First-passage behavior of the random-barrier model

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The previously proposed transport equation for the random-barrier model, which is the diffusion equation with resetting to positions visited in the past, is used here to calculate the first-passage times. The results obtained are compared with those obtained using the normal diffusion equation with an effective diffusion coefficient. It is shown that, under certain conditions, the equation with the effective diffusion coefficient can greatly overestimate the time of the first passage. In particular, the rate constant of a bimolecular diffusion-controlled reaction calculated from this equation can be significantly lower than the actual rate. This result can serve as one of the possible explanations for the high rates of diffusion-controlled reactions observed in an experiment.

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I. INTRODUCTION

The time it takes for a random walker to reach a target point is called the first-passage time (FPT). FPTs play an important role in many physical, chemical, and biological processes [1–5]. To date, methods have been developed for finding FPTs and determining their properties. However, the existing methods are applicable only for Markovian and some special types of non-Markovian processes [1,3,6–9].

Non-Markovian behavior of stochastic processes usually takes place in complex disordered environments. The microscopic mechanisms responsible for non-Markovianity are varied. One of the widespread mechanisms is static disorder [10].

Most of the theoretical models describing transport in media with static disorder use random walks on an ordered lattice, introducing disorder into the rates of transitions between lattice sites. Usually only transitions between nearest neighbors are considered. The two prototypical models are the random-barrier model and the random-trap model [10–12]. In the random-barrier model, the rates of transitions between neighboring sites w_{ij} and w_{ji} are symmetric, $w_{ji} = w_{ij}$. In the random-trap model, the transition rates w_i originating from the sites are given; they do not depend on the final sites. The random-barrier model belongs to the class of stationary models [13]. The diffusion slowdown observed in it is due to negative correlations between successive jumps. The random-trap model belongs to the class of nonstationary models [13]. In this model, the diffusion slowdown is due to the slowing down of the mobility of particles.

In papers [11,14,15], it was shown that averaged over an ensemble of configurations, the propagator of a disordered system, P_i, satisfies the generalized master equation

$$\frac{dP_i(t)}{dt} = \int_0^t \sum_j \Theta(t-\tau)[p_{ji}P_j(\tau) - p_{ii}P_i(\tau)]\mathrm{d}\tau. \qquad (1)$$

Here, $\Theta(t)$ is the memory function, which is expressed in terms of the transition rates w_{ij}; p_{ji} are the transition probabilities which are translationally invariant: $p_{ji} = p_{j-i}$. In the continuum limit, this equation reduces to a generalized diffusion equation

$$\frac{\partial\rho(\mathbf{r},t)}{\partial t} = h^2 \int_0^t \Theta(t-\tau)\nabla^2\rho(\mathbf{r},\tau)\mathrm{d}\tau, \qquad (2)$$

a particular form of which is the fractional diffusion equation [16]. Here, ∇^2 is the Laplace operator and h^2 is the constant.

Equation (2) gives the correct expression for the average propagator in both the random-trap model and the random-barrier model. However, it cannot be used to find other quantities in both models. In particular, the FPTs given by this equation are consistent with the random-trap model, but not with the random-barrier model [17]. Since this equation does not take negative correlations into account, it does not correctly describe the random-barrier model.

In Ref. [18], Eq. (2) was transformed in such a way that it takes negative correlations into account. The transformed equation has the form of a diffusion equation with source and sink describing the resetting to positions visited in the past:

$$\begin{aligned}\frac{\partial\rho(\mathbf{r},t)}{\partial t} =& D_0\nabla^2\rho(\mathbf{r},t) - r\rho(\mathbf{r},t)\\ &+ r\int_0^t \phi(t-\tau)\rho(\mathbf{r},\tau)\mathrm{d}\tau\\ &+ r\left[Q(t) - \int_0^t \phi(t-\tau)Q(\tau)\mathrm{d}\tau\right]\delta^d(\mathbf{r}). \qquad (3)\end{aligned}$$

Here, r is the rate of resetting; $\phi(t)$ is the memory function satisfying the normalization condition $\int_0^\infty \phi(\tau)\mathrm{d}\tau = 1$; $\delta^d(\mathbf{r})$ is the d-dimensional Dirac delta function; and $Q(t)$ is the survival probability: $Q(t) = \int \rho(\mathbf{r},t)\mathrm{d}\mathbf{r}$. Term $r\rho(\mathbf{r},t)$ describes the departure of a particle from point $\mathbf{r}$. Term $r\int_0^t \phi(t-\tau)\rho(\mathbf{r},\tau)$ describes the arrival of a particle at point $\mathbf{r}$. The probability of arriving at this point depends on the probability that the particle was at this point in the past, $\rho(\mathbf{r},\tau)$, and also on the time difference $t-\tau$. Term $r[Q(t) - \int_0^t \phi(t-\tau)Q(\tau)\mathrm{d}\tau]\delta^d(\mathbf{r})$ describes the arrival of a particle at the starting point $\mathbf{r} = \mathbf{0}$. The parameters of this equation are linked with the parameters of Eq. (2) by the relations

$$\Theta(s) = \frac{\Theta_\infty s}{s + r[1 - \phi(s)]} \tag{4}$$

and

$$D_0 = h^2 \Theta_\infty, \tag{5}$$

where $\Theta(s)$ and $\phi(s)$ are the Laplace transforms of $\Theta(t)$ and $\phi(t)$ [the Laplace transform of $f(t)$ is $f(s) = \int_0^\infty \exp(-st) f(t) \mathrm{d}t$]; $\Theta_\infty = \lim_{s\to\infty} \Theta(s)$.

In the case of diffusion in infinite space, the survival probability is equal to unity and Eq. (3) is equivalent to Eq. (2) (this is easy to see in the Laplace domain). On the contrary, in the case of diffusion in a bounded region with probability flows across the boundaries, the survival probability is not equal to unity and the solutions of Eq. (3) differ from the solutions of Eq. (2). It was shown in [18] that in this case the solutions of Eq. (3) correctly reflect the effect of negative correlations on the FPTs and, therefore, qualitatively agree with the random-barrier model.

This article considers the question of how the results given by Eqs. (2) and (3) differ in practically interesting cases. In particular, these equations are used to calculate the rate constant of a bimolecular diffusion-controlled reaction. The motivation for this question is as follows. First, in many physical systems, subdiffusion is due to negative correlations, at least in part [19–24]. Secondly, this fact is not taken into account in any way when determining the rate constant. Thirdly, the standard method for finding the rate constant using the Smoluchowski formula sometimes gives results that are very different from reality [25,26]. [The standard method is based on the normal diffusion equation. But in the case of transient subdiffusion, Eq. (2) gives the same results as the normal diffusion equation with an effective diffusion coefficient $D_\infty = h^2\Theta(s)|_{s=0}$.] It is natural to ask whether the discrepancies between the calculated rate constant and the real one are the result of using Eq. (2) corresponding to subdiffusion due to mobility slowing down in such cases when subdiffusion is actually due to negative correlations.

The main result of this article is as follows. If diffusion in some medium is slowing down, so that the diffusion coefficient decreases from a value of D_0 at times close to 0 to a value of D_∞ at large times, then the rate constant of a bimolecular diffusion-controlled reaction will depend on the mechanism that slows down diffusion. If the reason for slowing down diffusion is a mobility decrease, then the rate constant will be equal to $4\pi a D_\infty$, and if the reason is negative correlations, then it will be equal to $4\pi a D_0$. These two values differ by the ratio of the diffusion coefficients D_0/D_∞. Since this ratio can be very large [27], the value of the calculated rate constant can significantly depend on the assumptions regarding the diffusion slowing down mechanism.

The article is organized as follows. In Sec. II, we reproduce those results of work [18], which shows that Eq. (3) qualitatively correctly reflects the impact of negative correlations on FPTs. In this section, anomalous subdiffusion is considered, since relevant data are available for comparison. In Sec. III, using Eq. (3), we calculate the Laplace transform of the survival probability of a fixed spherical absorbing target (or trap) in the presence of a single diffusing particle and analyze the long-time asymptotics of the survival probability. In this and the next section, we focus on transient subdiffusion because we are interested in the rate constant of the stationary process. Anomalous subdiffusion is of no interest in this case, because Eq. (2) predicts the complete immobilization of particles. In Sec. IV, we consider many diffusive particles in the presence of a single trap and study the behavior of the survival probability of the trap. In Sec. V, we discuss the application of the results obtained to finding the rate constant of a bimolecular diffusion-controlled reaction.

II. MODEL TESTING

In this section, we demonstrate the suitability of Eq. (3) for modeling diffusion processes with negative correlations. To do this, we consider one-dimensional anomalous subdiffusion. In this case, the memory function $\Theta(s)$ behaves at small s as $\propto s^{1-\alpha}$ with the parameter α ranging from 0 to 1. Since the propagators given by Eqs. (2) and (3) are the same, the mean-square displacement (MSD) corresponding to Eq. (3) behaves as $\propto t^\alpha$.

Let us find the survival probability of a particle on a semi-infinite interval $x > 0$. The particle starts at the point $x_0 > 0$ at time $t = 0$. When it hits point $x_0 = 0$, it is absorbed. In the Laplace domain, one-dimensional Eq. (3) has the form

$$s\rho(x,s) - \delta(x) = D_0 \frac{\partial^2 \rho(x,s)}{\partial x^2} - \kappa\rho(x,s) + \kappa Q(s)\delta(x), \tag{6}$$

where

$$\kappa = r[1 - \phi(s)] = s\left[\frac{\Theta_\infty}{\Theta(s)} - 1\right]. \tag{7}$$

This equation coincides in form with the equation describing diffusion with resetting [28]. In our case, the "resetting rate" κ depends on the Laplace variable s; however, in the calculation of the survival probability, this dependence has no effect, so we can directly use the result of [28]. In [28], the following expression for the Laplace transform of the survival probability is obtained:

$$Q(s) = \frac{1 - \exp\left(-x_0\sqrt{\frac{s+\kappa}{D_0}}\right)}{s + \kappa\, \exp\left(-x_0\sqrt{\frac{s+\kappa}{D_0}}\right)}. \tag{8}$$

Substituting $D_0 = h^2\Theta_\infty$ and $\kappa = s[\frac{\Theta_\infty}{\Theta(s)} - 1]$, we get

$$Q(s) = \frac{1 - \exp\left(-x_0\sqrt{\frac{s}{h^2\Theta(s)}}\right)}{s + s\left[\frac{\Theta_\infty}{\Theta(s)} - 1\right]\exp\left(-x_0\sqrt{\frac{s}{h^2\Theta(s)}}\right)}. \tag{9}$$

If the memory function $\Theta(s)$ behaves at small s as $\propto s^{1-\alpha}$, then $Q(s)$ calculated by this formula will behave as $\propto s^{-\alpha/2}$, and the real-time survival probability $Q(t)$ behaves at large time as $\propto t^{(\alpha/2)-1}$. At the same time, the survival probability for normal diffusion behaves as $\propto t^{-1/2}$, i.e., decreases more slowly. Thus, Eq. (3) predicts an acceleration of the decrease of the survival probability by negative correlations. The validity of this prediction can be seen from the following reasoning. Negative correlations make it difficult for the particle to move away from the starting point. Therefore, at long times, the particle will be in some finite region containing the sink with a higher probability than in the absence of negative correlations. At the same time, in the presence of negative correlations, the particle mobility remains constant, the same as in their absence [29]. Therefore, all points in this region, including the sink, will be visited more often than in the case of normal diffusion, and the probability for a particle to survive at long times will be lower.

As is known, in the model of fractional Brownian motion (fBm) with MSD growing as $\propto t^{\alpha}$, the survival probability decreases according to the same law as predicted by Eq. (3): $Q(t) \propto t^{(\alpha/2)-1}$ [30]. Since, in the fBm model, diffusion slows down due to negative correlations, we can conclude that, in the example under consideration, Eq. (3) correctly reflects the effect of negative correlations on the FPT.

Recall that in the case of subdiffusion described by Eq. (2), the survival probability is determined by the formula

$$Q(s) = \frac{1 - \exp\left(-x_0\sqrt{\frac{s}{h^2\Theta(s)}}\right)}{s}. \tag{10}$$

If the memory function $\Theta(s)$ behaves at small s as $\propto s^{1-\alpha}$, then survival probability $Q(t)$ calculated by this formula will behave as $\propto t^{-\alpha/2}$, i.e., it decreases more slowly than in the case of normal diffusion.

Now we calculate the mean first-passage time for a particle starting at the point x_0 on the interval (a, b) with absorbing boundaries. Here we can also use the result for diffusion with resetting. In [31], the following expression was obtained for the Laplace transform of the survival probability:

$$Q(s) = \frac{1 - g(x_0, s)}{s + \kappa g(x_0, s)}, \tag{11}$$

where

$$g(x_0, s) = \frac{\exp\left[(b - x_0)\sqrt{\frac{s+\kappa}{D}}\right] + \exp\left[(x_0 - a)\sqrt{\frac{s+\kappa}{D}}\right]}{1 + \exp\left[(b - a)\sqrt{\frac{s+\kappa}{D}}\right]}. \tag{12}$$

The mean first-passage time is calculated by the formula $T = \lim_{s\to 0} Q(s)$. Substituting the expressions $D = h^2\Theta_\infty$ and $\kappa = s[\frac{\Theta_\infty}{\Theta(s)} - 1]$ into (11) and (12) and letting s tend to zero, we get a finite value for T:

$$T = \frac{(b - x_0)(x_0 - a)}{2h^2\Theta_\infty}. \tag{13}$$

As is known, Eq. (2) gives an infinite value of the mean first-passage time in the case under consideration [6]. The fact that for subdiffusion due to negative correlations the mean first-passage time should be finite, is confirmed by the corresponding result of the fBm model [32].

Thus, in the two considered cases, Eq. (3) gives qualitatively correct results. Therefore, it can be used to study the influence of negative correlations on the qualitative behavior of the FPTs.

III. THE SINGLE-PARTICLE PROBLEM

We consider an immobile target of radius a centered at the origin $\mathbf{r} = \mathbf{0}$ and a point particle performing random walks described by Eq. (3). If the particle ever hits the surface of the target both the particle and the target disappear. In the Laplace domain, Eq. (3) is written as

$$\begin{aligned} &s\rho(\mathbf{r}, s) - \delta^d(\mathbf{r} - \mathbf{r_0}) \\ &\quad = D_0\nabla^2\rho(\mathbf{r}, s) - \kappa\rho(\mathbf{r}, s) + \kappa Q(s)\delta^d(\mathbf{r} - \mathbf{r_0}). \end{aligned} \tag{14}$$

The boundary conditions at the surface of a spherical target and at infinity are

$$\rho(\mathbf{r}, s)_{|\mathbf{r}|=a} = 0, \tag{15}$$

$$\rho(\mathbf{r}, s)_{|\mathbf{r}|\to\infty} = 0. \tag{16}$$

Note that the survival probability of the particle (as well as target) $Q(r_0, s) = \int_{|\mathbf{r}|>a} \rho(\mathbf{r}, s)d\mathbf{r}$ depends only on the initial distance r_0 between the target center and the particle because of the spherical symmetry of the target. (Since we are considering an exterior problem, the condition $r_0 > a$ is satisfied.)

It is straightforward to show that the survival probability obeys the equation

$$sQ(r, s) - 1 = D_0\nabla^2 Q(r, s) - \kappa Q(r, s) + \kappa Q(r_0, s) \tag{17}$$

and the boundary conditions

$$Q(a, s) = 0, \tag{18}$$

$$Q(r, s)_{r\to\infty} = 1. \tag{19}$$

In Eq. (17), the variable r is assumed to be different from the initial position r_0. The equation is solved for arbitrary r and r_0 and eventually $r = r_0$ is assumed [28]. This problem was solved in work [33] and we can use the solution found there. Given the expressions for D_0 (5) and κ (7), the solution is written as

$$Q(r_0, s) = \frac{a^\nu K_\nu(\alpha a) - r_0^\nu K_\nu(\alpha r_0)}{sa^\nu K_\nu(\alpha a) + s\left(\frac{\Theta_\infty}{\Theta(s)} - 1\right)r_0^\nu K_\nu(\alpha r_0)}, \tag{20}$$

where K_ν is the modified Bessel function of the second kind, $\nu = 1 - \frac{d}{2}$, $\alpha = \sqrt{\frac{s}{h^2\Theta(s)}}$.

Equation (2) is usually used to describe slowing diffusion in media with static disorder. The solutions of this equation differ from the solutions of the normal diffusion equation, in the Laplace domain, in that the diffusion coefficient is not a constant, but a function of the Laplace variable s. When finding from these solutions the quantities related to large times, i.e., to small s, the same expressions are obtained as in the case of normal diffusion with a diffusion coefficient $D_\infty = \lim_{t\to\infty} D(t) = \lim_{s\to 0} h^2\Theta(s) = h^2\Theta_0$. From this it is concluded that, at long times, transient subdiffusion can be described by the normal diffusion equation with the diffusion coefficient D_∞. If this is done, then expression

$$Q_1(r_0, s) = \frac{a^\nu K_\nu(\beta a) - r_0^\nu K_\nu(\beta r_0)}{sa^\nu K_\nu(\beta a)} \tag{21}$$

is obtained for the survival probability, where $\beta = \sqrt{\frac{s}{h^2\Theta_0}}$ [27]. This expression can be obtained from (20) by substituting $\Theta_\infty = \Theta_0$ and $\Theta(s) = \Theta_0$.

Our further goal is to compare the results obtained by formulas (20) and (21). Since the explicit inversion of the

Laplace transforms (20) and (21) seems difficult, we will consider only the asymptotic behavior of the survival probability at long times.

A. $d = 1$

In the one-dimensional case, we can put $a = 0$. Given that $K_{1/2}(x) = \sqrt{\frac{\pi}{2x}} \exp(-x)$, we have

$$Q(r_0, s) = \frac{1 - \exp(-\alpha r_0)}{s\left[1 + \left(\frac{\Theta_\infty}{\Theta(s)} - 1\right)\exp(-\alpha r_0)\right]}. \tag{22}$$

The long-time behavior of time-dependent quantities corresponds to the limit $s \to 0$ for their Laplace transforms. In this limit we get

$$Q(r_0, s) \simeq \frac{\Theta_0}{\Theta_\infty} \frac{1 - \exp\left(-r_0\sqrt{\frac{s}{h^2\Theta_0}}\right)}{s}. \tag{23}$$

The inverse Laplace transform of this expression is

$$Q(r_0, t) \simeq \frac{\Theta_0}{\Theta_\infty} \mathrm{erf}\left\{\frac{r_0}{(4h^2\Theta_0 t)^{1/2}}\right\}. \tag{24}$$

This result differs from the result given by formula (21),

$$Q_1(r_0, t) \simeq \mathrm{erf}\left\{\frac{r_0}{(4h^2\Theta_0 t)^{1/2}}\right\}, \tag{25}$$

by the factor $\frac{\Theta_0}{\Theta_\infty}$.

B. $d = 2$

In two dimensions, we use the approximation $K_0(x)_{x\to 0} \simeq \ln\frac{1}{x}$. The leading term of expansion of (20) in the limit $s \to 0$ is

$$Q(r_0, s) \simeq \frac{\Theta_0}{\Theta_\infty} \ln\left(\frac{r_0}{a}\right) \frac{2}{s \ln\left(\frac{h^2\Theta_0}{s}\right)}. \tag{26}$$

Using the Tauberian theorem, we get

$$Q(r_0, t) \simeq \frac{\Theta_0}{\Theta_\infty} \ln\left(\frac{r_0}{a}\right) \frac{2}{\ln(h^2\Theta_0 t)}. \tag{27}$$

In this case also, the result differs from the result given by formula (21),

$$Q_1(r_0, t) \simeq \ln\left(\frac{r_0}{a}\right) \frac{2}{\ln(h^2\Theta_0 t)}, \tag{28}$$

by the factor $\frac{\Theta_0}{\Theta_\infty}$.

C. $d = 3$

Given that $K_{-1/2}(x) = K_{1/2}(x) = \sqrt{\frac{\pi}{2x}} \exp(-x)$, we have

$$Q(r_0, s) = \frac{1 - \frac{a}{r_0}\exp\left\{-(r_0 - a)\sqrt{\frac{s}{h^2\Theta(s)}}\right\}}{s\left[1 + \left(\frac{\Theta_\infty}{\Theta(s)} - 1\right)\frac{a}{r_0}\exp\left\{-(r_0 - a)\sqrt{\frac{s}{h^2\Theta(s)}}\right\}\right]}. \tag{29}$$

In this case, the ultimate survival probability $Q(r_0, t \to \infty) = \lim_{s\to 0} sQ(r_0, s)$ is nonzero:

$$Q(r_0, t \to \infty) = \frac{1 - \frac{a}{r_0}}{1 + \left(\frac{\Theta_\infty}{\Theta_0} - 1\right)\frac{a}{r_0}}. \tag{30}$$

As is known [34], formula (21) yields

$$Q_1(r_0, t \to \infty) = 1 - \frac{a}{r_0}. \tag{31}$$

The factor $\frac{1}{1+\left(\frac{\Theta_\infty}{\Theta_0}-1\right)\frac{a}{r_0}}$ in (30) takes values ranging from 1 to $\frac{\Theta_0}{\Theta_\infty}$ depending on the ratio $\frac{a}{r_0}$.

The result of this section is formulas (24), (27), and (30), giving the dependence of the survival probability on time for $d = 1, 2, 3$ in a model with negative correlations. A comparison of these formulas with the corresponding formulas for the model with the slowing down of the mobility of particles [formulas (25), (28), and (31)] shows that the survival probability always decreases faster in the model with negative correlations (in transient subdiffusion the ratio Θ_0/Θ_∞ is always less than 1).

IV. THE MANY-PARTICLE PROBLEM

Consider now the problem of many independent particles and the survival probability $Q(t)$ of the target. If N particles are uniformly distributed in volume V of Ω, then

$$Q(t) = \left\{\frac{1}{V}\int_\Omega Q(\mathbf{r}, t)d\mathbf{r}\right\}^N. \tag{32}$$

In the thermodynamic limit $N \to \infty$, $V \to \infty$ at fixed particle density $\rho = N/V$, the survival probability becomes [35]

$$Q(t) = \exp[-\rho a^d f(t)], \tag{33}$$

where

$$f(t) = \frac{1}{a^d}\int_{|\mathbf{r}|>a} [1 - Q(\mathbf{r}, t)]d\mathbf{r}. \tag{34}$$

The Laplace transform of (34) can be determined using (20):

$$f(s) = \frac{S_d}{a^d}\frac{\Theta_\infty}{s\Theta(s)} \int_a^\infty \frac{r^{d-1+\nu}K_\nu(\alpha r)}{a^\nu K_\nu(\alpha a) + \left(\frac{\Theta_\infty}{\Theta(s)} - 1\right)r^\nu K_\nu(\alpha r)}dr. \tag{35}$$

Here α is equal to $\sqrt{\frac{s}{h^2\Theta(s)}}$, as before, and

$$S_d = \frac{2\pi^{d/2}}{\Gamma(d/2)} \tag{36}$$

is the surface area of a d-dimensional unit sphere. Passing to the variable $z = \alpha r$, we get

$$f(s) = \frac{S_d}{(\alpha a)^d}\frac{\Theta_\infty}{s\Theta(s)} \times \int_{\alpha a}^\infty \frac{z^{d-1+\nu}K_\nu(z)}{(\alpha a)^\nu K_\nu(\alpha a) + \left(\frac{\Theta_\infty}{\Theta(s)} - 1\right)z^\nu K_\nu(z)}dz. \tag{37}$$

A. $d = 1$

In the one-dimensional case, expression (37) takes the form

$$f(s) = \frac{2}{\alpha a}\frac{\Theta_\infty}{s\Theta(s)} \int_{\alpha a}^\infty \frac{\exp(-z)}{\exp(-\alpha a) + \left(\frac{\Theta_\infty}{\Theta(s)} - 1\right)\exp(-z)}dz. \tag{38}$$

Calculating the integral, we obtain the leading term of expansion of (38) in the limit $s \to 0$:

$$f(s) \simeq \frac{2}{a}\sqrt{\frac{h^2\Theta_0}{s^3}}\frac{\Theta_\infty}{\Theta_\infty - \Theta_0}\ln\left(\frac{\Theta_\infty}{\Theta_0}\right). \tag{39}$$

The inverse Laplace transform of this expression is

$$f(t) \simeq \frac{4}{a}\sqrt{\frac{h^2\Theta_0 t}{\pi}}\frac{\Theta_\infty}{\Theta_\infty - \Theta_0}\ln\left(\frac{\Theta_\infty}{\Theta_0}\right). \tag{40}$$

The expression corresponding to formula (21) is obtained from here at $\Theta_\infty \to \Theta_0$:

$$f(t) \simeq \frac{4}{a}\sqrt{\frac{h^2\Theta_0 t}{\pi}}. \tag{41}$$

The factor $\frac{\Theta_\infty}{\Theta_\infty-\Theta_0}\ln(\frac{\Theta_\infty}{\Theta_0})$ in (40) takes values ranging from 1 to $\ln(\frac{\Theta_\infty}{\Theta_0})$, depending on the ratio $\frac{\Theta_\infty}{\Theta_0}$.

B. $d = 2$

In the two-dimensional case, expression (37) takes the form

$$f(s) = \frac{2\pi}{(\alpha a)^2 K_0(\alpha a)}\frac{\Theta_\infty}{s\Theta(s)}\int_{\alpha a}^{\infty}\frac{zK_0(z)}{1+\left(\frac{\Theta_\infty}{\Theta(s)}-1\right)\frac{K_0(z)}{K_0(\alpha a)}}\mathrm{d}z. \tag{42}$$

As s tends to zero, the expression $\frac{K_0(z)}{K_0(\alpha a)}$ tends to zero. Therefore, in the limit $s \to 0$, the integral reduces to $\int_0^\infty zK_0(z)\mathrm{d}z = 1$. Thus, the leading term of the expansion of (42) in this limit is

$$f(s) \simeq \frac{4\pi}{a^2}\frac{h^2\Theta_\infty}{s^2\ln\left(\frac{h^2\Theta_0}{sa^2}\right)}. \tag{43}$$

The inverse Laplace transform of this expression is

$$f(t) \simeq \frac{4\pi}{a^2}\frac{h^2\Theta_\infty t}{\ln\left(\frac{h^2\Theta_0 t}{a^2}\right)}. \tag{44}$$

This result differs from the result corresponding to formula (21),

$$f(t) \simeq \frac{4\pi}{a^2}\frac{h^2\Theta_0 t}{\ln\left(\frac{h^2\Theta_0 t}{a^2}\right)}, \tag{45}$$

by the factor $\frac{\Theta_\infty}{\Theta_0}$.

C. $d = 3$

In the three-dimensional case, expression (37) takes the form

$$f(s) = \frac{4\pi\ \exp(\alpha a)}{(\alpha a)^2}\frac{\Theta_\infty}{s\Theta(s)}\int_{\alpha a}^{\infty}\frac{z\exp(-z)}{1+\left(\frac{\Theta_\infty}{\Theta(s)}-1\right)\frac{\alpha a\exp(-z)}{z\exp(-\alpha a)}}\mathrm{d}z. \tag{46}$$

As s tends to zero, the expression $\frac{\alpha a\exp(-z)}{z\exp(-\alpha a)}$ tends to zero. Therefore, in the limit $s \to 0$, the integral reduces to $\int_0^\infty z\exp(-z)\mathrm{d}z = 1$. Thus, the leading term of the expansion of (46) in this limit is

$$f(s) \simeq \frac{4\pi}{a^2}\frac{h^2\Theta_\infty}{s^2}. \tag{47}$$

The inverse Laplace transform of this expression is

$$f(t) \simeq \frac{4\pi h^2\Theta_\infty t}{a^2}. \tag{48}$$

This result differs from the result corresponding to formula (21),

$$f(t) \simeq \frac{4\pi h^2\Theta_0 t}{a^2}, \tag{49}$$

by the factor $\frac{\Theta_\infty}{\Theta_0}$.

The result of this section is formulas (40), (44), and (48), giving the dependence of the survival probability on time for $d = 1, 2, 3$ in a model with negative correlations. A comparison of these formulas with the corresponding formulas for the model with the slowing down of the mobility of particles [formulas (41), (45), and (49)] shows that in the many-particle problem, as in the single-particle problem, the survival probability always decreases faster in the model with negative correlations.

V. DISCUSSION

This article compares the first-passage characteristics for two models of transient subdiffusion that have the same time dependence of the diffusion coefficient. In one model, the slowing down of diffusion is due to the slowing down of the mobility of particles, and in the other, it is due to negative correlations. It is shown that the survival probability always decreases faster in the model with negative correlations. This result is essentially not new. What is new is that it is obtained from consideration of transient subdiffusion rather than anomalous subdiffusion. For the case of anomalous subdiffusion, this result was known earlier. It is mentioned in the second section of this article. There, survival probabilities for the model with the slowing down of the mobility of particles, described by Eq. (2), and the fBm model, which is a model with negative correlations, are given. In addition, two models were compared in [17], for which the first passage characteristics are calculated directly without the use of a master equation. Qualitatively the same result was obtained: the survival probability decreases faster in the model with negative correlations than in the model with the slowing down of the mobility of particles.

The formulas obtained here can be used to calculate the rate constant of a bimolecular diffusion-controlled reaction. The rate constant k is related to the function $f(t)$ by the relation $k = a^d\frac{df(t)}{dt}$ [34]. From formulas (48) and (49) we find in the three-dimensional case $k = 4\pi aD_0$ for the model with negative correlations and $k = 4\pi aD_\infty$ for the model with the slowing down of the mobility of particles. Since the diffusion coefficient D_0 in real physical systems can be several orders of magnitude greater than D_∞ [27], the reaction rate constant calculated by the Smoluchowski formula using the coefficient D_∞ may be several orders of magnitude smaller than the real rate constant. Such a situation can arise when diffusion in the medium under consideration is slowing down and the slowing down is due to negative correlations. In this case, in the Smoluchowski formula, it is necessary to use not the coefficient D_∞, which characterizes the expansion of a cloud of particles at large times in an unlimited space, but the coefficient D_0, which characterizes the time-independent mobility of particles.

The result obtained here can potentially find application in biophysics as an alternative to the Berg–von Hippel model of facilitated diffusion [36]. The facilitated diffusion model was proposed just to explain why the real rate constant is several orders of magnitude higher than that predicted by the Smoluchowski formula. This model assumes that the increase in the reaction rate is associated with the presence of other stochastic search mechanisms besides three-dimensional diffusion. However, this model does not take into account the fact that three-dimensional diffusion in living cells is, as a rule, not ordinary diffusion, but transient subdiffusion [27]. Perhaps, in some cases, taking this fact into account will provide the desired explanation without using the model of facilitated diffusion.

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