Hopping Models of Charge Transfer in a Complex Environment: New Class of Coupled Memory Continuous-Time Random Walks

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(Dated: March 23, 2022)

Charge transport processes in disordered complex media are accompanied by anomalously slow relaxation for which usually a broad distribution of relaxation times is adopted. To account for those properties of the environment, a standard kinetic approach in description of the system is addressed either in the framework of continuous-time random walks (CTRW) or fractional diffusion. In this paper the power of the CTRW approach is illustrated by use of the probabilistic formalism and limit theorems that allow to predict the limiting distributions of the paths traversed by charges and to derive effective relaxation properties of the entire system of interest. Application of the method is discussed for non-exponential electron-transfer processes controlled by dynamics of the surrounding medium.

PACS numbers: 05.40+j, 82.20.Fd, 87.10.+e

I. INTRODUCTION

The stochastic formulation of transport phenomena in terms of a random walk process, as well as the description via the deterministic diffusion equation are two fundamental concepts in the theory of diffusion in complex systems. The best known examples are charge transport in amorphous semiconductors, rebinding kinetics in proteins, polarization fluctuations in inhomogeneous solvents, diffusion of contaminants in complex geological formations and diffusion of pollutants in large ecosystems. In all realms mentioned above, the complex structures, characterized by a large diversity of elementary units and strong interaction between them, exhibit a non-predictable or anomalous temporal evolution. The possibility of the dual description of the anomalous dynamical properties of such systems, based either on the random motion or on the differential equations for the probability density functions, has been considered in literature since the late 60s and gave rise to an extensive list of developed models 1 2 3.

In this paper we demonstrate the power of the mathematical tools underlying the concept of a continuous-time random walk (CTRW) by showing how the tool can be generalized to handle complicated situations such as diffusion-reaction schemes in complex system. The notion of the CTRW, a walk with a waiting time distribution governing the time interval between subsequent jumps of a random walker, has been introduced by Montroll and Weiss 1. The distribution of waiting times may stem from possible obstacles and traps that delay the particle’s motion and in consequence, introduce the memory effect into the kinetics. Especially fascinating in this approach was the idea of an infinite mean time between the jumps as in such a case a characteristic time scale of the process looses its common sense. This novel concept has been used by Montroll and Scher 2 to give a first explanation of experiments measuring transient electrical current in amorphous semiconductors. Since then the CTRW formalism has been successfully applied to describe fully developed turbulence, transport in fractal media, intermittent chaotic systems and relaxation phenomena. The common feature of the above mentioned applications is that they exhibit anomalous diffusion manifested by a non-Gaussian asymptotic distribution (propagator, diffusion front) of a distance reached at large times.

At the level of the CTRW modeling, the diverging mean waiting time leads to a subdiffusive motion with the mean square displacement growing as \( < r^2(t) > \propto t^\alpha \) with 0 < \( \alpha < 1 \). When applied to the theory of Brownian motion, the CTRW scenario leads to the fractional diffusion equation 4 5 that can be treated on an equal footing with the framework used for systems with normal diffusion.

Usually, in applications of the CTRW ideology, the analysis of the asymptotic distribution is presented within the approach that is based on a formal expression for the Fourier-Laplace transform of the propagator, or otherwise, use of the fractional calculus is required 6 as a legitimate tool. Here, we present an approach to a random walk analysis which is based directly on the definition of the cumulative stochastic process. Our aim is to show that despite of the extensive studies on CTRWs and their long history in physics, the powerful tool of the limit theorems 7 hidden behind the derivation of limiting distributions, has not been fully explored yet. We emphasize the possibilities of applications of that scenario...
in stochastic modeling of physical systems, in particular, in description of the charge transport in disordered materials.

A starting point in the CTRW analysis is the definition of a total path \( R(t) \) of a particle traversed up to the time \( t \) in accumulating number \( L(t) \) of jumps of a length \( R_j \). The number of jumps exerted in (generally random) time \( t \) can be defined either directly by assuming a specific counting process \( L(t) \) (with \( e.g. \) Poisson, negative binomial, geometric, etc. count distribution) or indirectly - by assuming the distribution of waiting times \( T_j \) between the jumps. In both approaches, under certain assumptions concerning the distribution of jumps \( R_j \) and the distribution of waiting times \( T_j \) (or number of jumps \( L(t) \)), the asymptotic distribution of the total path \( R(t) \) reached up to time \( t \) can be obtained by applying limit theorems of the probability theory. In contrast to the more popular Tauberian analysis of the Fourier-Laplace transform of \( R(t) \), such an approach precisely identifies classes of possible limiting distributions and offers an easy-to-follow scheme of generating various limiting results.

The dual description of the random walk and the relationship between the results obtained in both cases are exemplified in this work by discussing the biologically relevant charge transport processes in disordered media.

The paper is organized as follows: We begin in Section II with a brief discussion of models of non-exponential dielectric relaxation and their relation to solvent (medium) dynamics influencing the rates of the long-range electron transfer. Further, as a generalization of the McConnell formula we incorporate medium fluctuations in the expression for the electronic transfer matrix. Its form is analyzed in terms of an exponential of a sum of independent and identically distributed (\( i.i.d. \)) random variables with a random number \( L \) of virtual jumps between the donor and acceptor sites. By assuming the deviations from equilibrium of the atomic coordinates of a given pathway to be random contributions to the sum, we are able to investigate asymptotic forms of the tunneling matrix elements. Section III poses the problem in terms of a standard CTRW scenario which is generalized (Sections IV and V) for random walks subordinated to a compound step-counting process. Main results and conclusions of the analysis are presented in Sections VI and VII.

II. CHARGE TRANSPORT IN A COMPLEX ENVIRONMENT

Charge transport processes determine a variety of phenomena in physics, chemistry and biology. The study of the phenomenon has gradually developed together with general progress in theoretical physics and in fast high resolution spectroscopy, so that contemporary research deals nowadays with a broad class of systems, materials and environmental conditions. Of particular interest are the processes taking place in disordered materials, such as amorphous semiconductors, randomly arranged molecular wires, glasses or biological proteins where the charge transfer processes form the elementary steps in energy transport and production in almost all living cells. In all those cases, the actual transport process is coupled to local polarization fluctuations of the environment. For the situations that the relaxation of the polarization fluctuations of the surrounding medium has a simple “close-to-equilibrium” exponentially decaying form, the main energetic contributions to the charge transfer process come from the reorganization energy of the medium. In contrast, many observed charge transport processes, like electron transfer (ET) in complex solvents and proteins, or gating kinetics of biological channels, exhibit non-exponential kinetics resulting from the complex response to the interfering medium. A classical example are higher alcohols, for which the frequency dependent dielectric permittivity takes on a Cole-Davidson (CD) form:

\[
\phi^*_CD(\omega) = \frac{\epsilon^*(\omega) - \epsilon_{\infty}}{\epsilon_0 - \epsilon_{\infty}} = \frac{1}{1 + (i\omega\tau_p)^\gamma} = \int_0^\infty e^{-\omega t} \left[-\frac{d}{dt} \phi(t/\tau_p)\right] dt \tag{2.1}
\]

with \( 0 < \gamma < 1 \); \( \phi(t) \) standing for the correlation function of polarization fluctuations and \( \tau_p \) indicating a reciprocal proportional to the peak frequency of the dielectric loss. In the electron transfer (ET) theory, the time-correlation function \( \phi(t) \) is related to the Coulombic potential energy difference for a given configuration of all solvent (intervening medium) molecules in the states of reactants and products:

\[
\phi(t) = \langle (\delta \Delta E)^2 \rangle^{-1} \langle \delta \Delta E \delta \Delta E(t) \rangle \tag{2.2}
\]

with \( \Delta E(t) \) identified with a complex dynamic “reaction coordinate” describing the transfer. In a convenient dipole-approximation for medium molecules, the potential energy difference \( \Delta E \) would be given by

\[
\Delta E = -\int drP(r) [E_P(r - r_P) - E_R(r - r_R)] \tag{2.3}
\]

where \( P(r) \) stands for the medium orientational polarization at position \( r \). For a solvent in which the dipoles of the dielectric medium relax with a single relaxation time \( \tau_p \), the complex dielectric permittivity Eq. \( \tag{2.1} \) is given by the Debye (D) function

\[
\phi^*_D = \frac{\epsilon^*(\omega) - \epsilon_{\infty}}{\epsilon_0 - \epsilon_{\infty}} = \frac{1}{1 + (i\omega\tau_p)^\gamma} \tag{2.4}
\]

with \( \phi(t) \) expressed in terms of a single exponential function with a decay time \( \tau_p \). Other, equally likely fitted expressions exploited in dielectric spectroscopy of polymers and disordered solids estimate relaxation of \( \phi(t) \) by use of the Cole-Cole (CC) \( \tag{2.2} \) formula

\[
\phi^*_CC = \frac{\epsilon^*(\omega) - \epsilon_{\infty}}{\epsilon_0 - \epsilon_{\infty}} = \frac{1}{1 + (i\omega\tau_p)^\gamma} \tag{2.5}
\]
or the Havriliak-Negami (HN) function:
\[
\phi_{HN}^* = \frac{\epsilon(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1}{\alpha} \frac{1}{1 + (i\omega \tau^\alpha)^\gamma}
\]
(2.6)
where \(0 < \alpha < 1\) and \(0 < \gamma < 1\) are parameters determining the characteristics of the dielectric relaxation with \(\alpha\) representing the width and \(\gamma\) the skewness of the distribution of relaxation times [13]. Although the generic physical reasons for anomalous relaxation in complex systems are still under debate, both static models based on the inhomogeneity of the medium, - as well as the dynamic models, describing complex local dynamical processes have been successfully employed to describe relaxation behavior of fluctuations in such systems. In particular, the studies on the effect of protein dynamics on biological ET [9,17,22,23,24] have demonstrated sensitivity of the long distance tunneling mediated by the protein matrix on atomic configurations of the surroundings and pointed out possibility of an electron of emitting or absorbing phonons from the medium that would effectively result in an inelastic ET processes. In numerous chemical and biological examples of the ET reaction [9,22,23], a single electron is tunneling in an inhomogeneous medium over large distances of several angstroms. The intervening medium can be either a protein backbone or a sequence of cofactors embedded in a protein matrix. Due to a large separation between the donor and acceptor, direct electronic coupling between the chromophores is negligible, rendering thus the question on the effect of medium on enhancement of the electronic coupling [17]. A possible realization of the long-distance ET process is a transfer mediated through the medium which acts as a bridge providing virtual states for the tunneling electron [25]. Within the nonadiabatic-reaction scenario corresponding to a weak electronic coupling \(T_{DA}\) between the state of reactants \(D\) and products \(A\), the expression for the rate reads
\[
k_{ET} = \frac{2\pi}{h} T^2_{DA}(FC)
\]
(2.7)
where (FC) is the Franck-Condon nuclear factor associated with the nuclear modes activation barrier. In a conventional theory the Condon approximation is assumed, i.e. the electronic coupling \(T_{DA}\) is viewed as independent of the coordinates of the medium. To account for thermal fluctuations of the bridge or random intervening medium, the electronic coupling has to be a function of the modes of the medium. The simplest expression that can be proposed in such a case is the Mc Connell formula [24,25] which for a case of a linear bridge consisting of \(L\) orbitals leads to the tunneling matrix \(T_{DA}\)
\[
T_{DA} \approx \prod_{j} \beta_{j+1} \epsilon - \epsilon_j
\]
(2.8)
with \(\epsilon - \epsilon_j\) being the energy difference between the tunneling energy and the energy of the bridging orbital \(j\), \(L\) standing for the number of virtual jumps performed along the path and \(\beta_j\) denoting couplings between directly overlapping atomic orbitals of neighbouring atoms within the bridge. The above formula constitutes the essential part of the ET pathways models [17,24] in proteins, where the calculation of the effective electronic coupling is based on a general assumption that the electron wave function decay is softer for propagating through a chemical bond than through space jump. Since the coupling coefficients \(\beta\) are exponentially decreasing function of the distance between subsequent medium centers (atoms), the effective tunneling matrix can be recast in the form
\[
T_{DA}(r) = T^0_{DA} \prod_{j} \exp(-\alpha_j r_j) =
\]
\[
= T^0_{DA} \exp \left(-\sum_{j} \alpha_j r_j \right)
\]
(2.9)
where \(r_j\) are fluctuations of the atomic coordinates of the bridge, \(\alpha_j\) are constants characterizing strength of the coupling to a particular bridge mode \(j\) and \(T^0_{DA}\) corresponds to the average, equilibrium tunneling matrix. Such a representation of the effective tunneling matrix allows to use the notion of the continuous time random walk (CTRW) as a very convenient mathematical tool to analyze the decay with time of the donor state occupation density. In fact, the latter is commonly described by systems of phenomenological balance equations
\[
\frac{d}{dt} \begin{pmatrix}
P_1(t) \\
P_2(t)
\end{pmatrix} = - \begin{pmatrix}
k^+ & -k^- \\
k^- & k^-
\end{pmatrix} \begin{pmatrix}
P_1(t) \\
P_2(t)
\end{pmatrix}
\]
(2.10)
which relate the decay of the donor (acceptor) populations to the state-relaxation rate constants \(k^{+,-}\). Note, that corresponding populations \(P_{1,2}(t)\) in any of the electronic states (reactants or products) are dynamical quantities usually measured in the electron transfer kinetic experiment and are obtained by integrating the polarization energy dependent populations \(\rho(E,t)\) over configuration variable \(E(t)\):
\[
P_i(t) = \int_{-\infty}^{+\infty} dE \rho(E,t)
\]
(2.11)
In a standard ET theory approach [21,22,24] after assuming a disentanglement of reactive tunneling from the dynamics of diffusion, the elements of the evolution matrix Eq. (2.10) have the form of
\[
k^+ = \frac{k^+_{NA} k^+_{D}}{1 + k^+_{NA} k^+_{D} + k^-_{NA} k^-_{D}}
\]
(2.12)
where \(k_{NA}\) describes the crossing (nonadiabatic) kinetics and \(k_D\) is the rate constant of the diffusion in the
reactants’ (products’) basins. However, in a more general situations, where the matrix entries in Eq. (2.10)
are represented by time dependent functions, the redistribution of populations and consequently, the relaxation
of electron-donoring (accepting) states may follow a non-exponential law. Accordingly, the frequency character-
sistics of dielectric susceptibility \( \chi(\omega) \) connected to the temporal relaxation function of the induced state-polarization \( \mathbf{P}(t) = e_0 \chi(\omega) \mathbf{E}(t) = e_0 (e^\epsilon - 1) \mathbf{E}(t) \) where \( \mathbf{E}(t) = E_0 e^{-i\omega t} \) and the functional character of the dielectric permittivity \( e^\epsilon(\omega) \) may be inferred from the analysis
of relaxation of state populations in a frequency domain

\[
\chi(\omega) = \int_0^\infty e^{-i\omega t} d(-P_{1,2}(t)) \tag{2.13}
\]

In the forthcoming sections we present a dynamic framework which, within the CTRW scenario, leads to the empirically observed non-exponential relaxation dynamics.

III. PATHWAY ANALYSIS OF ET REACTIONS

As discussed above, with the matrix elements of a particular path \( T_{DA} \), the nature of matrix elements may be analyzed in terms of fluctuations in couplings or, alternatively, in contributions \( R_j \) to the total distance \( R \) traversed by a charge:

\[
R = \sum_{j=0}^{L(R)} R_j \geq R \tag{3.1}
\]

Here \( L(R) \) stands for a random counting process describing a (random) number of forward steps exerted by a particle before reaching a distance \( R \). Note, that such a formulation is identical with the assumption of a one-dimensional, biased (directed) random walk performed in an amorphous medium under the influence of a strong external field. The time \( T \) that particle needs to reach a fixed distance \( \mathcal{R} \) is given by \( T = \sum_{i=0}^{L(\mathcal{R})} T_i \) with \( T_i \) being a time spent by a hopping charge at the location \( \sum_{j=1}^{i-1} R_j \). By means of a conditional probability, the probability density \( p(T) \) for the distribution of times \( T \) to reach a distance \( \mathcal{R} \) reads

\[
p(T) = \sum_{j=1}^{\infty} p_1(L(R) = j)p_2 \left( \sum_{i=0}^{L(R)} T_i = T \mid L(R) = j \right) \tag{3.2}
\]

where \( p_2 \) stands for the probability distribution that the elapsed time is \( T \) provided exactly \( j \) steps have been performed to reach distance \( R \) and \( p_1 \) is probability to make \( j \) steps over the distance \( \mathcal{R} \). Here we assume, that the length of a given jump, as well as the waiting times elapsing between two successive jumps are drawn as independent random variables with densities

\[
\rho(r) = \beta e^{-\beta r}, \quad r > 0, \quad \tag{3.3}
\]

and

\[
\sigma(t) = L_{1/2}(t; 1, 1, 0) = \frac{1}{\sqrt{2\pi}} t^{-3/2} e^{-1/2t}, \quad t > 0, \tag{3.4}
\]

i.e. the model describes a charge moving only in one direction with a Poisson number of jumps and the Lévy-
Smirnov distribution \( L_{1/2}(t; 1, 1, 0) \) of waiting times. The probability density function \( p_2 \) in Eq. (3.2) is then given by a convolution of independent probability densities \( [\cdot] \)

\[
p_2(T) = L_{1/2}(T; j^2, 1, 0) \tag{3.5}
\]

and leads to a marginal probability density

\[
p(T) \mathcal{R} = e^{-\beta \mathcal{R}} T^{-3/2} \frac{\sum_{j=0}^{\infty} (\beta \mathcal{R})^j}{\sqrt{2\pi}} \frac{j!}{e^{-\frac{j^2}{2}}} \tag{3.6}
\]

FIG. 1: Density distribution function \( p(R) \mathcal{T} \) of distances traversed up to the time \( T \) in a one-dimensional random walk with \( \tau(t) \) given by a Lévy-Smirnov distribution Eq. (3.3).

FIG. 2: Density distribution function of times \( T \) needed to reach a distance \( \mathcal{R} \) in a one-dimensional random walk with a Lévy-Smirnov distribution Eq. (3.6) of waiting times for a jump.

Quite similarly, one can calculate \( p(R) \mathcal{T} \) with the condition \( T = \sum_{j=1}^{L(T)+1} T_j \geq T \) and \( p_2 \) given by a gamma
density distribution resulting from a sum of \( j \) independent and exponentially distributed random variables:

\[
p(R) = \sum_{j=1}^{\infty} p_1(L(T) = j)p_2 \left( \sum_{i=0}^{L(T)} r_i = R | L(T) = j \right) = \\
= \sum_{n=0}^{\infty} \frac{(\beta R)^n}{n!} e^{-\beta R} \frac{2}{\sqrt{2\pi T}} \int_{n}^{n+1} e^{-\frac{y^2}{2T}} dy
\]

(3.7)

Thus the sketched problem describes a 1-dim diffusion among traps with a broad (asymptotically, heavy-tailed) distribution \( \sigma(t) \) of trapping times, see Figures 1 and 2. This type of the “annealed” CTRW has been extensively studied in literature \([1, 3, 10, 24, 27]\). A 3-dim analogue with a broken unidirectionality of the transfer corresponds to a weak external field approximation. Figure 3 displays results of a 3-dim CTRW computer simulation: direction of a jump has been generated by sampling spherical coordinates \( \theta \) and \( \phi \) from uniform distributions defined on intervals \((0, \frac{\pi}{2})\) and \((0, 2\pi)\), respectively. Quite arbitrarily, the positive direction of the \( z \)-axis have been favoured by sampling the coordinates of a point \((\phi, \theta, -z)\) by those for \((\phi, \theta, z)\) and switching from \( z \) to \(-z\) with a probability 3/10. The upper panel of Figure 3 refers to the distribution of 3-dim waiting times for a subsequent jump was assumed in a form of a skewed (heavy-tailed) \( \text{Lévy-Smirnov distribution} \) describing higher probability of long trapping. In contrast, the lower panel represents results of simulations for a 3-dim CTRW with a preferential short mean time of waiting (a Weibull distribution) for a particle release from the trap:

\[
\sigma(t) = \alpha t^{\alpha-1} e^{-t^\alpha}
\]

(3.8)

where \( 0 < \alpha < 1 \). In a forthcoming section we investigate an extension of such an approach for the family of complex CTRW incorporating effects of clustering of carrier trapping sites in a disordered material under the study.

IV. CTRW SUBORDINATED TO A COMPOUND COUNTING PROCESS

As briefly mentioned in the preceding sections, the CTRW generalizes a simple random walk by implementing a random waiting time between jumps \([1, 4]\). This stochastic process is defined by the total distance \( R(\tau) \) reached by the particle at time \( \tau \geq 0 \) if the movement is generated by a sequence \((R_j, T_j), j = 1, 2, \ldots \) of jump parameters with \( R_j \) specifying both the length and the direction of the \( j \)-th jump and \( T_j > 0 \) denoting the waiting time for the next jump. We assume moreover that the sequence \((R_j, T_j), j = 1, 2, \ldots \) is formed by i.i.d. random vectors. The cumulative distance \( R(\tau) \) may be expressed as

\[
R(\tau) = \sum_{j=1}^{\nu(\tau)} R_j
\]

(4.1)

where

\[
\nu(\tau) = \min \{ k : \sum_{j=1}^{k} T_j > \tau \}
\]

(4.2)

The renewal process

\[
\left\{ \sum_{j=1}^{k} T_j, k = 1, 2, \ldots \right\}
\]

(4.3)

represents the instants of time at which subsequent jumps occur; the process \( \{ \nu(\tau), \tau \geq 0 \} \) counts the jumps. Hence, the introduced CTRW \( \{ R(\tau), \tau \geq 0 \} \) is the discrete-time random walk \( \{ \sum_{j=1}^{[\tau]} R_j, \tau \geq 0 \} \) subordinated to the renewal counting process \( \{ \nu(\tau), \tau \geq 0 \} \). It is decoupled if random variables \( T_j \) and \( R_j \) are independent; otherwise it incorporates statistical dependence between time and space steps. In general, the properties of \( \{ R(\tau), \tau \geq 0 \} \) are unknown. Nevertheless, the behavior of the CTRW for long time, or, equivalently, of the rescaled process \( R(t/\delta\tau)/f(\delta\tau) \), (where \( f(\delta\tau) \) is an appropriately chosen rescaling function) for the characteristic time scale \( \delta\tau \) decreasing to 0, can be determined quite
well. Systematic studies of the limiting total-distance distributions for the one-dimensional CTRWs have pointed on few possible distributions \[23, 29\]. Introducing a new class of coupled memory CTRWs with random-sum form of time/space steps, much broader class of possible limiting distributions can be obtained. Namely, let us consider the case when
\[
R_j = \sum_{k=1}^{M_j} \Delta R_{jk}, \quad T_j = \sum_{k=1}^{M_j} \Delta T_{jk},
\]
where sequences \(\{\Delta R_{jk}, j, k = 1, 2, \ldots\}\) and \(\{\Delta T_{jk}, j, k = 1, 2, \ldots\}\) of space/time random spans are independent and each of them consists of \(i.i.d\) positive random variables, and \(\{M_j, j = 1, 2, \ldots\}\) is a sequence of \(i.i.d\) positive integer-valued random variables. The nondegenerate distribution of \(M_j\), the number of summands, (i.e. the case when random variable \(M_j\) takes at least two different values with positive probabilities), provides a stochastic dependence between time and space steps. As a consequence, the CTRW resulting from the space/time-step family Eq.(4.4) is usually coupled. Moreover, it has an equivalent random-sum form since the total distance \(R(\tau)\) has the same distribution as the following random sum of distance increments
\[
R(\tau) = \sum_{k=1}^{L(\tau)} \Delta R_{1k}
\]
where the random index \(L(\tau)\) has the form
\[
L(\tau) = \sum_{j=1}^{N(K(\tau))} M_j,
\]
with the random number of summands defined as
\[
N(K(\tau)) = \min\{n : \sum_{j=1}^{n} M_j > K(\tau)\}
\]
for
\[
K(\tau) = \min\{n : \sum_{k=1}^{n} \Delta T_{1k} > \tau\}.
\]

Note, that the above definition of the CTRW process (cf. Eq.(1.4)) does not assume explicitly any precise relation between steps \(R_i\) and time lapses \(T_i\). Instead, possible coupling between those two random variables is incorporated \(via\) the counting process Eq.(4.6) summing contributions to the cumulative distance \(R(\tau)\) traversed during the walk. This particular construction of the random sum Eq.(4.7) allows calculating statistical properties of their distribution by use of the “nested” moment-generating function \(\Phi(s) = \langle s^{R(\tau)} \rangle\) which in this case fulfills the equation
\[
\Phi_R(s) = \Phi_L(\Phi_{\Delta R_{1k}}(s)) = \Phi_N(\Phi_M(\Phi_{\Delta R_{1k}}(s)))
\]
where the last equation follows by applying the technique of conditional averages.

V. DIFFUSION FRONT. LIMITING DISTRIBUTIONS

Let us consider now the rescaled total distance
\[
\tilde{R}(t) = \frac{R_M(t/\delta \tau)}{f(\delta \tau)}
\]
where \(\delta \tau\) is the characteristic time scale, and \(f(\delta \tau)\) is a rescaling function chosen appropriately. Applying limit theorems \[30\] one can evaluate the limiting position \(\tilde{R}(t)\) of the rescaled total distance reached as \(\delta \tau \to 0\). The characteristics of \(\tilde{R}(t)\) depends on assumptions set on the distributions of the variables \(\Delta R_{jk}, \Delta T_{jk}\) and \(M_j\). Below, following the regularization scheme Eq.(5.1) along with more detailed presentation and proofs included in ref.\[31\], we discuss briefly some examples which might be of practical use in modeling relaxation phenomena in disordered materials. We consider the case when \(\Delta R_{jk}\) and \(\Delta T_{jk}\) are independent and both positive.

(a) Let us first assume that both \(\Delta R_{jk}\) and \(\Delta T_{jk}\) have heavy-tailed distributions with \(c = c_1\) and \(c = c_2\), respectively, and the same \(r = \gamma\). (We say that the distribution of a positive random variable \(X\) has a heavy tail if for some \(c > 0 \) and \(0 < r < 1\)
\[
\lim_{x \to \infty} \frac{\Pr(X > x)}{(x/c)^r} = 1.
\]
In consequence, the expected value \(\langle X \rangle\) is infinite.)

- If the distribution of the random number \(M_j\) has a heavy tail with some \(c > 0 \) and \(r = \gamma\), then for any \(t > 0\)
\[
R(t/\delta \tau) \xrightarrow{d_{\delta \tau \to 0}} \tilde{R}(t) \xrightarrow{d_{\delta \tau \to 0}} \frac{t}{A} \frac{S_\alpha}{B_\gamma} \left( \frac{1}{B_\gamma} \right)^{1/\alpha}.
\]
Here ”\(\xrightarrow{d}\)” reads ”tends in distribution”, and ”\(\xrightarrow{a.s.}\)” denotes the equal distributions.

- If the numbers \(M_j\) have a finite expected value \(\langle M_j \rangle\) is finite, then for any \(t > 0\)
\[
R(t/\delta \tau) \xrightarrow{d_{\delta \tau \to 0}} \tilde{R}(t) \xrightarrow{d_{\delta \tau \to 0}} \frac{t}{A} \frac{S_\alpha}{B_\gamma}.
\]

(b) Assume that the expected values of both \(\Delta R_{jk}\) and \(\Delta T_{jk}\) are finite, and \(\langle \Delta R_{jk} \rangle = c_1, \langle \Delta T_{jk} \rangle = c_2\).

- If the distribution of \(M_j\) has a heavy tail with some \(c > 0 \) and \(r = \gamma\), then for any \(t > 0\)
\[
R(t/\delta \tau) \xrightarrow{d_{\delta \tau \to 0}} \tilde{R}(t) \xrightarrow{d_{\delta \tau \to 0}} \frac{t}{A} \frac{1}{B_\gamma}.
\]

- If \(\langle M_j \rangle < \infty\), then for any \(t > 0\)
\[
R(t/\delta \tau) \xrightarrow{\delta \tau \to 0} \tilde{R}(t) \frac{a.s.}{\delta \tau} = \frac{1}{A}
\]

Here ”\(\xrightarrow{a.s.}\)” reads ”tends with probability 1”. 
The random variables $B_\alpha$, $S_\alpha$, and $S_\alpha'$ in (5.3) - (5.6) are as follows:

- $S_\alpha$ and $S_\alpha'$ are identically distributed according to the completely asymmetric $\alpha$-stable law such that $\langle e^{-kS_\alpha} \rangle = e^{-k^\alpha}$;
- $B_\alpha$ is distributed according to the generalized arc-sine distribution with parameter $\gamma$ (i.e., the beta distribution with parameters $p = \gamma$ and $q = 1 - \gamma$) given by the density function
  \[
  f_\gamma(x) = \begin{cases} 
  \frac{1}{\Gamma(\gamma)} \frac{1}{(1-x)^{1-\gamma}} & \text{for } 0 < x < 1 \\
  0 & \text{otherwise};
  \end{cases} \tag{5.7}
  \]
- for any $0 < \alpha, \gamma < 1$ the random variables $B_\gamma$, $S_\alpha$, and $S_\alpha'$ are independent.

Armed with the above results, we are now in position to discuss properties of CTRW paths generated under mentioned constraints with the application of the formalism in the analysis of the relaxation responses in disordered materials.

VI. EMPIRICAL AND PHENOMENOLOGICAL RELAXATION RESPONSES

Relaxation in amorphous solids and ET processes in disordered molecular media represent nowadays intensively investigated subjects both in experimental and theoretical physics [4, 11, 12, 28, 32, 33]. In particular, a key probe of electron dynamics in disordered systems is the time of flight experiment (TOF) for the drift mobility. In the experiment, the thin film sample is located between two blocking contacts across which is maintained a potential drop, and a laser flash is used to create carriers that wander towards an appropriate electrode. During their drift through the sample, the electrons and holes encounter a variety of traps that affect their motion. The experiments show that in the disordered materials, the registered transient current follows an algebraic decay $I(t) \approx t^{-(\alpha+1)}$. In contrast, for Gaussian transport processes, the charge carriers move at a constant velocity and after a transient time, depending on the thickness of the sample and the applied external field, they become absorbed. In consequence, for normal transport processes typically observed in ordered materials, the current is given by a step-like function, whereas in disordered media the current $I(t)$ adheres to a universal (independent of the applied field and sample thickness) scaling curve. Similar conclusions are drawn from the ultrafast pump-probe laser spectroscopy and spectral hole burning experiments which are well advanced techniques used for nanostructures and comprise nowadays a standard tool to determine fast carrier dynamics and spectral and spatial diffusion of the carriers. A wide-ranging experimental information resulting from the latter [12, 32] has led to the concept that the classical phenomenology of relaxation processes breaks down in complex materials. It has been found that the Debye behavior [24] is hardly ever found in nature and that for many dielectrics the deviations from it may be relatively large [12, 13, 15].

For a long time a major effort has been diverted to a purely qualitative representation of the shape of the non-Debye dielectric functions in terms of certain mathematical expressions without, in any way, going into a physical significance of these representations. As pointed out by experimental studies almost all dielectric data are characterized well enough by a few empirical functions [11, 12, 13, 15, 16]. The most popular analytical expressions applied to the complex susceptibility or permittivity data is given by the Havriliak-Negami function (2.6). For $\alpha = 1$ and $\gamma < 1$, formula (2.6) takes the form of the Cole-Davidson function; for $\gamma = 1$ and $\alpha < 1$ it takes the form (2.5) of the Cole-Cole function, and for $\alpha = 1$ and $\gamma = 1$ one obtains the classical Debye form (2.4). Let us note that time-domain relaxation function $\phi(t)$ corresponding to formula (2.6) has the following series representation

\[
\phi(t) = 1 - \sum_{n=0}^{\infty} \frac{(-1)^n \Gamma(\gamma + n)(\omega pt)^{\alpha(\gamma+n)}}{n! \Gamma(1 + \alpha(\gamma+n))} \tag{6.1}
\]

referred to the generalized Mittag-Leffler distribution. In case of the CC function the series representation (6.1) is simplified to

\[
\phi(t) = 1 - \sum_{n=0}^{\infty} \frac{(-1)^n (\omega pt)^{\alpha(1+n)}}{n! \Gamma(1 + \alpha(1+n))} \tag{6.2}
\]

corresponding to the Mittag-Leffler distribution. The CD relaxation function is referred to the tail function of the gamma distribution with the scale parameter $\omega_p$ and the shape parameter $\gamma$, given by the density function

\[
g_\gamma(t) = \begin{cases} 
\frac{\omega_p}{\Gamma(\gamma)} (\omega pt)^{\gamma-1} e^{-\omega pt} & \text{for } t > 0, \\
0 & \text{otherwise.}
\end{cases} \tag{6.3}
\]

In order to derive relevant relaxation functions resulting from cases (5.3) - (5.6), considered above, we use the following relations: For any $0 < \alpha \leq 1$

\[
\langle e^{-kS_\alpha} \rangle = \langle e^{-kS_\alpha'} \rangle = e^{-k^\alpha} \tag{6.4}
\]

and for any $0 < \gamma \leq 1$ we have [31]

\[
\langle e^{-kB_\gamma} \rangle = \Pr(G_\gamma \geq k) \tag{6.5}
\]

where $S_1 = S'_1 = B_1 = 1$; $G_1 = E$ is exponentially distributed with mean 1; and for $\gamma < 1$ the random variable $G_\gamma$ is distributed according to the gamma distribution with the shape parameter $\gamma$ and the scale parameter 1. Assuming that for any $0 < \alpha, \gamma \leq 1$ the random variable
$G_\gamma$ is independent of $S_\alpha$, and by using the conditional-expectation tools, from formulae (6.4) and (6.5) one obtains

$$
\left< e^{-k} \left( \frac{S'_\alpha}{S_\alpha} \right)^{1/\alpha} \right> = \text{Pr}(G^{1/\alpha}_{1/\alpha} S_\alpha \geq k) \tag{6.6}
$$

and hence for $\tilde{R}(t)$ of the form (6.2) - (6.3) the corresponding relaxation function $\phi(t)$ equals

$$
\phi(t) = \left< e^{-k \tilde{R}(t)} \right> = \left< e^{-\frac{\alpha}{k/A}} \left( \frac{S'_\alpha}{S_\alpha} \right)^{1/\alpha} \right>
$$

$$
= \text{Pr}(A/k)G^{1/\alpha}_{1/\alpha} S_\alpha \geq t. \tag{6.7}
$$

where $k$ is an appropriate positive constant. For such a relaxation function we have the frequency domain response of the general form

$$
\phi^*(\omega) = \left< e^{-i\omega/\omega_p} G^{1/\alpha}_{1/\alpha} S_\alpha \right> \quad , \quad \omega_p = k/A, \tag{6.8}
$$

which includes the Havriliak-Negami with its special cases (see Table 1).

### VII. CONCLUSIONS

Relaxation processes deviating from the usual exponential behavior in time domain (and a classical Debye form in the frequency domain) occur in many physical, chemical and biological systems, such as supercooled liquids, viscoelastic solids, polymer melts and porous media, membranes and liquid crystals. They are usually described by some mathematical functions related to the fractional-order differential equations. Properties of relaxation processes in complex media are also important topics in the long-range transfer of an electron in polymeric and various biological materials [3, 31, 32, 36]. The kinetics of the charge transport in those media is determined by the nature of electronic coupling which for the long distances is mediated by sequential overlaps of atomic orbitals of the donor, the intervening medium (bridge), and the orbitals of the acceptor. Internal random motion of the medium may result in fluctuations of the tunneling barriers between subsequent transfer states and modulate the electronic coupling. Such an effect is formally due to the dependence of the electronic coupling on the nuclear coordinates of the medium and may express possible deviation from the usual Condon approximation [22, 24]. The influence of factors arising from the static and dynamic fluctuations in electronic coupling have been discussed in a number of papers [24, 18, 33, and references therein] related to the electron transport in proteins and polymers. All of them have claimed existence of nontrivial effective coupling resulting from averaging over environmental disorder.

In this paper we have extended previously proposed model [36] which accounts for long distance charge transfer hopping. Our approach is based on CTRW formalism in the representation of random sums of i.i.d elements which are deviations from equilibrium of the atomic coordinates of the intervening medium. In contrast to other works [2, 16, 27], the present approach is based on renewal theory and the limit theorems for random sums [7, 28, 23, 30, 31] of jumps instead of Tauberian theorems for the two-dimensional Laplace-Fourier transform. Dispersive kinetics, as discussed here, appears in situations when the environmental fluctuations become comparable or slower in the time-scale of the overall transition from the reactants’ to products’ states. In ordinary solvents, the medium relaxation is complete in several picoseconds. In contrast, in highly viscous liquids the relaxation modes can determine the rate of the fast ET kinetics. Theoretical treatment of such processes is based on analysis of slow, reorientational motions of the system which influence survival of populations in given electronic states. Our analysis maps the complex medium reorientation kinetics on a relaxation process of measurable reactants’ and products’ populations for states before and after the charge transfer. Diffusion of a charge (and response kinetics of the local polarization energy) can be then investigated by use of the generalized relaxation functions defined as moment generating functions for coupled memory random sums. A non-exponential, non-Debye decay of relaxing modes is a basic feature arising in such an approach and can be traced to the probabilistic pattern of contributing lengths of steps and waiting times in the charge hopping process.
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