM. For both models, the diffusion coefficient is linear in the electric field (at low fields) (see the insets in each figure).

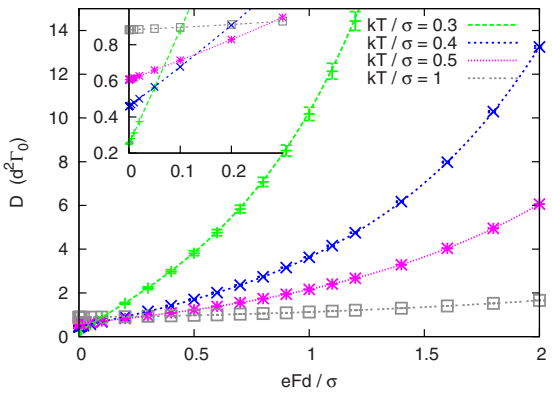

FIG. 2. (Color online) $D(F)$ in the RBM for different temperatures T. Curves show the analytical solution Eq. (54), while the symbols show numerical results [Eq. (80)] for chains with $N=10^7$ sites. Inset shows the low-field behavior.

VI. DISCUSSION AND CONCLUSIONS

Figures 2 and 3 demonstrate a full agreement between analytical results, Eqs. (54) and (71), and numerical ones based on Eq. (80). This result can be considered as evidence that the two definitions of the diffusion coefficient D, Eqs. (8) and (9), give the same quantity for hopping in one-dimensional disordered systems. The former definition expresses D via the variance of particle displacement during a random walk, while the latter one defines D as a ratio between the particle flow and the gradient of macroscopic concentration of particles. Although it seems to be obvious from a physical point of view that both definitions should give the same result, no formal proof has yet been known.

Computer simulations evidence that at low temperatures, the diffusion constant experiences significant fluctuations from one realization to another, even for systems containing millions of localized states. The reason of such a large fluc-

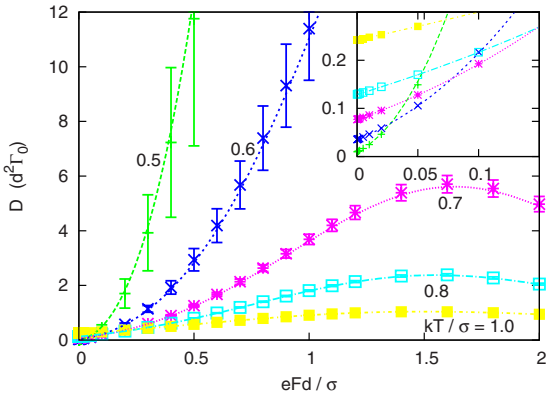

FIG. 3. (Color online) $D(F)$ in the REM for different temperatures T. Curves show the analytical solution [Eq. (71) with $m_1 \ldots m_{11}$ from the MA column in Table I]. Symbols show numerical results [Eq. (80)] for chains with $N=10^8$ sites. Inset shows the low-field behavior.

tuation in 1D hopping is essentially the same as in 3D hopping—it is the sensitivity of the diffusion coefficient to the very rare sites with low energies. We will discuss this phenomenon in detail in the following paper.[20] We also note that sample-to-sample fluctuations of *mobility* for all parameters presented in Figs. 2 and 3 are negligible.

The most striking property of the 1D diffusion is its linear dependence on electric field:

$$D(F) = D(0) + \alpha|F| + O(F^2), \tag{91}$$

where $\alpha \neq 0$. It means that the diffusion coefficient is a *nonanalytic* function of electric field. From general physical arguments, one can hardly expect such a behavior. Instead, one can expect that, as $D(F)$ is an even function, it can be expanded in a Taylor series with respect to F^2,

$$D(F) = D(0) + \beta F^2 + O(F^4). \tag{92}$$

The physical reason of this nonanalyticity is still unclear. As first steps to acquire an understanding of this phenomenon, we will try (i) to provide a *mathematical* explanation of it and (ii) to find out which systems demonstrate the linear field dependence of the diffusion coefficient and which systems lack this behavior.

From the mathematical point of view, the possibility for a nonanalytic dependence $D(F)$ can be seen from expressions (30) and (39) for the coefficients a_i and b_i as functions of $B \equiv \exp(eFd/kT)$. These expressions are series that converge at $B>1$ and diverge at $B \leq 1$. For $B<1$ (i.e., for negative eF), one can obtain converging series, applying a "mirror reflection" transformation ($i+k \rightarrow i-k$, $B \rightarrow B^{-1}$) to Eqs. (30) and (39). Therefore, a_i and b_i are defined by *different* series expansions for positive and negative values of the field. Moreover, at $eF>0$, the values a_i and b_i depend on quantities related to sites i, $i+1$, $i+2,\ldots$ (for example, on $\Gamma_{i+1,i+2}$, ε_{i+1}, etc.); on the contrary, for $eF<0$, these coefficients a_i and b_i depend on a different set of sites: i, $i-1$, $i-2,\ldots$. So, it is obvious that, in a disordered system, the function $a_i(F)$ for negative F cannot be obtained by analytic continuation of this function for positive F and vice versa. The same is true for $b_i(F)$. Keeping in mind that the mobility $\mu \equiv v/F$ and the diffusion coefficient D depend on a's and b's via Eq. (27), one can conclude that negative-field parts of the functions $\mu(F)$, $D(F)$ may not be analytic continuations of their positive-field parts. Consequently, a nonanalyticity of $\mu(F)$ and $D(F)$ at $F=0$ is possible.

It is evident from Figs. 2 and 3 and from Eqs. (54) and (79) that both the RBM and the REM demonstrate a linear low-field behavior of $D(F)$ according to Eq. (91). Moreover, Eq. (78) shows that the mobility $\mu(F)$ in the REM also contains a linear contribution with respect to F, while in the RBM the mobility is a smooth function of F [see Eq. (53)].

Parris *et al.*[25,29] considered a model of a 1D continuous medium with smooth disorder potential and obtained analytical expressions for $\mu(F)$ and $D(F)$. Although the low-field behavior of the mobility and of the diffusion coefficient were not discussed in detail,[25,29] one can learn from Eqs. (25) and (69) of Ref. 29 that this behavior is qualitatively the same as in our REM. The method of Refs. 25 and 29 is, however, not directly applicable to the Gaussian-disorder model considered here. Therefore, a separate derivation was necessary.

One-dimensional transport with Gaussian DOS has another peculiarity—namely, there are sites with arbitrarily high energies, which represent barriers for transport. Despite the fact that such barriers are very rare, their influence on the transport properties should be noticeable (unlike in the 2D and 3D cases, where a carrier can easily pass around these hard places). One can argue that this peculiarity might be responsible for the unusual nonanalytical behavior of $\mu(F)$ and $D(F)$. In order to check this assumption, we consider a 1D system with a *discrete* DOS $g(\varepsilon)$ allowing only two values of energy ($\varepsilon=-\sigma$ and $\varepsilon=\sigma$)

$$g(\varepsilon) = \frac{1}{2}\delta(\varepsilon+\sigma) + \frac{1}{2}\delta(\varepsilon-\sigma). \tag{93}$$

It is obvious that there are no high barriers in this system. Using our general expressions (50), (51), (70), and (71), we have calculated the dependencies $\mu(F)$ and $D(F)$ for this DOS for both RBM and REM. The results demonstrate qualitatively the same low-field behavior as in the case of Gaussian DOS. Therefore, the property of the nonanalyticity of μ and D cannot be attributed just to the presence of infinitely high barriers provided by the corresponding DOS.

We have also checked whether this nonanalyticity is related to the assumption of the *nearest-neighbor* hopping. We have considered the same random-energy model as discussed in Sec. IV, except that we allow transitions to distant states. The dependence of transition rates Γ_{ij} on distances r_{ij} between the sites is governed by the Miller-Abrahams expression (3). The mobility and diffusion coefficient as functions of electric field were calculated by a Monte Carlo algorithm described in the following paper.[20] Again, the results have shown linear low-field dependencies $\mu(F)$ and $D(F)$. Therefore one can conclude that the linear behavior of the diffusion coefficient, Eq. (91), is a robust property of 1D disordered systems.

On the contrary, at higher dimensions, there are no evidences of a linear field dependence of the diffusion coefficient. Both our Monte Carlo simulations (see the following paper, Ref. 20) and previous studies[24] clearly demonstrate a parabolic field dependence, Eq. (92), for 2D and 3D systems with Gaussian disorder. It is worth to note that a smooth dependence $D(F)$ should be obtained also in 1D systems *without disorder*—namely, in systems with periodically repeated site energies (and barrier heights). Indeed, such a system is equivalent to a *finite* chain (with periodical boundary conditions) considered by Derrida.[27] One can therefore use Derrida's formula for D, Eq. (80). This formula, in the case of finite chain length N, is an analytic function of the transition rates Γ_{ij} and consequently of the electric field. Our numerical studies also confirm that for small N, there is a region of parabolic dependence $D(F)$ around $F=0$. Thus, disorder is important for the nonanalytic behavior of $D(F)$.

Finally, we will discuss the applicability of Einstein's relation (1) for finite electric fields. Our analytical results, Eqs. (53), (54), (78), and (79), show that Einstein's relation is violated at any nonzero field F both in RBM and REM and that the deviation from Eq. (1) is proportional to $|F|$. One should note that this phenomenon is related to the discrete

nature of the systems, in which charge transport is dominated by hopping processes. For the opposite case of a continuous-medium model, the diffusion coefficient is known to obey a generalized version of the Einstein relation[25,29]

$$D(F) = \frac{kT}{e}\frac{dv}{dF}, \tag{94}$$

where $v(F)$ is the drift velocity. Our expressions for both RBM and REM, however, demonstrate that Eq. (94) is also violated in the general case and the deviation is also proportional to $|F|$. We argue that, generally, there are no exact connections between $D(F)$ and $\mu(F)$ at $F \neq 0$. Indeed, let us consider the REM. There are 11 quantities $m_1 \ldots m_{11}$ (see Sec. IV) dependent on statistics of the energy levels and on the electric field. The mobility depends on three of them (m_1, m_3, m_4) according to Eq. (70); the diffusion coefficient depends on all 11 quantities [see Eq. (71)]. For an arbitrary density of states, all the 11 quantities are independent of each other and cannot be reduced to each other. Consequently, there is no general way to reduce the diffusion coefficient to the mobility at nonzero electric field.

In conclusion, we have examined analytically and numerically two models of one-dimensional hopping transport—the RBM and the REM. Exact analytical solutions of field-dependent diffusion coefficient have been obtained for both models in the case of nearest-neighbor hopping. We have demonstrated that the nonanalytic field dependence (91) of the diffusion coefficient as well as the violation of the Einstein relation for any nonzero electric field are inherent properties of hopping transport in one-dimensional disordered systems.

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