# Anomalous two-state model for anomalous diffusion

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An anomalous two-state model (ATSM) with the anomalous long-tailed kinetics of transitions between states is proposed to describe the specific features of anomalous diffusion (AD) and AD-assisted transitions (ADAT) in the double-well potential. In the ATSM the system is assumed to undergo the conventional diffusion in both states but with different diffusion coefficients. The anomalous features of diffusion result from the modulation of the diffusion coefficient caused by transitions between ATSM states. The anomalous space-time evolution predicted by the ATSM is treated within the continuous time random walk theory. With the use of the proposed ATSM the transient behavior of the AD and the ADAT is analyzed in detail. We found a large variety of different (and sometimes peculiar) types of the space-time behavior of the free AD and ADAT. The free AD is found to be of subdiffusion or superdiffusion type for fairly long time depending on the relation between the parameters of the ATSM. The kinetics of the ADAT can be either conventional (exponential) or anomalous (of inverse power type) for different parameters of the model and time.

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## I. INTRODUCTION

The anomalous random walks, called hereafter anomalous diffusion (AD), manifest themselves in various physical situations. This kind of processes, as applied to some fields of physics, biology, and other sciences [1,2], is a subject of active studies in recent years. Since the work of Scher and Montroll [3], which analyzed the specific features of photoconductivity in disordered and glassy semiconductors, a lot of different transport processes and phenomena are considered.

Most clearly the peculiarities of the AD show themselves in the non-Fickean time dependence of the mean square of displacement [1]: $\overline{\Delta x^2}(t)=\overline{x^2}(t)-\overline{x}^2(t)\sim t^{\alpha}, \quad (\alpha\neq 1)$. The case $\alpha<1$, called subdiffusive, is typical for migration on fractals [1], motion of a probe particle in a polymer network [4]. The opposite case ($\alpha>1$) of enhanced diffusion, called superdiffusion, is observed in migration of tracers in rotating flows [5] and layered velocity fields [6], etc.

Recently, the effect of the AD on diffusion-assisted activated rate processes has also been discussed [7]. It is found that the AD can show itself in the nonexponential kinetics of the AD-assisted escaping from the well.

Usually the AD is described within the generalized Chapman-Kolmogorov equation [8,9] or the equivalent stochastic equation [10] that under some assumptions can be reduced to the fractional kinetic equations [2]. Very popular is also the continuous time random walk (CTRW) approach [11–13] in which the long-tailed waiting time and jump length probability distribution functions (PDF's) are assumed [2,9,14].

In regard to the CTRW approach, only one channel variant of this approach has mainly been discussed yet as applied to the AD [2], though the multistate extension opens a new ample scope for the analysis. In principle, the multistate variants of the CTRW theory have already been considered in literature [12] and applied to some physical processes. However, to the best of our knowledge no applications of this variant of the CTRW theory to the analysis of the AD and other related processes have been made so far.

The well known examples of multistate theories are based on the assumption of the Poissonian statistics of transitions between states [12] in which the evolution equation, called the stochastic Liouville equation (SLE), is Markovian. The SLE is a particular variant of the general non-Markovian equations of the non-Poissonian CTRW.

In this work we analyze the AD within the simplest variant of the multistate model, the two-state model (TSM), which suggests the conventional diffusion of a probe particle in both states but with different diffusion coefficients. The transitions between the states assumed in the TSM result in the time modulation of the diffusion coefficient and thus in the nonconventional random walks of the particle. Our work mainly concerns the discussion of the special type of the TSM, the anomalous TSM (ATSM) presuming the non-Poissonian transition statistics with the long-tailed waiting time PDF's. Within the proposed ATSM the space/time evolution of the particle is described using the CTRW theory.

Some variants of the ATSM for the AD have already been discussed earlier within the projection operator formalism [2,15]. This approach enables one to reduce the multistate kinetic equations to the single-state one but with a memory term. After this reduction, however, some interesting information on the inter-relation between the kinetics of TSM transitions and the stochastic motion turns out to be essentially masked. At the same time, the analysis of this relation is very instructive and useful for deeper understanding of the specific features of the AD. An important advantage of the complete consideration within the ATSM, which is the main goal of the proposed work, is in the possibility to demonstrate and thoroughly analyze the effect of the TSM-transition kinetics on the peculiar properties of the AD.

The analysis within the ATSM shows that the specific features of the AD strongly depend on the properties of the waiting time PDF's. First of all these features manifest themselves in some peculiarities of the kinetics of transitions between the two states. The peculiarities significantly affect the characteristic properties of the AD. To illustrate these effects we will thoroughly discuss the free AD and AD-assisted transitions in a double-well potential. In both cases the anomalous specific features of the transition kinetics strongly influence the kinetics of the processes giving rise to some unusual properties of subdiffusive or superdiffusive character that shows themselves, in particular, in strongly nonexponential transition kinetics in a double-well potential.

## II. TWO-STATE MODEL

We consider the one-dimensional stochastic motion of a probe particle in the external potential $U(x)$ represented hereafter in terms of the dimensionless function $u(x) = U(x)/(k_B T)$, where $T$ is the temperature of the system. The particle is assumed to occupy the two states, 1 or 2, in which it undergoes the conventional diffusive motion in the potential $u(x)$, however, with different diffusion coefficients. The diffusion is described by the Smoluchowsky equations for the coordinate PDF's $\rho_j(x,t)(j=1,2)$

$$\dot{\rho}_j = -\hat{L}_j \rho_j, \tag{2.1}$$

where

$$\hat{L}_j = -(w_j \lambda_j^2)\boldsymbol{\nabla}(\boldsymbol{\nabla} + \boldsymbol{\nabla} u) = -D_j^0 \boldsymbol{\nabla}(\boldsymbol{\nabla} + \boldsymbol{\nabla} u) \tag{2.2}$$

are the Smoluchowsky operators in which $\boldsymbol{\nabla} = \partial/\partial x$, and $w_j$ and $\lambda_j$ are the characteristic rates and lengths of diffusive jumps that are combined into the diffusion coefficients $D_j^0 = w_j \lambda_j^2$ in the states $j=1,2$.

In this TSM, diffusion of the particle is suggested to be modulated by the stochastic $(1 \leftrightarrow 2)$ transitions between TSM states. The specific features of the space-time evolution of the particle predicted by the TSM are essentially determined by the statistics of these transitions.

The TSM assuming the Poissonian statistics of $(1 \leftrightarrow 2)$ transitions has already been considered in a number of earlier investigations [12]. In this case the space-time evolution of the system is described by the Markovian equation for the vector of PDF's $\rho(x|t) = [\rho_1(x|t), \rho_2(x|t)]^{\mathrm{T}}$:

$$\dot{\rho} = -\hat{L}\rho - \hat{w}\rho, \tag{2.3}$$

in which

$$\hat{L} = \begin{bmatrix} \hat{L}_1 & 0 \\ 0 & \hat{L}_2 \end{bmatrix} \quad \text{and} \quad \hat{w} = \begin{bmatrix} w_1 & -w_2 \\ -w_1 & w_2 \end{bmatrix} \tag{2.4}$$

with $w_{1,2}$ being the rates of $(1 \leftrightarrow 2)$ transitions. Equation (2.3) is called the SLE.

The main purpose of our study is to analyze ATSM in which $(1 \leftrightarrow 2)$-transition statistics is non-Poissonian with the long-tailed waiting time PDF's $W_1(t)$ and $W_2(t)$ of transitions from the states 1 and 2, respectively. In what follows we will approximate $W_{1,2}(t)$ by

$$W_j(t) = \frac{1}{2\pi i}\int_{-i\infty}^{i\infty} d\epsilon \frac{e^{\epsilon t}}{1+\phi_j(\epsilon)} \text{with } \phi_j(\epsilon) = \left(\frac{\epsilon}{w_j}\right)^{\nu_j}. \tag{2.5}$$

We will also assume that $0 < \nu_j \leqslant 1$.

The stochastic properties of transitions can equivalently be characterized by the probabilities $P_j(t)$ not to make any transitions until time $t$ [naturally, $P_j(0)=1$]:

$$P_j(t) = \int_t^\infty d\tau W_j(\tau), \quad \text{i.e., } W_j(t) = -\dot{P}_j(t). \tag{2.6}$$

In the approximation (2.5) $P_j(t)$ is written as

$$P_j(t) = \frac{1}{2\pi i}\int_{-i\infty}^{i\infty} d\epsilon \frac{e^{\epsilon t}}{\epsilon + \epsilon \phi_j^{-1}(\epsilon)} = E_{\nu_j}[-(w_j t)^{\nu_j}], \tag{2.7}$$

where

$$E_\nu(-x) = \frac{1}{2\pi i}\int_{-i\infty}^{i\infty} dz \frac{e^z}{z + x z^{1-\nu}} \tag{2.8}$$

is the Mittag-Leffler function [16] that for $0 < \nu < 1$ monotonically decreases with the increase of $x$ and has the following asymptotic properties: $E_\nu(-x) \approx 1 - x/\Gamma(\nu+1)$ for $|x| \ll 1$ and $E_\nu(x \to -\infty) \approx 1/x$.

In accordance with Eqs. (2.6)–(2.8), the PDF's $W_j(t)$ monotonically decrease as $t$ is increased with $W_j(t) \sim 1/t^{1+\nu_j}$ at $t \to \infty$, and is singular at $t \to 0$: $W_j(t) \sim 1/t^{1-\nu_j}$. Notice that the singularity can be eliminated by taking, for example, $\phi_j(s) = \xi_j s + s^{\nu_j}$ for which $W_j(0) = \xi_j^{-1}$.

The evolution of the system, predicted by the ATSM, is conveniently described within the CTRW approach [11,13]. In this approach the vector of PDF's $\rho(x|t) = [\rho_1(x|t), \rho_2(x|t)]^{\mathrm{T}}$ satisfies the integral equations [11]

$$\eta(t) = \hat{W}(t)\hat{G}(t)\rho_0 + \int_0^t d\tau \hat{W}(\tau)\hat{G}(\tau)\eta(t-\tau), \tag{2.9}$$

$$\rho(t) = \hat{P}(t)\hat{G}(t)\rho_0 + \int_0^t d\tau \hat{P}(\tau)\hat{G}(\tau)\eta(t-\tau). \tag{2.10}$$

Here $\rho_0 = \rho(t=0)$ and $\eta = (\eta_1, \eta_2)^{\mathrm{T}}$ is the auxiliary vector, that describes the evolution of the PDF $\rho(x,t)$ as a result of only one transition during the time $t$. In Eqs. (2.9) and (2.10) we also introduced the operator

$$\hat{G}(t) = \exp(-\hat{L}t) \tag{2.11}$$

of evolution between two consecutive transitions [in which $\hat{L}$ is given by Eq. (2.4)] and two matrices $\hat{W}$ and $\hat{P}$ defined as

$$\hat{W}(t) = \begin{bmatrix} 0 & W_2(t) \\ W_1(t) & 0 \end{bmatrix}, \quad \hat{P}(t) = \begin{bmatrix} P_1(t) & 0 \\ 0 & P_2(t) \end{bmatrix}. \tag{2.12}$$

Equations (2.9) and (2.10) can be considered as a non-Poissonian generalization of the SLE (2.3). Naturally, in the Poissonian case, $W_j(t)=w_j\exp(-w_j t)$ they reduce to the SLE (2.3).

Most conveniently Eqs. (2.9) and (2.10) are represented with the Laplace transformation in time, that for any function of time $g(t)$ is conventionally denoted as $\widetilde{g}(\epsilon)=\int_0^\infty dt\, g(t)\exp(-\epsilon t)$,

$$\widetilde{\eta}=\widetilde{WG}\rho_0+\widetilde{WG}\,\widetilde{\eta} \quad \text{and} \quad \widetilde{\rho}=\widetilde{PG}\rho_0+\widetilde{PG}\,\widetilde{\eta}. \tag{2.13}$$

The solution of Eqs. (2.13) is given by

$$\rho(t)=\hat{T}(t)\rho_0, \quad \text{or} \quad \widetilde{\rho}(\epsilon)=\widetilde{T}(\epsilon)\rho_0, \tag{2.14}$$

where the Laplace transform $\widetilde{T}(\epsilon)$ is the $(2\times 2)$ matrix with

$$\widetilde{T}_{ij}=(\hat{\phi}_i+\delta_{ij}\hat{\phi}_1\hat{\phi}_2)/(\hat{\omega}_i\hat{\phi}),(i,j=1,2), \tag{2.15}$$

in which $\delta_{ij}$ is the Kronecker symbol ($\delta_{ij}=0$ for $i\neq j$ and $\delta_{jj}=1$),

$$\hat{\omega}_j=\epsilon+\hat{L}_j, \quad \hat{\phi}_j=\phi_j(\hat{\omega}_j)=(\hat{\omega}_j/w_j)^{\nu_j}, \tag{2.16}$$

and $\hat{\phi}=\hat{\phi}_1+\hat{\phi}_2+\hat{\phi}_1\hat{\phi}_2$. It is easily seen that the evolution matrix $\hat{T}(t)$ ensures the conservation of the total population of both states.

To clarify the specific features of the ATSM we begin our discussion with the analysis of the kinetics of $(1\leftrightarrow 2)$ transitions (in the absence of diffusion).

## III. KINETICS OF TRANSITIONS

The proposed ATSM predicts very important peculiarities of the kinetics of $(1\leftrightarrow 2)$ transitions in the absence of diffusion, when $\hat{L}_1=\hat{L}_2=0$. In this case $\hat{\omega}_1=\hat{\omega}_2=\epsilon$, and the above-mentioned conservation rule for the total populations of the states is written as

$$\widetilde{T}_{1j}(\epsilon)+\widetilde{T}_{2j}(\epsilon)=1/\epsilon, \quad \text{i.e.,} \quad T_{1j}(t)+T_{2j}(t)=1. \tag{3.1}$$

### A. Asymptotic relations

First, let us consider the asymptotic (at $t\rightarrow\infty$) behavior of $\hat{T}(t)$. It is determined by the analytic properties of $\widetilde{T}(\epsilon)$ at $\epsilon\rightarrow 0$:

$$\widetilde{T}_{ij}(\epsilon)\overset{\epsilon\rightarrow 0}{\rightarrow}\frac{(\epsilon/w_i)^{\nu_i}}{\epsilon[(\epsilon/w_1)^{\nu_1}+(\epsilon/w_2)^{\nu_2}]}. \tag{3.2}$$

For example, the limiting value

$$\hat{T}_l=\hat{T}(t\rightarrow\infty)=\lim_{\epsilon\rightarrow 0}\epsilon\widetilde{T}_{ij}(\epsilon) \tag{3.3}$$

can be represented as

$$\hat{T}_l=\frac{1}{N}\begin{bmatrix} w_2^\nu & w_2^\nu \\ w_1^\nu & w_1^\nu \end{bmatrix}, \quad \hat{T}_l=\begin{bmatrix} 0 & 0 \\ 1 & 1 \end{bmatrix} \quad \text{and} \quad \hat{T}_l=\begin{bmatrix} 1 & 1 \\ 0 & 0 \end{bmatrix} \tag{3.4}$$

$(N=w_1^\nu+w_2^\nu)$, for $\nu_1=\nu_2=\nu,\nu_1>\nu_2$, and $\nu_1<\nu_2$, respectively.

These seemingly astonishing results (3.4), especially for the case $\nu_1\neq\nu_2$, are, in reality, quite clear. The fact is that at very long times the PDF's $W_j(t)$ (2.5) describe the transitions with strongly different rates: independently of the relation between $w_1$ and $w_2$ the effective asymptotic (at $t\rightarrow\infty$) rate is smaller for transitions from the state $j$ with smaller $\nu_j$. Moreover, the difference between the effective rates increases as $t\rightarrow\infty$. Naturally, the population of the state with slower transitions approaches 1 and, correspondingly, the population of the second state decreases to zero.

Noteworthy is also the important property of the transition kinetics predicted by the ATSM. In the case $\nu_1=\nu_2$ the system relaxes to the equilibrium state that is determined by $\hat{T}_l$. For $\nu_1\neq\nu_2$, however, the limiting matrix $\hat{T}_l$ (3.3) does not represent the equilibrium state. Furthermore, the equilibrium state does not exist in this case. This fact is very important for the analysis of anomalous processes. In particular, this means that for $\nu_1\neq\nu_2$ it is impossible to introduce the conventional averages over equilibrium state such as correlation functions that imply the existence of the stationary equilibrium state.

In general, at very long times $t\gg w_{1,2}^{-1}$ the matrix $\hat{T}(t)$ monotonically approaches $\hat{T}_l$. However, according to Eq. (3.2), in some cases the nonmonotonic behavior of $T_{ij}(t)$ is also expected at intermediate times. Analysis shows (see below) that this nonmonotony appears when the additional rate parameter

$$w_0=w_1(w_1/w_2)^{\nu_2/\delta}=w_2(w_1/w_2)^{\nu_1/\delta}, \tag{3.5}$$

in which $\delta=\nu_1-\nu_2$, is small enough: $w_0\ll w_{1,2}$. It is easily seen that this relation is observed only in two cases $w_1\ll w_2,\nu_1>\nu_2$ and $w_1\gg w_2,\nu_1<\nu_2$.

### B. Transient kinetics

To demonstrate the above-mentioned peculiarities let us consider the $(1\leftrightarrow 2)$-transition kinetics over a wide range of times. Because of the conservation rule (3.1) and the symmetry of the problem in respect to the exchange the state numbers $(1\leftrightarrow 2)$ to understand the behavior of all elements $T_{ij}(t)$ it is sufficient to analyze the only one, for example, $T_{22}(t)$ whose Laplace transform

$$\widetilde{T}_{22}(\epsilon)=\left[\epsilon+\frac{\epsilon}{(\epsilon/w_2)^{\nu_2}}\frac{(\epsilon/w_1)^{\nu_1}}{1+(\epsilon/w_1)^{\nu_1}}\right]^{-1}. \tag{3.6}$$

#### *1. The limit $w_1\ll w_2$*

*a. In the case $\delta=\nu_1-\nu_2>0$*

$$\widetilde{T}_{22}(\epsilon)=[\epsilon+\epsilon(w_2/\epsilon)^{\nu_2}]^{-1}\text{at} \quad \epsilon\gtrsim w_1, \tag{3.7}$$

$$\tilde{T}_{22}(\epsilon)=[\epsilon+\epsilon(\epsilon/w_0)^{\delta}]^{-1}\text{at}\quad \epsilon<w_1, \tag{3.8}$$

where $w_0$ is defined in Eq. (3.5) ($w_0 \ll w_{1,2}$). Therefore

$$T_{22}(t)=P_2(t)=E_{\nu_2}(-(w_2 t)^{\nu_2})\quad \text{at}\quad t<1/w_1, \tag{3.9}$$

$$T_{22}(t)=1-E_{\delta}(-(w_0 t)^{\delta})\quad \text{at}\quad t>1/w_1. \tag{3.10}$$

In deriving Eq. (3.10) we applied the relation

$$E_{\nu}(x)=1-E_{-\nu}(x^{-1}) \tag{3.11}$$

that can easily be obtained using the evident formula

$$(z+xz^{1-\nu})^{-1}=z^{-1}-(z+x^{-1}z^{1+\nu})^{-1}. \tag{3.12}$$

*b. In the case* $\delta=\nu_1-\nu_2<0$

$$\tilde{T}_{22}(\epsilon)=[\epsilon+\epsilon(w_2/\epsilon)^{\nu_2}]^{-1}\text{at}\quad \epsilon \gtrsim w_2, \tag{3.13}$$

$$\tilde{T}_{22}(\epsilon)=[\epsilon+\epsilon(\epsilon/w_0)^{\delta}]^{-1}\text{at}\quad w_2 \gtrsim \epsilon \gtrsim w_1. \tag{3.14}$$

Thus at $t<1/w_1$ we get again

$$T_{22}(t)=P_2(t)=E_{\nu_2}(-(w_2 t)^{\nu_2}) \tag{3.15}$$

[see Eq. (3.9)], but at $t>1/w_1$ $T_{22}(t)\sim 1/t^{|\delta|}$ instead of $T_{22}(t)\sim 1/t^{\nu_2}$ predicted by Eq. (3.15).

### *2. The limit* $w_1 \gg w_2$

*a. In the case* $\delta=\nu_1-\nu_2>0$

$$\tilde{T}_{22}(\epsilon)=\epsilon^{-1}[1+o((w_2/w_1)^{\nu_2})] \tag{3.16}$$

and therefore

$$T_{22}(t)=1+o((w_2/w_1)^{\nu_2}). \tag{3.17}$$

*b. In the case* $\delta=\nu_1-\nu_2<0$

$$\tilde{T}_{22}(\epsilon)\approx\epsilon^{-1}\quad \text{at}\quad \epsilon\gtrsim w_2, \tag{3.18}$$

$$\tilde{T}_{22}(\epsilon)\approx[\epsilon+\epsilon(\epsilon/w_0)^{\delta}]^{-1}\quad \text{at}\quad w_2 \gg \epsilon, \tag{3.19}$$

where $w_0=w_2(w_2/w_1)^{\nu_2/|\delta|}\ll w_2$. This means that over a wide range of times with high accuracy

$$T_{22}(t)=E_{|\delta|}(-(w_0 t)^{|\delta|}) \tag{3.20}$$

with the asymptotic dependence $T_{22}(t)\sim 1/t^{|\delta|}$.

### *3. Qualitative features*

The behavior of $T_{22}(t)$ in all cases considered above are schematically shown in Fig. 1. It is seen that the nonmonotonic time dependence $T_{22}(t)$ is observed both for $w_1 \gg w_2$ and $w_1 \ll w_2$ (when $\delta>0$). In the first case the amplitude of the nonmonotonic part of $T_{22}(t)$ is very small in the whole region of time. In the second case, however, the nonmonotonic behavior of $T_{22}(t)$ is markedly pronounced: $T_{22}(t)$ first drops almost to 0 and then increases back to 1. This strange behavior results from the anomalous long-tailed time dependence of $W_j(t)$. Recall that all conventional kinetic models, even non-Poissonian (with $\nu_1=\nu_2$), predict monotonic relaxation to the equilibrium.

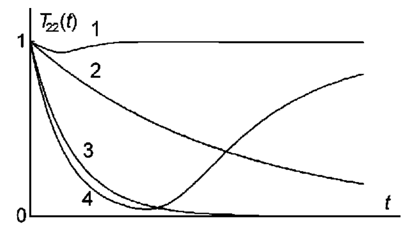


FIG. 1. Qualitative behavior of $T_{22}(t)$ for (1) $w_1 \gg w_2$, $\nu_1>\nu_2$; (2) $w_1 \gg w_2, \nu_1<\nu_2$; (3) $w_1 \ll w_2, \nu_1<\nu_2$, and (4) $w_1 \ll w_2, \nu_1>\nu_2$.

## IV. GENERAL FORMULA FOR THE MEAN SQUARE DISPLACEMENT

The peculiarities of the $(1\leftrightarrow 2)$ transition kinetics quite pronouncedly manifest themselves in the mobility of the probe particle when $\hat{L}_{1,2}\neq 0$. To illustrate these manifestations, for definiteness, in what follows we will consider the case

$$\hat{L}_1\neq 0 \quad \text{and} \quad \hat{L}_2=0 \tag{4.1}$$

in which the strongest anomalous effects on the mobility are expected. These effects substantially depend on the values of $w_j$ and $\nu_j$, and lead to a large variety of different forms of $T_{ij}(x,t)$ behavior. Here, for simplicity, we discuss mainly the limiting cases of large difference between the rates $w_j$.

In general, the ATSM predicts the finite value of the mean square of displacement

$$\sigma(t)\equiv\overline{\Delta x^2}(t)=\overline{x^2}(t)-\overline{x}^2(t)=\sigma_1(t)\rho_{0_1}+\sigma_2(t)\rho_{0_2}, \tag{4.2}$$

where $\rho_{0_j}$ are the components of the initial PDF vector $\rho_0$. The analysis of the time dependence $\overline{\Delta x^2}(t)$ gives valuable information on the specific features of the AD described by the ATSM. For our further analysis it is more convenient to use the first derivative $\dot{\sigma}(t)$ and its dimensionless components $D_j(t)(j=1,2)$,

$$\dot{\sigma}(t)=d(\overline{\Delta x^2})/dt \quad \text{and} \quad D_j(t)=\dot{\sigma}_j(t)/(2w_1\lambda_1^2), \tag{4.3}$$

in which $w_1\lambda_1^2=D_1^0$ is the diffusion coefficient in the state 1 [see Eq. (2.2)].

In the case of free diffusion $\overline{\Delta x^2}(t)$ can be conveniently represented in terms of the Fourier transform in the coordinate $x$: $\mathcal{T}_{ij}(k,t)=\int_{-\infty}^{\infty}dx\,\tilde{T}_{ij}(x,t)e^{ikx}$,

$$\sigma_j(t)=-\partial^2(\mathcal{T}_{1j}+\mathcal{T}_{2j})/\partial k^2|_{k=0}. \tag{4.4}$$

With the use of Eqs. (2.15) one can derive the following expressions for the Laplace transforms $\tilde{\sigma}_j(\epsilon)$:

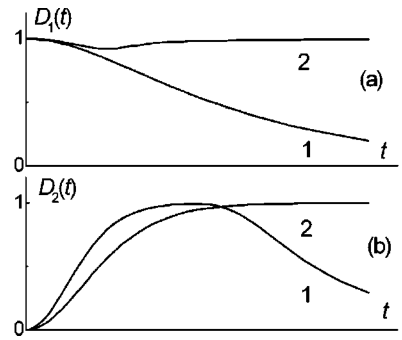


FIG. 2. Qualitative behavior of $D_1(t)$ (a) and $D_2(t)$ (b) for $w_1 \ll w_2$ as well as: $\nu_1 > \nu_2$; (1), and $\nu_1 < \nu_2$; (2).

$$\tilde{\sigma}_1(\epsilon) = \frac{1+\phi_2(\epsilon)}{\epsilon\Psi(\epsilon)} \quad \text{and} \quad \tilde{\sigma}_2(\epsilon) = \frac{1}{\epsilon\Psi(\epsilon)}, \tag{4.5}$$

in which

$$\Psi(\epsilon) = \Phi(\epsilon)/\phi_1(\epsilon) = 1 + \phi_2(\epsilon) + \phi_2(\epsilon)/\phi_1(\epsilon). \tag{4.6}$$

Formula (4.5) is very suitable for the analysis of the characteristic properties of the mean square displacement.

## V. THE BEHAVIOR OF THE MEAN SQUARE DISPLACEMENT

The time dependencies of the first derivatives of the dimensionless mean square displacements: $D_j(t) = \dot{\sigma}_j(t)/(2w_1\lambda_1^2)$, $(j=1,2)$, are schematically shown in Figs. 2 and 3 for $w_1 \ll w_2$ and $w_1 \gg w_2$, respectively.

The strongly nonmonotonic behavior of $D_j(t)$ for $w_1 \ll w_2$ and $\delta > 0$ (Fig. 2) clearly results from that of the state populations predicted by the ATSM as it is demonstrated in Sec. III. Similar nonmonotonic behavior of $D_j(t)$ is also found in the case $w_1 \gg w_2$ and $\delta < 0$ (Fig. 3). As in the former case it is caused by the nonmonotonic behavior of the corresponding kinetic curves predicted the ATSM.

Below in this section we will present simple analytical formulas for the dependencies displayed in Figs. 2 and 3.

### A. Short times $t \lesssim [\max(w_1,w_2)]^{-1}$

*a. The limit* $w_1 \ll w_2$. At $t \lesssim w_2^{-1}$ the behavior of $D_1(t)$ and $D_2(t)$ is independent of the sign of $\delta$. The times $t \lesssim w_2^{-1}$ correspond to $\epsilon \gtrsim w_2$ at which $\Psi(\epsilon) \approx 1/[1+\phi_2(\epsilon)]$ and therefore we obtain $D_j(t)$,

$$D_1(t) \approx 1, D_2(t) \approx 1 - P_2(t) = 1 - E_{\nu_2}(-(w_2 t)^{\nu_2}). \tag{5.1}$$

*b. The limit* $w_1 \gg w_2$. As in the case of $w_1 \ll w_2$, for $w_1 \gg w_2$ at short times $t \lesssim w_1^{-1}$, which correspond to $\epsilon \gtrsim w_1$ and $\Psi(\epsilon) \approx \phi_2(\epsilon)$ with $\phi_2(\epsilon) \gg 1$, the behavior of $D_1(t)$ and $D_2(t)$ does not depend on the sign of $\delta$ either,

$$D_1(t) \approx P_1(t) = E_{\nu_1}(-(w_1 t)^{\nu_1}), D_2(t) \approx (w_2 t)^{\nu_2}. \tag{5.2}$$

### B. Long times $t \gg [\min(w_1,w_2)]^{-1}$

#### 1. The limit $w_1 \ll w_2$

*a. The case* $\delta = \nu_1 - \nu_2 > 0$. In the case $\delta > 0$ the rate $w_0$, defined in Eq. (3.5), satisfies inequality $w_0 \ll w_{1,2}$ and significantly controls the long time $(t \gg w_1^{-1})$ behavior of $D_j(t)$. Both $D_1(t)$ and $D_2(t)$ are monotonically increasing functions depending only on $\delta$. General formulas yield $\Psi(\epsilon) \approx 1 + (w_0/\epsilon)^\delta$ and

$$D_1(t) \approx D_2(t) \approx E_\delta(-(w_0 t)^\delta). \tag{5.3}$$

*b. The case* $\delta < 0$. The long time $(t \gg w_1^{-1})$ behavior of $\sigma_1(t)$ and $\sigma_2(t)$ for $\delta < 0$ differs from that for $\delta > 0$ because in the case $\delta < 0$ for small $\epsilon \ll w_1$ the term $(\epsilon/w_0)^{|\delta|} \ll 1$ and thus $\Psi(\epsilon) \approx 1$. This gives

$$D_1(t) \approx D_2(t) \approx 1. \tag{5.4}$$

It is important to note that, as in the case $\delta > 0$, at long times the behavior of $D_1(t)$ and $D_2(t)$ is the same.

#### 2. The limit $w_1 \gg w_2$

*a. The case* $\delta = \nu_1 - \nu_2 > 0$. At $\epsilon \lesssim w_2$, which determine this long time $(t > w_2^{-1})$ behavior, $\Psi(\epsilon) \approx \phi_2(\epsilon)\phi_1^{-1}(\epsilon)$, i.e.,

$$D_1(t) \approx D_2(t) \approx \sin(\pi\delta)\Gamma(1-\delta)/(w_0 t)^\delta. \tag{5.5}$$

*b. The case* $\delta < 0$. In this case the rate $w_0$ is small: $w_0 \ll w_{1,2}$, and essentially determines the long time kinetics. At $\epsilon < w_2$ corresponding to $t \gg w_2^{-1}$ we have $\Psi(\epsilon) \approx 1 + \phi_2(\epsilon)/\phi_1(\epsilon)$ and therefore

$$D_1(t) \approx D_2(t) \approx 1 - E_{|\delta|}(-(w_0 t)^{|\delta|}). \tag{5.6}$$

It is worth noting that in the limit $w_1 \gg w_2$ (similarly to $w_1 \ll w_2$) the functions $D_1(t)$ and $D_2(t)$ coincide with each other at long times $t \gg w_2^{-1}$ independently of the sign of $\delta$.

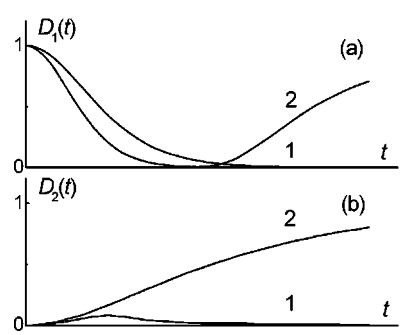


FIG. 3. Qualitative behavior of $D_1(t)$ (a) and $D_2(t)$ (b) for $w_1 \gg w_2$ as well as: $\nu_1 > \nu_2$; (1), and $\nu_1 < \nu_2$; (2).

## VI. QUALITATIVE FEATURES OF THE SPATIAL PDF

The expressions (5.1)–(5.6) help us to understand some important features of the time evolution of the spatial PDF $\rho(x,t)$.

The general analysis shows that at short times $t \lesssim [\max(w_1,w_2)]^{-1}$ the time evolution of $\rho(x,t)$ strongly depends on the initial state $\rho_0$. At long times $t\gg w_{1,2}$, however, the spatial PDF is independent of $\rho_0$ and is mainly determined by the relation between the parameters $\nu_j$, $(j=1,2)$. Here we will analyze the behavior of $\rho(x,t)$ by expressing it in terms of the evolution operator $\exp(-\hat{L}_1)t$ of the conventional diffusion in the state 1 whose properties are quite well known [17].

### A. Short times $t\lesssim[\max(w_1,w_2)]^{-1}$

#### 1. The case $w_1\ll w_2$

*a. The initial condition* $\rho_0=(1,0)^{\mathrm{T}}$. For $\rho_0=(1,0)^{\mathrm{T}}$ spatial evolution is determined by $\tilde{T}_{11}$ represented as $\tilde{T}_{11}\approx 1/\hat{\omega}_1=(\epsilon+\hat{L}_1)^{-1}$. This operator describes conventional free diffusion in the state 1: $\hat{T}_{12}(t)\approx\exp(-\hat{L}_1 t)$.

*b. The initial condition* $\rho_0=(0,1)^{\mathrm{T}}$. For $\rho_0=(0,1)^{\mathrm{T}}$ the evolution is governed by the element $\tilde{T}_{12}\approx(\epsilon+\hat{L}_1)^{-1}[1+\phi_2(\epsilon)]^{-1}$. The corresponding time-dependent operator is written as

$$\hat{T}_{12}(t)\approx\int_0^t d\tau\, e^{-\hat{L}_1\tau}W_2(t-\tau). \tag{6.1}$$

#### 2. The case $w_1\gg w_2$

*a. The initial condition* $\rho_0=(1,0)^{\mathrm{T}}$. For $\rho_0=(1,0)^{\mathrm{T}}$ spatial evolution is described by $\tilde{T}_{11}\approx\phi_1(\hat{\omega}_1)\hat{\omega}_1^{-1}[1+\phi_1(\hat{\omega}_1)]^{-1}$ and $\tilde{T}_{21}\approx\epsilon^{-1}[1+\phi_1(\hat{\omega}_1)]^{-1}$. The corresponding time-dependent operators are given by

$$\hat{T}_{11}(t)\approx e^{-\hat{L}_1 t}P_1(t)=e^{-\hat{L}_1 t}E_{\nu_1}(-(w_1 t)^{\nu_1}), \tag{6.2}$$

$$\hat{T}_{21}(t)\approx\int_0^t d\tau\, W_1(\tau)e^{-\hat{L}_1\tau} \tag{6.3}$$

*b. The initial condition* $\rho_0=(0,1)^{\mathrm{T}}$. For $\rho_0=(0,1)^{\mathrm{T}}$ the evolution at $t\lesssim w_1^{-1}$ is governed by the elements $\tilde{T}_{12}\approx\phi_1(\hat{\omega}_1)\phi_2^{-1}(\epsilon)[1+\phi_1(\hat{\omega}_1)]^{-1}\hat{\omega}_1^{-1}$ and $\tilde{T}_{22}\approx\epsilon^{-1}(1-\hat{\omega}_1\tilde{T}_{12})$, which in the time dependent form are represented as

$$\hat{T}_{12}(t)\approx\int_0^t d\tau\, W_2(t-\tau)P_1(\tau)e^{-\hat{L}_1\tau}, \tag{6.4}$$

$$\hat{T}_{22}(t)\approx P_2(t)+\int_0^t d\tau[1-P_2(t-\tau)]W_1(\tau)e^{-\hat{L}_1\tau}. \tag{6.5}$$

### B. Long times $t>\tau_m=[\min(w_0,w_1,w_2)]^{-1}$

In general, for $t\gtrsim[\min(w_1,w_2)]^{-1}$ the behavior of $T_{ij}(t)$ are fairly complicated, however, for $t\gg\tau_m=[\min(w_0,w_1,w_2)]^{-1}$ it can be obtained in analytical form quite easily.

#### 1. The case $\delta=\nu_1-\nu_2>0$

For $\delta=\nu_1-\nu_2>0$ in the long-time limit only the state 2 is strongly populated [see Eq. (3.4)], however, both states make strong contributions to the spatial evolution at $t\gg\tau_m$, $(\epsilon\ll\tau_m^{-1})$: $\tilde{T}_1(\epsilon)=\tilde{T}_{11}(\epsilon)\approx\tilde{T}_{12}(\epsilon)\approx\phi_1(\hat{\omega}_1)[\hat{\omega}_1\phi_2(\epsilon)]^{-1}$ and $\tilde{T}_2(\epsilon)=\tilde{T}_{21}(\epsilon)\approx\tilde{T}_{22}(\epsilon)\approx\epsilon^{-1}-\phi_1(\hat{\omega}_1)[\epsilon\phi_2(\epsilon)]^{-1}$ with $\hat{\omega}_1=\epsilon+\hat{L}_1$.

The corresponding time-dependent operators $\hat{T}_1(t)$ and $\delta\hat{T}_2(t)=\hat{T}_2(t)-\hat{1}$ are written as

$$\hat{T}_1(t)\sim\int_0^t d\tau\,\hat{U}_1(\tau)F_1(t-\tau), \tag{6.6}$$

$$\delta\hat{T}_2(t)\sim-\int_0^t d\tau\,\hat{U}_2(\tau)F_2(t-\tau), \tag{6.7}$$

where $\hat{U}_j(t)\sim(w_1 t)^{1-\nu_1-j}\exp(-\hat{L}_1 t)$ and $F_j(t)\sim t^{\nu_1+j-2}$. It can be shown that the long-time contributions of both $\hat{T}_1(t)$ and $\delta\hat{T}_2(t)$ to $\overline{\Delta x^2}(t)$ depend on $t$ as $t^{1-\delta}$ and must be taken into account. The prediction of Eqs. (6.6) and (6.7) for the long-time asymptotics of $\overline{\Delta x^2}(t)$ is, evidently, in agreement with the general results (5.3)–(5.6), as expected.

It is important to note that in the long time limit $t\gtrsim w_0^{-1}$ there appears the intermediate asymptotics that corresponds to the Lévy-type coordinate behavior [2,18] of the spatial PDF $\rho(x,t)$ (see below).

#### 2. The case $\delta=\nu_1-\nu_2<0$

For $\delta<0$ at long times $t>\tau_m=[\min(w_0,w_1,w_2)]^{-1}$ the system mainly populates the state 1. It is easily seen that with high accuracy $\sim w_1/w_2\ll 1$ the elements $\hat{T}_{11}(t)$ and $\hat{T}_{12}(t)$, which determine the space-time evolution of the system for $\rho_0=(1,0)^{\mathrm{T}}$ and $\rho_0=(0,1)^{\mathrm{T}}$, respectively, are given by $\hat{T}_{11}(t)\approx\hat{T}_{12}(t)\approx\exp(-\hat{L}_1 t)$. In other words, the theory predicts that in the long-time limit $t>\tau_m$ the system undergoes the conventional free diffusion in the state 1 with the diffusion coefficient $D_1^0=w_1\lambda_1^2$ (independently of $\rho_0$).

### C. The anomalous Lévy-type motion at intermediate times

The detailed analysis of the results presented above shows that in two regions of parameters of the model the dependence of $\rho(x,t)$ on $x$ is of the long-range inverse-power type, typical for Lévy flights [2,18]: (1) $\delta>0$ (independently of the relation between $w_1$ and $w_2$) at long times $t\gg\tau_m$, and (2) $w_1\gg w_2$ (independently of the relation between $\nu_1$ and $\nu_2$) for $w_1^{-1}<t\lesssim w_2^{-1}$.

The size of the areas of this behavior (in $x$ coordinate) is very large, but is different in these two cases: $\sqrt{D_1 t}>x>\sqrt{D_1/w_0}$ and $\sqrt{D_1/\min(w_0,w_2)}\gtrsim x>\sqrt{D_1/w_1}$ in the cases (1) and (2), respectively.

The anomalous Lévy-type long-range $x$ dependence of $\rho(x,t)$ occurs because in the two mentioned cases for $\epsilon$, that govern the behavior of $\rho(x,t)$, one gets $\epsilon<\|\hat{L}_1\|$, $\phi_1(\epsilon)<\phi_2(\epsilon)$, but $\|\phi_1(\hat{\omega}_1)\|\approx\|\phi_1(\hat{L}_1)\|\sim\phi_2(\epsilon)$. Taking into account these inequalities we arrive at the approximate expressions for $\widetilde{T}_{22}$ and $\widetilde{T}_{21}$ that determine the evolution of the system in both cases

$$\widetilde{T}_{22}=\frac{\phi_2(\epsilon)\epsilon^{-1}}{\phi_2(\epsilon)+\hat{\mathcal{L}}} \quad \text{and} \quad \widetilde{T}_{21}=\widetilde{T}_{22}\frac{1}{1+\phi_1(\hat{L}_1)}, \tag{6.8}$$

where

$$\hat{\mathcal{L}}=\frac{\phi_1(\hat{L}_1)}{1+\phi_1(\hat{L}_1)}=\int_0^\infty d\tau(1-e^{-\hat{L}_1\tau})W_1(\tau). \tag{6.9}$$

It should be noted that in the case $w_1 \ll w_2, \delta>0$ the expressions (6.8) are valid only for $\|\hat{L}_1\|/w_1 \ll 1$, i.e., for $\|\phi_1(\hat{L}_1)\| \ll 1$. Thus in this case $\hat{\mathcal{L}} \approx \phi_1(\hat{L}_1)$ and $\widetilde{T}_{22} \approx \widetilde{T}_{21}$.

The expression (6.8) is the Green's function of the non-Markovian equation

$$\dot{G}_{2j}=-\int_0^t d\tau\, \gamma(t-\tau)\hat{\mathcal{L}}G_{2j}, (j=1,2) \tag{6.10}$$

in which

$$\gamma(t)=\frac{1}{2\pi i}\int_{-i\infty}^{i\infty} d\epsilon \frac{\epsilon}{\phi_2(\epsilon)}e^{\epsilon t} \tag{6.11}$$

is a slowly decreasing memory function: $\gamma(t) \sim 1/t^{2-\nu_2}$. Some caution is required in the treatment of the integral in Eq. (6.11). To avoid the analysis of divergences it should be considered as a first derivative of $\Gamma(t)=-\int_t^\infty d\tau\, \gamma(\tau) \sim 1/t^{1-\nu_2}$.

The physical meaning of two operators $\hat{\mathcal{L}}$ and $[1+\phi_1(\hat{L}_1)]^{-1}$ in Eqs. (6.8) is simple: $\hat{\mathcal{L}}$ is the operator of diffusive jumps $1-\exp(-\hat{L}_1 t)$ (in the state 1) averaged over the PDF $W_1(t)$ [see Eq. (6.9)], while the term $[1+\phi_1(\hat{L}_1)]^{-1}=\int_0^\infty d\tau \exp(-\hat{L}_1\tau)W_1(\tau)$ in the expression for $\widetilde{T}_{21}$ represents the distribution of particles that appeared in the state 2 as a result of transitions from the state 1 at short times.

The inverse power-type dependence of $G_{2j}(x,t)$ on $x$: $G_{2j}(x,t) \sim x^{-(1+2\nu_1)}$, typical for the Lévy-type processes [10,18] (with $\overline{\Delta x^2}=\infty$), results from the power-type dependence $\phi_1(\hat{L}_1)=(\hat{L}_1/w_1)^{\nu_1}$ with $\nu_1<1$ . This fact can be clearly demonstrated using the expression for the Fourier transform $\widetilde{G}_{2j}(k,t)$ of $G_{2j}(x,t)$,

$$\widetilde{G}_{2j}(k,t)=\{\epsilon+[\epsilon/\phi_2(\epsilon)]\widetilde{\mathcal{L}}(k)\}^{-1}, \tag{6.12}$$

whose behavior at small $k$ is nonanalytical: $\widetilde{G}_{2j}(k,t) \sim \widetilde{\mathcal{L}}(k) \sim k^{2\nu_1}$. The finiteness of the exact value $\overline{\Delta x^2}$ found in Sec. V testifies that in the two considered cases it is determined by large $x$ outside the region of Lévy-type behavior, where $G_{2j}(x,t)$ rapidly decreases with the increase of $x$.

Thus, the obtained results show that, (1) the anomalous coordinate behavior of $\rho(x,t)$ is governed by the PDF $W_1(t)$: for $\nu_1<1$ the motion is of Lévy type (with $\overline{\Delta x^2}=\infty$), while for $\nu_1=1$ it represents the conventional diffusion with finite $\overline{\Delta x^2}$; (2) the anomalous properties of the time evolution, for example, the anomalous time dependence $\overline{\Delta x^2}(t) \sim t^{\nu_2}$ (for $\nu_1=1$), are controlled by the PDF $W_2(t)$.

## VII. TRANSITIONS IN THE DOUBLE-WELL POTENTIAL

The peculiarities predicted by the ATSM significantly manifest themselves not only in the free AD but also in AD-assisted activated rate processes, for example, in the kinetics of transitions in the double-well potential.

### A. General expressions

For simplicity, let us consider the double-well potential $u(x)$ is symmetric, and assume that the wells (at $x>0$ and $x<0$), denoted hereafter as $(+)$ and $(-)$, are separated by a high barrier of the inverse parabola shape, located at $x=0$ with the activation energy $E_a \gg k_B T$. The state 2 is taken to be immobile in accordance with Eq. (4.1). We also assume, for definiteness, that initially the particle is located in the well $(+)$.

In the considered high barrier limit, $E_a \gg k_B T$, in the spectrum of the operator $\hat{L}_1$ the eigenvalue

$$\epsilon_1=w_t \approx [(\lambda_1^2 w_1)(\omega_b\omega_\pm)/(\pi\overline{v^2})]e^{-E_a/k_BT}, \tag{7.1}$$

corresponding to the first "excited" state [17] that is responsible for the kinetics of $(+\leftrightarrow-)$ transitions, is much smaller than all others, describing equilibration within the wells: $\epsilon_1 \ll \epsilon_j$ $(j \geq 2)$. In Eq. (7.1) $\omega_b$ and $\omega_\pm$ are frequencies of the potential $u(x)$ at a top of the barrier and near the bottom of the wells, respectively, and $\overline{v^2}=2k_BT/m$ is the average thermal velocity of the particle.

After the short time $\tau_r \sim 1/\epsilon_{j\geq 2}$ of equilibration in the well $(+)$ the transition kinetics is described by the two eigenvalues

$$\epsilon_0 \equiv \epsilon_s=0 \quad \text{and} \quad \epsilon_a \equiv \epsilon_1, \tag{7.2}$$

and the corresponding eigenfunctions [17]

$$\phi_s(x)=\frac{e^{-u(x)}}{2Z} \text{and} \quad \phi_a(x) \approx A_a\phi_s(x)\int_0^x dz\, e^{u(z)}, \tag{7.3}$$

in which $Z=\int_{w_\pm}dx \exp[-u(x)]$ is the partition function of particles in the wells (whose areas are denoted as $w_\pm$) and $A_a=\sqrt{2m\omega_b^2/\pi}$ is the normalization constant in which $m$ is the mass of the particle. The functions $\phi_s(x)$ and $\phi_a(x)$ can also be represented in the form

$$\phi_s=\frac{1}{2}(\phi_+ + \phi_-) \quad \text{and} \quad \phi_a \approx \frac{1}{2}(\phi_+ - \phi_-), \tag{7.4}$$

where

$$\phi_\pm(x) \approx \phi_s(x)\theta(\pm x), \tag{7.5}$$

with $\theta(x)$ being the Heaviside step function, are the quasi-equilibrium spatial PDF's in the corresponding wells.

Initial population of the well $(+)$ (independently of the TSM state $j$) means that $\rho_0=\phi_+$.

The kinetics of $(+\leftrightarrow-)$ transitions is determined by the matrix $\hat{T}(t)$ [see Eqs. (2.15)]. Using the bra-ket notation the representation of $\hat{T}(t)$ in the $(\phi_s,\phi_a)$ basis can be written as

$$\hat{T}\equiv\hat{T}_r=|\phi_s\rangle\langle\phi_s|\hat{T}^s+|\phi_a\rangle\langle\phi_a|\hat{T}^a, \tag{7.6}$$

where

$$\langle\phi_s|=1,\langle\phi_a|\approx\mathrm{sgn}(x) \tag{7.7}$$

(i.e. $\langle\phi_\pm|\approx 1$), and

$$\hat{T}^s=\hat{T}_{\hat{L}_1=0} \quad \text{and} \quad \hat{T}^a=\hat{T}_{\hat{L}_1=w_t}. \tag{7.8}$$

The populations of $(\pm)$ wells are thus given by

$$\hat{n}^{\pm}(t)=\int_{w_\pm}dx\,\rho(x|t) \tag{7.9}$$

$$=\langle\phi_\pm|\hat{T}_r(t)|\rho_0\rangle=\frac{1}{2}[\hat{T}^s(t)\pm\hat{T}^a(t)], \tag{7.10}$$

where $w_\pm$ denote the integration regions within the wells. These populations are, actually, $(2\times2)$ matrices in the space of ATSM states $j$. Therefore the total populations

$$N_j^{\pm}(t)=n_{1j}^{\pm}(t)+n_{2j}^{\pm}(t)=\frac{1}{2}[1\pm Q_j(t)], \tag{7.11}$$

where $Q_j(t)=T_{1j}^a(t)+T_{2j}^a(t)$. In Eq. (7.11) we took into account the conservation rule $T_{1j}^s+T_{2j}^s=1$ [see Eq. (3.1)].

Formula (7.11) is the main result of this section. It expresses the kinetics of $(+\leftrightarrow-)$ transitions, i.e., the time-dependent populations $N_j^{\pm}(t)$, in terms of the matrix elements of $\hat{T}(t)$ that can be obtained by solving Eqs. (2.9) and (2.10). In the ATSM considered these matrix elements are given by Eqs. (2.15).

It is also worth noting that because of the population conservation rule $N_j^+(t)+N_j^-(t)=1$ it is sufficient to analyze only one of functions $N_2^{\pm}(t)$, for example, the transition probability $N_j^-(t)$.

In general, the analysis of the transition kinetics is similar to that carried out in Sec. VI for the free AD. As in the case of the free AD, at short times the kinetics strongly depends on the initial ATSM state. At the same time the characteristic properties of long-time asymptotics of the transition kinetics is independent of the initial state and mainly determined by the parameters $\nu_j$.

The kinetics of $(+\leftrightarrow-)$ transitions, evidently, results from the superposition of strongly nonexponential anomalous transitions between ATSM states and exponential transitions between the wells of the potential. The specific features of this kinetics can straightforwardly be obtained with the use Eq. (7.11) and formulas derived in Sec. VI. One should only take into account that the expressions for $T_{ij}^a(t)$ are given by the corresponding formulas of Sec. VI with $\hat{L}_1=w_t$.

To illustrate the specific features of $(+\leftrightarrow-)$-transition kinetics let us consider the particular case $w_1\gg w_2$, as an example. In this case the largest variety of these specific features is expected. Similar analysis can easily be done in the opposite limit $w_1\ll w_2$ as well.

### B. The transition kinetics for $w_1\gg w_2$

According to the general results of Sec. VI at short times the specific features of transition kinetics are expected to substantially depend on the initial state $j$ of the ATSM, while at long time they are mainly determined by the relation between $\nu_1$ and $\nu_2$. Therefore, similar to the case of the free AD we will analyze the short and long-time limits separately. In reality, however, instead of the time limits, we will consider different values of the rate $w_t$ of conventional diffusion-assisted transitions between wells in the state 1 [see Eq. (7.2)] because this is just the rate $w_t$ that determines the main time domain $(t\sim w_t^{-1})$ of the transition kinetic dependencies $N_{1,2}^{\pm}(t)$.

#### 1. The kinetics for $w_t\gtrsim w_1$ (short times)

For large $w_t\gtrsim w_1$, i.e., for short times, the specific features of the transition kinetics can easily be understood with the use of general expression derived in Sec. VI A 2.

*a. The initial state* 1. $\rho_0=(1,0)^{\mathrm{T}}$. For $\rho_0=(1,0)^{\mathrm{T}}$ one gets from Eqs. (6.4) and (6.5) (with the replacement $\hat{L}_1$ by $w_t$)

$$N_1^-(t)=\tfrac{1}{2}w_t\int_0^t d\tau\,P_1(\tau)e^{-w_t\tau}. \tag{7.12}$$

*b. The initial state* 2. $\rho_0=(0,1)^{\mathrm{T}}$. For $\rho_0=(0,1)^{\mathrm{T}}$ Eqs. (6.4) and (6.5) yield (with the same replacement $\hat{L}_1$ by $w_t$)

$$N_2^-(t)=\int_0^t d\tau\,W_2(t-\tau)N_1^-(\tau). \tag{7.13}$$

#### 2. The kinetics for $w_1>w_t\gtrsim w_2$ (intermediate times)

In the wide region of relatively small values of $w_t$ $(w_1>w_t\gtrsim w_2)$ and corresponding times $w_2^{-1}\gtrsim t>w_1^{-1}$ the transition kinetics $N_j^{\pm}(t)$ is obtained in a simple and quite universal analytical form, i.e., independent of the initial condition $\rho_0$ and the relative values of $\nu_1$ and $\nu_2$ (the sign of $\delta=\nu_1-\nu_2$). However, the region of $w_t$ values, in which this kinetics is valid, depends on the sign of $\delta$. For both signs this region can roughly be represented as $w_1>w_t\gtrsim w_2$, but, as the detailed analysis shows, the low boundary of the region is, actually, lower than $w_2$ and somewhat different for positive and negative $\delta$ (see below).

The general formulas (2.15) show that at times $w_2^{-1}\gtrsim t>w_1^{-1}$ the kinetics is determined by the corresponding Laplace transform at $\epsilon\lesssim w_t$. In this region of $\epsilon$ we have the following relations: $\tilde{T}_{21}^a(\epsilon)\gg\tilde{T}_{11}^a(\epsilon)$ and $\tilde{T}_{22}^a(\epsilon)\gg\tilde{T}_{12}^a(\epsilon)$. This means that for the initial conditions $\rho_0=(1,0)^{\mathrm{T}}$ and $\rho_0$

$=(0,1)^{\mathrm{T}}$ the kinetics of $(+\leftrightarrow-)$ transitions is determined by the elements $\tilde{T}^a_{21}(\epsilon)$ and $\tilde{T}^a_{22}(\epsilon)$, respectively, which are written as

$$\tilde{T}^a_{12}(\epsilon)[1+\phi_1(w_t)]\approx\tilde{T}^a_{22}(\epsilon)\approx[\epsilon+\xi\epsilon/\phi_2(\epsilon)]^{-1}, \tag{7.14}$$

where

$$\xi=\phi_1(w_t)/[1+\phi_1(w_t)]. \tag{7.15}$$

The extra term $1/[1+\phi_1(w_t)]$ in the expression for $\tilde{T}^a_{12}$ in Eq. (7.14) describes the decrease of the amplitude of the kinetic function (without changing the shape) due to fast initial transitions during the time period $t\lesssim w_1^{-1}$.

Noteworthy is that in the most interesting high barrier limit the relation $w_t\ll w_1$ is quite realistic and therefore $\tilde{T}^a_{12}\approx\tilde{T}^a_{22}$ and $\xi\approx\phi_1(w_t)=(w_t/w_1)^{\nu_1}\ll 1$.

The inverse Laplace transformation of $\tilde{T}^a_{12}(\epsilon)$ and $\tilde{T}^a_{22}(\epsilon)$ gives for the kinetics

$$N_1^-(t)\approx N_2^-(t)\approx\frac{1}{2}\{1-E_{\nu_2}(-\xi(w_2t)^{\nu_2})\}. \tag{7.16}$$

Formula (7.16) predicts the population $N_2^-(t)$ of the well $(-)$ monotonically increasing with the increase of $t$ [with $N_2^-(0)=0$] and slowly approaching the value $N_2^-(\infty)=\frac{1}{2}$: $\frac{1}{2}-N_2^-(t)\sim t^{-\nu_2}$.

In the end it is worth adding some comments on the region of validity of the expression (7.16), i.e., actually, of the relation $\phi_1(\epsilon+w_t)\approx\phi_1(w_t)$ (i.e., $\epsilon<w_t$) applied to derive formula (7.14). The region of validity of this relation depends on the sign of $\delta$.

*a. The case* $\delta=\nu_1-\nu_2>0$. For $\delta>0$ the time evolution of the corresponding time-dependent elements $T^a_{12}(t)$ and $T^a_{22}(t)$ is mainly determined by $\epsilon\sim w_2(w_t/w_1)^{\nu_1/\nu_2}=w_t(w_2/w_1)(w_t/w_1)^{\nu_1/\nu_2-1}\ll w_t$ and, thus, with high accuracy we can put $\phi_1(\epsilon+w_t)\approx\phi_1(w_t)$ for any values of $w_t<w_1$. This means that for $\delta>0$ the simple analytical formula (7.16) is valid over a very wide range of transition rates $w_t\ll w_1$ and, correspondingly, for any times $t>w_1^{-1}$.

*b. The case* $\delta<0$. In this case $w_0\ll w_{1,2}$ and the kinetics significantly depends on the relation between the transition rate $w_t$ and $w_0$. In particular, there appears the low boundary of validity region for the anomalous kinetics (7.16) given by inequality $w_t\gtrsim w_0$ (but $w_t<w_1$). This estimation results from the above mentioned condition $\epsilon\sim w_2(w_t/w_1)^{\nu_1/\nu_2}<w_t$. Thus, for $\delta<0$ the region of validity of Eq. (7.16) is $w_1\gg w_t>w_0$.

### *3. The kinetics for* $\delta<0$ *and* $w_t<w_0$ *(long times)*

For $\delta<0$ [unlike the case $\delta>0$, when Eq. (7.16) is valid at any small $w_t$] the specific features of the kinetics strongly change as $w_t$ decreases from $w_t>w_0$ to $w_t<w_0$ (recall that for $\delta<0$ one gets $w_0\ll w_{1,2}$). In the limit $w_t<w_0$ the main time domain of the kinetics is $t\gtrsim w_0^{-1}$. The kinetics itself is independent of the initial condition $\rho_0$ and significantly different from that for $w_t\gtrsim w_0$. The fact is that in the region of $\epsilon\lesssim w_0$ corresponding to the times $t\gtrsim w_0^{-1}$

$$\tilde{T}_{21}(\epsilon)\approx\tilde{T}_{22}(\epsilon)\approx\frac{\phi_2(\epsilon)}{\epsilon\phi_1(\epsilon+w_t)}, \tag{7.17}$$

$$\tilde{T}_{11}(\epsilon)\approx\tilde{T}_{12}(\epsilon)\approx\frac{1}{\epsilon+w_t}\left[1-\frac{\phi_2(\epsilon)}{\phi_1(\epsilon+w_t)}\right], \tag{7.18}$$

and therefore $Q_j(t)=T^a_{1j}(t)+T^a_{2j}(t)$ is represented as

$$Q_j=\exp(-w_tt)+q_j(t), \tag{7.19}$$

where $q_j(t)$ are the functions of small absolute value ($q_j\ll 1$), independent of $j$ and, of inverse power-type form.

The behavior of $q_j(t)$ can be understood by considering, for example, $T_2(t)=T_{21}(t)\approx T_{22}(t)$. The inverse Laplace transform of the expression (7.17) yields

$$T_2(t)\sim\frac{1}{(w_0t)^{|\delta|}}\int_0^1 dx\,x^{\nu_1-1}(1-x)^{-\nu_2}e^{-(w_tt)x}. \tag{7.20}$$

For $w_tt\ll 1$ and $w_tt\gg 1$ one gets $T_2(t)\sim(w_0t)^{-|\delta|}$ and $T_2(t)\sim(w_0/w_1)^{\nu_1}(w_0t)^{-\nu_2}$, respectively. Similar evaluation predicts the same inverse power type behavior of the function $\delta T_1(t)=e^{-w_tt}-T_{11}(t)\approx e^{-w_tt}-T_{12}(t)$. Thus the transition kinetics is given by

$$N_1^-(t)\approx N_2^-(t)\approx\tfrac{1}{2}[1-e^{-w_tt}-q(t)], \tag{7.21}$$

where $q(t)\approx q_1(t)\approx q_2(t)$ and

$$q(t)\sim(w_0t)^{-|\delta|}\quad\text{for}\quad w_{1,2}^{-1}\ll t\ll w_t^{-1}, \tag{7.22}$$

$$q(t)\sim(w_0t)^{-\nu_2}\quad\text{for}\quad t\gg w_t^{-1}. \tag{7.23}$$

Formula (7.21) shows that for small $w_t<w_0$ initially the transition kinetics is exponential, but at long times when $e^{-w_tt}<q(t)$ the exponential kinetics is changed by the anomalous inverse power-type one (7.23). The intermediate asymptotics (7.22) does not seem to be distinguishable against a background of the main exponential part at $t\sim w_t^{-1}$.

## VIII. DISCUSSION

In this work we thoroughly analyzed the ATSM for AD. The TSM assumes that the probe particle undergoes conventional diffusion in two states, denoted as 1 and 2, which differ in the value of the diffusion coefficient. The motion is modulated by the stochastic transitions between these two states. The discussed anomalous variant of the TSM implies the long-tailed statistics of stochastic $(1\leftrightarrow 2)$ transitions. The effect of these transitions on the AD is described within the CTRW theory.

In our analysis we have used simple approximation (2.6) and (2.7) for the PDF's $W_j(t)$, though the most general results obtained are fairly universal and insensitive to the behavior of the PDF's at small times. We also restricted ourselves to the particular case of the model, in which one state, state 2, is immobile (the diffusion coefficient $D_2^0=0$), and the strongest anomalous effects are expected. Although, it should be noted that these effects, evidently, persist for quite long time in the case $D_2^0\neq 0$ as well, if $D_2^0\ll D_1^0$.

The characteristic properties of the AD has been discussed very actively last years. The large number of different models of the AD have been proposed in literature [2] though they usually analyze the asymptotic (at $t\to\infty$) properties of diffusion. The proposed ATSM enables one to describe selfconsistently the processes over a wide region of times from $t=0$ to $t\to\infty$. This means that the model proposes the possibility to describe not only asymptotic properties (at $t\to\infty$) but the transient processes at finite times as well. The ATSM also allows for the rigorous analysis of the subtle details of the crossover from different regimes of evolution. It gives a new insight into the applicability of various approximate approaches proposed in literature, for example, usually applied approaches based on the one-state CTRW [2].

The majority of the above mentioned works discuss only free diffusion, because of the complexity of the problems including interaction potential. This has been demonstrated in some recent works studied the AD in the presence of linear potential and parabolic well [2,14,19]. The kinetics of AD-assisted escaping from the well has also been considered, but with the use qualitative scaling arguments in the theory based on fractional diffusion equation [2]. Within the proposed ATSM we have analyzed not only the free AD case but also the AD-assisted transitions in the double-well potential, as an example of processes in the presence of interaction potential. It is found that the specific features of the kinetics of anomalous transitions between the states of the ATSM strongly manifest themselves in transitions in the double-well potential. Below some important manifestations are briefly discussed.

### A. Free diffusion

The results of Sec. V and VI show that the ATSM predicts very large variety of types of anomalous diffusion, depending on the relation between the rates $w_1$ and $w_2$, and the exponents $\nu_1$ and $\nu_2$. The specific features of the AD predicted by the ATSM turn out to be closely related to those of the kinetics of $(1\leftrightarrow 2)$ transitions (see Sec. II). Generally speaking the free AD, which in our work is characterized by the time-dependent effective diffusion coefficients $D_j(t)$, $(j=1,2)$ [see Eq. (4.3)], is determined by the population of the mobile state 1, i.e., $D_j(t)$ increase as the population of this state is increased and vice versa.

*a. Anomalous diffusion at short times.* In the short-time limit $t\lesssim[\max(w_1,w_2)]^{-1}$ the value of the effective diffusion coefficients $D_j(t)$ strongly depend on the initial condition $\rho_0$, i.e., on ATSM state *j*, as it is shown in Sec. V and VI.

(1) For the mobile initial state (1) $[\rho_0=(1,0)^{\mathrm{T}}]$ the motion is either the conventional diffusion in the state 1 (for $w_1\ll w_2$) or the subdiffusion with decreasing effective diffusion coefficient $D_1(t)$, which follows the $(1\to 2)$-transitions kinetics: $D_1(t)\sim 1/(w_1 t)^{\nu_1}$ (for $w_1\gg w_2$).

(2) For the immobile initial state (2) $[\rho_0=(0,1)^{\mathrm{T}}]$ the diffusion is anomalous both for $w_1\ll w_2$ and for $w_1\gg w_2$ and can be thought as superdiffusion with the increasing diffusion coefficient $D_2(t)$. The increase is controlled either by the rate $w_2$, resulting in a relatively fast saturation (for $w_1\ll w_2$), or by the rate $w_0\ll w_{1,2}$ that describes slow increase of $D_2(t)$ without saturation.

*b. Anomalous diffusion at long times.* Most pronouncedly anomalous properties of the AD manifest themselves in the long time limit $t\gg[\min(w_1,w_2)]^{-1}$. Moreover, these properties are independent of the initial condition $\rho_0$ and mainly determined by the sign of $\delta=\nu_1-\nu_2$. Some details of the asymptotic behavior, however, depend on the relation between $w_1$ and $w_2$ as well.

(1) For $\delta>0$ the effective diffusion coefficients $D_j(t)$ are the slowly decreasing functions of time: $D_1(t)\approx D_2(t)\sim(w_0 t)^{-\delta}$, corresponding to subdiffusion. The dependence of the exponent of this function on $\delta$ shows that in this limit the kinetics results from the interplay of transitions between states 1 and 2.

(2) For $\delta<0$ the long time asymptotic behavior of the system is determined by the conventional diffusion in the mobile state 1 mainly populated at long times in this case. Noteworthy is, however, that for $w_1\gg w_2$ this limit is achieved only at very long times $t\gg w_0^{-1}$. At shorter times $t\lesssim w_0^{-1}$ the diffusion coefficients $D_1(t)\approx D_2(t)\sim(w_0 t)^{|\delta|}$, representing superdiffusion over a wide range of times.

*c. The anomalous Lévy-type coordinate behavior.* In Sec. VI C we have described the interesting slow inverse-power coordinate behavior of the PDF $\rho(x,t)$ typical for so called Lévy-type stochastic processes [18]. It is important to emphasize that this anomalous behavior is localized in space though the corresponding coordinate region can be very large. Besides, in some cases the region size grows in time. Because of the localization this behavior does not manifest itself in the divergence of $\overline{\Delta x^2}(t)$, which is always finite (see Sec. V) and determined in this case by the coordinates outside the region of anomalous behavior. The results obtained show that the Lévy-type behavior of $\rho(x,t)$ can be reproduced without real flights using the conventional diffusion-like processes whose diffusion coefficient, however, is modulated by the anomalous process with the long-tailed waiting time PDF [for example, the PDF of the form (2.5)]. Some similar ideas have recently been proposed in Refs. [20,21] within the one state CTRW approach.

### B. The transitions in the double-well potential

In our work, for brevity, we considered only the case $w_1\gg w_2$ in which the largest variety of types of kinetics is expected. The opposite case $w_1\ll w_2$ can be treated quite similarly.

#### 1. The short-time transition kinetics

At short times $t\lesssim w_1^{-1}$ the kinetics of $(+\leftrightarrow-)$ transitions $N_j^-(t)$, predicted by the ATSM, is quite simple and can easily be understood within the conventional terms as in the case of free diffusion. In accordance with Eq. (7.12), for the initial state $\rho_0=(1,0)^{\mathrm{T}}$ the kinetics is determined by the interplay of two processes: the diffusion-assisted transition over a barrier in the state 1 with the rate $w_t$ and transitions to the immobile state 2. For $\rho_0=(0,1)^{\mathrm{T}}$, however, the process consists of two stages: the transition from the state 2 to the state 1 represented by the term $W_2(t-\tau)$ and the subsequent transitions over a barrier described by the function $N_1^-(\tau)$ [see Eq. (7.13)]. The only difference of the short time anomalous kinetics from the conventional one is in its nonanalytical dependence on the parameters of the model and time.

### 2. The long-time transition kinetics

The anomalous long time transition kinetics, observed for relatively small $w_t \ll w_1$, is independent of the initial state $\rho_0$ and substantially differs from the conventional one.

(1) In general, this kinetics is strongly non-exponential over a wide region of time, as it is demonstrated by Eqs. (7.16) and (7.19). Only in the particular case of $\delta<0$ and very small $w_t<w_0$ the initial part of the kinetics appears to be exponential.

Similar to the case of the free AD, the most important specific features of the kinetics of $(+\leftrightarrow-)$ transitions can qualitatively be understood by taking into account that they are closely related to those of the kinetics of $(1\leftrightarrow 2)$ transitions in the ATSM. For example, the nonexponential kinetics (7.16) is a clear manifestation of the very similar kinetics of $(1\leftrightarrow 2)$ transitions at corresponding times. The exponential kinetics found for $\delta<0$ at not very long times and small $w_t$ results from the high population of the diffusive state 1 at these times, predicted by the ATSM. The universal long time asymptotic behavior $N_j^-(t)-\frac{1}{2}\sim t^{-\nu_2}$, which follows from Eqs. (7.16) and (7.19), can also be considered as the effect of anomalous $(1\leftrightarrow 2)$ transitions that control the $N_j^-(t)$ at long times.

(2) According to Eq. (7.16) the anomalous kinetics is characterized by the transition rate

$$w_c \approx w_2 \xi^{1/\nu_2} \sim w_t^{\nu_1/\nu_2} \sim \exp[-E_e/(k_B T)], \qquad (8.1)$$

where $E_e=(\nu_1/\nu_2)E_a$ is the effective activation energy. In principle, the energy $E_e$ can significantly differ from $E_a$ if $\nu_1 \gg \nu_2$ or $\nu_1 \ll \nu_2$. This is the important effect of the AD on the activated rate processes.

(3) Notice that formula (7.16) can also be derived with the use of the non-Markovan Eq. (6.10). This gives some additional insight into the physical meaning of both the kinetics (7.16) and Eq. (6.10). For the particular case $\nu_1=1$ (which implies $\delta=1-\nu_2>0$) formula similar to Eq. (7.16) has recently been obtained in Ref. [7], though at somewhat more qualitative level and without the analysis of the applicability region.

## IX. CONCLUSIONS

This paper concerns detailed analysis of the ATSM for anomalous diffusion and diffusion-assisted transitions in a double well potential. The model assumes that the probe particle can be in two states, undergoing conventional diffusion in both states but with different diffusion coefficients $D_1^0$ and $D_2^0$. The specific features of anomalous diffusion result from transitions between these states described by the long-tailed waiting time PDF's $W_{1,2}(t)$.

The analysis shows that the ATSM provides new insight into the problem of formation of the AD and AD-assisted transitions and can be considered as the additional tool for analysis of anomalous transport. It allows one to investigate not only asymptotic (at $t\to\infty$) properties of the process but also the transient phenomena at the short and intermediate time regions that are determined by the characteristic rates $w_1$ and $w_2$ of the change of $W_1(t)$ and $W_2(t)$, respectively. The short time (at $t<[\max(w_1,w_2)]^{-1}$) properties of the AD are not universal and strongly depend on the initial state of the ATSM (given by $\rho_0$). At intermediate times, $[\max(w_1,w_2)]^{-1} \gg t \gtrsim [\min(w_1,w_2)]^{-1}$, however, the properties are independent of the initial ATSM state. It is important to note that for some relation between the parameters of the ATSM at intermediate times the anomalous properties can manifest themselves in the Lévy-type long-range coordinate behavior of the distribution $\rho(x,t)$ in the large region of coordinates. The long time ($t \gg [\min(w_0,w_1,w_2)]^{-1}$) specific features the free AD are mainly determined by the exponents $\nu_j$ in the asymptotic dependencies $W_j(t)\sim 1/t^{\nu_j}$, $(j=1,2)$. At these times, depending on the sign of $\delta=\nu_1-\nu_2$, the effective diffusion coefficients $D_j(t)$ are either independent of $t$, $D_j(t)\approx D_1^0$ (for $\delta<0$), or slowly decrease with the increase of time, $D_j(t)\sim 1/t^{\delta}$ (for $\delta>0$).

The ATSM discussed in this work can, in principle, be generalized to include larger number of states and used for the analysis fairly complicated processes. The nonmonotonic $(1\leftrightarrow 2)$-transition kinetics predicted by the ATSM leads to a very nontrivial kinetic behavior of multistate systems. The investigation of this kind of processes is now in progress.

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