Non-Markovian stochastic Liouville equation and its Markovian representation

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The non-Markovian variant of the stochastic Liouville equation (SLE) is studied within the continuous time random walk approach (CTRWA). The CTRWA-based non-Markovian SLE is shown to be equivalently represented by the corresponding conventional Markovian SLE. This Markovian representation provides a rigorous method for deriving the non-Markovian SLE and allows for a physically clear interpretation of the specific features of this SLE. It also enables one to develop convenient non-Markovian models useful for applications, some of which are discussed in detail. Special attention is given to the discussion of anomalous long-tailed CTRW processes and non-Markovian SLE. The obtained results are applied to the analysis of the effect of rate fluctuations on chemical reaction kinetics. It is shown, in particular, that the anomalous fluctuations not only influence the reaction rate but also change the reaction kinetics itself.

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I. INTRODUCTION

The modern theory of relaxation in dynamical systems is based on a number of well known approaches. One of the most widely applied is the short correlation time approximation leading to the Bloch equation [1] or its classical analogs. This approach is very well known in the relaxation theory (see, for example, Ref. [2]). It allows for a rigorous derivation of Bloch-type equations, which are of special importance for theoretical studies in magnetic resonance [3], optics [2], etc.

An essential generalization of the theory beyond the short correlation time approximation (to describe the effect of finite correlation times) can be attained with the so called stochastic Liouville equation (SLE) which allows for a description of relaxation under the assumption of the Markovian nature of fluctuations [4]. The approaches based on the SLE appeared to be very powerful and useful in the analysis of a large variety of relaxation phenomena [2,3]. It is worth noting, however, that the Markovian approximation implies negligibly weak memory effects in the stochastic processes which control fluctuations. In reality, however, this assumption is often not fulfilled, for example, in highly disordered glassy materials [5].

In this work we discuss the non-Markovian variant of the SLE, which takes into account the memory effects. These effects are usually analyzed by two approaches: the generalized Langevin equation [2,6] and the continuous time random walk approach (CTRWA) [7–9]. In our consideration, we will apply the second one, CTRWA, based on the concept of independent renewals [10] governing sudden stochastic changes in the system (migration jumps, dephasing in dynamic systems, etc.), which are characterized by the probability distribution function (PDF) of waiting time of renewals [7–9].

The non-Markovian generalizations of the SLE have not been discussed in detail so far. Some recent studies dealt with this type of the SLE, but considered only its simple two-state variant [11]. In our work, we analyze the general multistate non-Markovian SLE. The detailed analysis is made with the use of the equivalent Markovian representation of the non-Markovian SLE, which allows one to derive an analytical expression for the PDF (or density matrix) of the relaxing system, as well as propose simple approaches for describing relaxation in the multistate systems. Here, we will concentrate on three of them: the two-state model, the Fokker-Plank approximation, and the sudden relaxation model. We will thoroughly discuss possible applications of the obtained results and proposed models.

It is also shown that the Markovian representation provides a deep insight into the specific features of the CTRWA-based SLE and offers the possibilities to analyze them in terms of those for the conventional Markovian SLE. Within this representation, some analytical expressions for waiting time PDFs via kinetic functions of the equivalent Markovian process are derived, which provide a simple interpretation of stationary and nonstationary variants of the SLE and clarify the relation between these two variants.

To illustrate the obtained general results, we study the manifestation of anomalous long-tailed fluctuations of the reaction rate on the kinetics of the first-order chemical reactions. This process is analyzed within all three above-mentioned models. The long-tailed fluctuations, the most representative example of non-Markovian processes with anomalously long memory [12,13], are shown to strongly affect the reaction kinetics. Unlike Markovian fluctuations, for which the kinetics is always exponential at large times and the effect of fluctuations reduces mainly to the change of rate, non-Markovian fluctuations influence the kinetics itself.

II. FORMULATION OF THE PROBLEM

We consider the kinetics of relaxation in a dynamical system caused by fluctuating interactions. The evolution of the system is assumed to be governed by the (classical or quantum) fluctuating operator $L(t)$. In general, the relaxation kinetics in this system is described by the PDF $\rho(t)$ (or density matrix for quantum systems) that satisfies the linear equation

$$\dot{\rho} = -L(t)\rho. \tag{2.1}$$

In this work, we concentrate on classical processes in which $L(t)$ is a classical fluctuating operator. In general, however,

the expression for the operator $L(t)$ can be written both for classical and quantum systems, for which $L\rho=\{H,\rho\}$ and $L\rho=i\hbar[H,\rho]$, respectively, where $\{H,\rho\}$ are the Poisson brackets corresponding to the classical Hamiltonian H, and $[H,\rho]=H\rho-\rho H$ is the commutator with the quantum Hamiltonian H.

Before proceeding to the analysis of system evolution, we need to specify the mechanism of $\hat{L}(t)$ fluctuations. In what follows, we assume that the fluctuations result from stochastic jumps between the states $|\nu\rangle\equiv|x_\nu\rangle$ in the (discrete or continuum) space $\{x_\nu\}$ with different $L=L_\nu$ which are conveniently combined into the matrix

$$\hat{L}=\sum_\nu |x_\nu\rangle L_\nu\langle x_\nu|. \tag{2.2}$$

Hereafter, we will use the ''bra-ket'' notation for the states in the $\{x\}$ space that appears to be fairly suitable for treating relaxation phenomena determined by non–self-adjoint evolution operators [14].

The general solution of Eq. (2.1) can be written in terms of the T-ordered evolution operator,

$$\rho(t)=T\left[\exp\left(-\int_0^t d\tau\hat{L}(\tau)\right)\right]\rho_i. \tag{2.3}$$

The macroscopic evolution of the system is essentially determined by the average evolution operator

$$\hat{\mathfrak{S}}(t)=\left\langle T\left[\exp\left(-\int_0^t d\tau\hat{L}(\tau)\right)\right]\right\rangle_x, \tag{2.4}$$

in which averaging is made over the fluctuations of $L(t)$, i.e., over the realizations of the stochastic process in the $\{x_\nu\}$ space. Both for Markovian and non-Markovian fluctuations, $\hat{\mathfrak{S}}(t)$ is expressed in terms of the so called conditional evolution operator $\hat{\mathcal{G}}(x,t|x_i,t_i)$ averaged over the initial distribution $P_0(x_i)$ of the system in the $\{x\}$ space:

$$\hat{\mathfrak{S}}(t)=\int\int dx dx_i\,\hat{\mathcal{G}}(x,t|x_i,t_i)P_0(x_i). \tag{2.5}$$

In general, the evaluation of $\hat{\mathcal{G}}(x,t|x_i,t_i)$ is a very complex problem. In some approximations, however, it is considerably simplified.

The important example of these approximations is the Markovian approach in which the fluctuations of $\hat{L}(t)$ are assumed to result from Markovian stochastic jumps between the states $|x_\nu\rangle$ in the $\{x_\nu\}$ space. These jumps are known to be completely characterized by the PDF $P(x,t|x_i,t_i)$ that satisfies the master equation [2]

$$\dot{P}=-\hat{\mathcal{L}}P, \quad \text{with} \quad P(x,t_i|x_i,t_i)=\delta_{xx_i}, \tag{2.6}$$

where $\hat{\mathcal{L}}$ is the linear operator which, in principle, can be time dependent, i.e., the process in the $\{x\}$ space can be nonstationary. In our discussion, however, we restrict ourselves to stationary processes only. The principal simplification of the problem results from the fact that in the Markovian model (2.6), the evolution operator $\hat{\mathcal{G}}(x,t|x_i,t_i)$ satisfies the SLE:

$$\dot{\hat{\mathcal{G}}}=-(\hat{L}+\hat{\mathcal{L}})\hat{\mathcal{G}} \ \text{ with } \ \hat{\mathcal{G}}(x,t_i|x_i,t_i)=\delta_{xx_i}. \tag{2.7}$$

The main objective of this work, however, is to analyze the systems with non-Markovian fluctuations of $\hat{L}(t)$. Below, we will show that in this case, the analysis can be done by treating the fluctuations within the CTRWA resulting in the non-Markovian variant of the SLE.

III. NON-MARKOVIAN FLUCTUATIONS

One of the most popular methods of modeling the non-Markovian fluctuations is based on the CTRWA [7–9]. Here, we discuss the CTRWA-based non-Markovian SLE in the conventional probabilistic formulation and derive it rigorously within the equivalent Markovian approach.

A. CTRWA-based non-Markovian SLE

In the CTRWA, the non-Markovian features of $\hat{L}(t)$ fluctuations show themselves in the non-exponential PDF of waiting time $W(t)$ of stochastic changes of $\hat{L}$ resulting from jumps between states $|\nu\rangle\equiv|x_\nu\rangle$ in the space $\{x_\nu\}\equiv\{x\}$. Depending on physical situation, two types of CTRWA are often considered: nonstationary (n) and stationary (s) [7]. They differ in the waiting time PDF $W_f(t)$ of the statistics of the very first change of the interaction. In the n case, it equals the PDF $W_n(t)$ of further changes: $W_f(t)=W_n(t)$, while in the s case $W_f(t)=W_s(t)\neq W_n(t)$. In the general multistate variant of the CTRWA, the fluctuations are characterized by the matrices $\hat{W}_n(t)$ and $\hat{W}_f(t)$, which satisfy the relations $W_{\mu_{jj}}=0$ and $\int_0^\infty dt\Sigma_{\nu'}W_{\mu_{\nu\nu'}}(t)=1$ for $\mu=n,s$. In the s-CTRWA, $\hat{W}_s(t)$ is closely related to $\hat{W}_n(t)$ [15],

$$W_{s_{\nu\nu'}}(t)=W_{s_{\nu\nu'}}(t)=\int_t^\infty d\tau W_{n_{\nu\nu'}}(\tau)/\overline{t}_{\nu'}, \tag{3.1}$$

where $\overline{t}_\nu=\int_0^\infty d\tau\tau[\Sigma_{\nu'}W_{n_{\nu'\nu}}(\tau)]$.

The conventional CTRW process (i.e., $\hat{L}=0$) is described by the conditional PDFs $\hat{\mathcal{G}}_\mu(t)$ for $\mu=n,s$ which satisfy some integral equations [7–9]. The evolution of the system with fluctuating $\hat{L}(t)$, whose fluctuations are governed by the CTRW process, appears to be described by an integral equation, as well, which can be called the non-Markovian SLE. It has been derived in Ref. [11], not quite rigorously using probabilistic arguments in analogy with the Markovian case. In the most general form, it is written as a system of two equations

$$\hat{\mathcal{R}}(t)=\hat{W}_\mu(t)e^{-\hat{L}t}+\int_0^t d\tau\hat{W}_n(\tau)e^{-\hat{L}\tau}\hat{\mathcal{R}}(t-\tau), \tag{3.2}$$

$$\hat{\mathcal{G}}_\mu(t)=\hat{P}_\mu(t)e^{-\hat{L}t}+\int_0^t d\tau\hat{P}_n(\tau)e^{-\hat{L}\tau}\hat{\mathcal{R}}(t-\tau), \quad (3.3)$$

in which $\hat{\mathcal{R}}(t')$ is the auxiliary matrix describing the state of the system after transition at time t and

$$P_{\mu_{\nu\nu'}}=\delta_{\nu\nu'}\int_t^\infty d\tau\sum_{\nu''} W_{\mu_{\nu''\nu}}(\tau) \quad (\mu=n,s) \quad (3.4)$$

are the (diagonal) matrices of probabilities of not observing any fluctuations during time t. These equations can formally be solved by the Laplace transformation defined as $\tilde{f}(\epsilon)=\int_0^\infty dt f(t)\exp(-\epsilon t)$ for any function $f(t)$:

$$\hat{\tilde{\mathcal{G}}}(\epsilon)=\hat{\tilde{P}}_\mu(\hat{\Omega})+\hat{\tilde{P}}_n(\hat{\Omega})[1-\hat{\tilde{W}}_n(\hat{\Omega})]^{-1}\hat{\tilde{W}}_\mu(\hat{\Omega}), \quad (3.5)$$

where

$$\hat{\Omega}=\epsilon+\hat{L} \text{ and } \hat{\tilde{W}}_\mu(\hat{\Omega})=\int_0^\infty dt\hat{W}_\mu(t)e^{-\hat{\Omega}t}. \quad (3.6)$$

Notice, however, that, in general, the PDF matrices $\hat{\tilde{W}}_\mu$ do not commute with $\hat{L}$ so that formula (3.5) is, in reality, a fairly complex matrix expression.

A much deeper insight into the problem as well as simplified and physically more clear expressions for $\hat{\tilde{\mathcal{G}}}(\epsilon)$ can be obtained with the Markovian representation of the CTRWA discussed below. In addition, this representation is, actually, the most rigorous method for the derivation of the non-Markovian SLE (3.2) and (3.3).

B. Markovian representation of the CTRWA

In accordance with the above formulation (Sec. II), we assume that the system can occupy the states $|\nu\rangle\equiv|x_\nu\rangle$ (of the space $\{x_\nu\}\equiv\{x\}$), in which the evolution of the system is determined by the operators L_ν [see Eq. (2.2)]. The kinetics of $(\nu\to\nu')$ transitions, however, is assumed to be controlled by the Markovian process in another space $\{q_j\}$ governed by the operator $\hat{\Lambda}$. The corresponding PDF $\sigma(j,t)$ satisfies the equation

$$\dot{\sigma}=-\hat{\Lambda}\sigma \quad (3.7)$$

describing evolution in $\{q_j\}$ space and equilibration if the operator $\hat{\Lambda}$ has the equilibrium state $|e_q\rangle$ $(\hat{\Lambda}|e_q\rangle=0)$:

$$|e_q\rangle=\sum_j p^e_{q_j}|j\rangle, \ \langle e_q|=\sum_j \langle j|(\langle e_q|e_g\rangle=1), \quad (3.8)$$

where p^e_j are the equilibrium population probabilities.

The control of transitions between ν states by the q_j process is assumed to proceed as follows. $(\nu\to\nu')$ transitions occur with the rate $\kappa_{\nu'\nu}$ whenever the system visits the transition state $|t\rangle$ in the $\{q_j\}$ space. The transitions are also assumed to be accompanied by the change in $|j\rangle$ state, i.e., by the transition $|t\rangle\to|n\rangle$ in the $\{q_j\}$ space. Notice that the states $|t\rangle$ and $|n\rangle$ are not only pure j states but any linear combinations of pure states.

A further general discussion implies $|n\rangle\neq|t\rangle$, but in the discussion of some particular cases we will assume $|n\rangle=|t\rangle$ for simplicity. For the same reason, we also suggest that the $\{q_j\}$ space is the same for all ν states, as well as that the operator $\hat{\Lambda}$ and the states $|t\rangle$ and $|n\rangle$ are independent of the state in the $\{x_\nu\}$ space.

In this model $\{x_\nu\otimes q_j\}$ evolution of the system is described by the PDF matrix $|\hat{\rho}\rangle$ obeying the SLE

$$|\dot{\hat{\rho}}\rangle=-(\hat{\Lambda}+\hat{L}+\hat{K}_d-\hat{K}_o)|\hat{\rho}\rangle, \quad (3.9)$$

in which $\hat{L}$ is defined in Eq. (2.1), and

$$\hat{K}_d=\hat{\kappa}_d\otimes|t\rangle\langle t| \text{ and } \hat{K}_o=\hat{\kappa}_o\otimes|n\rangle\langle t| \quad (3.10)$$

are the transition matrices in the $\{x_\nu\otimes q_j\}$-space diagonal $(\hat{K}_d)$ and nondiagonal $(\hat{K}_o)$ in the $\{x_\nu\}$ subspace with

$$\hat{\kappa}_d=\sum_\nu |\nu\rangle\kappa_{\nu\nu}\langle\nu|, \quad \hat{\kappa}_o=\sum_{\nu,\nu'\neq\nu}|\nu\rangle\kappa_{\nu\nu'}\langle\nu'|, \quad (3.11)$$

and $\kappa_{\nu\nu}=\Sigma_{\nu'(\neq\nu)}\kappa_{\nu'\nu}$. Equation (3.9) should be solved with the initial condition

$$|\hat{\rho}\rangle_{t=0}=|i\rangle\sum_\nu |\nu\rangle\langle\nu| \text{ with } |i\rangle=\sum_j p^i_j|j\rangle, \quad (3.12)$$

and $\langle e_q|i\rangle=\Sigma_j p^i_{q_j}=1$.

The function of interest for our analysis is the Laplace transformed PDF $\hat{\tilde{\mathcal{G}}}$ in the $\{x_\nu\}$ space:

$$\hat{\tilde{\mathcal{G}}}=\langle e_q|\hat{\tilde{\rho}}\rangle=\sum_j \hat{\tilde{\rho}}_j, \text{ where } \hat{\tilde{\rho}}_j=\langle j|\hat{\tilde{\rho}}\rangle. \quad (3.13)$$

It is determined by $|\hat{\tilde{\rho}}(\epsilon)\rangle$ satisfying the equation

$$|\hat{\tilde{\rho}}\rangle=\hat{G}|i\rangle+\hat{G}\hat{K}_o|\hat{\tilde{\rho}}\rangle, \quad (3.14)$$

where

$$\hat{G}=(\hat{\Omega}+\hat{\Lambda}+\hat{K}_d)^{-1}, \text{ with } \hat{\Omega}=\epsilon+\hat{L}. \quad (3.15)$$

Substitution of the particular solution of Eq. (3.14),

$$\hat{\tilde{\rho}}_0=\langle t|\tilde{\rho}\rangle=\hat{G}_i+\hat{G}_n(1-\hat{\kappa}_o\hat{G}_n)^{-1}\hat{\kappa}_o\hat{G}_i, \quad (3.16)$$

in which

$$\hat{G}_n=\langle t|\hat{G}|n\rangle \text{ and } \hat{G}_i=\langle t|\hat{G}|i\rangle, \quad (3.17)$$

back into Eq. (3.14) yields the CTRWA-like expression [see Eq. (3.5)]

$$\hat{\tilde{\mathcal{G}}}=\hat{\tilde{P}}_i(\hat{\Omega})+\hat{\tilde{P}}_n(\hat{\Omega})[1-\hat{\tilde{W}}_n(\hat{\Omega})]^{-1}\hat{\tilde{W}}_i(\hat{\Omega}), \quad (3.18)$$

where

$$\hat{\tilde{W}}_\mu=\hat{\kappa}_o\hat{G}_\mu, \quad \hat{\tilde{P}}_\mu=\hat{\Omega}^{-1}(1-\hat{\kappa}_d\hat{G}_\mu) \quad (\mu=n,i). \tag{3.19}$$

It is noteworthy that the matrices $\hat{G}_n$ and $\hat{G}_i$ can be expressed in terms of the Green's function

$$\hat{g}=(\hat{\Omega}+\hat{\Lambda})^{-1} \quad (\hat{\Omega}=\epsilon+\hat{L}) \tag{3.20}$$

by solving the equation

$$(\hat{\Omega}+\hat{\Lambda})\hat{G}=1-\hat{K}_d\hat{G}: \tag{3.21}$$

$$\hat{G}_\mu=(1+\hat{g}_t\hat{\kappa}_d)^{-1}\hat{g}_\mu, \text{ where } \hat{g}_\mu=\langle t|\hat{g}|\mu\rangle, \tag{3.22}$$

with $\mu=n,i$, and $\hat{g}_t=\langle t|\hat{g}|t\rangle$.

Formulas (3.19) offer the representation of the matrices $\hat{W}_i(t)$ and $\hat{W}_n(t)$ in terms of the Green's function $\hat{G}$ for the (controlling) process in the $\{q_j\}$ space: $\hat{W}_i(t)$ is the PDF matrix for the times of the first visits of the $|t\rangle$ state, while $\hat{W}_n(t)$ is that for the times of revisits of this state.

The proposed Markovian representation enables us to rewrite the non-Markovian SLE (3.18) in a form very suitable for our further applications

$$\hat{\tilde{\mathcal{G}}}=\hat{\tilde{P}}_i+\hat{\Omega}^{-1}\hat{\gamma}\hat{\tilde{\mathcal{G}}}_0\hat{\tilde{W}}_i, \text{ where } \hat{\tilde{\mathcal{G}}}_0=(\hat{\gamma}+\hat{\mathcal{L}})^{-1}, \tag{3.23}$$

with

$$\hat{\mathcal{L}}=\hat{\kappa}_d-\hat{\kappa}_o \text{ and } \hat{\gamma}=\hat{\kappa}_d(1-\hat{\tilde{W}}_d)/\hat{\tilde{W}}_d. \tag{3.24}$$

In expression (3.24), $\hat{\gamma}$ is represented in terms of the Laplace transform $\hat{\tilde{W}}_d$ of universal PDF matrix $W_d(t)$ (diagonal in the $\{x_\nu\}$ space), which is directly related to $\hat{P}_n(t)$: $\hat{W}_d(t)=-d\hat{P}_n(t)/dt$. With the use of Eqs. (3.19) and (3.22), $\hat{\tilde{W}}_d=\hat{\kappa}_d\hat{G}_n$ can be written as

$$\hat{\tilde{W}}_d=\frac{1}{1+\hat{\Phi}}, \text{ where } \hat{\Phi}=\frac{\hat{g}_t-\hat{g}_n}{\hat{g}_n}+\frac{1}{\hat{\kappa}_d\hat{g}_n}, \tag{3.25}$$

so that

$$\hat{\gamma}=\hat{\kappa}_d\hat{\Phi}=\hat{\kappa}_d\hat{g}_n^{-1}(\hat{g}_t-\hat{g}_n)+\hat{g}_n^{-1}. \tag{3.26}$$

Notice that $\hat{\tilde{W}}_n$ is also expressed in terms of the matrix $\hat{\tilde{W}}_d$: $\hat{\tilde{W}}_n=(\hat{\kappa}_o/\hat{\kappa}_d)\hat{\tilde{W}}_d=(1-\hat{\mathcal{L}}/\hat{\kappa}_d)\hat{\tilde{W}}_d$.

Formula (3.23) shows the important property of $\hat{\tilde{\mathcal{G}}}$: its dependence on the transition matrices $\hat{\kappa}_d$ and $\hat{\kappa}_o$ mainly reduces to that on the matrix $\hat{\mathcal{L}}$. The only possible additional effect of $\hat{\kappa}_d$ can result from the $\hat{\kappa}_d$ dependence of $\hat{\gamma}$ which, however, is negligible in the realistic limit of fairly small $\|\hat{\kappa}_d\|$ and in the particular case $|n\rangle=|t\rangle$ of special interest for further discussion.

So far, we have assumed that the transition states $|t\rangle$ and $|n\rangle$ are the same for all states in the $\{x_\nu\}$ space. However, the CTRW-type formulas (3.18)–(3.22) are also applicable for ν-dependent states $|t_\nu\rangle$ and $|n_\nu\rangle$. One should only change the definition of matrices $\hat{G}_\mu$ and $\hat{g}_\mu(\mu=n,i)$. The ν dependence of the operator $\hat{\Lambda}$ can also be taken into account (see below).

According to Eqs. (3.18) and (3.19), the initial state $|i\rangle$ in the $\{q_j\}$ space manifests itself only in the waiting time PDF matrix $\hat{W}_i(t)$, so that, in particular, we have the following.

(1) The *n*-CTRWA implies [7–9] $|i\rangle=|n\rangle$ and, therefore, $\hat{\tilde{W}}_i=\hat{\tilde{W}}_n$ and $\hat{\tilde{P}}_i=\hat{\tilde{P}}_n$ with

$$\hat{\tilde{W}}_n=(\hat{\kappa}_o/\hat{\kappa}_d)\hat{\tilde{W}}_d, \quad \hat{\tilde{P}}_n=\hat{\Omega}^{-1}(1-\hat{\tilde{W}}_d), \tag{3.27}$$

so that

$$\hat{\tilde{\mathcal{G}}}=\hat{\tilde{\mathcal{G}}}_n=(\hat{\Omega}^{-1}\hat{\gamma})\hat{\tilde{\mathcal{G}}}_0=[\hat{\Omega}+\hat{\mathcal{L}}(\hat{\Omega}/\hat{\gamma})]^{-1}. \tag{3.28}$$

(2) The *s*-CTRWA is realized only if the operator $\hat{\Lambda}$ has the equilibrium eigenstate $|e\rangle$ and $|i\rangle=|e\rangle$:

$$\hat{\tilde{W}}_i=\hat{\tilde{W}}_s=(\hat{\kappa}_o/\hat{\kappa}_d)\hat{\tilde{P}}_n/\hat{\tau}, \text{ where } \hat{\tau}=\hat{g}_n\hat{\Phi}/p_t^e, \tag{3.29}$$

with $p_t^e=\langle t|e\rangle$. In this expression, $\hat{\tau}$ is the matrix of average times (diagonal in the $\{x_\nu\}$ space) which, in principle, depends on Ω. Notice that, in general, formula (3.29) does not agree with Eq. (3.1) defining the PDF matrix $\hat{W}_s(t)$. The agreement is observed only in the case $|n\rangle=|t\rangle$ when $\hat{\Phi}=1/(\hat{\kappa}_d\hat{g}_t)$ and $\hat{\tau}=1/(\hat{\kappa}_d p_t^e)$. Substitution of Eq. (3.29) into Eq. (3.18) yields

$$\hat{\tilde{\mathcal{G}}}=\hat{\tilde{\mathcal{G}}}_s=\hat{\Omega}^{-1}(1-\hat{\tilde{W}}_e)+\hat{\tilde{\mathcal{G}}}_n\hat{\tilde{W}}_e, \tag{3.30}$$

where $\hat{\tilde{W}}_e=p_t^e/(\hat{\Omega}\hat{g}_n)$.

IV. SIMPLE MODELS AND APPROXIMATIONS

A. Models for controlling process in the $\{q_j\}$ space

Here, we consider the two simple models of the controlling process in the $\{q_j\}$ space. These models enable one to describe a large variety of CTRW processes (including anomalous) in terms of the proposed Markovian representation and are of significance in further analysis.

For simplicity, we discuss only the case $|n\rangle=|t\rangle$, which is sufficient for our applications. However, if necessary, the general expressions for $|n\rangle\neq|t\rangle$ can straightforwardly be obtained with the use of formulas of Sec. III B.

Before discussing the models we would like to note that the specific features of the time dependence of the PDF matrices $\hat{W}_\mu(t)$ and $\hat{P}_\mu(t)(\mu=n,s,i)$ are represented by $\hat{W}_d(t)=-d\hat{P}_n(t)/dt$, which is diagonal in the basis of ν states (i.e., commuting with $\hat{L}$). Therefore for simplicity of further notations, we will restrict ourselves to the case

$$\hat{L}=0, \text{ i.e., } \hat{\Omega}=\epsilon. \tag{4.1}$$

The corresponding formulas for $\hat{L}\neq 0$ can be obtained from those derived below by replacing ϵ with $\hat{\Omega}$.

1. Model of coupled kinetic states

In the model of coupled kinetic states, the controlling Markovian process in the $\{q_j\}$ space is determined by

$$\hat{\Lambda}=w_t^+|t\rangle\langle t|+\sum_{j\neq t} w_j^-|j\rangle\langle j|-\sum_{j\neq t}(w_j^-|t\rangle\langle j|+w_j^+|j\rangle\langle t|), \tag{4.2}$$

where w_j^- and w_j^+ are the rates of $|j\rangle\rightarrow|t\rangle$ and $|t\rangle\rightarrow|j\rangle$ stochastic jumps, respectively, with $w_t^+=\Sigma_{j\neq t}w_j^+$. This model is quite appropriate for describing structural changes in some disordered systems of type of glasses in which the processes are controlled by conformational jumps with rates widely distributed in their values.

In model (4.2), one can easily find $\hat{g}_t$, $\hat{g}_n$, and $\hat{g}_i$ for any initial state $|i\rangle$ and by this means get

$$\hat{\tilde{W}}_d=(1+\hat{\Phi})^{-1} \text{ with } \hat{\Phi}=[\epsilon+\phi(\epsilon)]/\hat{\kappa}_d \tag{4.3}$$

and $\phi=\Sigma_{j\neq t}w_j^+/(\epsilon+w_j^-)$.

This model gives some insight into the specific features of CTRW, in particular, anomalous CTRW [12,13] with long-tailed waiting time PDF $W_d(t)$. Most conveniently they can be analyzed in the case of continuum $\{q_j\}$ space. Suggesting that $j\in[0,\infty)$ and that the transition state $|t\rangle$ corresponds to $j_t=0$, we obtain, for example, for $w_j^{\pm}=w_t^{\pm}j^{\alpha_{\pm}}(\alpha_->1+\alpha_+)$,

$$\hat{\phi}(\epsilon)=\epsilon\int dj w_j^+/(\epsilon+w_j^-)=\xi w_t^+(\epsilon/w_t^-)^{\alpha}, \tag{4.4}$$

where $\alpha=(1+\alpha_+)/\alpha_-<1$ and $\xi=\pi/[\alpha_-\sin(\pi\alpha)]$.

Formula (4.4) means that in the considered (anomalous) case $\alpha<1$, the PDF $\hat{W}_d(t)$ is of long-tailed behavior: $\hat{W}_d(t)\sim 1/(w_t^-t)^{1+\alpha}$.

2. Model of diffusionlike processes in the $\{q_j\}$ space

The controlling process in the $\{q_j\}$ space can also be modeled by diffusionlike stochastic migration. This quite realistic model can be formulated in the discrete and continuum forms for any dimensionality n_q of the $\{q_j\}$ space.

(*a*) *Discrete* $\{q_j\}$ *space*. In the simplest discrete model,

$$\hat{\Lambda}=\sum_{i=1}^{n_q} w_i\sum_{j_i}|j_i\rangle(2\langle j_i|-\langle j_i+1|-\langle j_i-1|). \tag{4.5}$$

The Green's function $\hat{g}(\epsilon)=(\epsilon+\hat{\Lambda})^{-1}$ for this $\hat{\Lambda}$ and its matrix elements $\hat{g}_\mu$ for $(\mu=xst,n,i)$, defined in Eq. (3.22), is obtained analytically by the Fourier transformation in j_i (see, for example, Ref. [7]. Especially, simple expressions are found in the case $|n\rangle=|t\rangle$: $\hat{g}_n=\hat{g}_t=\hat{g}_0(\epsilon)=\int_0^\infty dt\, e^{-\epsilon t}\Pi_{i=1}^{n_q}e^{-2w_it}I_0(2w_it)$. This formula predicts an anomalous behavior of $\hat{W}_d(t)$ at $t\rightarrow\infty$: for $\epsilon\rightarrow 0$, $\hat{g}_0(\epsilon)\sim\text{const}+\xi_q\epsilon^{n_q/2-1}$ and, therefore, for $n_q<2$ $\hat{W}_d(t)\sim 1/t^{2-n_q/2}$.

(*b*) *Continuum* $\{q_j\}$ *space*. In the continuum case, the diffusion model can be formulated in the form of the model of two kinetically coupled states [16]: the state $|m\rangle$ in which the system undergoes migration in the continuum $\{q_j\}$ space of dimensionality $n_q\leqslant 2$ and the transition state $|t\rangle$ defined above. In the case of spherically symmetric diffusion,

$$\hat{\Lambda}=[D_q\hat{\Lambda}_q+w_m\delta(q-l)]|m\rangle\langle m|+w_t|t\rangle \times\langle t|-S_l^{-1}w_t\delta(q-l)|m\rangle\langle t|-S_lw_m\hat{\mathcal{P}}_q^l|t\rangle\langle m|, \tag{4.6}$$

where $S_l=S_{n_q}l^{n_q-1}$ is the surface area of the sphere with radius l of the transition state, in which S_{n_q} is the surface area of the sphere of unit radius, $\hat{\Lambda}_q=-(d^2/dq^2-V_{n_q}/q^2)$ with $V_{n_q}=(\frac{1}{2}n_q-1)^2-\frac{1}{4}$ is the radial part of the operator describing diffusion in the $\{q_j\}$ space with the diffusion coefficient D_q, and $\hat{\mathcal{P}}_q^l$ is the projection operator in the $\{q_j\}$ space defined by the relation $\hat{\mathcal{P}}_q^l\rho(q)=\rho(l)$ for any function $\rho(q)$.

Within model (4.6), the PDF $\hat{W}_d(t)$ can be obtained in an analytical form [16]. In particular, for $|n\rangle=|t\rangle$,

$$\hat{\tilde{W}}_d=(1+\hat{\Phi})^{-1} \text{ with } \hat{\Phi}(\epsilon)=[\epsilon+\phi_q(\epsilon)]/\hat{\kappa}_d, \tag{4.7}$$

where the dependence

$$\phi_q(\epsilon)=D_q(w_t/w_m)\langle l|(\epsilon/D_q-\hat{\Lambda}_q)^{-1}|l\rangle^{-1} \tag{4.8}$$

is determined by the Green's function $\langle l|(\epsilon/D-\hat{\Lambda}_q)^{-1}|l\rangle$, which should be obtained for the reflective boundary condition at $x=l$ [16]: $d\rho(q)/dq|_{q=l}=0$.

Noteworthy is that formula (4.7) is similar to that obtained in model (4.2) [see Eq. (4.3)], as expected. The only difference is in the definition of $\hat{\phi}(\epsilon)$. It is also important to note that the discussed model, which assumes free diffusion in infinite space, leads to the anomalous variant of the CTRWA: at small ϵ, we get $\phi(\epsilon)\sim\epsilon^{\alpha}$ [17], where $\alpha=1-n_q/2$ for $n_q<2$, and hence at long times $\hat{W}_d(t)\sim 1/t^{1+\alpha}$, in agreement with the prediction of the discrete model. At intermediate times, however, $\hat{W}_d(t)$ exponentially depends on t: $\hat{W}_d(t)\sim\exp(-\hat{\kappa}_dt)$ [16].

3. The Mittag-Leffler approximation for $W_d(t)$

The complexity of the problems under study often does not permit a detailed analysis of the physical nature of the controlling process (in the $\{q_j\}$ space). In these cases, it is reasonable to apply semiempirical approximations for $\hat{W}_d(t)$.

In particular, anomalous processes are conveniently analyzed by approximating $W_d(t)$ with the Mittag-Leffler function. In the simplest variant of this approximation,

$$\hat{\tilde{W}}_d=(1+\hat{\Phi})^{-1} \text{ with } \hat{\Phi}(\epsilon)=(w/\hat{\kappa}_d)(\epsilon/w)^{\alpha}, \quad (4.9)$$

where $0<\alpha\leqslant 1$ and w is the rate parameter that determines the population relaxation, so that

$$\hat{W}_d(t)=-\dot{\hat{P}}_n(t)=-\dot{E}_{\alpha}[-(\hat{\kappa}_d/w)(wt)^{\alpha}]. \quad (4.10)$$

Here,

$$E_{\alpha}(-x)=\frac{1}{2\pi i}\int_{-i\infty}^{i\infty}dz\,\frac{e^z}{z+xz^{1-\alpha}} \quad (4.11)$$

is the Mittag-Leffler function [18]. For $0<\alpha<1$, it is a monotonically decreasing function of x with $E_{\alpha}(-x)\approx 1-x/\Gamma(\alpha+1)$ for $|x|\ll 1$ and $E_{\alpha}(x\to-\infty)\approx 1/x$. The approximation Eqs. (4.9)–(4.11), allows one to analyze the effect of anomalous long-tailed $\hat{W}_d(t)(\sim 1/t^{1+\alpha})$ predicted by the physically sensible models discussed above.

Notice that the dependence $\hat{\Phi}\sim 1/\hat{\kappa}_d$ suggested in formula (4.9) is very important. It reproduces a similar behavior predicted by the above-discussed realistic models for the controlling process (in the $\{q_j\}$ space) in the considered case $|n\rangle=|t\rangle$. The behavior $\hat{\Phi}\sim 1/\hat{\kappa}_d$ also ensures the independence of $\hat{\gamma}=\hat{\kappa}_d\hat{\Phi}$ from $\hat{\kappa}_d$, which is proved to be valid for $|n\rangle=|t\rangle$ (see Sec. III B).

B. Models for transition matrix $\hat{\mathcal{L}}$ in the $\{x_\nu\}$ space

The general expressions (3.18)–(3.23) for arbitrary transition matrices $\hat{\kappa}_n$ and $\hat{\kappa}_o$ are fairly complex because of cumbersome matrix operations. To get a deeper insight into the effects under study, in what follows we will use simplified models of transitions in the $\{x_\nu\}$ space taking into account that in the considered case $|n\rangle=|t\rangle$, the problem reduces to the analysis of different models for $\hat{\mathcal{L}}$.

(*a*) *Two-state model*. In the two-state model [11], the operator $\hat{\mathcal{L}}$ is a (2×2) matrix with elements

$$\mathcal{L}_{11}=-\mathcal{L}_{21}=\kappa_1 \text{ and } \mathcal{L}_{22}=-\mathcal{L}_{12}=\kappa_2. \quad (4.12)$$

In this model, the matrix $\hat{\mathcal{G}}$ [see Eq. (3.5)] is obtained analytically and is somewhat different for stationary *s* and nonstationary *n* processes:

$$\hat{\tilde{G}}_{\mu_{jj}}=\hat{\tilde{P}}_{f_j}+\hat{\tilde{P}}_{n_j}\hat{\tilde{\Delta}}_j^{-1}\hat{\tilde{W}}_{n_{3-j}}\hat{\tilde{W}}_{\mu_j} \quad (j=1,2), \quad (4.13)$$

$$\hat{\tilde{G}}_{\mu_{ij}}=\hat{\tilde{P}}_{n_i}\hat{\tilde{\Delta}}_i^{-1}\hat{\tilde{W}}_{\mu_j} \quad (i\neq j;\ \ i,j=1,2), \quad (4.14)$$

where $\mu=n,s$ and $\hat{\Delta}_j=1-\hat{\tilde{W}}_{n_{3-j}}\hat{\tilde{W}}_{n_j}$.

Noteworthy is that model (4.12) is equivalent to the two-state variant of the strong relaxation model (see below).

(*b*) *Fokker-Planck continuum model*. In the case of continuum $\{x_\nu\}$ space, we can use the simplest model based on the Fokker-Planck approximation for $\mathcal{L}$:

$$\hat{\mathcal{L}}=-D_x\boldsymbol{\nabla}_x(\boldsymbol{\nabla}_x+\boldsymbol{\nabla}_x u), \quad (4.15)$$

which treats the fluctuation process as diffusion with the coefficient D_x in some effective potential $u(x)$ in $\{x_\nu\}$ space.

In model (4.15), the main problem reduces to obtaining the Green's function $\hat{\tilde{\mathcal{G}}}_0=(\hat{\gamma}+\hat{\mathcal{L}})^{-1}$ [Eq. (3.23)]. In general, this problem is fairly complex even for relatively simple Fokker-Planck–type operators $\mathcal{L}$. However, in some cases, which are interesting for applications, $\hat{\tilde{\mathcal{G}}}_0$ can be found analytically. Below, we will discuss some examples of analytically solvable models.

(*c*) *Strong relaxation model*. An important generalization of the analysis to the continuum case can be made within the strong relaxation model which assumes sudden equilibration of the system $\{x_\nu\}$ space and enables one to consider both discrete and continuum cases fairly easily. In general, in representation (3.23) of the non-Markovian SLE, this model corresponds to

$$\hat{\mathcal{L}}=\hat{\gamma}_0(1-\hat{P}_e), \text{ where } \hat{P}_e=|e_x\rangle\langle e_x|. \quad (4.16)$$

The operator $\hat{P}_e$ determines the projection on the equilibrium state $|e_x\rangle$ in the $\{x_\nu\}$ space:

$$|e_x\rangle=\sum_\nu p^e_{x_\nu}|\nu\rangle, \quad \langle e_x|=\sum_\nu \langle\nu|, \quad (4.17)$$

in which $p^e_{x_\nu}$ is the probability of population of the state $|\nu\rangle$ (so that $\langle e_x|e_x\rangle=1$).

A great advantage of the strong relaxation model is in that this model allows for the representation of the Green' s function $\hat{\mathcal{G}}_0$ [Eq. (3.23)] in the analytical form

$$\hat{\tilde{\mathcal{G}}}_0=\frac{1}{\hat{\gamma}+\hat{\mathcal{L}}}=\left(1+\hat{\tilde{W}}_g\frac{\hat{P}_e}{1-\langle\tilde{W}_g\rangle}\right)\hat{\gamma}_0^{-1}\hat{\tilde{W}}_g. \quad (4.18)$$

Here $\langle\tilde{W}_g\rangle=\langle e_x|\hat{\tilde{W}}_g|e_x\rangle$ and

$$\hat{\tilde{W}}_g=(1+\hat{\gamma}_g)^{-1} \text{ with } \hat{\gamma}_g=\hat{\gamma}/\hat{\gamma}_0. \quad (4.19)$$

Recall that in the case of two states, the strong relaxation model reduces to the two-state model discussed above.

V. APPLICATION TO THE ANALYSIS OF GATING

A. General remarks

To illustrate the proposed models and general results, we will apply them to the analysis of the well known problem of manifestation of reaction rate fluctuations in the kinetics of some biochemical reactions. Strictly speaking, the process, implied in this example, is not dynamical; however, from mathematical point of view the corresponding problem proves to be very similar to that analyzed above (see below).

The effect of rate fluctuations on reaction kinetics, called gating, is intensively studied for many years (see, for example, Ref. [19], and references therein). A number of different models for gating have been proposed [19], which, however, are based on the conventional assumption of fairly fast decay of the rate fluctuations. In this case, the kinetics is

exponential at long times. As for the manifestations of possible anomalous specific features of rate fluctuations, they have not been analyzed so far, to the best of our knowledge, though the effect of such properties on some biochemical reactions (which shows itself in strongly nonexponential reaction kinetics) is well established [13,19].

This anomalous nonexponential reaction kinetics is believed to result from the complexity of the structure and dynamical properties of large biomolecules [13]. The most popular and successful models of biomolecules assume structural analogy of the molecules with glasses. Within these assumptions the above-proposed two Markovian models for the controlling process (the models of kinetically coupled states and diffusionlike process) look quite reasonable. They allow us to interpret the reasons for the anomalous behavior of waiting time PDFs and relate the parameters describing this behavior to the kinetic parameters for elementary processes in biomolecules.

In this work, we will study the effect of anomalous rate fluctuations using the simplest first-order reaction with the fluctuating rate $k(t)$ as an example. The kinetics of this reaction, i.e., the number $C_g(t)$ of survived particles, is given by the expression similar to Eq. (2.4):

$$C_g(t)=\left\langle \exp\left[-\int_0^t d\tau k(\tau)\right]\right\rangle_k=\langle e_x|\hat{C}(t)|i_\nu\rangle, \quad (5.1)$$

where the brackets $\langle\cdots\rangle_k$ mean averaging over fluctuations of the rate k, and $|i_\nu\rangle=\Sigma_\nu p_\nu^i|\nu\rangle$ is the initial state vector in the $\{x\}$ space. Within the CTRWA and the Markovian representation, the problem reduces to the analysis of solution of the non-Markovian SLEs (3.23) for the Laplace transform of the PDF matrix $\hat{C}(t)$:

$$\hat{\tilde{C}}=\hat{\tilde{P}}_i+\hat{\Omega}^{-1}\hat{\gamma}\hat{C}_0\hat{\tilde{W}}_i, \text{ with } \hat{\tilde{C}}_0=(\hat{\gamma}+\hat{\mathcal{L}})^{-1}, \quad (5.2)$$

in which $\hat{\Omega}$ is expressed in terms of the matrix of reaction rates $\hat{k}$ as follows:

$$\hat{\Omega}=\epsilon+\hat{k}, \text{ where } \hat{k}=\sum_\nu |\nu\rangle k_\nu\langle\nu|. \quad (5.3)$$

In our work, we will mainly concentrate on the discussion of anomalous long-tailed fluctuations of $k(t)$ for which $\hat{W}_d(t)\sim 1/t^{1+\alpha}$, with $\alpha<1$, and therefore we will restrict ourselves to the nonstationary variant of the non-Markovian SLE only. Recall that this variant corresponds to $\hat{\tilde{P}}_i=\hat{\tilde{P}}_n$ and $\hat{\tilde{W}}_i=\hat{\tilde{W}}_n$. At intermediate times, however, the behavior $\hat{W}_d(t)$ can be close to exponential, as expected from the models for the controlling process proposed above [see, for example, Eq. (4.7)].

B. Two-state model

A relatively simple expression for $\hat{C}(t)$ can be obtained in the two-state model discussed in Sec. IV (the states are denoted as $|1\rangle$ and $|2\rangle$). Here, we discuss the most interesting case in which one of the states, say $|2\rangle$, is nonreactive, i.e., $k_2=0$ and $\hat{\Omega}=\epsilon+k|1\rangle\langle 1|$. In fact, the effect of anomalous $(1\leftrightarrow 2)$ transitions on $\hat{C}(t)$ has already been analyzed in Ref. [11]. A large variety of different types of kinetics $C_g(t)$ have been found, depending on the initial condition and the relation between parameters of the model, such as nonmonotonic and strongly nonexponential behavior of $C_g(t)$.

In accordance with the goal of our work to analyze the manifestation of anomalous gating, we will discuss the predictions of the two-state model within the Mittag-Leffler approximation for $\hat{W}_d(t)$ defined by Eqs. (4.9)–(4.11). In this approximation, the general formulas (4.13) and (4.14) result in the following expression for $\tilde{C}_g(\epsilon)$ [11]:

$$\tilde{C}_g=\Omega_1^{-1}R_1+\Omega_2^{-1}R_2, \quad (5.4)$$

where

$$R_\nu=Z_\nu/(Z_1+Z_2) \text{ with } Z_\nu=\phi_\nu+p_\nu^0\phi_1\phi_2. \quad (5.5)$$

In the parameters Z_ν,

$$\phi_\nu(\epsilon)=(w/\kappa_\nu)(\Omega_\nu/w)^\alpha \quad (\Omega_1=\epsilon+k,\Omega_2=\epsilon). \quad (5.6)$$

In the absence of reaction $(\hat{k}=0)$, expressions (5.4)–(5.6) describe the relaxation of the system to the equilibrium state

$$|e_x\rangle=p_1^e|1\rangle+p_2^e|2\rangle \text{ with } p_\nu^e=\tau_\nu/(\tau_1+\tau_2), \quad (5.7)$$

in which $\tau_\nu=\kappa_\nu^{-1}$, for $\nu=1,2$. The anomalous kinetics of relaxation is represented as [11]

$$|\rho(t)\rangle=\hat{P}_n(t)|\rho_0\rangle=E_\alpha[-(\hat{\kappa}_d/w)(wt)^\alpha]|\rho_0\rangle. \quad (5.8)$$

The reaction kinetics $C_g(t)$ for $\hat{k}\neq 0$ significantly depends on the initial condition (i.e., p_1^0 and p_2^0), as well as on the relation between the rate w and k.

(*a*) *The case* $w\gg k$. In the case of sufficiently large transition rates for any initial state $|i\rangle\neq|e_x\rangle$, the first stage of the process is the anomalous relaxation to the equilibrium state $|e_x\rangle$ according to Eq. (5.8). The long time stage (at $t\gtrsim 1/k$) comprises the slow reactive decrease of population of the slightly perturbed equilibrium state. Evolution of the system at this stage is described by $\tilde{\rho}_\nu(\epsilon)$ at $\epsilon\lesssim k\ll w$. A simple analysis shows that for these values of ϵ, $\tilde{\rho}_1\approx p_1^e/(\epsilon+k)$ and $\tilde{\rho}_2\approx p_2^e/[\epsilon+(p_1^e k/\epsilon)^\alpha]$. This means that at $t\gtrsim 1/k$, reaction is also nonexponential and is approximately described by a linear combination of the exponential and the Mittag-Leffler functions:

$$C_g(t)\approx p_1^e e^{-kt}+p_2^e E_\alpha[-(\bar{k}t)^\alpha], \quad (5.9)$$

where $\bar{k}=k(\kappa_2/\kappa_1)$.

(*b*) *The case* $w\ll k$. In the opposite limit of large reaction rate, the kinetics $C_g(t)$ is also described by an expression of the type of Eq. (5.9), but with other kinetic parameters. The exponential term $p_1^0 e^{-kt}$ represents the first fast decay of initial population of state 1 at short times $t\sim k^{-1}$. At longer times $t\sim w^{-1}>k^{-1}$, the kinetics is described by nearly irre-

versible relaxation transitions $(2\rightarrow 1)$ whose contribution to $C_g(t)$ can be written as $p_2^0 E_\alpha[-(\kappa_2/w)(wt)^\alpha]$. Combining these two terms into the final expression, one gets

$$C_g(t)\approx p_1^0 e^{-kt}+p_2^0 E_\alpha[-(\kappa_2/w)(wt)^\alpha]. \qquad (5.10)$$

Expressions (5.9) and (5.10) show that [except for the intermediate relaxation stage (5.8)] in the presence of anomalous gating, the reaction kinetics $C_g(t)$ is typically exponential at short times $[C_g(t)\sim e^{-kt}]$, but is anomalous long-tailed $[C_g(t)\sim 1/t^{1+\alpha}]$ at long times.

C. Fokker-Planck continuum model

A relatively simple analysis of the problem can also be made in some continuum models for which the space $\{x_\nu\}\equiv\{x\}$ is assumed to be a one-dimensional continuum.

In our analysis, we will use the simplest model for stochastic fluctuations in the $\{x\}$ space based on the Fokker-Planck approximation in which $\hat{\mathcal{L}}=-D_x\boldsymbol{\nabla}_x(\boldsymbol{\nabla}_x+\boldsymbol{\nabla}_x u)$. For a general analysis of the kinetics $C_g(t)$, one does not need to specify the explicit analytic form of $u(x)=U(x)/(k_BT)$. We will only assume that $u(x)\equiv u(|x|)$ is the even function of the shape of a potential well with the bottom at $x=x_b=0$ and $u(x)\rightarrow\infty$ as $|x|\rightarrow\infty$ [for example, $u(x)\sim x^2$].

Recall that, for the sake of simplicity, we restrict ourselves to the discussion of the case $|n\rangle=|t\rangle$ in which the matrix $\hat{\gamma}=\hat{\kappa}_d\hat{\Phi}$ is independent of $\hat{\kappa}_d$. For definiteness, we also assume that initially the system is prepared in the equilibrium state in the $\{x\}$ space, i.e. $|i_\nu\rangle=|e_x\rangle$.

The kinetics $C_g(t)$ is essentially determined by the reactivity $k(x)$. In the considered case of non-Markovian fluctuations, which corresponds to the long-tailed PDF $\hat{W}_d(t)\sim 1/t^{1+\alpha}$ (with $\alpha<1$), the problem becomes fairly complex for x-dependent reactivity. Even in the parabolic model $k(x)\sim x^2$, analytically solvable for Markovian fluctuations [20], the kinetics cannot be found in the analytical form in the non-Markovian case. In what follows, we will consider the physically reasonable and analytically solvable model, which is often applied for the description of gating (see Ref. [19], and references therein):

$$k(x)=k_0\theta(|x|-x_0) \text{ with } k_0\rightarrow\infty. \qquad (5.11)$$

At the coordinates $\pm x_0$ at the onset of fast reaction, the potential $u(x)$ is assumed to be large enough: $u(\pm x_0)\gg 1$.

In accordance with the results of Sec. V, the problem of calculation of the PDF $C(x,x_i|t)$ reduces to obtaining the Green's function $\hat{\tilde{\mathcal{G}}}_n=[\Omega(x)+\hat{\mathcal{L}}\Omega(x)/\hat{\gamma}(\Omega(x))]^{-1}$, where $\Omega(x)=\epsilon+k(x)$. It is easily seen that for the stepwise $k(x)$ [Eq. (5.11)], one gets $\hat{\tilde{\mathcal{G}}}_n=0$ for $x\geqslant x_0$ and

$$\hat{\tilde{\mathcal{G}}}_n=[\epsilon+\epsilon\hat{\mathcal{L}}/\hat{\gamma}(\epsilon)]^{-1} \text{ for } x\leqslant x_0, \qquad (5.12)$$

where

$$\hat{\mathcal{L}}=\hat{\mathcal{L}}_g=-D_x\boldsymbol{\nabla}_x(\boldsymbol{\nabla}_x+\boldsymbol{\nabla}_x u_g), \qquad (5.13)$$

in which the potential

$$u_g(x)=u(x)\,\theta(x_0-|x|)-u_0\,\theta(|x|-x_0), \qquad (5.14)$$

with $u_0\gg 1$, is of the shape of the potential well with barriers at $x\sim\pm x_0$. This means that the problem under study reduces to that of escaping from the well of the potential $u_g(x)$ by diffusion over the barriers.

In the considered limit $u(x_0)\gg 1$ for the assumed initial state $|i_\nu\rangle=|e_x\rangle$, this kinetics can easily be obtained analytically [11]:

$$\tilde{C}_g(\epsilon)=[\epsilon+w_g\epsilon/\gamma(\epsilon)]^{-1}, \qquad (5.15)$$

where

$$w_g=2D_x\left[\int_{x\in\{b\}}dx e^{-u_g(x)}\int_{x\sim x_0}dx e^{u_g(x)}\right]^{-1} \qquad (5.16)$$

is the lowest eigenvalue of the operator $\mathcal{L}_g$, which determines the rate of escaping from the well $u_g(x)$ [21]. In expression (5.16), the first and second integrals are taken over the regions near the bottom $\{b\}$ of the well $(x\sim x_b=0)$ and near the barrier at $x\sim x_0$, respectively. Interestingly, formula for $\tilde{C}_g(\epsilon)$ is very similar to that for the PDF $\hat{\tilde{P}}_n(\epsilon)=[\epsilon+\epsilon/\Phi(\epsilon)]^{-1}$. The only difference is in the additional coefficient $w_g/\hat{\kappa}_d$ in Eq. (5.15). This means that the kinetic function $C_g(t)$ is close to $P_n(t)$.

In particular, in the Mittag-Leffler approximation (4.9) for which $\gamma(\epsilon)=w(\epsilon/w)^\alpha$ for $\alpha<1$,

$$C_g(t)=E_\alpha[-(w_g/w)(wt)^\alpha]. \qquad (5.17)$$

It is important to note that, according to this expression, $C_g(t)$ anomalously slowly decreases at long times: $C_g(t)\sim 1/t^\alpha$.

It is worth noting that in the presence of anomalous gating the reaction kinetics $C_g(t)$ is expected to strongly depend on the functional form of $k(x)$. This fact will become quite clear if one takes into account that for sharply changing $k(x)$ [given by Eq. (5.11)], $C_g(t)$ is a slowly decreasing function: $C_g(t)\sim 1/t^\alpha$, while for constant $k=k_0$ the kinetics $C_g(t)$ is exponential: $C_g(t)\sim\exp(-k_0t)$. Unfortunately, it is difficult to analyze the dependence of $C_g(t)$ on $k(x)$ within the Fokker-Plank approximation. From this point of view, the strong relaxation model proposed above proves to be very helpful.

D. Strong relaxation model

The general results obtained in Sec. IV B within the strong relaxation model allow us to derive an analytical expression for the reaction kinetics $C_g(t)$. Here, we will consider the most interesting case of the continuum $\{x\}$ space and assume that the relaxation rate γ_0 is independent of x.

In principle, some details of the reaction kinetics at early stage depend on the initial state $|i_\nu\rangle$ in the $\{x\}$ space, however, for definiteness and simplicity, we will analyze only the case of the equilibrium initial state $|i_\nu\rangle=|e_x\rangle$, in which the Laplace transform of the kinetics is given by

$$\tilde{C}_g=\langle e_x|(\hat{\gamma}/\hat{\Omega})\hat{\tilde{\mathcal{G}}}_0|e_x\rangle=\langle\tilde{P}_g\rangle/(1-\langle\tilde{W}_g\rangle), \quad (5.18)$$

where, according to Eq. (4.19),

$$\hat{\tilde{W}}_g=(1+\hat{\gamma}_g)^{-1} \text{ and } \hat{\tilde{P}}_g=[\hat{\Omega}(1+1/\hat{\gamma}_g)]^{-1}, \quad (5.19)$$

with $\hat{\gamma}_g=\hat{\gamma}/\gamma_0$. In formula (5.18) [following Eq. (4.18)], we introduce the notation $\langle B\rangle$ for the averages of the operators $\hat{B}=\hat{\tilde{W}}_g,\hat{\tilde{P}}_g$:

$$\langle B\rangle=\langle e_x|\hat{B}|e_x\rangle=Z_u^{-1}\int dxB(x)e^{-u(x)}, \quad (5.20)$$

in which $Z_u=\int dxe^{-u(x)}$ is the partition function.

Expressions (5.18)–(5.20) reduce the problem of obtaining the kinetics $C_g(t)$ to that of evaluating the integrals in $\langle\tilde{P}_g\rangle$ and $\langle\hat{\tilde{W}}_g\rangle$.

1. Some exact limiting results

(*a*) *Anomalous reaction kinetics for stepwise k(x)* [Eq. (5.11)]. For stepwise dependence of the reactivity on x: $k(x)=k_0\theta(|x|-x_0)$ with $k_0\to\infty$, the parameters $\langle\hat{\tilde{P}}_g\rangle$ and $\langle\hat{\tilde{W}}_g\rangle$ can easily be evaluated analytically. Substitution of these parameters into Eq. (5.18) yields

$$\tilde{C}_g=(1-p_r)[\epsilon+p_r\epsilon/\gamma_g(\epsilon)]^{-1}, \quad (5.21)$$

where

$$p_r=2\int_{x_0}^{\infty}\frac{dx}{Z_u}e^{-u(x)} \text{ with } Z_u=\int_{-\infty}^{\infty}dxe^{-u(x)} \quad (5.22)$$

is the population of reactive states in the equilibrium state. Within the Mittag-Leffler approximation (4.9), in which $\gamma(\epsilon)=w(\epsilon/w)^{\alpha}$ for $\alpha<1$,

$$C_g(t)=(1-p_r)E_{\alpha}[-p_r(\gamma_0/w)(wt)^{\alpha}]. \quad (5.23)$$

For $p_r\ll 1$, this expression agrees with formula (5.17) obtained above in the Fokker-Planck model with the rate w_b replaced by the average reaction rate $p_r\gamma_0$.

(*b*) *Exponential reaction kinetics for k(x) independent of x*. In the trivial case of $k(x)=k_0$ independent of x, we get $\tilde{P}_g=(\epsilon+k_0)^{-1}(1-\tilde{W}_g)$ and, therefore, $C_g(t)=\exp(-k_0t)$, as expected.

2. Nonexponential reaction kinetics for $k(x)\sim|x|^{\alpha_r}$

In the case $k(x)=k_0(|x|/x_b)^{\alpha_r}$, the expression for $C_g(t)$ cannot be obtained analytically, in general. However, some interesting conclusions can be made by analyzing the asymptotic (at $t\to\infty$) behavior of $C_g(t)$, which is determined by $\tilde{C}_g(\epsilon)$ at $\epsilon\to 0$. It is easixsly seen that in the leading order in $\epsilon\to 0$, we can write $\tilde{C}_g\approx\langle\tilde{P}_g\rangle/(1-\langle\tilde{W}_g\rangle_0)$, with $\langle\tilde{W}_g\rangle_0=\langle\tilde{W}_g\rangle_{\epsilon=0}$, i.e.,

$$C_g(t)\overset{t\to\infty}{\approx}(1-\langle\tilde{W}_g\rangle_0)^{-1}P_g(t)\langle e^{-k(x)t}\rangle, \quad (5.24)$$

where $\langle e^{-k(x)t}\rangle=Z_u^{-1}\int_{-\infty}^{\infty}dxe^{-[u(x)+k(x)t]}$ and

$$\langle e^{-k(x)t}\rangle\overset{t\to\infty}{\approx}\frac{1}{Z_u}\int_{-\infty}^{\infty}dxe^{-k(x)t}\sim 1/t^{1/\alpha_r}. \quad (5.25)$$

Therefore, within the Mittag-Leffler approximation in which $P_g(t)=E_{\alpha}[-(\gamma_0/w)(wt)^{\alpha}]$ one obtains

$$C_g(t)\overset{t\to\infty}{\sim}1/t^{\alpha+1/\alpha_r}. \quad (5.26)$$

It is worth noting that the potential $u(x)$ does not affect the obtained asymptotic behavior of $C_g(t)$. It is only determined by the specific features of the dependence $k(x)$ and anomalous fluctuations of reactivity.

Formula (5.26) clearly demonstrates the important manifestation of the functional form of reactivity $k(x)$ in the reaction kinetics. In accordance with the above general conclusions, for slow dependence $k(x)$ (for small α_r) the kinetic function $C_g(t)$ sharply decreases at $t\to\infty$ approaching the exponential function in the limit $\alpha_r\to 0$, as predicted above.

In particular, in the case of anomalous reactivity fluctuations (i.e., for $\alpha<1$) whose statistics cannot be described by any characteristic time, the reaction kinetics has nevertheless a finite average time τ_g if $\alpha_r<1/(1-\alpha)$:

$$\tau_g=\int_0^{\infty}dtC_g(t)=\tilde{C}_g(\epsilon=0)=\frac{\langle\tilde{P}_g\rangle_0}{1-\langle\tilde{W}_g\rangle_0}, \quad (5.27)$$

where

$$\langle\tilde{W}_g\rangle_0=\langle\tilde{W}_g\rangle_{\epsilon=0}=\frac{1}{Z_u}\int dx\frac{e^{-u(x)}}{1+\gamma_g(x)}, \quad (5.28)$$

$$\langle\tilde{P}_g\rangle_0=\langle\tilde{P}_g\rangle_{\epsilon=0}=\frac{1}{Z_u}\int dx\frac{e^{-u(x)}}{k(x)[1+\gamma_g^{-1}(x)]}, \quad (5.29)$$

with $\gamma_g(x)=\gamma(k(x))/\gamma_0$. It is easily seen that the condition $\alpha_r<1/(1-\alpha)$ ensures the convergence of the integral in Eq. (5.29) for $\langle\tilde{P}_g\rangle_0$ at $x\to 0$.

The expressions similar to Eq. (5.27) can be written for any higher moments of the kinetics $C_g(t)$ in terms of derivatives of $\tilde{C}_g(\epsilon)$. The existence conditions for these moments are easily determined from Eq. (5.26).

In general, the parameters $\langle\tilde{W}_g\rangle_0$ and $\langle\tilde{P}_g\rangle_0$ and, therefore, τ_g can be calculated only numerically. In some simple models, the representation in an analytical form is, in principle, also possible. For example, in the Mittag-Leffler approximation and for $u(x)$: $u(x)=u_0\theta(|x|-x_u)$, with $u_0\to\infty$, both $\langle\tilde{W}_g\rangle_0$ and $\langle\tilde{P}_g\rangle_0$ are expressed in terms of the incomplete Euler B functions [22] (closely related to the hypergeometric functions). Unfortunately, even in this simplified model, a formula for τ_g is fairly cumbersome and inconvenient for the analysis.

VI. DISCUSSION AND SUMMARY

In this work, we proposed the non-Markovian variant of the SLE, which describes the effect of non-Markovian fluctuations of the parameters of dynamical systems on the evolution of these systems. In the case of Markovian fluctuations, the SLE is well known and is successfully applied to a lot of problems of the relaxation theory. As for the non-Markovian case, the corresponding SLE has not been discussed so far, to the best our knowledge.

Here, we have analyzed the effect of non-Markovian fluctuations of parameters within the CTRWA. This approach makes it possible to derive the integral equation for the PDF (or density matrix) of the system that can be considered as a generalization of the conventional (Markovian) SLE to the non-Markovian case.

It is shown that the CTRWA-based non-Markovian SLE can equivalently be represented in terms of some Markovian SLE. This representation provides a deep insight into the specific features of non-Markovian processes. It allows for the formulation and analysis of some realistic non-Markovian models and approximations useful for discussion of normal and anomalous relaxation phenomena.

Below, we summarize the most important results of this analysis.

(1) The Markovian representation gives the most rigorous method for derivation of the CTRWA-based non-Markovian SLE. It also provides a physically clear interpretation of the important functions and parameters of the underlying CTRWA, and enables us to develop convenient ways of the numerical solution of the non-Markovian SLE reducing it to the Markovian one. This problem will be discussed in detail elsewhere [23]. Here, we restrict ourselves to a few remarks only. First, the Markovian representation allows for the analysis of the physical meaning of renewals, applied in the CTRWA, in terms of revisits of the transition state $|t\rangle$ in the $\{q_j\}$ space [see Eqs. (3.18)–(3.22)]. Second, this representation shows that the stationary CTRWA exists only if the corresponding Markovian controlling process (in the $\{q_j\}$ space) is stationary (i.e., has an equilibrium state) and the initial state $|i\rangle$ is in equilibrium. As for the conventional nonstationary CTRWA, it is realized for $|i\rangle=|t\rangle$. Third, the controlling Markovian processes in the $\{q_j\}$ space, which do not have the equilibrium states, represent anomalous CTRWA and anomalous non-Markovian SLE corresponding to the long-tailed behavior of the PDF $W_d(t\to\infty)\sim 1/t^{1+\alpha}$. Fourth, the Markovian representation allows, in principle, for the extension of the non-Markovian SLE to the case of quantum controlling processes, such as non-adiabatic charge transfer reactions [21], etc.

(2) The proposed Markovian representation is especially useful for the analysis of the multistate models in $\{x_\nu\}$ space. With the use of this representation, the problem of evaluating the PDF matrix under study $\hat{\mathcal{G}}(t)$ is reduced to obtaining the Green's function $\hat{\tilde{\mathcal{G}}}_0=(\hat{\gamma}+\hat{\mathcal{L}})^{-1}$ [see Eqs. (3.23) and (3.24)], in which the matrix $\hat{\gamma}$ and operator $\hat{\mathcal{L}}$ are expressed in terms of the parameters of the model. It is important to note that in some cases (mainly considered in this work), the matrix $\hat{\gamma}$ is a universal function of ϵ, independent of the transitions rates $\hat{\kappa}_{d,o}$. In these cases, the dependence of $\hat{\mathcal{G}}(t)$ on the rates $\hat{\kappa}_{d,o}$ reduces to that on $\hat{\mathcal{L}}=\hat{\kappa}_d-\hat{\kappa}_o$ only, so that the problems of modeling $\hat{\gamma}$ and $\hat{\mathcal{L}}$, which are determined by the processes in $\{q_j\}$ and $\{x_\nu\}$ spaces, respectively, can be analyzed separately (see Sec. IV).

(3) To illustrate high efficiency of the proposed methods and models we applied them in the analysis of the effect of rate fluctuations on the kinetics $C_g(t)$ of the first-order chemical reactions. This effect, usually called gating, is known to be very important in some biochemical reactions [19]. In our work, we concentrated on the discussion of the manifestation of possible anomalous long-tailed fluctuations sometimes observed in biochemical processes. Some interesting results are obtained with the proposed models, in particular, within the Mittag-Leffler approximation properly describing anomalous behavior of waiting time PDF $W_d(t)\sim 1/t^{1+\alpha}$,$(\alpha<1)$.

In the simple two-state model (Sec. V B), the reaction kinetics $C_g(t)$ is found to be represented as a superposition of exponential and long-tailed anomalous terms. Naturally, the exponential term mainly contributes to $C_g(t)$ at relatively short times, while the long time asymptotic behavior is determined by the anomalous term. The situation is especially interesting in the limit of large rates of transitions between states (larger than the reaction rate in the reactive state), in which the characteristic rate of the anomalous part of the reaction kinetics is significantly affected by the transition rates.

A more realistic analysis, however, should be based on continuum models of transitions in the $\{x_\nu\}$ space. In our work, we analyzed the predictions of two of them: the Fokker-Planck model and the sudden relaxation time model. One of the most important predictions of both models comprises in the strong dependence of the reaction kinetics on the mathematical form of $k(x)$. In our analysis, we assumed $k(x)\sim|x|^{\alpha_r}$. The kinetics is found to change from strongly anomalous long-tailed to exponential with the increase of α_r from $\alpha_r\ll 1$ to $\alpha_r\gg 1$, i.e., as the dependence $k(x)$ becomes sharper. The specific features of this change of the kinetics are analyzed within the strong relaxation model. In particular, it is shown that at large $\alpha_r>1/(1-\alpha)$, the kinetics is anomalous long tailed and cannot be described by any characteristic time. At smaller $[\alpha_r<1/(1-\alpha)]$, however, it is characterized by the average reaction time τ_g defined by Eqs. (5.27)–(5.29).

This work mainly concerns with the analysis of manifestations of anomalous long-tailed fluctuations (with $\alpha<1$). However, the obtained general results, in particular, formulas for reaction kinetics in the presence of gating (Sec. V), are valid for any type of stochastic fluctuations including conventional Poissonian. For example, for non-Poissonian fluctuations with $W_d(t\to\infty)\sim 1/t^{1+\alpha}$ and $\alpha>1$, the reaction kinetics $C_g(t)$ still depends on the form of $k(x)$, but as α is increased this dependence becomes less pronounced, disappearing at $\alpha\gg 1$.

In conclusion, the proposed non-Markovian SLE and its Markovian representation enable one to analyze the effects

of non-Markovian fluctuations of parameters on the kinetics relaxation in dynamical systems. To illustrate the results of our work, we discussed the effect non-Markovian anomalous fluctuations of the rate on the kinetics of gating, taking into account formal mathematical equivalence of this problem to that for dynamical systems. However, there are a number of other important processes that can be studied with the use of the non-Markovian SLE: spin selective diffusion-assisted reactions of paramagnetic particles (radicals, triplet excitons, etc.) [24], nonadiabatic reactions governed by stochastic motion along the reaction coordinates [21], stochastic processes observed by single-molecule spectroscopy [25], etc. Analysis of some of these processes is now in progress.

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