Subordinated stochastic processes with aged operational time

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In this paper, subordinated stochastic processes are considered, where the renewal process acting as the operational time. It is assumed that the observation of the process begins at a certain time after the start of the renewal process. A recurrence formula was derived for calculating the multipoint probability density functions of the aged renewal process. Two-point correlation functions for certain subordinated stochastic processes, particularly for the generalized Ornstein-Uhlenbeck process, were calculated. A model of relaxation in a disordered medium with traps and obstacles is proposed.

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I. INTRODUCTION

Subordination is a mathematical method that broadens the applicability of classical transport models [1–7]. In this method, the clock time of a stochastic process $X(t)$ is randomized by introducing a new time $s = S(t)$. The resulting process $Y(t) = X[S(t)]$ is said to be subordinated to the parent process $X(s)$, and s is commonly referred to as the leading process or the operational time. The operational time introduced in this way considers the heterogeneity of the medium in which the process takes place.

If the processes $X(s)$ and $S(t)$ are independent and if their multipoint probability density functions (PDFs) $P_n^X(x_1,s_1;\ldots;x_n,s_n)$ and $P_n^S(t_1,s_1;\ldots;t_n,s_n)$ are known, the multipoint probability density functions of the resulting process can be calculated by integration [8]:

$$P_n^Y(x_1,t_1;\ldots;x_n,t_n) = \int_0^\infty ds_1 \ldots \int_0^\infty ds_n \times P_n^X(x_1,s_1;\ldots;x_n,s_n) \times P_n^S(t_1,s_1;\ldots;t_n,s_n). \quad (1)$$

A widely known example of a subordinated stochastic process is the continuous time random walk (CTRW). In this model, ordinary random walks play the role of the parent process, and the renewal process plays the role of the operational time.

The CTRW model describes a slowing diffusion caused by traps (binding sites). A characteristic feature of this kind of slowing diffusion is nonstationarity; its properties depend on the instant at which the observation begins. From a physical perspective, this feature is explained by the fact that the initial distribution over different states differs from the equilibrium distribution.

Another kind of slowing diffusion corresponds to the motion in the presence of obstacles (i.e., in a labyrinthine or crowded environment). In this case, the initial (equiprobable) distribution coincides with the equilibrium distribution, and the nonstationarity effect is absent. The process has stationary increments. This kind of slowing diffusion can be described by various models, such as the random walks on fractals, the Lorentz model, and the random barrier model [9–11]. Besides those described above, there are other types of slowing diffusion, which are described by other mathematical models, such as the fractional Brownian motion, the generalized Langevin equation, and the time-dependent diffusion coefficient [9,10].

In real physical systems, various mechanisms are often present simultaneously, which cause the slowing of diffusion. In such cases, an individual model is unable to adequately describe the process, and it is necessary to combine two or more models. If one of the mechanisms slowing the diffusion is a delay in the traps, the combined model can be constructed using the subordination method, and the renewal process can be taken as the operational time. The choice of the parent process depends on the other mechanisms present for slowing the diffusion. These types of combined models have been proposed in Refs. [12] and [13]. The multipoint probability density functions for the renewal process, allowing the calculation of multipoint correlation functions for such combined models, were calculated in Ref. [8]. There are examples of successful application of this type of combined models to describe experimental data. For instance, in Ref. [14], it is shown that CTRW on fractals adequately represents the diffusion process of molecules in a plasma membrane.

In previous works, it was assumed that the waiting time distribution of the first event coincides with the waiting time distribution of the second and subsequent events. This means that at the beginning of the observation, the residence time (the time elapsed since the last event) is equal to zero. This assumption is valid if the beginning of the observation coincides with the time of the creation of the system, for example, in a time-of-flight experiment. However, experiments are often performed on preexisting systems. For example, in biological experiments, such as fluorescence correlation spectroscopy (FCS) or fluorescence recovery after photobleaching (FRAP), the initial state of the system is in equilibrium. In such cases, it is more realistic to assume that the residence time was zero before a certain period of time or that the ensemble of walkers is in equilibrium with the environment.

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In this paper, we derive the multipoint probability density functions of the renewal process when the observation of the process begins at a certain time after the start of the process (aged renewal process). Subsequently, we consider several applications of the formulas obtained. In particular, we propose a model of relaxation in a disordered medium containing traps and obstacles.

II. AGED RENEWAL PROCESS

As a starting point, we use the Markov representation of the renewal process. $\xi_n(t,\tau)$ is set as the probability density of n events and residence time τ at time t after the beginning of the observation. Analogously to the CTRW model [15–17], the balance equation can be written as:

$$\frac{\partial \xi_n(t,\tau)}{\partial t} + \frac{\partial \xi_n(t,\tau)}{\partial \tau} = -\omega(\tau)\xi_n(t,\tau), \tag{2}$$

where $\omega(\tau)$ is the rate at which events occur.

Events are counted from the beginning of the observation, thus the initial condition can be written in the form of $\xi_n(0,\tau) = \delta_{n0} f_0(\tau)$, where δ_{n0} is the Kronecker symbol and $f_0(\tau)$ is the initial distribution of the residence times. If the renewal process starts at time $-t_0$, $f_0(\tau) = \kappa(t_0 - \tau)\Psi(\tau)$, where $\kappa(t_0)$ is the probability of an event at time t_0 after the start of the renewal process, and $\Psi(\tau) \stackrel{def}{=} \exp[-\int_0^\tau \omega(y)dy]$ is the survival probability. The boundary condition at $\tau = 0$ differs from the corresponding condition of the CTRW model in that only one-sided transitions $n-1 \to n$ occur:

$$\xi_n(t,0) = \int_0^\infty \omega(\tau)\xi_{n-1}(t,\tau)d\tau. \tag{3}$$

We performed Laplace transform on the time variable t and discrete Laplace transform on variable n: (In this paper, the original functions and their transforms can be distinguished by their arguments.)

$$\xi(u_1,k_1,\tau) = \sum_{n=0}^{\infty}\int_0^\infty \exp(-k_1 n - u_1 t)\xi_n(t,\tau)dt, \tag{4}$$

As a result of the transformations, Eqs. (2), and (3) become

$$\frac{\partial \xi(u_1,k_1,\tau)}{\partial \tau} = -[\omega(\tau)+u]\xi(u_1,k_1,\tau) + f_0(\tau), \tag{5}$$

$$\xi(u_1,k_1,0) = F_1, \tag{6}$$

where $F_1 = \exp(-k_1)\int_0^\infty \omega(\tau)\xi(u_1,k_1,\tau)d\tau$. The solution of these equations is

$$\xi(u_1,k_1,\tau) = \Psi(\tau)\exp(-u_1\tau) \times \left[F_1 + \int_0^\tau \frac{\exp(u_1 y)}{\Psi(y)} f_0(y)dy\right]. \tag{7}$$

To evaluate the integral, we regard parameter t_0 as a variable and perform the Laplace transform $t_0 \to \lambda$. Thus, the function $f_0(\tau)$ takes the form $f_0(\tau,\lambda) = \Psi(\tau)\frac{\exp(-\lambda\tau)}{1-\psi(\lambda)}$ [18–20], where $\psi(\lambda)$ is the Laplace transform of the waiting time distribution $\psi(t_0)$ [$\psi(t_0) \stackrel{def}{=} -\frac{d\Psi(t_0)}{dt_0}$].

The calculations yield:

$$\xi(u_1,k_1,\tau) = \Psi(\tau)\left[F_1\exp(-u_1\tau) + \frac{\exp(-\lambda\tau) - \exp(-u_1\tau)}{[1-\psi(\lambda)][u_1-\lambda]}\right], \tag{8}$$

$$F_1 = \frac{\exp(-k_1)\phi(u_1,\lambda)}{1-\exp(-k_1)\psi(u_1)}, \tag{9}$$

where

$$\phi(u_1,\lambda) = \frac{\psi(\lambda)-\psi(u_1)}{[1-\psi(\lambda)][u_1-\lambda]} \tag{10}$$

is the forward recurrence time [18]. The one-point PDF, $P_1(u_1,k_1) \stackrel{def}{=} \int_0^\infty \xi(u_1,k_1,\tau)d\tau$, can be written as:

$$P_1(u_1,k_1) = \frac{\exp(-k_1)\phi(u_1,\lambda)}{1-\exp(-k_1)\psi(u_1)}\Psi(u_1) + \Phi(u_1,\lambda), \tag{11}$$

where $\Phi(u_1,\lambda) = \frac{\Psi(\lambda)-\Psi(u_1)}{[1-\psi(\lambda)][u_1-\lambda]} = \frac{1}{u_1\lambda} - \frac{1-\phi(u_1,\lambda)}{u_1}$. Performing Laplace inversion $\lambda \to t_0$, gives the same expression, but with replacements $\phi(u_1,\lambda) \to \phi(u_1,t_0)$ and $\Phi(u_1,\lambda) \to \Phi(u_1,t_0)$. It should be noted that the limiting forms of the function $\phi(u_1,t_0)$ are $\phi(u_1,t_0=0) = \lim_{\lambda\to\infty}\lambda\phi(u_1,\lambda) = \psi(u_1)$ (nonaged system) and $\phi(u_1,t_0=\infty) = \lim_{\lambda\to 0}\lambda\phi(u_1,\lambda) = \frac{1-\psi(u_1)}{\bar{\tau}u_1}$ (system in full equilibrium), where $\bar{\tau} = \int_0^\infty \tau\psi(\tau)d\tau$ is the mean residence time. By taking the continuum limit [i.e., replacing $\exp(-k_1)$ by $1-k_1$] and performing Laplace inversion $k_1 \to s_1$ (the operational time s_1 is a continuous extension of the number of events n), the following can be obtained:

$$P_1(u_1,s_1) = \frac{\phi_1(1-\psi_1)}{u_1\psi_1^2}\exp\left(-s_1\frac{1-\psi_1}{\psi_1}\right) + \frac{\psi_1-\phi_1}{u_1\psi_1}\delta(s_1). \tag{12}$$

Here, we introduce the abbreviated notation of $\psi_1 = \psi(u_1)$, $\phi_1 = \phi(u_1,t_0)$. This one-point PDF can be used in Eq. (1) to obtain the one-point PDFs of the subordinated processes. In the case of the non-aged system, Eq. (12) reduces to the well-known formula $P_1(u_1,s_1) = \frac{(1-\psi_1)}{u_1\psi_1}\exp(-s_1\frac{1-\psi_1}{\psi_1})$ [7,21].

As can be seen, the dynamics of the two-component process $[n(t),\tau(t)]$ is Markovian. If the state of the system at time t_1 is known, the conditional probability at any time $t_2 > t_1$ can be obtained by solving Eqs. (2) and (3). This allows us to find the multipoint PDFs of the renewal process.

The joint PDF $P_2(t_1,n_1;\sigma,\Delta)$ is defined such that there are n_1 events at time t_1 and $\Delta = n_2 - n_1$ events during the time interval $\sigma = t_2 - t_1$. The Laplace transform of this PDF, $P_2(u_1,k_1;u_2,k_2)$, can be obtained in the same way as $P_1(u_1,k_1)$ was obtained, if $\xi(\sigma=0,k_2,\tau) = \xi(u_1,k_1,\tau)$ is considered as the initial condition. In this case, Eq. (7) takes the form:

$$\xi(u_2,k_2,\tau) = \Psi(\tau)\exp(-u_2\tau) \times \left[F_2 + \int_0^\tau \frac{\exp(u_2 y)}{\Psi(y)}\xi(u_1,k_1,y)dy\right]. \tag{13}$$

The expression for F_2 is

$$F_2 = \exp(-k_2)\int_0^\infty \omega(\tau)\xi(u_2,k_2,\tau)d\tau, \tag{14}$$

and the PDF $P_2(u_1,k_1;u_2,k_2)$ is calculated from $P_2(u_1,k_1;u_2,k_2) = \int_0^\infty \xi(u_2,k_2,\tau)d\tau$. Substituting Eq. (8) into Eq. (13) and solving Eqs. (13) and (14) gives:

$$\xi(u_2,k_2,\tau) = \Psi(\tau)\left\{F_2\exp(-u_2\tau)+\frac{\exp(-u_1\tau)-\exp(-u_2\tau)}{u_2-u_1}\times\left[F_1-\frac{1}{[1-\psi(\lambda)][u_1-\lambda]}\right]+\frac{\exp(-\lambda\tau)-\exp(-u_2\tau)}{[u_2-\lambda][1-\psi(\lambda)][u_1-\lambda]}\right\}, \quad (15)$$

$$F_2 = \frac{\exp(-k_2)}{1-\exp(-k_2)\psi(u_2)}\times\left[F_1\frac{\psi(u_1)-\psi(u_2)}{u_2-u_1}+\frac{\phi(u_1,\lambda)-\phi(u_2,\lambda)}{u_2-u_1}\right], \quad (16)$$

and

$$P_2(u_1,k_1;u_2,k_2) = F_2\Psi(u_1) + F_1\frac{\Psi(u_1)-\Psi(u_2)}{u_2-u_1}+\frac{\Phi(u_1,\lambda)-\Phi(u_2,\lambda)}{u_2-u_1}. \quad (17)$$

If the function P_2 is known, the Laplace transform of the function P_2^S appearing in Eq. (1) can be found: $P_2^S(u_1,k_1;u_2,k_2) = P_2(u_1+u_2,k_1+k_2;u_2,k_2) + P_2(u_1+u_2,k_1+k_2;u_1,k_1)$ [22]. The resulting complex expressions are not presented as the function P_2 is sufficient to calculate the correlation functions [23].

By taking the continuum limit in Eq. (17) [i.e., replacing $\exp(-k_1)$ by $1-k_1$ and $\exp(-k_2)$ by $1-k_2$] and performing Laplace inversions $k_1 \to s_1$, $k_2 \to \Delta$, and $\lambda \to t_0$ (Δ is a continuous variable equal to $s_2 - s_1$), the following results can be obtained:

$$\begin{aligned}P_2(u_1,s_1;u_2,\Delta) &= \frac{\Phi_2-\Phi_1}{u_1-u_2}\delta(s_1)\delta(\Delta)\\&+\frac{\Psi_2-\Psi_1}{u_1-u_2}\frac{\phi_1}{\psi_1}\left[\frac{1}{\psi_1}\exp\left(-s_1\frac{1-\psi_1}{\psi_1}\right)-\delta(s_1)\right]\delta(\Delta)\\&+\frac{\Psi_2}{\psi_2}\frac{\phi_2-\phi_1}{u_1-u_2}\left[\frac{1}{\psi_2}\exp\left(-\Delta\frac{1-\psi_2}{\psi_2}\right)-\delta(\Delta)\right]\delta(s_1)\\&+\frac{\Psi_2}{\psi_2}\frac{\psi_2-\psi_1}{u_1-u_2}\left[\frac{1}{\psi_2}\exp\left(-\Delta\frac{1-\psi_2}{\psi_2}\right)-\delta(\Delta)\right]\\&\times\frac{\phi_1}{\psi_1}\left[\frac{1}{\psi_1}\exp\left(-s_1\frac{1-\psi_1}{\psi_1}\right)-\delta(s_1)\right], \quad (18)\end{aligned}$$

where $\psi_2 = \psi(u_2)$, $\phi_2 = \phi(u_2,t_0)$, $\Psi_i = \frac{1-\psi_i}{u_i}$, and $\Phi_i = \frac{1-\phi_i}{u_i}$ $(i = 1,2)$. This function can be used to calculate the Laplace transforms of the two-point correlation functions of the subordinated process. If the correlation function of the parent process $\langle x_1^k x_2^m\rangle^X(s_1,s_2) \overset{def}{=} \langle x^k(s_1)x^m(s_2)\rangle$ is known, the Laplace transform of the correlation function of the subordinated process can be calculated from the equation:

$$\langle x_1^k x_2^m\rangle^Y(u_1,u_2) = \int_0^\infty ds_1\int_0^\infty d\Delta\langle x_1^k x_2^m\rangle^X(s_1,s_1+\Delta)\times P_2(u_1,s_1;u_2,\Delta). \quad (19)$$

This expression follows from Eq. (1).

Hence, a two-point PDF was obtained. For PDFs of order n higher than two, the indices in Eqs. (12) and (13) have to be increased successively by one and these equations have to be solved. After finding $\xi(u_n,k_n,\tau)$ and F_n, the n-point PDF P_n can be acquired from the relation $P_n(u_1,k_1;\ldots;u_n,k_n) = \int_0^\infty \xi(u_n,k_n,\tau)d\tau$. If P_n is known, P_n^S can be obtained.

III. CERTAIN DIRECT CONSEQUENCES

The mean-squared displacement (MSD) of the subordinated process is calculated using the one-point PDF from Eq. (12): $\langle x^2\rangle^Y(u_1) = \int_0^\infty ds_1\langle x^2(s_1)\rangle^X P_1(u_1,s_1)$. The result is

$$\langle x^2\rangle^Y(u_1) = \frac{\phi_1(1-\psi_1)}{u_1\psi_1^2}f\left(\frac{1-\psi_1}{\psi_1}\right), \quad (20)$$

where $f(u_1)$ is the Laplace transform of $\langle x^2(s_1)\rangle^X$. For the fully equilibrated system (i.e., where $\phi_1 = \frac{1-\psi_1}{\bar{\tau}u_1}$)

$$\langle x^2\rangle^Y_{eq}(u_1) = \frac{(1-\psi_1)^2}{\bar{\tau}u_1^2\psi_1^2}f\left(\frac{1-\psi_1}{\psi_1}\right), \quad (21)$$

and it follows from this that if the MSD of the parent process is a linear function of time (i.e., if $f(u_1) = \frac{\text{const.}}{u_1^2}$), the MSD of the subordinated process is also a linear function of time. This is the case in the CTRW model [11]. For a nonaged system (i.e., where $\phi_1 = \psi_1$), the well-known result $\langle x^2\rangle^Y_{ne}(u_1) = \frac{1-\psi_1}{u_1\psi_1}f(\frac{1-\psi_1}{\psi_1})$can be obtained.

Let the parent process be a certain process with stationary increments. For such processes, the MSD during a certain time interval $\langle[x(s_2)-x(s_1)]^2\rangle^X$ is equal to $\langle x^2(s_2-s_1)\rangle^X$ [9]. As $\langle[x(s_2)-x(s_1)]^2\rangle^X$ is a linear combination of the correlation functions, Eq. (19) can be applied to it, with a result of

$$\langle[x_2-x_1]^2\rangle^Y(u_1,u_2) = \frac{\phi_2(1-\psi_1)-\phi_1(1-\psi_2)}{\psi_2(u_1-u_2)(1-\psi_1)}\times\frac{1-\psi_2}{u_2\psi_2}f\left(\frac{1-\psi_2}{\psi_2}\right). \quad (22)$$

In the case of a fully equilibrated system

$$\langle[x_2-x_1]^2\rangle^Y_{eq}(u_1,u_2) = \frac{(1-\psi_2)^2}{\bar{\tau}u_1u_2^2\psi_2^2}f\left(\frac{1-\psi_2}{\psi_2}\right). \quad (23)$$

This shows that $\langle[x(t_2)-x(t_1)]^2\rangle^Y_{eq}$ is only a function of the time difference $t_2 - t_1$. In the case of a nonaged system

$$\langle[x_2-x_1]^2\rangle^Y_{ne}(u_1,u_2) = \frac{\psi_2-\psi_1}{\psi_2(u_1-u_2)(1-\psi_1)}\times\frac{1-\psi_2}{u_2\psi_2}f\left(\frac{1-\psi_2}{\psi_2}\right). \quad (24)$$

If the parent process is a simple Brownian motion [i.e., if $f(u_1) = \frac{\text{const.}}{u_1^2}$], this expression reduces to

$$\langle[x_2-x_1]^2\rangle^Y_{ne}(u_1,u_2) = \text{const.}\left\{\frac{1}{u_1-u_2}\left[\frac{\psi_2}{u_2(1-\psi_2)}-\frac{\psi_1}{u_1(1-\psi_1)}\right]-\frac{\psi_1}{u_1u_2(1-\psi_1)}\right\}. \quad (25)$$

In real time, the known CTRW relation [9]

$$\langle [x(t_2) - x(t_1)]^2 \rangle^Y_{ne} = \langle x^2 \rangle^Y_{ne}(t_2) - \langle x^2 \rangle^Y_{ne}(t_1) \quad (26)$$

is obtained.

In stationary state, the normalized two-point correlation function of the standard Ornstein-Uhlenbeck process is $\langle x(s_1)x(s_2)\rangle = \exp[-\gamma(s_2 - s_1)]$ [24]. By substituting this expression into Eq. (19), the Laplace transform of the two-point stationary correlation function of the generalized Ornstein-Uhlenbeck process can be obtained:

$$\langle x_1 x_2 \rangle^Y(u_1,u_2) = \frac{1}{u_1 u_2} - \frac{\phi_2(1-\psi_1) - \phi_1(1-\psi_2)}{u_2(u_1-u_2)(1-\psi_1)} \times \frac{\gamma}{1-\psi_2+\gamma\psi_2}. \quad (27)$$

Three cases are considered: (i) $t_0 = 0$. The Laplace transform of the single-time correlation function $\langle x(0)x(t_2)\rangle^Y$ can be obtained either by using the one-point distribution in Eq. (12) or from the relation $\langle x_1x_2\rangle^Y(t_1 = 0,u_2) = \lim_{u_1\to\infty} u_1 \times \langle x_1x_2\rangle^Y(u_1,u_2)$. The result is

$$\langle x_1 x_2 \rangle^Y(t_1 = 0,u_2) = \frac{1}{u_2}\frac{1-\psi_2+\gamma(\psi_2-\phi_2)}{1-\psi_2+\gamma\psi_2}. \quad (28)$$

This expression was previously obtained in Ref. [23]. (ii) Fully equilibrated system. By substituting $\phi_i = \frac{1-\psi_i}{\bar{\tau}u_i}$ into Eq. (27),

$$\langle x_1 x_2 \rangle^Y_{eq}(u_1,u_2) = \frac{1}{u_1 u_2}\left[1 - \frac{\gamma}{\bar{\tau}u_2}\frac{1-\psi_2}{1-\psi_2+\gamma\psi_2}\right] \quad (29)$$

can be obtained. In this case, the correlation function $\langle x(t_1)x(t_2)\rangle^Y_{eq}$ is only a function of the time difference $t_2 - t_1$. (iii) Nonaged system. This case was considered in Ref. [24]. To show that our approach yields the same results, Eq. (27) was transformed with $\phi_i = \psi_i$ into:

$$\langle x_1 x_2 \rangle^Y_{ne}(u_1,u_2) = \frac{1}{u_1-u_2}\left[\frac{1}{u_2+\gamma\theta_2} - \frac{1}{u_1+\gamma\theta_1}\right] \times \left[\frac{\gamma\psi_1}{1-\psi_1} + 1\right], \quad (30)$$

where $\theta_i = \frac{u_i\psi_i}{1-\psi_i}$. With the function ψ_i corresponding to the anomalous subdiffusion ($\psi_i = \frac{1}{1+u_i^\alpha}$), $\frac{\psi_1}{1-\psi_1} = u_1^{-\alpha}$ and $\theta_i = u_i^{1-\alpha}$. By substituting these expressions into Eq. (30) and performing Laplace inversion, the obtained result coincides with that obtained in Ref. [24]:

$$\langle x(t_1)x(t_2)\rangle^Y_{ne} = \frac{1}{\Gamma(\alpha)}\int_0^{t_1} dt t^{\alpha-1} E_\alpha[-\gamma(t_2-t)^\alpha] + \frac{1}{\gamma}E_\alpha(-\gamma t_2^\alpha), \quad (31)$$

where $\Gamma(x)$ is the Gamma function and $E_\alpha(x)$ is the Mittag-Leffler function.

IV. NON-DEBYE RELAXATION

In Laplace space (u,λ), the correlation function in Eq. (28) (denoted here by Γ) satisfies the following equation:

$$u\Gamma(u,\lambda) - \frac{1}{\lambda} = -\gamma\Theta(u)\Gamma(u,\lambda) + \gamma\left[\frac{\Theta(u)}{u\lambda} - \frac{1}{\lambda-u}\left(\frac{\Theta(u)}{u} - \frac{\Theta(\lambda)}{\lambda}\right)\right]. \quad (32)$$

In real-time space, this takes the form of

$$\frac{\partial\Gamma(t,t_0)}{\partial t} = -\gamma\int_0^t d\tau\Theta(t-\tau)\Gamma(\tau,t_0) + \gamma\left[\int_0^t d\tau\Theta(\tau) - \int_0^{t+t_0} d\tau\Theta(\tau)\right]. \quad (33)$$

If, as is usually the case in physical systems [25], function $\psi(t)$ is a composition of exponentials

$$\psi(t) = \int_0^\infty d\nu[\nu\rho(\nu)\exp(-\nu t)], \quad (34)$$

then the function $\Theta(t)$ has the following representation [26]:

$$\Theta(t) = \langle\nu\rangle\delta(t) - Q(t), \quad (35)$$

where $Q(t)$ is a positive function and the integral $\int_0^\infty d\tau Q(\tau)$ is equal to $\langle\nu\rangle - \frac{1}{\langle\frac{1}{\nu}\rangle}$. [Angular brackets mean averaging by the function $\rho(\nu)$.] As the arithmetic mean is greater than the harmonic mean, the inhomogeneous term in Eq. (33) is non-negative. For $t_0 = 0$, it is identically equal to zero. With increasing t_0 (i.e., with increasing age of the system), it grows while keeping the sum of the right-hand side of the equation negative. Thus, the greater the age of the system, the slower Γ relaxes to the equilibrium value.

Let us consider a particular example where the function $\psi(t)$ is the sum of two exponentials:

$$\psi(t) = \rho_1\nu_1\exp(-\nu_1 t) + \rho_2\nu_2\exp(-\nu_2 t) \quad (36)$$

with

$$\nu_1,\nu_2 > 0, \rho_1 \in (0,1), \rho_2 = 1-\rho_1. \quad (37)$$

In such a case, the correlation function $\Gamma(t)$ has the form of

$$\Gamma(t) = \beta_1\exp(-\mu_1 t) + \beta_2\exp(-\mu_2 t), \quad (38)$$

where

$$\mu_{1,2} = \frac{1}{\sigma} + \xi a \pm \sqrt{\left(\frac{1}{\sigma}+\xi a\right)^2 - \frac{\xi}{\sigma}}, \quad (39)$$

$$\beta_{1,2} = \frac{\mu_{1,2} - \xi[1+(a-1)\exp(-\frac{t_0}{\sigma})]}{\mu_{1,2}-\mu_{2,1}}, \quad (40)$$

$$\xi = \frac{\gamma}{\bar{\tau}}, \bar{\tau} = \frac{\rho_1}{\nu_1} + \frac{\rho_2}{\nu_2}, \quad (41)$$

$$\sigma = \frac{1}{\nu_1\nu_2\bar{\tau}}, a = \bar{\tau}(\rho_1\nu_1 + \rho_2\nu_2). \quad (42)$$

The derivative of the function in Eq. (38) at zero is equal to $-\xi[1+(a-1)\exp(-\frac{t_0}{\sigma})]$ and the integral of this function from zero to infinity is equal to $\frac{1}{\xi} + \sigma(a-1)[1-\exp(-\frac{t_0}{\sigma})]$. With the increasing of t_0, the absolute value of the derivative decreases, and the value of the integral increases. The absolute value of the product of these quantities is always greater than one. In the limit of $t_0 = \infty$, it is $1 + \xi\sigma(a-1)$. For certain combinations of the parameters of the initial distribution in Eq. (36), this quantity can be quite large. This means that the equilibrium correlation function can differ substantially from the classical exponential function. (For an exponential function, the product of the derivative at zero and the integral from zero to infinity is -1.) As is well known, the correlation function of an unbiased CTRW in the equilibrium state following classical laws. It is usually concluded from this that for large times, the CTRW with the function $\psi(t)$ having a finite first moment, does not differ from the CTRW with the exponential function $\psi(t)$. The example considered shows that this is not the case for a biased CTRW.

Equations (28), (32), and (33) are valid for any quantity that relaxes according to an exponential law in the parent process. For example, the relaxation of the dielectric polarization of a disordered medium can be described by these equations. In this case, the polarization of the medium, which satisfies the assumptions of Debye's theory plays the role of the parent process.

In the relaxation experiment, a constant external driving was applied to the system at a time $t = -\infty$ such that the equilibrium condition prevails by the time $t = 0$. At $t = 0$, an external driving was turned off and the relaxation process started. Obviously, such a process corresponds to the case $t_0 = \infty$ and must be described by Eq. (28) with the function ϕ equal to $\frac{1-\psi}{\bar{\tau}u}$:

$$\Gamma(u) = \frac{1}{u}\left[1 - \frac{\gamma}{\bar{\tau}}\frac{1}{u + \gamma\Theta(u)}\right]. \tag{43}$$

The following shape function $[\Phi(\omega) \overset{def}{=} 1 - i\omega\Gamma(i\omega)]$ corresponds to this relaxation equation:

$$\Phi(\omega) = \frac{\gamma}{\bar{\tau}}\frac{1}{i\omega + \gamma\Theta(i\omega)}. \tag{44}$$

Here, ω is the frequency of the harmonic external driving.

In previous works, the following equations are used to describe the non-Debye relaxation within the framework of the CTRW model:

$$\Gamma(u) = \frac{1}{u + \gamma\Theta(u)}, \tag{45}$$

$$\Phi(\omega) = \frac{\gamma\Theta(i\omega)}{i\omega + \gamma\Theta(i\omega)}. \tag{46}$$

In earlier studies, the function corresponding to the anomalous subdiffusion $\Theta(u) = \text{const.} \times u^{1-\alpha}$ was used only [27]. In a recent study [7], other possibilities were considered. Equations (45) and (46) can be derived, for example, in the framework of the generalized Debye theory [28]. In this theory, the generalized equation of rotational diffusion is written as

$$\frac{\partial W(t,\varphi)}{\partial t} = \Delta^2 \int_0^t d\tau\Theta(t-\tau)\frac{\partial W(\tau,\varphi)}{\partial\varphi}, \tag{47}$$

where φ is the angular coordinate, $W(t,\varphi)$ is the probability where the coordinate is equal to φ at time t, and Δ is the elementary angular spacing. This equation can be solved by using the initial condition

$$W(0,\varphi) = \frac{1}{2\pi}\left[1 + \frac{\mu F}{k_B T}\cos(\varphi)\right]. \tag{48}$$

A time-dependent solution is sought in the form of

$$W(t,\varphi) = \frac{1}{2\pi}\left[1 + \Gamma(t)\frac{\mu F}{k_B T}\cos(\varphi)\right]. \tag{49}$$

Substitution of Eq. (49) into Eq. (47) gives function $\Gamma(t)$, which is the original one of the function in Eq. (45) with $\gamma = \Delta^2$. The function in Eq. (46) can be found from the generalized drift-diffusion equation

$$\frac{\partial W(t,\varphi)}{\partial t} = \Delta^2\int_0^t d\tau\Theta(t-\tau)\frac{\partial^2 W(\tau,\varphi)}{\partial\varphi^2} + \Delta^2\frac{\partial}{\partial\varphi}\left[\int_0^t d\tau\Theta(t-\tau) \times\frac{\mu F}{k_B T}\sin(\varphi)\exp(i\omega\tau)W(\tau,\varphi)\right], \tag{50}$$

which is valid for a weak field $\mu F \ll k_B T$. An ω-dependent solution can be sought in the form of

$$W(t,\varphi) = \frac{1}{2\pi}\left[1 + \Phi(\omega)\frac{\mu F}{k_B T}\exp(i\omega t)\cos(\varphi)\right]. \tag{51}$$

Substitution of Eq. (51) into Eq. (50) gives the function in Eq. (46) with $\gamma = \Delta^2$.

Two comments have to be made here. First, Eq. (47) is valid both in the CTRW model and in the random barrier model [26,29]. However, in the CTRW model it is valid only for an equiprobable initial distribution. With an equilibrium initial distribution, the inhomogeneous term must be present in the equation [11]

$$\frac{\partial W(t,\varphi)}{\partial t} = \Delta^2\int_0^t d\tau\Theta(t-\tau)\frac{\partial^2 W(\tau,\varphi)}{\partial\varphi^2} - \Delta^2\left[\int_0^t d\tau\Theta(\tau) - \frac{1}{u\bar{\tau}}\right]\frac{\partial^2 W(0,\varphi)}{\partial\varphi^2}. \tag{52}$$

In the random barrier model, this equation is valid for both the equiprobable and the equilibrium initial distributions (in this model these two distributions coincide). It follows from this that if Eq. (47) is applied to a process with an equilibrium initial distribution, the description is carried out within the framework of the random barrier model. Second, Eq. (50) is valid within the framework of the random barrier model [30]. The framework of the CTRW model is not suitable for this case. In this model, the drift-diffusion equation has the following form [31]:

$$\frac{\partial W(t,\varphi)}{\partial t} = \Delta^2\int_0^t d\tau\Theta(t-\tau)\frac{\partial^2 W(\tau,\varphi)}{\partial\varphi^2} + \Delta^2\frac{\partial}{\partial\varphi}\left[\frac{\mu F}{k_B T}\sin(\varphi)\exp(i\omega t) \times\int_0^t d\tau\Theta(t-\tau)W(\tau,\varphi)\right]. \tag{53}$$

This equation differs from Eq. (50) in that the time-dependent force is outside the integral. It is easy to verify that Eqs. (52) and (53) imply Eqs. (43) and (44), respectively. Based on the foregoing, it can be concluded that Eqs. (45) and (46) describe relaxation in the random barrier model, and that Eqs. (43) and (44) describe relaxation in the CTRW model.

Using the subordination method, we can construct a model describing the relaxation in a medium containing both traps and obstacles. To this end, we apply the subordination procedure to the expression, describing the relaxation in the random barrier model: $\Gamma_{mix}(u) = \int_0^\infty ds\Gamma(s)P_1(u,s)$. Here, $\Gamma_{mix}(u)$ is the relaxation function for the mixed model and $\Gamma(s)$ is the original one of relaxation function in Eq. (45). For the fully equilibrated system we find

$$\Gamma_{mix}(u) = \frac{1}{u}\left[1 - \frac{\gamma}{\bar{\tau}}\frac{\Theta_b(u)}{u + \gamma\Theta_t(u)\Theta_b(u)}\right], \tag{54}$$

where $\Theta_b(u) = \Theta[\frac{1-\psi(u)}{\psi(u)}]$ is the memory function corresponding to the barriers and $\Theta_t(u) = \frac{u\psi(u)}{1-\psi(u)}$ is the memory function corresponding to the traps. The shape function corresponding to this relaxation function is as follows:

$$\Phi_{mix}(\omega) = \frac{\gamma}{\bar{\tau}}\frac{\Theta_b(i\omega)}{i\omega + \gamma\Theta_t(i\omega)\Theta_b(i\omega)}. \tag{55}$$

These expressions for the relaxation and shape functions can also be derived from the dynamic equations describing diffusion and drift-diffusion processes in a medium containing traps and obstacles. (Such equations can be derived from the mean-field approximation in the framework of the lattice model [32].)

Relations in Eqs. (54) and (55) contain two unknown functions, $\Theta_t(u)$ and $\Theta_b(u)$. Finding these functions theoretically is impossible, thus these can only be found on the basis of experimental data. For this, at least two experimental curves are required, and these curves have to be independent. One such curve may be $\Phi_{mix}(\omega)$ or its equivalent $\Gamma_{mix}(t)$. For another curve, it is expected that a response of the system to a nonperiodic perturbation can be used.

Let us show that the expression in Eq. (55) with a realistic functions $\Theta_t(u)$ and $\Theta_b(u)$ is capable of reproducing qualitatively the experimental dependence $\Phi_{exp}(\omega)$. Suppose that $\psi(t)$ is given by formula in Eq. (38) with the density

$$\rho(\nu) = \frac{\bar{\tau}}{\pi Z^{\frac{1}{2n}}}\sin\left[\frac{1}{n}\arcsin\left(\frac{\sin[n\pi]}{Z^{\frac{1}{2}}}\right)\right], \tag{56}$$

where $\bar{\tau}$ is the mean residence time, $0 < n \leqslant 1$, and $Z = 1 + (\bar{\tau}\nu)^{2n} + 2(\bar{\tau}\nu)^n\cos(n\pi)$. The Laplace image of $\psi(t)$ has the form of [33]

$$\psi(u) = 1 - \bar{\tau}s[1 + (\bar{\tau}s)^n]^{-\frac{1}{n}} \tag{57}$$

and the memory function $\Theta_t(u)$ can be written as

$$\Theta_t(u) = \frac{[1 + (\bar{\tau}s)^n]^{\frac{1}{n}}}{\bar{\tau}} - u. \tag{58}$$

Suppose that the memory function $\Theta_b(u)$ has a similar form:

$$\Theta_b(u) = [1 + (\tau_b s)^m]^{\frac{1}{m}} - \tau_b u \tag{59}$$

with m and τ_b being positive parameters, $0 < m \leqslant 1$. Substituting Eqs. (58) and (59) into (55), we obtain the shape function as

$$\Phi_{mix}(\omega) = \frac{1}{\frac{\bar{\tau}i\omega}{\gamma\{[1+(\tau_b i\omega)^m]^{\frac{1}{m}} - \tau_b i\omega\}} + [1 + (\bar{\tau}i\omega)^n]^{\frac{1}{n}} - \bar{\tau}i\omega}. \tag{60}$$

The low-frequency dependence of the function $\Phi_{mix}(\omega) \sim 1 - \frac{1}{n}(\bar{\tau}i\omega)^n$ agrees with the experiment. The high-frequency dependence $\Phi_{mix}(\omega) \sim [\frac{m\bar{\tau}}{\gamma\tau_b^{1-m}}(i\omega)^m + \frac{\bar{\tau}^{1-n}}{n}(i\omega)^{1-n}]^{-1}$ can reproduce both the typical relaxation behavior and the less typical relaxation behavior [34] with the appropriate combinations of parameters n and m.

It is worth noting the general property of the expression in Eq. (55). If the memory function corresponding to the barriers $\Theta_b(i\omega)$ is equal to a constant, then the high-frequency dependence of the function $\Phi_{mix}(\omega)$ is $\Phi_{mix}(\omega) \sim (i\omega)^{-1}$. For this dependence to have the form $\Phi_{mix}(\omega) \sim (i\omega)^{-k}$ with $0 < k < 1$, it is necessary that the function $\Theta_b(i\omega)$ is not a constant. Thus, the experimental high-frequency dependence of the form $\Phi_{exp}(\omega) \sim (i\omega)^{-k}$ with $0 < k < 1$ indicates that the obstacles affect the relaxation process. In terms of the relaxation function, the conclusion is as follows: If the experimental relaxation function behaves like $\Gamma_{exp}(t) \sim 1 - \text{const.} \times t^k$ with $0 < k < 1$ at small times, then the obstacles have an effect on the relaxation process.

V. CONCLUSIONS

In this study, a class of subordinated stochastic processes are introduced, in which the aged renewal process acts as the operational time. Such stochastic processes can be used to model various processes in disordered media with complex structures. As an example, non-Debye relaxation in media containing traps and obstacles is considered. It is shown that the theoretical expression for the relaxation function contains two functional parameters, one corresponding to the traps and the other corresponding to the obstacles. The practical determination of these parameters requires independent experiments in addition to traditional relaxation experiments.

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