Wait-and-switch relaxation model: Relationship between nonexponential relaxation patterns and random local properties of a complex system

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The wait-and-switch stochastic model of relaxation is presented. Using the "random-variable" formalism of limit theorems of probability theory we explain the universality of the short- and long-time fractional-power laws in relaxation responses of complex systems. We show that the time evolution of the nonequilibrium state of a macroscopic system depends on two stochastic mechanisms: one, which determines the local statistical properties of the relaxing entities, and the other one, which determines the number (random or deterministic) of the microscopic and mesoscopic relaxation contributions. Within the proposed framework we derive the Havriliak-Negami and Kohlrausch-Williams-Watts functions. We also discuss the influence of the random-walk characteristics of migrating defects on the homogeneous and heterogeneous relaxation scenarios and show the origins of the stretched-exponential integral kernel in the integral representation of the ensemble-averaged relaxation function.

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I. INTRODUCTION

Experimental investigations have established the relaxation response of various materials (amorphous semiconductors and insulators, polymers, molecular solid solutions, glasses, etc.) to be nonexponential in nature [1–4]. Relaxation data, obtained by different experimental techniques, appear to be characterized well enough by the frequency-domain Havriliak-Negami (HN) function

$$\phi^*_{HN}(\omega) = \frac{1}{[1 + (i\omega/\omega_p)^a]^b}, \tag{1}$$

and the time-domain Kohlrausch-Williams-Watts (KWW) relaxation function

$$\Phi_{KWW}(t) = \exp[-(\omega_p t)^a], \tag{2}$$

where ω_p is the material characteristic constant and $0 < a, ab < 1$. By means of the well-known frequency-time-domain relation

$$\phi^*(\omega) = \int_0^\infty \exp(-i\omega t) d(1 - \Phi(t)), \tag{3}$$

it is easy to show that while both empirical functions share a common, short-time power-law property

$$f(t) = -d\Phi(t)/dt = \begin{cases} (\omega_p t)^{ab-1} & \text{for HN}, \\ (\omega_p t)^{a-1} & \text{for KWW}, \end{cases} \tag{4}$$

their long-time asymtoptics are considerably different:

$$f(t) = -d\Phi(t)/dt = \begin{cases} (\omega_p t)^{-a-1} & \text{for HN}, \\ \exp[-(\omega_p t)^a] & \text{for KWW}. \end{cases} \tag{5}$$

As a consequence, in theoretical attempts to modeling the dielectric (also magnetic or mechanical) relaxation phenomena, it has been unanimously assumed that the above unique properties of the response function $f(t)$, independent of any special details of the examined systems, reflect a kind of a general behavior of the relaxing materials. This idea has stimulated the proposal of several relaxation models that differ mainly in mathematical interpretations [5–11] of the relaxation function $\Phi(t)$; i.e., a function in terms of which the experimental evidence is analyzed. While different theoretical approaches can lead to the KWW and Cole-Cole (a special case of the HN function when $b=1$) functions, for a long time they have failed in modeling the HN relaxation function. The latter has been recently obtained within the cluster model [12,13] and in the diffusion framework by introducing a new fractional Fokker-Planck operator [14] and a new type of "clustered" continuous time random walk [15]. These results are, however, insufficient for understanding the origins of the two, short- and long-time, power laws observed in a majority [2–4] of the physical systems studied. The empirical facts call hence for a completely novel approach to relaxation phenomena and, to some extent, also photoconduction, photoluminescence, and chemical reaction kinetics [4].

In the framework of probabilistic attempts to study the origins of the universal power-law properties of nonexponential relaxations, the idea of a complex system [16] that is characterized through a large diversity of elementary units and strong interactions between them is of special importance. The main feature of all dynamical processes in such systems is their stochastic background. Hence, it is natural to expect that the universal behavior of complex systems is governed by "averaging principles" like, e.g., the law of large numbers. However, it turns out to be very difficult to develop this intuition in concrete examples of stochastic sys-

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tems. The difficulty lies in a rigorous mathematical description of the relationship between the local random characteristics of a complex system and the intrinsic random behavior of the system as a whole [5,8,9]. The need to understand the connections between the experimentally observed power laws and the statistical properties of individual molecular contributions requires the introduction of advanced stochastic methods into relaxation theory [9,10]. As shown in [9], a general formalism of limit theorems of probability theory plays an important role in constructing tools to relate the random properties of the entities contributing to the macroscopic relaxation response, regardless of the specific nature of the system considered.

It is commonly accepted that the most natural attempt to model relaxation is based on diffusion of defects in the system under consideration [17,18]. In this approach, vacancies such as microscopic cavities or random orientation of crystallites diffuse within the system and when they meet an imposed direction of a dipole moment (in general, an initially prepared excited state) the latter is allowed to relax. On the other hand, to interpret the nonexponential relaxation behavior of complex dipolar, hydrogen-bounded liquids a "wait-and-switch" relaxation mechanism has been proposed [19]. This idea, verified by computer simulation studies of water [20,21], is based on the assumption that the reorientation of a dipole moment follows an activated jump mechanism. At any given time the direction of the dipole moment corresponds to an energy minimum; different dipole orientations are separated by potential energy barriers. A dipole of the network waits (in general, for a random period of time) until a favorable condition for reorientation exists—i.e., until an additional neighbor is in a suitable position. The transition of the dipole from its initial state is hence determined by the period in which the additional neighbor approaches.

Following both ideas, we introduce a mathematically rigorous wait-and-switch model for the random transition of an object in the medium of migrating defects and relate it to the behavior of a relaxing complex system. We propose a stochastic mechanism of relaxation based on the well-known assumption [17] that the transition of a dipole from its initial state occurs instantaneously when one from a set of migrating defects reaches the dipole for the first time. We show how the random characteristics of the surrounding medium and the spatiotemporal jump parameters of the diffusing defects influence the properties of the random relaxation rate of a single dipole and, in consequence, the behavior of the macroscopic dipolar system.

The proposed formalism, based on limit theorems of probability theory, clarifies why the universal response should exist at all. Our approach provides stochastic schemes underlying the asymptotic short- and long-time properties of the relaxation responses. Within the proposed framework we derive the HN and KWW functions. In Sec. II we introduce the notion of the relaxation function as the probability of the first passage of the system. We emphasize the importance of this concept as a basic mathematical tool by means of which the rigorous description of the stochastic transition of a complex system is possible. In Sec. III we discuss the defect-diffusion origins of the statistical properties of a relaxing dipole. In Sec. IV we discuss the physical meaning of the domain of attraction of completely asymmetric Lévy-stable laws and explain its relation to the homogeneous and heterogeneous scenarios of relaxation introduced recently in [22,23]. In this context we clarify the role of the stretched-exponential kernel in the integral representation of the ensemble-averaged relaxation function. We show that this form cannot be responsible for the homogeneous and heterogeneous scenarios as assumed in [22,23]. We also show that the relaxation properties of an entire system may be represented by a random effective relaxation rate which contains information on the internal stochastic nature of the investigated system. In Secs. V and VI, we present the powerful formalism of limit theorems of probability theory which allows us to derive explicit formulas even with restricted information on local properties of the system. We relate the statistical conditions, yielding the well-known empirical HN and KWW functions, to the spatiotemporal scaling properties of a relaxing system.

II. IRREVERSIBLE STOCHASTIC TRANSITION OF A MACROSCOPIC SYSTEM

To formulate the wait-and-switch stochastic model of relaxation, we need to introduce the notion of the relaxation function defined as the survival probability of a nonequilibrium initial state of a relaxing system.

Let us consider a macroscopic complex system undergoing irreversible transition from the initial state A, imposed at time $t=0$, to the relaxed state B at a random instant of time. The initial and relaxed states differ in some physical parameter, so that the transition $A \to B$ is defined as a time-dependent change of this particular parameter (note that changes in all other parameters may also influence the transition). Let $\mu_A(t)\Delta t$ denote the time-dependent probability that the system as a whole will undergo the transition from state A during the time interval $(t,t+\Delta t)$ if the transition has not occurred before time t. The probability $\mu_A(t)\Delta t$, expressed in terms of a random waiting time $\tilde{\theta}$ for the system's transition, reads

$$\mu_A(t)\Delta t = \Pr(t \leq \tilde{\theta} < t + \Delta t | \tilde{\theta} \geq t) + o(\Delta t),$$

where $o(\Delta t)$ is the probability of two or more transitions of the system in the time interval $(t,t+\Delta t)$. The above conditional probability can be rewritten as

$$\mu_A(t)\Delta t = -\frac{\Pr(\tilde{\theta} \geq t + \Delta t) - \Pr(\tilde{\theta} \geq t)}{\Pr(\tilde{\theta} \geq t)} + o(\Delta t),$$

where $\Pr(\tilde{\theta} \geq t)$ denotes the probability that the system as a whole will not make a transition from its original state for at least time t after entering it at $t=0$. In the limit of $\Delta t \to 0$ we get the differential kinetic equation fulfilled by the relaxation function $\Phi(t)=\Pr(\tilde{\theta} \geq t)$:

$$\frac{d\Phi(t)}{dt} = -\mu_A(t)\Phi(t), \tag{6}$$

where $\mu_A(t)$ is a transition rate of the relaxing system.

Let the considered system contain N identical objects, each waiting for transition from the initial state for a random time interval. For the ith object $(1 \le i \le N)$ we denote this time interval by $\theta_{iN} = A_N \theta_i$, where A_N is the system's characteristic size-dependent scaling constant. We assume that the nonnegative waiting times $\{\theta_1, \theta_2, \ldots\}$ form a sequence of independent and identically distributed (i.i.d.) random variables. The objects change their initial states in a certain order that can be expressed by means of order statistics $\theta_{(1)} \le \cdots \le \theta_{(N)}$, which is a nondecreasing rearrangement of waiting times θ_{iN} [24]. Note that the first-order statistics of the sample, $\theta_{1N}, \ldots, \theta_{NN}$, equals $\theta_{(1)} = \min(\theta_{1N}, \ldots, \theta_{NN})$ and denotes the waiting time for transition of the fastest relaxing object. The notion of the order statistics allows us to write explicitly, for a fixed size N of the system, the random number $\eta(t)$of individual transitions that have occurred in the system up to time t. Namely, the event that no single transition has happened prior to time t reads

$$\{\eta(t) = 0\} = \{\theta_{(1)} > t\}.$$

Similarly, the event that the number of transitions equals k reads

$$\{\eta(t) = k\} = \{\theta_{(k)} \le t, \theta_{(k+1)} > t\}, \quad \text{for } k = 1, \ldots, N-1,$$

and the event that all N objects have changed their initial states reads

$$\{\eta(t) = N\} = \{\theta_{(N)} \le t\}.$$

It follows that the probability $\Pr(\widetilde{\theta_N} \ge t)$ of not a single transition occurring in the considered system up to time t can be expressed as

$$\begin{aligned} \Pr(\widetilde{\theta_N} \ge t) &= \Pr(\eta(t) = 0) \\ &= \Pr(\theta_{(1)} \ge t) \\ &= \Pr(A_N \min(\theta_1, \ldots, \theta_N) \ge t), \end{aligned} \tag{7}$$

where $\widetilde{\theta_N}$ denotes the waiting time for the system's transition. In practice, the survival probability of the macroscopic system may be approximated by the following weak limit:

$$\Pr(\tilde{\theta} \ge t) = \lim_{N\to\infty} \Pr(\widetilde{\theta_N} \ge t). \tag{8}$$

As a consequence, the relaxation function

$$\begin{aligned} \Phi(t) = \Pr(\tilde{\theta} \ge t) &= \lim_{N\to\infty} \Pr(A_N \min(\theta_1, \ldots, \theta_N) \ge t) \\ &= \lim_{N\to\infty} \prod_{i=1}^{N} \Pr(\theta_i \ge t/A_N) \end{aligned} \tag{9}$$

is equal to the probability that the first passage of the system as a whole from its initial state has not happened prior to time t. The normalizing constants A_N introduced beforehand ensure the convergence in Eq. (9).

The above probabilistic representation of the relaxation function shows a rigorous dependence of the effective relaxation response on two mechanisms: one, which determines the individual survival probability $\Pr(\theta_i \ge t)$, and the other one, which determines the number N (deterministic or random) of the relaxation contributions.

III. STATISTICAL PROPERTIES OF THE INDIVIDUAL WAITING TIMES

As has been shown recently [25], the transition of a single dipole from its initially imposed state depends on random characteristics of the surrounding medium and the statistical properties of the spatiotemporal jump parameters of diffusing defects. This result is based on the well-known "target" assumption [17] that relaxation of a dipole occurs as soon as one from a set of defects, moving along the defect-dipole direction, reaches the dipole for the first time. Using extreme value theory [26] and the "random-variable" formalism [15,27,28] of the continuous-time random walk (CTRW) [29], we have shown [25] that the individual survival probability $\Pr(\theta_i \ge t)$ equals the weighted average of a stretched exponential decay function with respect to the distribution $F_L(l)$ of the distance L, which has to be traveled by the defects to reach the dipole:

$$\Pr(\theta_i \ge t) = \int_0^\infty \exp(-Ct^{\lambda'} l^{-\alpha}) dF_L(l) = \langle \exp(-Ct^{\lambda'} L_i^{-\alpha}) \rangle, \tag{10}$$

where $C = t_0^{-\lambda'} b_R^{\alpha}$. The power-law exponents α and λ' are determined by the spatiotemporal properties of the investigated CTRW. The result (10) is valid if we take the following two forms of the CTRW as a model of the defect diffusion.

(I) A random walk with a heavy-tailed distribution of jump sizes R_j,

$$\Pr(R_j \ge r) \overset{r\to\infty}{\sim} (r/b_R)^{-\alpha}, \quad \text{for some } 0 < \alpha < 1, \quad b_R > 0, \tag{11}$$

and a finite-mean distribution of interjump waiting times T_j,

$$\langle T_j \rangle = \mu_T < \infty . \tag{12}$$

(II) A random walk with heavy-tailed distributions of both, jump sizes R_j and interjump waiting times T_j,

$$\begin{aligned} &\Pr(R_j \ge r) \overset{r\to\infty}{\sim} (r/b_R)^{-\alpha}, \quad \text{for some } 0 < \alpha < 1, \quad b_R > 0, \\ &\Pr(T_j \ge t) \overset{t\to\infty}{\sim} (t/b_T)^{-\lambda}, \quad \text{for some } 0 < \lambda < 1, \quad b_T > 0. \end{aligned} \tag{13}$$

The exponent λ', introduced in formula (10), takes the values $\lambda' = 1$ for type I and $\lambda' = \lambda$ for type II of the CTRW. The heavy-tailed distributions assumed for the jump sizes and the interjump waiting times yield infinite expected values of the corresponding random variables.

As is clear from Eq. (10), the stretched exponential kernel in this formula reduces to the exponential one if the diffusion of defects follows a biased Lévy flight [10]—i.e., type I of the CTRW. Observe that also in the more general case II, when $\lambda' = \lambda$, the stretched-exponential integral kernel in Eq.

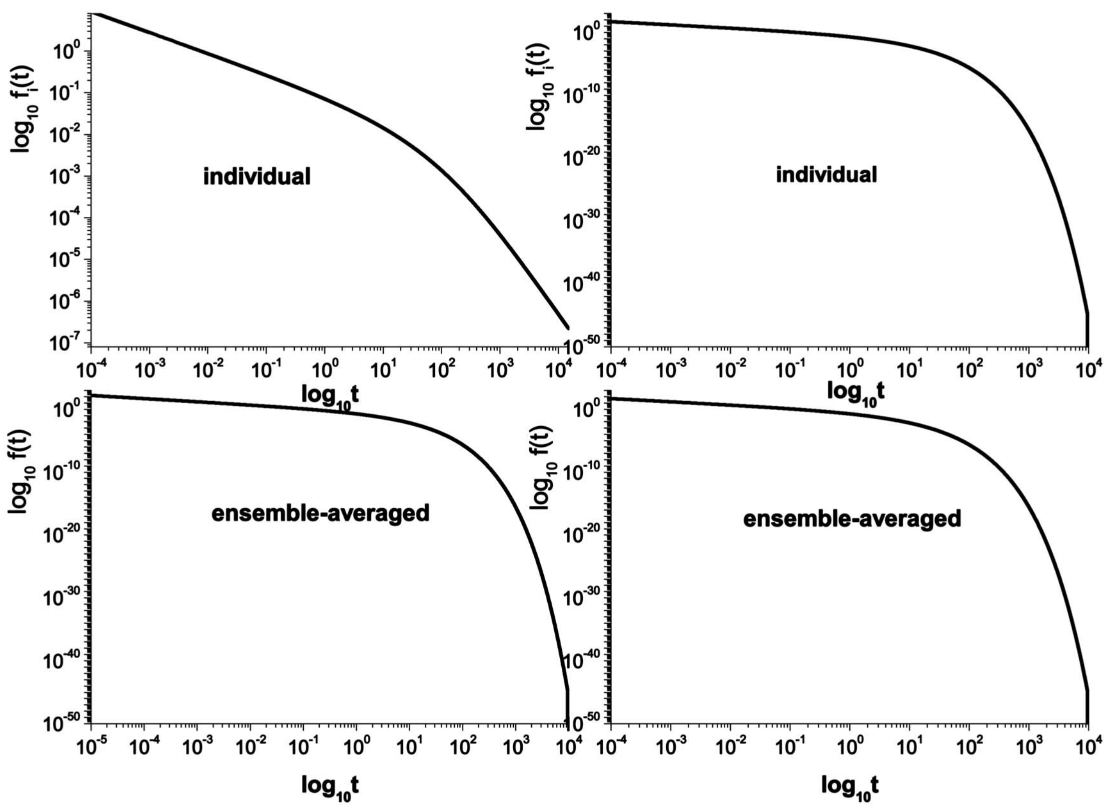

FIG. 1. Illustration of two different relaxation patterns of the KWW relaxation response. The left panels outline a heterogeneous relaxation scenario in which the relaxation rates of individual contributions are distributed according to a heavy-tailed Pareto distribution, and the ensemble-averaged behavior represents a Lévy-stable distribution of effective relaxation rate. Both responses share a common short-time power-law property but their long-time asymptotics are considerably different. The right panels refer to a homogeneous scenario in which the distribution of all individual relaxation rates is identical with the Lévy-stable distribution of the effective one. Both responses share common short- and long-time asymptotic properties.

(10) can be reduced to the exponential one. Using the well-known formula [30,31] for the Laplace transform of a completely asymmetric Lévy-stable distribution $\mathcal{S}_a(x)$,

$$\exp(-Ct^a) = \int_0^\infty \exp(-C_1 tx) d\mathcal{S}_a(x) = \langle \exp(-C_1 \mathcal{S}_a t)\rangle, \quad \text{for some } 0 < a < 1, \tag{14}$$

we have

$$\Pr(\theta_i \geq t) = \langle \exp(-Ct^{\lambda'} L_i^{-\alpha})\rangle = \langle \exp(-C_1 L_i^{-\alpha/\lambda'} \mathcal{S}_{\lambda'} t)\rangle, \tag{15}$$

where $C = t_0^{-\lambda'} b_R^{\alpha}$ and $C_1 = C^{1/\lambda'}$. Now, the survival probability $\Pr(\theta_i \geq t)$ of the ith object can be written as the weighted average of an exponentially decaying function with respect to the distribution of the random variable β_i, having the meaning of a relaxation rate with physical dimension $[s^{-1}]$:

$$\Pr(\theta_i \geq t) = \langle \exp(-\beta_i t)\rangle. \tag{16}$$

The explicit form of the individual relaxation rate reads

$$\beta_i = C_1 L_i^{-\alpha/\lambda'} \mathcal{S}_{\lambda'} \tag{17}$$

and contains information on the stochastic nature of the investigated complex system. Namely, it reflects the local random characteristics of the medium and the spatiotemporal properties of the anomalous diffusion processes.

IV. HOMOGENEOUS AND HETEROGENEOUS PATTERNS OF RELAXATION

It follows from formulas (9) and (16) that the system's waiting time $\tilde{\theta}$ is determined by the individual relaxation rates β_i:

$$\begin{aligned}\Pr(\tilde{\theta} \geq t) &= \lim_{N\to\infty} \prod_{i=1}^{N} \Pr\left(\theta_i \geq \frac{t}{A_N}\right) \\ &= \lim_{N\to\infty} \left\langle \exp\left(-\beta_1 \frac{t}{A_N}\right) \times \cdots \times \exp\left(-\beta_N \frac{t}{A_N}\right)\right\rangle \\ &= \lim_{N\to\infty} \left\langle \exp\left(-\sum_{i=1}^{N} \frac{\beta_i}{A_N} t\right)\right\rangle.\end{aligned}$$

As a consequence, the relaxation function $\Phi(t)$ can be writ-

TABLE I. Relaxation functions for a system with a fixed number of relaxation contributions. The influence of the defect-diffusion mechanism on the homogeneous scenario of relaxation is shown (note the role of the stable distribution in the individual relaxation rates).

	$\lambda'=1$		$\lambda'=\lambda$	
	$\kappa<\alpha$	$\kappa\geq\alpha$	$\kappa<\alpha$	$\kappa\geq\alpha$
β_i distribution	a-stable with $a=\frac{\kappa}{\alpha}$	δ-Dirac function	a-stable with $a=\lambda\frac{\kappa}{\alpha}$	a-stable with $a=\lambda$
$\Pr(\theta_i\geq t)$	KWW	D	KWW	KWW
$\widetilde{\beta}$ distribution	a-stable with $a=\frac{\kappa}{\alpha}$	δ-Dirac function	a-stable with $a=\lambda\frac{\kappa}{\alpha}$	a-stable with $a=\lambda$
$\Pr(\widetilde{\theta}\geq t)$	KWW	D	KWW	KWW
System type	homogeneous	homogeneous	homogeneous	homogeneous

ten in a form similar to that given by Eq. (16):

$$\Phi(t)=\Pr(\widetilde{\theta}\geq t)=\langle\exp(-\widetilde{\beta}t)\rangle, \tag{18}$$

where $\widetilde{\beta}$ denotes the effective relaxation rate and is equal to the sum of the individual relaxation rates β_i of all N contributions to the relaxation process,

$$\widetilde{\beta}=\lim_{N\to\infty}\frac{1}{A_N}\sum_{i=1}^{N}\beta_i. \tag{19}$$

The same result can be derived even if the set of contributions does not contain a deterministic number N but a random number ν_N of relaxing entities. In this case we have a more general formula

$$\widetilde{\beta}=\lim_{N\to\infty}\frac{1}{A_N}\sum_{i=1}^{\nu_N}\beta_i. \tag{20}$$

The deterministic number N of contributions in Eq. (19) may be treated as a special case of the random number ν_N in Eq. (20), in the sense that its probability density function is of the δ-Dirac form.

According to limit theorems of probability theory [32], the existence of the limiting rate $\widetilde{\beta}$ is determined [33] by the following asymptotic property of the distribution $F_L(l)$:

$$F_L(l)\sim(l/b_L)^{\kappa},\quad \text{as } l\to 0, \tag{21}$$

for some $\kappa>0$. As a consequence, the random variable $L_i^{-\alpha}$ belongs to the domain of attraction of a one-sided Lévy-stable law $\mathcal{S}_\eta$ with the index of stability η determined by parameters κ and α: namely, $\eta=\min\{\kappa/\alpha,1\}$. For $\kappa\geq\alpha$—i.e., for $\eta=1$—the distribution of an appropriately normalized sum of $L_i^{-\alpha}$ becomes degenerate, which yields a constant value of random variable $L_i^{-\alpha}$ with probability 1. The distribution of the individual relaxation rates defined in Eq. (17) is then heavy tailed and belongs to the domain of attraction of a completely asymmetric Lévy-stable distribution [30,31]. Let us remark that the distribution of a Lévy-stable random variable is heavy tailed itself and hence a Lévy-stable random variable belongs to its own domain of attraction [30,34]. Consequently, if β_i belongs to the domain of attraction of a completely asymmetric Lévy-stable random variable, then the heterogeneous pattern of relaxation is realized; however, if β_i is itself a Lévy-stable random variable, then the homogeneous pattern holds. From the physical point of view, the relaxation pattern is considered to be homogeneous if the local and the ensemble-averaged dynamics are the same [22,23]. Using the notion of relaxation rates, we conclude that in the homogeneous case the effective relaxation rate has to be distributed according to the same probability law as the individual relaxation rates.

Note that the idea of dynamical heterogenity [22,23] has been associated with the form of the kernel $h(t,\tau)$ in the integral representation of the ensemble-averaged relaxation function

$$\Phi(t)=\int_0^\infty g(\tau)h(t,\tau)d\tau, \tag{22}$$

where $g(\tau)$ is the relaxation time probability density function. According to this, the purely heterogeneous picture follows from the exponential kernel $h(t,\tau)=e^{-t/\tau}$, whereas the purely homogeneous picture from the kernel $h(t,\tau)$ proportional to the relaxation function $\Phi(t)$. The latter holds if the probability density $g(\tau)$ of the effective relaxation time is of the δ-Dirac form. As an example, the KWW function $\Phi(t)=\exp[-(t/\tau)^a]$ and the integral kernel $h(t,\tau)=\exp[-(t/\tau)^{a_{intr}}]$ (with $0<a<1$ and $a\leq a_{intr}<1$) have been considered in [22,23]. In this particular case the degree of heterogeneity was measured by the parameter $\gamma=(a_{intr}-a)/(1-a)$, chosen in such a way that it vanishes in the homogeneous limit (since $a_{intr}=a$) and is equal to 1 in the heterogeneous limit (since $a_{intr}=1$). As a conclusion, it has been suggested [22,23] that other nonexponential forms of the relaxation function may be alternatively given by other forms of the "intrinsic" function $h(t,\tau)$. However, as shown in Sec. III, the form of the kernel in the integral representation of the relaxation function (18) results naturally from the defect-diffusion scenario and, in general, is of a stretched-exponential form. Moreover, using the relationship (14) we can easily interchange the stretched-exponential intrinsic function with the exponential one. Hence, the dynamical homogeneity and heterogeneity of the relaxation process cannot

TABLE II. Relaxation functions for a system with a fixed number of relaxation contributions. The influence of the defect-diffusion mechanism on the homogeneous and heterogeneous scenarios of relaxation is shown (note the role of the heavy-tailed distribution in the individual relaxation rates).

	$\lambda'=1$		$\lambda'=\lambda$	
	$\kappa<\alpha$	$\kappa\geq\alpha$	$\kappa<\alpha$	$\kappa\geq\alpha$
β_i distribution	heavy tail with $a=\frac{\kappa}{\alpha}$	δ-Dirac function	heavy tail with $a=\lambda\frac{\kappa}{\alpha}$	a-stable with $a=\lambda$
$\Pr(\theta_i\geq t)$	other/not KWW	D	other/not KWW	KWW
$\widetilde{\beta}$ distribution	a-stable with $a=\frac{\kappa}{\alpha}$	δ-Dirac function	a-stable with $a=\lambda\frac{\kappa}{\alpha}$	a-stable with $a=\lambda$
$\Pr(\widetilde{\theta}\geq t)$	KWW	D	KWW	KWW
System type	heterogeneous	homogeneous	heterogeneous	homogeneous

be connected with the form of the kernel in Eq. (22). The different scenarios of relaxation are rather determined by the stochastic structure of the effective relaxation rate $\widetilde{\beta}$. To clarify this point, in the next section we derive the KWW relaxation function within both the homogeneous and heterogeneous scenarios.

V. FIRST PASSAGE OF A MACROSCOPIC SYSTEM WITH A FIXED NUMBER OF RELAXATION CONTRIBUTIONS

In this section we consider a system with a deterministic number of contributing entities. It is a rigorous result [9] that the only possible probability distributions for the effective relaxation rate (19) are completely asymmetric Lévy-stable laws, with the parameter $0<a<1$, leading to the KWW relaxation function (2). The corresponding response function $f_{KWW}(t)=-d\Phi_{KWW}(t)/dt$ exhibits the short-time power-law property $(\omega_p t)^{-n}$, $n=1-a$, determined by the long-tail exponent a of the individual relaxation rates distribution. Taking now into account the properties of distributions belonging to the domain of attraction of completely asymmetric Lévy-stable laws, we come to the conclusion that in the proposed framework the stretched-exponential function can be derived in two ways, representing the homogeneous (a) and heterogeneous (b) patterns of relaxation.

(a) The homogeneous relaxation—i.e., the scenario in which "all local contributions are identical to the ensemble average" [22,23]—is realized if the relaxation rate (17) is a positive Lévy-stable random variable. For this scenario the random variable $L_i^{-\alpha}$ in Eq. (17) has to be a positive Lévy-stable variable $\mathcal{S}_\eta$ (including the degenerate case when $\eta=1$). In such a case the effective relaxation rate $\widetilde{\beta}$ for each N is of the form

$$\widetilde{\beta}=\frac{1}{A_N}\sum_{i=1}^{N}\beta_i, \tag{23}$$

which yields

$$\widetilde{\beta}\overset{d}{\sim}\mathcal{S}_{\eta\lambda'}, \tag{24}$$

and consequently the KWW relaxation function (2) with the stretching parameter $a=\eta\lambda'$. In this scenario (see Fig. 1) the stretched-exponential survival probabilities (16) of all local relaxation contributions are identical with the one of the ensemble average (18).

(b) On the other hand, if the distribution of the individual relaxation rates (17) is heavy tailed—i.e., it belongs to the domain of attraction of a completely asymmetric Lévy-stable law, but β_i is not a Lévy-stable random variable itself—the heterogeneous scenario occurs. For this scenario it is sufficient that $L_i^{-\alpha}$ is a heavy-tailed random variable with the exponent equal to η. In such a case the effective relaxation rate of the form

$$\widetilde{\beta}=\lim_{N\to\infty}\frac{1}{A_N}\sum_{i=1}^{N}\beta_i. \tag{25}$$

yields the effective relaxation rate

$$\widetilde{\beta}\overset{d}{\sim}\mathcal{S}_{\eta\lambda'}, \tag{26}$$

which leads to the KWW relaxation function with the stretching parameter $a=\eta\lambda'$, the same as in the homogeneous scenario. In this scenario (see Fig. 1) the macroscopic relaxation (18) follows the stretched-exponential pattern while the local relaxation contributions (16) do not. However, both local contributions and the ensemble average share a common short-time asymptotic property determined by the

TABLE III. Microscopic stochastic scenarios leading to the empirical HN relaxation response.

β_i distribution	Heavy tail with $a=\kappa/\alpha$	Heavy tail with $a=\lambda\kappa/\alpha$	Heavy tail with $a=\lambda$
N_i distribution	Heavy tail with $a=\kappa/\alpha$	Heavy tail with $a=\lambda\kappa/\alpha$	Heavy tail with $a=\lambda$
M_j distribution	Heavy tail with $a=b$	Heavy tail with $a=b$	Heavy tail with $a=b$
Relaxation function $\phi^*(\omega)$	HN with parameters κ/α and b	HN with parameters $\lambda\kappa/\alpha$and b	HN with parameters λ and b

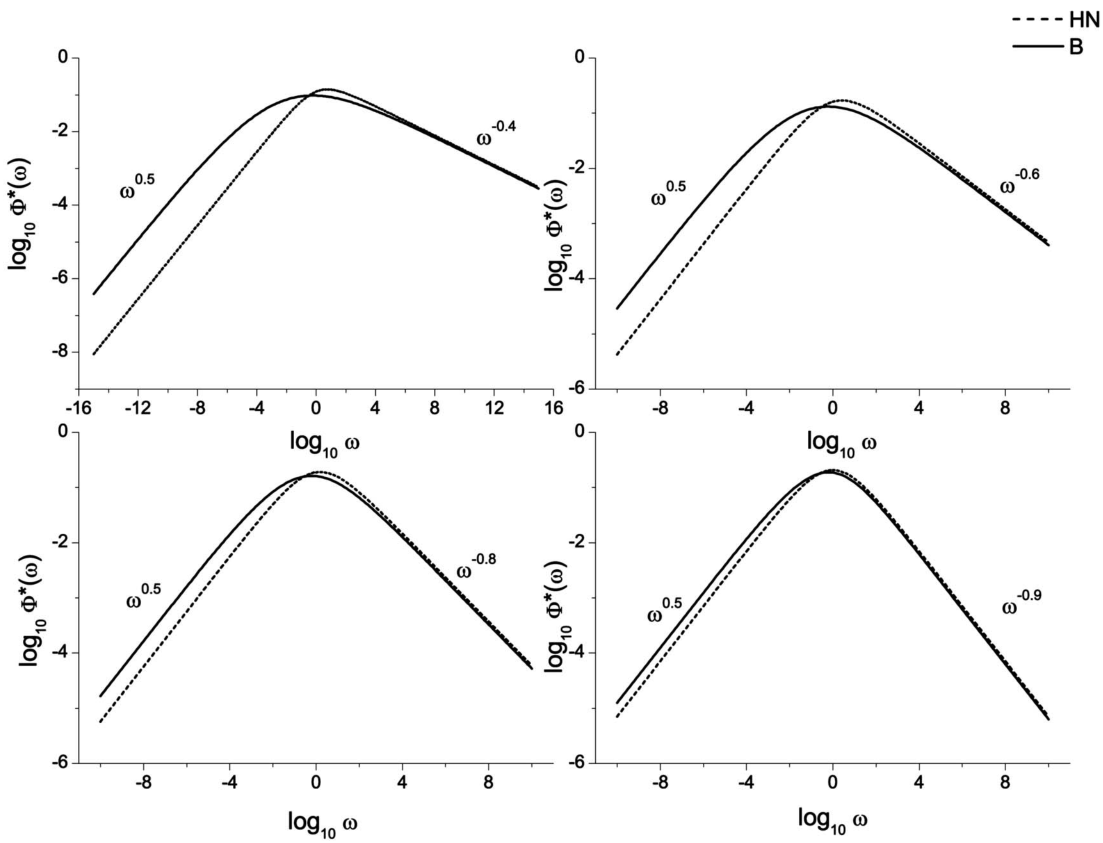

FIG. 2. Frequency-domain comparison of the HN and Burr relaxation functions with the same power-law characteristics. Parameters a, b, and c are chosen in such a way that the long-time (i.e., low-frequency) power-law exponent $(-m-1)$ is equal to 0.5 and the short-time (i.e., high-frequency) exponent $(n-1)$ is increasing from 0.4 (top left) to 0.9 (bottom right).

domain of attraction of a completely asymmetric Lévy-stable law. The long-time differences depend on the limiting properties of the choosen individual relaxation rate distribution.

The above analysis leads to a conclusion that both scenarios of the KWW relaxation do not follow from the integral representation of the relaxation function. A particular scenario is determined by the stochastic structure, Eqs. (23) and (25), of the effective relaxation rate $\tilde{\beta}$. All special cases depending on values of the model parameters are collected in Tables I and II.

VI. FIRST PASSAGE OF A MACROSCOPIC SYSTEM WITH A RANDOM NUMBER OF RELAXATION CONTRIBUTIONS

In Sec. V the simplest case of a system with a fixed number of independent relaxation contributions has been discussed. As a result, the KWW response, characterized by the short-time power law only, has been obtained. It is natural to expect, however, that in a complex system the number of objects directly engaged in a relaxation process is random and that the random number of contributions may have an impact on the relaxation pattern. Hence, in this section, we discuss the first passage of a macroscopic system with a random number of relaxation contributions. From a mathematical point of view, the number of contributions may be determined either directly, given an explicit distribution of ν_N, e.g., Poisson, geometric, negative-binomial, etc., or indirectly, given a stochastic scenario determining the distribution of ν_N. As has been recently shown [12,13,25] both approaches may yield the long-time power-law property of the relaxation response $f(t)$.

If one considers a system in which the random number ν_N of relaxation contributions to the effective relaxation rate (20) is determined by the negative-binomial law [35], hence introducing aggregation of the considered contributions (for details see [25,36]), then the following form of the relaxation function (18) is obtained:

$$\Phi_B(t) = \frac{1}{\left[1 + \frac{1}{c}(At)^a\right]^c}, \tag{27}$$

where $A>0$, $0<a<1$ and $c>0$ are related to the Lévy-stable and negative-binomial laws, respectively. The above function is equal to the tail $[1-F_B(t)]$ of the well-known [35] Burr distribution $F_B(t)$, in this case the system's transition time distribution. The Burr formula (27) is a generalization of relaxation functions proposed to describe the relaxation phenomena in which the long-time Nutting law [11,37] has been observed. The response function $f_B(t)$ corresponding Eq. (27) obeys the universal two power-law relation

$$f_B(t) = \begin{cases} (At)^{a-1} & \text{for } t \to 0, \\ (At)^{-ac-1} & \text{for } t \to \infty, \end{cases} \tag{28}$$

if only $c < 1/a$. Observe that in this approach, the randomness in the number of relaxation contributions, reflected by the parameter c, does not influence the short-time system evolution but yields the slowing down in the long-time behavior. Additionally, as a limiting case (for $c \to \infty$) we obtain the KWW relaxation function $\Phi_{KWW}(t)$.

To determine the distribution of the random number of relaxation contributions leading to the HN function the correlated-cluster stochastic scheme [12,13,25] may be used. Within this scheme, a system consisting of a large fixed number N of objects, divided into a random number K_N of randomly sized clusters, is considered. The size of the ith cluster is assumed to be equal to the number N_i of interacting entities in the cluster, and its relaxation behavior is represented by the relaxation rate β_i. In such a system, the cluster sizes, if represented by i.i.d. random variables $N_1, N_2, \ldots$, determine the random number of clusters. Namely, the number K_N of clusters is equal to the smallest index k for which the sum $N_1 + N_2 + \cdots + N_k$ of k cluster sizes exceeds the system size N. As a consequence, the distribution of the random number of clusters can be derived from the distribution of cluster sizes. If we additionally assume that the relaxation of clusters exhibits collective behavior [2,4], then the appearance of L_N mesoscopic, randomly sized regions of correlated clusters can be expected. The size of the jth"supercluster" is assumed to be equal to the number M_j of interacting clusters in the region, and its relaxation behavior is represented by the relaxation rate $\overline{\beta_j}$. Repeating the above arguments, we conclude that the sizes of those regions, represented by i.i.d. random variables $M_1, M_2, \ldots$, determine the number L_N of mesoscopic regions. It is equal to the smallest index l for which the sum $M_1 + M_2 + \cdots + M_l$ of l region sizes exceeds K_N, the number of clusters in a system of size N. The relaxation rate $\overline{\beta_j}$ of the jth region, containing M_j clusters, is defined by the normalized sum of individual relaxation contributions $\beta_1/A_N, \beta_2/A_N, \ldots$. Thus, the relaxation rate of a supercluster reads

$$\overline{\beta_j} = \sum_{i=1}^{M_j} \beta_i / A_N \tag{29}$$

and, consequently, the effective rate $\tilde{\beta}$, representing the relaxation behavior of the entire system, consists of the contributions $\overline{\beta_1}, \overline{\beta_2}, \ldots$ of all L_N mesoscopic regions—i.e.,

$$\tilde{\beta} = \lim_{N \to \infty} \sum_{j=1}^{L_N} \overline{\beta_j}. \tag{30}$$

The effective relaxation rate (30) can be rewritten in a form similar to Eq. (20), where the random number of components, determined by the number and sizes of correlated cluster regions, is given by the following formula

$$\nu_N = \sum_{j=1}^{L_N} M_j. \tag{31}$$

The proposed scheme requires dealing with stochastically independent sequences of random variables N_i, M_j, and β_i. Each sequence has to consist of i.i.d. random variables, the distributions of which can be either heavy tailed or with a finite expected value. An appropriate combination of different statistical properties of the cluster sizes N_i and their relaxation rates β_i, and also the correlated region sizes M_j, leads to the well-known HN, CC, CD, and KWW empirical responses (for details, see [12,13]). The complete scenario leading to the HN function (1) in the proposed wait-and-switch stochastic framework is given in Table III. Let us note that in contrast to former results, present considerations bring into light different defect-diffusion origins of the HN power-law exponents.

VII. CONCLUSIONS

Extensive studies of relaxation processes for a wide range of materials have made clear that complex systems exhibit nonexponential behavior characterized well enough by the HN and KWW functions. However, the justification of these functions has been provided rather by their applicability as fitting functions than by theoretical investigations.

In this paper we present a probabilistic, "random-variable" attempt to modeling the HN and KWW cases of relaxation. In the proposed model we combine the relaxation mechanism, based on a diffusion of defects in the system under consideration, with the wait-and-switch scenario of random transitions of its elements from their initial excited states. The basic mathematical tool required in this approach is the formalism of limit theorems of probability theory, which provides a rigorous link between the microscopic statistical properties of real objects forming the system and the macroscopic world of relaxation phenomena. This link takes the form of the effective relaxation rate, in general, equal to a random sum of independent and identically distributed individual relaxation rates. Such a stochastic structure of the effective relaxation rate follows from the notion of the relaxation function as the probability of the first passage of the system from its nonequilibrium state. Within this framework we show how the local characteristics of the medium and the spatiotemporal jump parameters of the diffusing defects influence the properties of the individual rates and, in consequence, the relaxation behavior of the entire complex system.

In the KWW case, the short-time power law of this response results from both spatial (reflected by parameters α and κ) and temporal (reflected by λ') characteristics of the diffusion scheme. As the number of relaxing contributions is deterministic in this case, the long-time power-law response is not obtained. In order to find stochastic schemes yielding also the long-time power-law response, observed in the majority of dielectric materials, we have to introduce randomness in the number of relaxation contributions. Depending on the distribution of the number of contributions, we derive the time-domain Burr and the frequency-domain HN functions (see Fig. 2). The corresponding response functions in both cases exhibit the short- and long-time power-law asymptotics; however, the origins of them are different.

In the framework of the wait-and-switch model, we show that the first passage survival probability simply equals the weighted average of an exponentially decaying function. This relation clarifies the origins of the exponential kernel in this historically oldest definition of the nonexponential relaxation function. It also follows that homogeneous and heterogeneous scenarios of relaxation are not determined by the form of the kernel function but by the stochastic structure of the effective relaxation rate.

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