Hopping models of charge transfer in a complex environment: Coupled memory continuous-time random walk approach

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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 (CTRWs) 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 one to rigorously predict the limiting distributions of the paths traversed by charges and to derive effective relaxation properties of the entire system of interest. In particular, the standard CTRW scenario is generalized to a new class of coupled memory CTRWs that effectivly can lead to the well known Havriliak-Negami response. Application of the method is discussed for nonexponential electron-transfer processes controlled by dynamics of the surrounding medium.

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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 nonpredictable 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 1960s and gave rise to an extensive list of developed models [1–3].

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 as a 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 [4] 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 abovementioned 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 $\langle r^2(t)\rangle \propto t^{\alpha}$ with $0<\alpha<1$. When applied to the theory of Brownian motion, the CTRW scenario leads to the fractional diffusion equation [5,6] 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 [3] 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 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. The main objective is to present a clear random walk scheme leading to the nonexponential polarization relaxation expressed in terms of the well-known Havriliak-Negami function. Our effort is therefore directed toward bringing into light statistical conditions underlying the rigorous results and

to dicuss their physical content. 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 (generally random) number of jumps exerted in 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 paper is organized as follows. We begin in Sec. II with a brief discussion of models of nonexponential 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 (IID) 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. Sections III and IV pose the problem in terms of a standard CTRW scenario which is generalized (Secs. V and VI) for random walks subordinated to a compound step-counting process. Main results and conclusions of the analysis are presented in Secs. VII and VIII.

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 [8], 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 [9,10]. In contrast, many observed charge transport processes, such as electron transfer (ET) in complex solvents [5,8,11–16] and proteins [17–20], or gating kinetics of biological channels [21], exhibit nonexponential 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) [12] form

$$\phi^*_{\mathrm{CD}}(\omega) = \frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1}{(1 + \mathrm{i}\omega/\omega_p)^\gamma} \tag{1}$$

with $0 < \gamma < 1$ and ω_p indicating the peak frequency of the dielectric loss. The frequency-dependent dielectric permittivity corresponds to $\phi(t)$, the correlation function of polarization fluctuations, by means of the Fourier transform

$$\phi^*(\omega) = \int_0^\infty e^{-\mathrm{i}\omega t}\left[-\frac{d}{dt}\phi(\omega_p t)\right]dt. \tag{2}$$

In the electron transfer (ET) theory, the time-correlation function $\phi(t)$ is related [9,10,22] to the excess polarization fluctuations $\delta E(t)$ which contribute to the total free energies of the sites donoring and accepting the transferred charge

$$\phi(t) = \langle(\delta\Delta E)^2\rangle^{-1}\langle\delta\Delta E\,\delta\Delta E(t)\rangle. \tag{3}$$

The variations of $E(t)$ are expressed by the Coulombic potential energy difference for a given configuration of all solvent (intervening medium) molecules in the states of reactants and products and are commonly identified with a complex dynamic "reaction coordinate" describing the transfer. In a convenient dipole-approximation for medium molecules, the potential energy difference ΔE would be given by [22]

$$\Delta E = -\int d\mathbf{r}\cdot\mathbf{P}(\mathbf{r})[E_P(\mathbf{r}-\mathbf{r}_P) - E_R(\mathbf{r}-\mathbf{r}_R)], \tag{4}$$

where $\mathbf{P}(\mathbf{r})$ stands for the medium orientational polarization at position $\mathbf{r}$. For a solvent in which the dipoles of the dielectric medium relax with a single relaxation time $\tau_p = 1/\omega_p$, the complex dielectric permittivity (2) is given by the Debye (D) function

$$\phi^*_D(\omega) = \frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1}{1 + \mathrm{i}\omega/\omega_p} \tag{5}$$

with $\phi(t)$ expressed in terms of a single exponential function with a decay time τ_p. Other, equally likely fitted expressions [15,16] exploited in dielectric spectroscopy of polymers and disordered solids estimate relaxation of $\phi(t)$ by use of the Cole-Cole (CC) [11] formula

$$\phi^*_{\mathrm{CC}}(\omega) = \frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1}{1 + (\mathrm{i}\omega/\omega_p)^\alpha} \tag{6}$$

or the Havriliak-Negami (HN) [13] function

$$\phi^*_{\mathrm{HN}}(\omega) = \frac{\epsilon(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1}{[1 + (\mathrm{i}\omega/\omega_p)^\alpha]^\gamma}, \tag{7}$$

where $0 < \alpha < 1$ and $0 < \gamma < 1$ are parameters determining the characteristics of the dielectric relaxation with α repre-

senting the width and γ 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 [9,19,20,23] 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 the forthcoming section, we present a brief review of the ET issues leading to interpretation of the charge transfer in terms of the generalized random walk scenario.

III. ELECTRON TRANSFER MODELS AND THE CTRW METHODOLOGY

In numerous chemical and biological examples of the ET reaction [9,20,23], a single electron is tunneling in an inhomogeneous medium over large distances of several Å. 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 [17,18].

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 [24]. In many situations, such as the nucleotide base stacks, the charge transfer is effectively confined to one dimension. However, the mechanisms of such charge transfer processes are not fully understood and with respect to the long-range molecular ET in DNA they have become a subject of a constant debate [25].

The decay of the donor state occupation is commonly described by systems of phenomenological balance equations

$$\frac{d}{dt}\begin{pmatrix} P_1(t) \\ P_2(t) \end{pmatrix} = -\begin{pmatrix} k^+ & -k^- \\ -k^+ & k^- \end{pmatrix}\begin{pmatrix} P_1(t) \\ P_2(t) \end{pmatrix} \tag{8}$$

which relate the experimentally observable decay of the donor (acceptor) populations to the effective state-relaxation rate constants $k^{+,-}$. In a standard ET theory approach [22,23] after assuming a disentanglement of reactive tunneling from the dynamics of diffusion, the elements of the evolution matrix (8) have the form of

$$k^+ = \frac{k_{NA}^+}{1 + k_{NA}^+/k_D^+ + k_{NA}^-/k_D^-}, \tag{9}$$

where k_{NA} describes the crossing (nonadiabatic) kinetics and k_D is the rate constant of the diffusion in the reactants' (products') basins. 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 $E(t)$:

$$P_i(t) = \int_{-\infty}^{+\infty} dE\, \rho(E,t). \tag{10}$$

In general situations, where the matrix entries in Eq. (8) are represented by time-dependent functions, the redistribution of populations and consequently, the relaxation of electron-donoring (accepting) states may follow a nonexponential law. Accordingly, the frequency characteristics of dielectric susceptibility $\chi(\omega)$ connected to the temporal relaxation function of the induced state-polarization $\mathbf{P}(t) = \epsilon_0 \chi(\omega)\mathbf{E}(t) = \epsilon_0[\epsilon^*(\omega) - 1]\mathbf{E}(t)$, where $\mathbf{E}(t) = \mathbf{E}_0 e^{-i\omega t}$ and the functional character of the dielectric permittivity $\epsilon^*(\omega)$ may be inferred from the analysis of relaxation of state populations in a frequency domain

$$\chi(\omega) = \int_0^{\infty} e^{-i\omega t} d[-P_{1,2}(t)]. \tag{11}$$

Within the nonadiabatic-reaction approach corresponding to a weak electronic coupling T_{DA} between the state of donoring D and accepting A centers, the expression for the rate reads

$$k_{NA} = \frac{2\pi}{\hbar} T_{DA}^2 \varrho(\mathrm{FC}), \tag{12}$$

where $\varrho(\mathrm{FC})$ is the Franck-Condon nuclear factor representing weighted density distribution of energy gaps arising from thermal excitations and 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 McConnell formula [23,24] which for a case of a linear bridge consisting of L orbitals leads to the tunneling matrix T_{DA}

$$T_{DA} \approx \prod_{j=1}^{L} \frac{\beta_{j,j+1}}{\epsilon - \epsilon_j} \tag{13}$$

with $\epsilon - \epsilon_j$ being the energy difference between the tunneling energy and the energy of the bridging orbital j, and β_{ij} denoting couplings between directly overlapping atomic orbitals of neighboring atoms within the bridge. The number of orbitals, L, is equivalent to the number of virtual jumps performed along the path. The above formula (13) constitutes the essential part of the ET pathways models [18,23] 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 β are exponentially decaying functions of the distance

between subsequent medium centers (atoms), the effective tunneling matrix can be recast in the form

$$T_{DA} = T^0_{DA}\prod_{j=1}^{L} \exp(-\alpha_j r_j) = T^0_{DA}\exp\left(-\sum_{j=1}^{L}\alpha_j r_j\right) = T^0_{DA}\exp\left(-\sum_{j=1}^{L} R_j\right), \quad (14)$$

where r_j are fluctuations of the atomic coordinates of the bridge, α_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. 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 $R(t)$ reached by the particle at time $t \geqslant 0$ if the movement is generated by a sequence $\{(R_j, T_j), j=1,2,\ldots\}$ assumed to be formed by IID random vectors with R_j specifying both the length and the direction of the jth jump and $T_j > 0$ denoting the waiting time for the next jump. Note that T_j is a time spent by the particle in the location $\Sigma_{i=1}^{j} R_i$, reached as the result of j subsequent jumps. CTRW is called decoupled if random variables T_j and R_j are independent and coupled if one incorporates statistical dependence between time and space steps. The cumulative distance $R(t)$ may be expressed as

$$R(t) = \sum_{j=1}^{L(t)} R_j, \quad (15)$$

where

$$L(t) = \min\left\{ l : \sum_{j=1}^{l} T_j > t \right\} \quad (16)$$

meaning that $L(t)=l$ iff $\Sigma_{j=1}^{l-1} T_j \leqslant t < \Sigma_{j=1}^{l} T_j$. The renewal process

$$\left\{ \sum_{j=1}^{l} T_j, l = 1,2,\ldots \right\} \quad (17)$$

represents the instants of time at which subsequent jumps occur, hence the process $\{L(t), t \geqslant 0\}$ counts the jumps, and $L(t)=l$ if exactly l jumps occurred until time t. The introduced CTRW $\{R(t), t \geqslant 0\}$ is the discrete-time random walk $\{\Sigma_{j=1}^{[t]} R_j, t \geqslant 0\}$ subordinated to the renewal counting process $\{L(t), t \geqslant 0\}$ defined by Eq. (16). In case of the one-dimensional decoupled CTRW the space steps are independent of the counting process, and the probability distribution of $R(t)$ can be given by its characteristic function which in this case fullfils the equation

$$\varphi_{R(t)}(\mathrm{s}) = \langle e^{isR(t)} \rangle = \Phi_{L(t)}[\varphi_R(\mathbf{s})], \quad (18)$$

where $\Phi_{L(t)}(\mathbf{s}) = \langle \mathbf{s}^{L(t)} \rangle$ is the "nested" moment-generating function of $L(t)$ and $\varphi_R(\mathbf{s})$ is the characteristic function of R_i. In the forthcoming sections we present a dynamic framework which, within the CTRW scenario, leads to the empirically observed non-exponential relaxation dynamics and anomalous diffusion.

IV. PATHWAY ANALYSIS OF ET REACTIONS

As discussed above, with the matrix elements of a particular path T_{DA}, the nature of disorder may be analyzed in terms of fluctuations in couplings or, alternatively, in contributions R_j to the total distance traversed by a charge. In the framework of the CTRW model, the total distance $R(t)$ has a form given by Eq. (15). The properties of the CTRW process $\{R(t), t \geqslant 0\}$ follow from the assumptions set on the probability distributions of the random vectors (R_j, T_j) and, in general, are very difficult to analytical studies. In its simplest version, the decoupled CTRW with the exponential distribution of the waiting times between the jumps and the distribution of the jump lengths with finite first moment and variance is known to have independent increments and, consequently, the Markov property. In such a case, in a continuous limit one ends with the regular diffusion process of charges. In this section, we examine another example of the decoupled CTRWs with some chosen distributions of the waiting times and the jump lengths. First, we consider the case when the length R_j of a given jump, and the waiting time T_j elapsing between two corresponding successive jumps are drawn as independent random variables with densities

$$\rho(\mathrm{R}) = \beta e^{-\beta \mathrm{R}}, \quad \mathrm{R} > 0 \quad (19)$$

and

$$\sigma(\mathrm{T}) = s_{1/2}(\mathrm{T};1,1,0) = \frac{1}{\sqrt{2\pi}}\mathrm{T}^{-3/2} e^{-1/2\mathrm{T}}, \quad \mathrm{T} > 0, \quad (20)$$

i.e., the model describes a charge moving only in one direction with a Poisson number of jumps needed to exceed the level R and the Lévy-Smirnov [(1/2) stable] distribution of waiting times. Here, for a stable distribution characterized by the set of parameters $\alpha, \beta, \sigma, \mu$ (the stability index α, the scale parameter σ, the skewness β, and the shift μ) we use the notation $s_\alpha(x;\sigma,\beta,\mu)$ representing its density function (for details, see the Appendix).

In the considered case, by means of the conditional probability, we obtain the explicit form of the probability density function $p(\mathrm{R})_\mathrm{T}$ of the total distance $R(\mathrm{T})$ reached at time T. Namely, for $p_1(i) = \Pr[L(\mathrm{T}) = i]$ being the probability to make i steps until time T, and $p_2(\mathrm{R}|i)$ standing for the conditional probability density of $R(\mathrm{T}) = \Sigma_{j=0}^{L(\mathrm{T})} R_j$ given $L(\mathrm{T}) = i$ we have

$$p(\mathrm{R})_\mathrm{T} = \sum_{i=1}^{\infty} p_1(i) p_2(\mathrm{R}|i) = \sum_{n=0}^{\infty} \frac{(\beta \mathrm{R})^n}{n!} e^{-\beta R} \frac{2}{\sqrt{2\pi \mathrm{T}}} \int_n^{n+1} e^{-(y^2/2\mathrm{T})} dy \quad (21)$$

since for the decoupled CTRW $p_2(\mathrm{R}|i)$ is a density function of $\Sigma_{j=1}^{i} R_j$ that in the considered case has a gamma distribu-

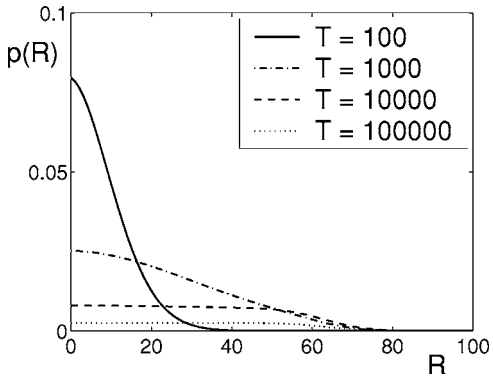

FIG. 1. Probability density function $p(\mathrm{R})_{\mathrm{T}}$, Eq. (21), of distances traversed up to the time T in a one-dimensional CTRW with the waiting times assumed to have the Lévy-Smirnov distribution (20).

tion resulting from a sum of i independent and exponentially distributed random variables. The shapes of the obtained density functions corresponding to some chosen values of T are displayed in Fig. 1.

On the other hand, we can ask for another counting process $\{L_1(\mathrm{R}), \mathrm{R} \geqslant 0\}$ describing random numbers of forward steps exerted by a particle before exceeding the fixed distance R. Hence

$$L_1(\mathrm{R}) = \max\left\{ l : \sum_{j=1}^{l} R_j \leqslant \mathrm{R} \right\}, \tag{22}$$

i.e., we have

$$\sum_{j=1}^{L_1(\mathrm{R})} R_j \leqslant \mathrm{R} < \sum_{j=1}^{L_1(\mathrm{R})+1} R_j. \tag{23}$$

The random time $T(\mathrm{R})$ that the particle needs to exceed the fixed distance R is given by $T(\mathrm{R}) = \Sigma_{i=1}^{L_1(\mathrm{R})} T_i$ with the waiting time T_i being a time spent by a hopping charge at the location $\Sigma_{j=1}^{i} R_j$. By means of a conditional probability, the probability density $p(\mathrm{T})_{\mathrm{R}}$ for the distribution of time $T(\mathrm{R})$ to reach a distance R reads in accordance with the basic assumptions of the CTRW [1] and analogically to Eq. (21) as

$$p(\mathrm{T})_{\mathrm{R}} = \sum_{j=1}^{\infty} p_1(j) p_2(\mathrm{T}|j), \tag{24}$$

where in this case $p_1(j) = \Pr[L_1(\mathrm{R}) = j]$ is the probability that exactly j steps have been performed to reach the distance R, and $p_2(\mathrm{T}|j)$ is a conditional probability density of $T(\mathrm{R}) = \Sigma_{i=1}^{L_1(R)} T_i$ provided $L_1(\mathrm{R}) = j$. Due to the known properties of sums of stable random variables, in the considered case, the conditional probability density function $p_2(\mathrm{T}|j)$ in Eq. (24) is given by the probability density of a rescaled Lévy-Smirnov distribution

$$p_2(\mathrm{T}) = s_{1/2}(\mathrm{T}; j^2, 1, 0) \tag{25}$$

resulting in

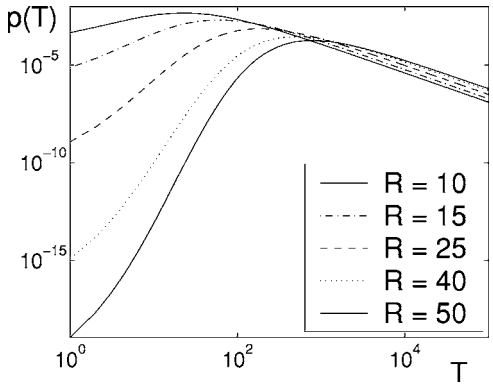

FIG. 2. Probability density function $p(\mathrm{T})_{\mathrm{R}}$, Eq. (26), of time needed to reach the distance R in a one-dimensional random walk with the Lévy-Smirnov distribution (20) of waiting times for a jump.

$$p(\mathrm{T})_{\mathrm{R}} = e^{-\beta \mathrm{R}} \frac{\mathrm{T}^{-3/2}}{\sqrt{2\pi}} \sum_{j=0}^{\infty} \frac{(\beta \mathrm{R})^j}{j!} j e^{-j^2/2\mathrm{T}}. \tag{26}$$

The shapes of the obtained density functions for some chosen values of R are presented in Fig. 2.

The sketched problem describes a one-dimensional diffusion among traps with a broad (asymptotically heavy-tailed) distribution $\sigma(\mathrm{T})$ of trapping times. This type of the "annealed" CTRW has been extensively studied in literature [1,8,16,26,27]. 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. Below, as another example of CTRW, we study a three-dimensional analog with a broken unidirectionality of the transfer that corresponds to a weak external field approximation. Figure 3 displays results of a three-dimensional CTRW computer simulation. Direction of a jump has been generated by sampling spherical coordinates θ and ϕ from uniform distributions defined on intervals $(0, \pi/2)$ and $(0, 2\pi)$, respectively. Quite arbitrarily, the positive direction of the z axis have been favored by sampling the coordinates of a point $(\phi, \theta, -z)$ by using those

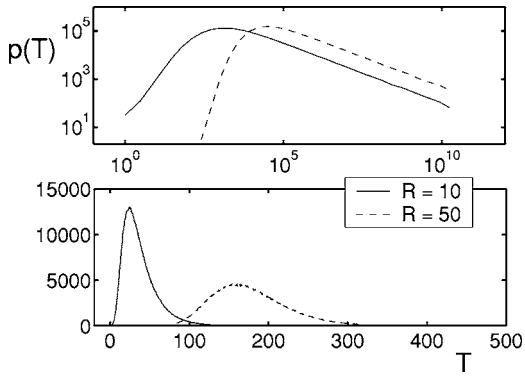

FIG. 3. Probability density function $p(\mathrm{T})_{\mathrm{R}}$ of time needed to reach a distance R in a three-dimensional CTRW with the Lévy-Smirnov distribution (20) (upper panel) and the Weibull distribution (27) (lower panel) of waiting times for a jump.

for (ϕ,θ,z) and switching from z to $-z$ with a probability 3/10. The upper panel of Fig. 3 refers to the distribution of the time required to reach the distance R when the distribution of waiting times for the subsequent jump was assumed in a form of a skewed (heavy-tailed) Lévy-Smirnov distribution describing higher probability of long trapping. In contrast, the lower panel represents the results of simulations for a three-dimensional CTRW with a preferential short mean time of waiting for a particle release from the trap, modeled by an asymmetric Weibull distribution

$$\sigma(\mathrm{T}) = \alpha \mathrm{T}^{\alpha-1} e^{-\mathrm{T}^{\alpha}}, \quad \mathrm{T} > 0, \tag{27}$$

where $0<\alpha<1$. Comparison of both sets of simulated data points out a critical difference between the two kinetic schemes: particles which are preferentially trapped for short times diffuse more efficiently and reach the same distance in space in a much shorter time than the particles with a nonzero probability of an infinite waiting time for a release from a trap. Moreover, the probability density function $p(\mathrm{T})_{\mathrm{R}}$ of arrival times is characteristically overdispersed in such a case, in contrast to the situation when the mean time of trapping is preferentially short.

It is worthy mentioning here that the character of random motion in complex media or on complex disordered structures depends strongly on the involved topologies and, depending on the underlying microscopic dynamics, may result in either subdiffusive [5,20] or superdiffusive [28,29] behavior. For example, particles trapped in one of conformational states of the multidimensional energy landscape of the protein may exhibit a power-law distribution of trapping time [20] resulting in subdiffusion. In contrast, charge carriers hopping along a polymer in a complex folding state may jump to a neighboring location which is close in the Euclidean space but far distant in chemical coordinates [28,29], leading effectively to the superdiffusive (Lévy flight) motion. This observation is further used to infer possible statistics of R_i and T_i parameters in a generalized form of the CTRWs.

V. RANDOM WALK SUBORDINATED TO A COMPOUND COUNTING PROCESS

As mentioned in the previous section, the statistical properties of CTRW processes are very difficult to study. Nevertheless, the behavior of the CTRW for long time or, equivalently, of the rescaled process $R(t/\delta\tau)/f(\delta\tau)$ for the characteristic time scale $\delta\tau$ decreasing to 0 [with an appropriately chosen rescaling function $f(\delta\tau)$], can be determined quite well. Systematic studies of the limiting total-distance distributions for the one-dimensional CTRWs have pointed on few possible distributions [30,31]. Recently, introducing a new class of coupled memory CTRWs incorporating effects of clustering of carrier trapping sites in a disordered material under the study, a much broader class of possible limiting distributions has been obtained [32]. The proposed new class of the CTRW processes involves the idea of the aggregation of M_j subsequent steps of the initial decoupled CTRW, M_j being a random number. Namely, to obtain a new, coupled CTRW we transform some initial space/time-step sequence $\{(R_i,T_i), i=1,2,\ldots\}$ (with independent R_i and T_i) into a new family $\{(\overline{R_j},\overline{T_j}), j=1,2,\ldots\}$ by means of the following "coarse-graining" procedure [32]

$$(\overline{R_1},\overline{T_1}) = \sum_{i=1}^{M_1} (R_i,T_i),$$

$$(\overline{R_j},\overline{T_j}) = \sum_{i=M_1+\ldots+M_{j-1}+1}^{M_1+\ldots+M_j} (R_i,T_i), \quad j=2,3,\ldots . \tag{28}$$

Formula (28) describes assembling space/time steps into clusters of random sizes $M_1,M_2,\ldots$. The resulting random vector $(\overline{R_j},\overline{T_j})$ has a probability distribution given by the joint characteristic function

$$\varphi(s,y) = \langle e^{i(s\cdot\overline{R_j}+y\overline{T_j})}\rangle = \Phi_M[\varphi_{R,T}(s,y)], \tag{29}$$

where $\Phi_M(s)=\langle s^{M_j}\rangle$ is the "nested" moment-generating function of M_j, and $\varphi_{R,T}(s,y)$ is the joint characteristic function of (R_i,T_i). Assuming that $\{M_j, j=1,2,\ldots\}$ is a sequence of IID positive integer-valued random variables and that this sequence is independent of the step family $\{(R_i,T_i), i=1,2,\ldots\}$, the spatiotemporal clustering (28) provides $\{(\overline{R_j},\overline{T_j}), j=1,2,\ldots\}$ being a sequence of IID random vectors such that $\overline{T_j}>0$. Therefore the resulting sequence can be considered as a new family of space/time steps that by means of the general formula (16) leads to a new CTRW process. Although no precise functional relation between the time and space steps $\overline{T_j}$ and $\overline{R_j}$ is explicitly assumed, the nondegenerate distribution of M_j, the cluster sizes (i.e., the case when random variable M_j takes at least two different values with positive probabilities), incorporates a stochastic dependence between the steps. As a consequence, the CTRW $\{R(t), t\geqslant 0\}$ resulting from the space/time-step family defined by Eq. (28) is usually coupled. Moreover, it has an equivalent form [32]

$$R(t) = \sum_{k=1}^{L_C(t)} R_k \tag{30}$$

of the discrete-time random walk $\{\Sigma_{j=1}^{[t]} R_j, t\geqslant 0\}$ subordinated to the compound counting process $\{L_C(t), t\geqslant 0\}$ defined as

$$L_C(t) = \sum_{j=1}^{N[L(t)]} M_j. \tag{31}$$

Here the renewal counting process $L(t)$ is as in Eq. (16) and the random number of summands in Eq. (31) is given by

$$N(\tau) = \min\left\{ n : \sum_{j=1}^{n} M_j > \tau \right\} \tag{32}$$

for τ being an "operational" time (number of steps), as discussed, e.g., in Ref. [33].

Note, that the subordinated-random-walk form (30) of the coupled CTRW process defined above shows that this process can be treated as the walk with somehow modified time lapses. Possible coupling between the space steps R_i and the modified time lapses is incorporated via the counting process

(31) summing contributions to the cumulative distance $R(t)$ traversed during the walk. Since the space steps R_i are independent of the compound counting process $L_C(t)$, the discussed form (30) of $R(t)$ allows us to calculate the characteristic function of the cumulative-distance distribution. Namely, similarly to Eq. (18), for the considered coupled CTRW, we obtain

$$\varphi_{R(t)}(s) = \Phi_{L_C(t)}[\varphi_R(s)], \tag{33}$$

where $\Phi_{L_C(t)}(s)$ is the "nested" moment-generating function of the compound counting process $L_C(t)$, and $\varphi_R(s)$, as in Eq. (18), is the characteristic function of R_i.

VI. DIFFUSION FRONT: LIMITING DISTRIBUTIONS

In this section we consider the coupled memory CTRW $\{R(t), t \geqslant 0\}$ obtained from the clustered space/time step family Eq. (28); however, we study the rescaled total distance of such a walk

$$\widetilde{R}_{\delta\tau}(t) = \frac{R(t/\delta\tau)}{f(\delta\tau)}, \tag{34}$$

where $\delta\tau$ is the characteristic time scale, and $f(\delta\tau)$ is a rescaling function chosen appropriately. Applying limit theorems [32,34] one can evaluate the limiting position $\widetilde{R}(t)$ of the rescaled total distance $\widetilde{R}_{\delta\tau}(t)$ reached as $\delta\tau \to 0$. The characteristics of $\widetilde{R}(t)$ depend on assumptions set on the distributions of the variables R_i, T_i, and M_j. Below, following the regularization scheme Eq. (34) along with a more detailed presentation and proofs included in Refs. [32,34,35], we discuss briefly the examples which—as shall be shown in the next section—are of practical use in modeling relaxation phenomena in disordered materials. All the examples concern the case of one-dimensional CTRW with the positive space steps R_i.

(a) Let us first assume that both R_i and T_i have heavy-tailed distributions with $c=c_1$ and $c=c_2$, respectively, and the same $r=\alpha$. We say that the distribution of a positive random variable X has a *heavy tail* if for some $c>0$ and $0<r<1$

$$\lim_{x\to\infty} \frac{\Pr(X>x)}{(x/c)^{-r}} = 1. \tag{35}$$

As a 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 $t>0$

$$\frac{R(t/\delta\tau)}{1/\delta\tau} \xrightarrow[\delta\tau\to 0]{d} \widetilde{R}(t) \overset{d}{=} \frac{t}{A}\frac{\mathcal{S}'_\alpha}{\mathcal{S}_\alpha}\left(\frac{1}{\mathcal{B}_\gamma}\right)^{1/\alpha}. \tag{36}$$

Here "$\xrightarrow{d}$" reads "tends in distribution" and "$\overset{d}{=}$" denotes the equal distributions.

If the numbers M_j have a finite expected value ($\langle M_j \rangle < \infty$), then for any $t>0$

$$\frac{R(t/\delta\tau)}{1/\delta\tau} \xrightarrow[\delta\tau\to 0]{d} \widetilde{R}(t) \overset{d}{=} \frac{t}{A}\frac{\mathcal{S}'_\alpha}{\mathcal{S}_\alpha}. \tag{37}$$

(b) Assume that the expected values of both R_i and T_i are finite, and $\langle R_i \rangle = c_1$, $\langle T_i \rangle = c_2$.

If the distribution of M_j has a heavy tail with some $c>0$ and $r=\gamma$, then for any $t>0$

$$\frac{R(t/\delta\tau)}{1/\delta\tau} \xrightarrow[\delta\tau\to 0]{d} \widetilde{R}(t) \overset{d}{=} \frac{t}{A}\frac{1}{\mathcal{B}_\gamma}. \tag{38}$$

If $\langle M_j \rangle < \infty$, then for any $t>0$

$$\frac{R(t/\delta\tau)}{1/\delta\tau} \xrightarrow[\delta\tau\to 0]{\text{a.s.}} \widetilde{R}(t) = \frac{1}{A}. \tag{39}$$

Here "$\xrightarrow{\text{a.s.}}$" reads "tends with probability 1."

The random variables $\mathcal{B}_\gamma$, $\mathcal{S}_\alpha$, and $\mathcal{S}'_\alpha$ in Eqs. (36)–(39) are as follows. $\mathcal{S}_\alpha$ and $\mathcal{S}'_\alpha$ are identically distributed according to the completely asymmetric α-stable law such that $\langle e^{-k\mathcal{S}_\alpha} \rangle = e^{-k^\alpha}$, i.e., the stable distribution corresponding to the density function $s_\alpha(x;\sigma,1,0)$ with $\sigma^\alpha = \cos(\pi\alpha/2)$, see the Appendix. $\mathcal{B}_\gamma$ is distributed according to the generalized arcsine distribution with parameter γ (i.e., the beta distribution with parameters $p=\gamma$ and $q=1-\gamma$) given by the density function

$$f_\gamma(x) = \begin{cases} \dfrac{x^{\gamma-1}(1-x)^{-\gamma}}{\Gamma(\gamma)\Gamma(1-\gamma)} & \text{for } 0<x<1, \\ 0 & \text{otherwise.} \end{cases} \tag{40}$$

For any $0<\alpha,\gamma<1$ the random variables $\mathcal{B}_\gamma$, $\mathcal{S}_\alpha$, and $\mathcal{S}'_\alpha$ 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.

VII. 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 [5,15,17,19,20,31,36,37]. 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 $I(t) \approx (\omega_p t)^{-(\alpha+1)}$. 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 steplike 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. Wide-ranging experimental information resulting from the latter [15,37] 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 (5) is hardly ever found in nature and that for many dielectrics the deviations from it may be relatively large [11,13,15]. In the context of ET rate constant, the experiments reflecting ensemble average over donor-acceptor complexes have been recently analyzed [19,20], pointing out that the nonexponential decay of the donor population is a result of averaging over the distribution of relaxation times and static heterogeneity, typical for the glass-forming solvents.

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 [11–13,15,16]. The most popular analytical expression applied to the complex susceptibility or permittivity data is given by the Havriliak-Negami function (7). For $\alpha=1$ and $\gamma<1$, formula (7) takes the form (1) of the Cole-Davidson function; for $\gamma=1$ and $\alpha<1$ it takes the form (6) of the Cole-Cole function, and for $\alpha=1$ and $\gamma=1$ one obtains the classical Debye form (5). Let us note that the time-domain relaxation function $\phi(t)$ corresponding to formula (7) by means of relation (2) has the following series representation:

$$\phi(\omega_p t) = 1 - \sum_{n=0}^{\infty} \frac{(-1)^n \Gamma(\gamma+n)}{\Gamma(\gamma) n! \Gamma[1+\alpha(\gamma+n)]} (\omega_p t)^{\alpha(\gamma+n)} \quad (41)$$

referred to the generalized Mittag-Leffler distribution. In case of the CC function the series representation (41) is simplified to

$$\phi(\omega_p t) = 1 - \sum_{n=0}^{\infty} \frac{(-1)^n}{\Gamma[1+\alpha(1+n)]} (\omega_p t)^{\alpha(1+n)} \quad (42)$$

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

$$g_\gamma(t) = \begin{cases} \dfrac{\omega_p}{\Gamma(\gamma)} (\omega_p t)^{\gamma-1} e^{-\omega_p t} & \text{for } t > 0, \\ 0 & \text{otherwise.} \end{cases} \quad (43)$$

In order to derive relevant relaxation functions resulting from cases (36)–(39), considered above, we use the following relations. For any $0<\alpha\leqslant 1$

$$\langle e^{-k\mathcal{S}_\alpha} \rangle = \langle e^{-k\mathcal{S}'_\alpha} \rangle = e^{-k^\alpha} \quad (44)$$

and for any $0<\gamma\leqslant 1$ we have [35]

$$\langle e^{-k\mathcal{B}_\gamma} \rangle = \Pr(G_\gamma \geqslant k), \quad (45)$$

where $\mathcal{S}_1=\mathcal{S}'_1=\mathcal{B}_1=1$, $G_1=E$ is exponentially distributed with mean 1, and for $\gamma<1$ the random variable G_γ is distributed according to the gamma distribution with the shape parameter γ and the scale parameter 1. Assuming that for any $0<\alpha,\gamma\leqslant 1$ the random variable G_γ is independent of $\mathcal{S}_\alpha$, and by using the conditional-expectation tools, from formulas (44) and (45) one obtains

$$\langle e^{-k[\mathcal{S}'_\alpha/\mathcal{S}_\alpha (1/\mathcal{B}_\gamma)^{1/\alpha}]} \rangle = \Pr(G_\gamma^{1/\alpha} \mathcal{S}_\alpha \geqslant k) \quad (46)$$

and hence for $\tilde{R}(t)$ of the form (36)–(39) the corresponding relaxation function $\phi(t)$ equals

$$\phi(t) = \langle e^{-k\tilde{R}(t)} \rangle = \langle e^{-t(k/A)[\mathcal{S}'_\alpha/\mathcal{S}_\alpha (1/\mathcal{B}_\gamma)^{1/\alpha}]} \rangle = \Pr[(A/k) G_\gamma^{1/\alpha} \mathcal{S}_\alpha \geqslant t], \quad (47)$$

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

$$\phi^*(\omega) = \langle e^{-i(\omega/\omega_p) G_\gamma^{1/\alpha} \mathcal{S}_\alpha} \rangle = \frac{1}{[1+(i\omega/\omega_p)^\alpha]^\gamma}, \quad \omega_p = k/A, \quad (48)$$

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

The above equations (47) and (48) along with the asymptotic properties of the total displacement, as discussed in Sec. VI, constitute the center result of this paper. Let us emphasize that in the framework of the CTRWs, the mathematically rigorous generalization of the Debye response (5) to the Havriliak-Negami one (7), requires introduction of a new class of coupled memory walks in which the coupling between the space steps and time lapses is incorporated via the counting process $L_C(t)$ [see Eqs. (30) and (31)]. The only crossover of the proposed model with classical CTRW [1,4,5] appears in the case of the Debye and the Cole-Cole responses in which the coupling with the finite mean values of the random number M_i (see Table I) leads asymptotically to the same results as in the case of the decoupled CTRWs.

Interestingly, within the adopted random walk model, assumptions leading to the Havriliak-Negami response require not only the heavy-tail property of space and time increments, but also a heavy-tail statistics of the cluster number M_j. The column of Assumptions in Table I contains a detailed information about the statistical character of specific random walks proposed in the study. The rigorous probabilistic representation of the corresponding relaxation functions is displayed in the last column (response). As it is already known from investigations in the similar context of the complex fractional dynamics [5,6,38], in the Debye and Cole-Cole cases, the corresponding relaxation functions reflect the tails of the exponential and Mittag-Leffler distributions, respectively. In two other cases, i.e., in the Cole-Davidson and Havriliak-Negami responses, the

TABLE I. Special cases of the frequency-domain responses (48) (c_0 is a positive constant).

Assumptions			Response
R_i	T_i	M_j	$\phi^*(\omega)$
heavy tail	heavy tail	heavy tail	Havriliak-Negami
$r=\alpha$	$r=\alpha$	$r=\gamma$	$\langle e^{-i(\omega/\omega_p)G_\gamma^{1/\alpha}S_\alpha}\rangle$
$c=\omega_p c_0/k$	$c=c_0$	$c>0$	$\alpha,\gamma<1$
heavy tail	heavy tail		Cole-Cole
$r=\alpha$	$r=\alpha$	$\langle M_j\rangle<\infty$	$\langle e^{-i(\omega/\omega_p)E^{1/\alpha}S_\alpha}\rangle$
$c=\omega_p c_0/k$	$c=c_0$		$\alpha<1,\ \gamma=1$
$\langle R_i\rangle=$	$\langle T_i\rangle=$	heavy tail	Cole-Davidson
$\omega_p c_0/k<\infty$	$c_0<\infty$	$r=\gamma$	$\langle e^{-i(\omega/\omega_p)G_\gamma}\rangle$
		$c>0$	$\alpha=1,\ \gamma<1$
$\langle R_i\rangle=$	$\langle T_i\rangle=$		Debye
$\omega_p c_0/k<\infty$	$c_0<\infty$	$\langle M_j\rangle<\infty$	$\langle e^{-i(\omega/\omega_p)E}\rangle$
			$\alpha=1,\ \gamma=1$

corresponding relaxation functions are the tails of the gamma and the generalized Mittag-Leffler distributions, respectively. All of them follow from one coupled memory random walk scheme represented at the level of experimental observations by a mixture of generalized gamma and completely asymmetric Lévy stable distributions [see Eqs. (47) and (48)].

VIII. 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 [15,16,40]. Anomalous relaxation kinetics is also an important topic in the analysis of ET reactions in polymeric and protein materials [5,17,20,23,40–42]. In the latter, the kinetics of the charge transport has been demonstrated to be influenced by factors arising from the static heterogeneity and dynamic fluctuations [17,19,20,23,25] and modeled by several different approaches [17,23,36,41,42].

Among various formalisms used to describe relaxation processes in disordered, amorphous polymers or glass forming liquids, models based on kinetic Fokker-Planck-Smoluchowski (FPSE) equation [5,39] have been considered. Similar to the Debye description which formulates the relaxation kinetics in terms of the Brownian motion relying on the diffusion limit of a discrete time random walk that leads to a standard FPSE, the continuous time walks have been demonstrated to give rise to the fractional FPSE [5]. In particular, it has been shown that the Cole-Cole relaxation pattern arises naturally from the solution of a fractional FPSE in the configuration space. Such an equation is obtained in the limit of a large sequence of jump times in fractal time random walks [5,30,31,39]. Another attempt to fractionalizing the FPSE has been presented recently [39]. In order to incorporate the Cole-Davidson and Havriliak-Negami relaxation behaviors in a fractional FPSE, the authors proposed a scheme of derivation of a FPSE-like kinetic equation for an impulse response starting from the fractional ordinary differential equation. In principle, the technique is based on a mere replacement of the partial derivative in the FPSE by a fractional time derivative of a given order and does not stem from a microscopic description of the Cole-Davidson or the Havriliak-Negami process. In contrast, the methodology presented in this paper allows us to formulate rigorous statistical requirements underlying asymptotical behavior of CTRW leading to the anomalous Cole-Davidson or the Havriliak-Negami relaxation scenarios.

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APPENDIX

The Lévy-stable distributions are defined by the property that the normalized sum of independent random variables X_1, X_2 distributed according to the same α-stable distribution has the same distribution as each component, i.e., the property that for any $a,b>0$

$$aX_1 + bX_2 \overset{d}{=} cX + d, \tag{A1}$$

for X distributed as X_1 and some constants $c>0, d$, where $\overset{d}{=}$ denotes equality in a distribution sense. The stable distributions are the only one possesing the above property. Each of them can be described by the probability density function. Real constants c,d in Eq. (A1), that allow for rescaling and shifting of the initial probability distribution, depend on a,b. It is a well-known fact that $c=(a^\alpha+b^\alpha)^{1/\alpha}$ for some $\alpha \in (0,2]$. The parameter α of a stable distribution is called the stability index. To indicate a stable distribution one needs three other parameters; however, they can be chosen in vari-

ous ways [7,43]. In this paper we adhere to the parameterization for which the characteristic function of the stable law with the index of stability α is given by

$$\phi(k) = \exp\left[-\sigma^{\alpha}|k|^{\alpha}\left(1 - i\beta\,\mathrm{sgn}(k)\tan\frac{\pi\alpha}{2}\right) + i\mu k \right],$$

$$\text{for } \alpha \neq 1,$$

$$\phi(k) = \exp\left[-\sigma|k|\left(1 + i\beta\frac{2}{\pi}\,\mathrm{sgn}(k)\ln|k|\right) + i\mu k \right], \quad \text{for } \alpha = 1, \tag{A2}$$

with the skewness parameter $\beta \in [-1,1]$, the scale parameter $\sigma \in (0,\infty)$, and the shift $\mu \in (-\infty,\infty)$. Thus $\phi(k)$ corresponds to the four-parameter stable density function $s_{\alpha}(x;\sigma,\beta,\mu)$:

$$\phi(k) = \int_{-\infty}^{+\infty} e^{-ikx} s_{\alpha}(x;\sigma,\beta,\mu)dx. \tag{A3}$$

The analytical expressions of the stable probability density functions [corresponding to Eq. (A2)] can be given only in few cases. In particular, for $\alpha=2$ and any β (e.g., $\beta=0$), we get the Gaussian probability density with mean μ and variance $2\sigma^2$:

$$s_2(x;\sigma,0,\mu) = \frac{1}{2\sigma\sqrt{\pi}}\exp\left(-\frac{(x-\mu)^2}{4\sigma^2}\right), \tag{A4}$$

whereas $\alpha=1$, $\beta=0$ and $\alpha=\frac{1}{2}$, $\beta=1$ yield the Cauchy distribution

$$s_1(x;\sigma,0,\mu) = \frac{\sigma}{\pi}\frac{1}{(x-\mu)^2+\sigma^2}. \tag{A5}$$

and the Lévy-Smirnov $(x>\mu)$ distribution

$$s_{1/2}(x;\sigma,1,\mu) = \left(\frac{\sigma}{2\pi}\right)^{1/2}(x-\mu)^{-3/2} \times \exp\left(-\frac{\sigma}{2(x-\mu)}\right), \tag{A6}$$

respectively.

In general, the stable probability density functions with $\alpha \neq 1$ are known to have an asymptotic power-law behavior $s_{\alpha}(x) \sim |x|^{-(\alpha+1)}$ as $|x| \to \infty$. (For $\beta=1$ or -1 this property concerns only x tending to ∞ or $-\infty$, respectively.) The stability property implies that the sum of independent stable variables X_1, X_2 sampled from a given distribution $s_{\alpha}(x;\sigma,\beta,\mu)$ has again a stable density function $s_{\alpha}(x;\sigma',\beta',\mu')$ with indices

$$\sigma' = (\sigma_1^{\alpha} + \sigma_2^{\alpha})^{1/\alpha},$$

$$\beta' = \frac{\beta_1\sigma_1^{\alpha} + \beta_2\sigma_2^{\alpha}}{\sigma_1^{\alpha} + \sigma_2^{\alpha}},$$

$$\mu' = \mu_1 + \mu_2. \tag{A7}$$

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