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2007 J. Phys.: Condens. Matter 19 065117

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Specific features of the kinetics of fractional-diffusion assisted geminate reactions

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Received 4 July 2006, in final form 21 July 2006

Published 22 January 2007

Online at stacks.iop.org/JPhysCM/19/065117

Abstract

Specific features of the kinetics of geminate reactions assisted by dispersive (subdiffusive) relative motion of reacting particles are analysed in detail. The analysis is made for different long-range dependences of the reactivity $k(r)$ on the interparticle distance r : square box, exponential, and inverse power type. The kinetics is obtained by analytical solution of the non-Markovian master equation and by direct numerical simulation of the process. The reaction kinetics is shown to be anomalous, namely, significantly different from that predicted for processes assisted by normal diffusion. The difference manifests itself both in static and time dependent characteristics of the kinetics depending on the form of $k(r)$ and on the anomaly parameter $\alpha < 1$ (which determines the time dependence of the mean square displacement $\langle r^2(t) \rangle \sim t^\alpha$). The anomalous kinetic peculiarities are most clearly demonstrated with the initial distance (r_0) dependence of reaction probability $\varphi_r(r_0)$. For localized $k(r)$ (square box and exponential) it is similar to that known for normal diffusion $\varphi_r(r_0) \sim 1/r_0$. For $k(r) \sim 1/r^m$, however, the behaviour of $\varphi_r(r_0)$ depends on $n = \alpha m$: at $n > 3$ the function $\varphi_r(r_0)$ is similar to that for localized $k(r)$, but at $3 > n > 2$ we found $\varphi_r(r_0) \sim 1/r_0^{n-2}$. A similar change-over is also observed for the long time part $n_s(t)$ of the kinetics $N(t)$ (the number of surviving pairs). For localized $k(r)$ it is universal: $n_s(t) \sim 1/t^{\alpha/2}$. For $k(r) \sim 1/r^m$ and $3 > n > 2$, the decay of $n_s(t)$ proves to be more dispersive: $n_s(t) \sim 1/t^{\alpha(1-2/n)}$. Possible applications of the present results are discussed.

1. Introduction

Subdiffusion occurs by spatial restrictions of motion of random walkers caused by fractal structures or by the distribution of hopping frequency of random walks or both [1–3]. Reaction

kinetics depends on the distribution of reactants, which cannot be characterized solely by the mean square displacements under subdiffusive transport because the distribution can be distorted from Gaussian [3]. Therefore, it is important to know the origin of subdiffusive transport when we consider reactions. We focus our attention on reactions in subdiffusive media where the hopping frequency is distributed. An example is photoluminescence in amorphous semiconductors in which photoluminescence originates from radiative recombination of electrons and holes in band-tail states [4, 5]. The hopping transport can be described by the fractional diffusion equation [2, 6, 7],

$$\dot{\rho}(\vec{r}, t) = {}_0D_t^{1-\alpha} D_\alpha \nabla^2 \rho(\vec{r}, t), \quad (1)$$

where the Riemann–Liouville fractional derivative is defined by

$${}_0D_t^{1-\alpha} f(t) = \frac{1}{\Gamma(\alpha)} \frac{\partial}{\partial t} \int_0^t dt_1 \frac{f(t_1)}{(t-t_1)^{1-\alpha}}. \quad (2)$$

${}_0D_t^{1-\alpha}$ operates on an arbitrary function $f(t)$ by convolution and can be interpreted as a memory effect. The conventional Markovian diffusion equation results from an exponential waiting time distribution function. Since reaction in the absence of transport is also Markovian, the theoretical method to treat reaction under normal diffusion has been well established [8]. However, if the transport is dissipative and has a long-ranged memory as shown in equation (1), reaction interferes with diffusion for finite reactivity. The kinetics of reactions, which are assisted by dispersive diffusion described by the fractional diffusion equation, have been considered only recently [9–21]. For contact reactions, the whole time kinetics of the survival probability is well described by the result of the fractional reaction–diffusion equation [18],

$$\dot{\rho}(\vec{r}, t) = {}_0D_t^{1-\alpha} [D_\alpha \nabla^2 \rho(\vec{r}, t) - k^\alpha \delta(r-R) \rho(\vec{r}, t)], \quad (3)$$

where the fractional derivative ${}_0D_t^{1-\alpha}$ operates on both terms in square brackets.

However, problems arise when it is generalized to include spatial dependence of reactivity. Under long-range reaction a fractional reaction–diffusion equation similar to equation (3) is derived for an auxiliary quantity which is related to but different from the real density [20]. In fact, the fractional reaction–diffusion equation for the real probability density is more complicated than the above fractional reaction–diffusion equation [15–17]. The equation has already been presented in the Laplace domain and solved approximately by applying some methods of quantum scattering theory [16, 17]. In this article, we show for the square box reactivity that the fractional reaction–diffusion equation for the real density reproduces the numerical results of direct Brownian motion simulation. Although this fractional reaction–diffusion equation is exact, it is difficult to solve for other spatial dependence of reactivity. We introduce an approximation, examine its validity and investigate the interference of dispersive diffusion with three types of long-range reactivity, i.e. square box sink, exponential sink and inverse-power type sink on the basis of the approximation.

2. Fractional reaction–diffusion equations

We consider the geminate reaction of a pair of particles, denoted as A and B, which undergo dispersive (subdiffusive) relative diffusion in the three dimensional space. The reaction is modelled by the first order decay process with isotropic long-range decay rate $k(\vec{r}) \equiv k(r)$ depending on the distance r between particles. We assume, in addition, that one of these particles, say particle B, does not move, staying at rest at $\vec{r}_B = 0$, so that the evolution of the system in the coordinate space is determined by that of particle A in the space $\{\vec{r}\}$ of relative AB-coordinate \vec{r} .

The kinetics of geminate reaction is known to be completely described by the probability density function (PDF) $\rho(\vec{r}, t)$. In the case of conventional (Markovian) diffusion of particle A, $\rho(\vec{r}, t)$ is known to satisfy an equation similar to the so called stochastic Liouville equation (SLE). In the considered model of non-Markovian dispersive relative migration of particles the problem of obtaining $\rho(\vec{r}, t)$ is more complicated. Recall that dispersive migration is the stochastic motion for which the mean square displacement $\langle r^2(t) \rangle \sim t^\alpha$, where $\alpha < 1$.

For dispersive (non-Markovian) migration $\rho(\vec{r}, t)$ is shown to satisfy some equation as well [15–17]. This equation is derived within the continuous time random walk (CTRW) approach and can be considered as a simple particular variant of the non-Markovian generalization of the Markovian SLE. It is worth recalling that in the CTRW approach relative migration is modelled by the process of stochastically independent jumps controlled by the waiting time PDF $\psi(t)$ [15–17, 22] (for simplicity we assume that $\psi(t)$ is independent of r). In general, for any function $\psi(t)$ the non-Markovian SLE is conveniently expressed in terms of the Laplace transform $\hat{\rho}(\vec{r}, s) = \int_0^\infty dt \exp(-st)\rho(\vec{r}, t)$ [15–17] (some comments on the alternative derivation of this equation are presented in the appendix):

$$(s + k(\vec{r}))\hat{\rho} = \lambda^2 [\nabla^2/(2d)] [\hat{M}(s + k(\vec{r}))\hat{\rho}] + \rho_0(\vec{r}), \quad (4)$$

where the Laplace transform of the memory function is defined as

$$\hat{M}(s) = s\hat{\psi}(s)/[1 - \hat{\psi}(s)] \quad (5)$$

and λ is the characteristic jump length of the migration.

In equation (4) $\rho_0(\vec{r})$ is the initial distribution of pairs. In what follows we will assume that initially pairs are created isotropically at a distance r_0 , i.e.

$$\rho_0(\vec{r}) = (4\pi r_0^2)^{-1} \delta(r - r_0). \quad (6)$$

Within the CTRW approach dispersive migration is realized for a special type of the long-tailed PDF $\psi(t)$, whose long-time behaviour is represented as

$$\psi(t) \simeq \alpha \Gamma(\alpha + 1) / (\gamma_r^\alpha t^{\alpha+1}), \quad (7)$$

with γ_r being the characteristic rate of jumps. For PDF (7) one can find a simple expression for the Laplace transform of the memory function: $\lambda^2 \hat{M}(s)/(2d) \simeq D_\alpha s^{1-\alpha}$ at small s , where $D_\alpha \equiv (\sin \pi\alpha/2d\pi\alpha)\gamma_r^\alpha \lambda^2$ is the generalized diffusion coefficient [23]. It is easily seen that for this type of $\psi(t)$, equation (4) can be represented in the form of the fractional reaction–diffusion equation

$$\dot{\rho} = D_\alpha \nabla^2 \left[e^{-k(\vec{r})t} {}_0D_t^{1-\alpha} (e^{k(\vec{r})t} \rho) \right] - k(\vec{r}) \rho. \quad (8)$$

In the above equation, the non-Markovian kernel ${}_0D_t^{1-\alpha}$ is influenced by reaction due to the interference of reaction with dispersive transport.

In our work we will mainly be interested in calculating the survival probability given by $N(t, \vec{r}_0) = \int d\vec{r} \rho(\vec{r}, t)$, where the integration is taken over the region outside the perfectly reflecting boundary. In the presence of the reflecting boundary condition, the decrease per unit time in the survival probability should obey $\dot{N}(t, \vec{r}_0) = - \int d^3r k(\vec{r})\rho(\vec{r}, t)$. By transformation of the volume integral into a surface one for the volume integration of equation (8) we can find that the perfectly reflecting boundary condition is expressed as

$$\vec{n} \cdot \nabla [e^{-k(\vec{r})t} {}_0D_t^{1-\alpha} (e^{k(\vec{r})t} \rho)]|_{r=R} = 0, \quad (9)$$

where $\vec{n} = \vec{r}/|\vec{r}|$ is the vector normal to the contact sphere. In the Laplace domain, the perfectly reflecting boundary condition is expressed as

$$\vec{n} \cdot \nabla [\hat{M}(s + k(\vec{r}))\hat{\rho}]|_{r=R} = 0. \quad (10)$$

Equation (4) can be formally solved in operator form [16]. In particular in the case of dispersive migration the solution is given by

$$\hat{\rho}(\vec{r}, s) = [s + k(\vec{r})]^{\alpha-1} \{ [s + k(\vec{r})]^\alpha - D_\alpha \nabla^2 \}^{-1} \rho_0. \quad (11)$$

The solution can only be obtained for the box model of $k(r)$ (see section 3). One can also solve this equation in the limit of small s with the use of methods of the quantum scattering theory developed to describe the low-energy scattering [16, 17]. The small- s solution allows one to obtain the long-time behaviour of the reaction kinetics $N(t)$.

But here we would like to briefly analyse the approximation recently proposed, which is based on some modification of the exact equation (4) [20]. This approximation appears to be fairly accurate for small s , i.e. reproduces quite well the asymptotic behaviour of $N(t)$ for a large variety of dependences $k(r)$ and also enables one to solve the problem analytically for exponential $k(r)$.

The key points of this approach can conveniently be understood by comparison of the found expression:

$$\hat{\rho}_a(\vec{r}, s) = k^{\alpha-1}(\vec{r}) [s^\alpha + k^\alpha(\vec{r}) - D_\alpha \nabla^2]^{-1} \rho_0 \quad (12)$$

with the exact one (11). It is seen that $\hat{\rho}(\vec{r}, s = 0) = \hat{\rho}_a(\vec{r}, s = 0)$ so that the approximation (12) reproduces correctly all steady state characteristics of the reaction kinetics. In addition, the applied approximation $[s + k(\vec{r})]^\alpha \approx s^\alpha + k^\alpha(\vec{r})$ is quite accurate in both limits $k \gg |s|$ and $k \ll |s|$. As for the approximation $[s + k(\vec{r})]^{\alpha-1} \approx k^{\alpha-1}(\vec{r})$, it is also quite reasonable for small $|s|$ (corresponding to long times), taking into account that in the expression for the reaction rate $-\dot{N}(t) \sim \int d^3r k(r) \rho(r, t)$ the contribution of small $k(r)$ at large r is truncated by the term $k(r)$ in the integrand. In this approximation, the solution is obtained from that of the corresponding reaction–diffusion equation under normal diffusion by substituting $D_1 \rightarrow s^{1-\alpha} D_\alpha$ and $k(\vec{r}) \rightarrow s^{1-\alpha} k^\alpha(\vec{r})$ after Laplace transformation [20]. Therefore, we can obtain analytical approximate solutions for a number of different $k(r)$ -dependences. Perhaps one of the most important of them is exponential: $k(r) = k_0 \exp(-\beta r)$ (see below) [20]. It is evident that in this case the replacement $k(r)$ by $k^\alpha(r)$ reduces just to the change of β for $\alpha\beta$.

Unfortunately the approximation (12) does not reproduce the exact formula at $|s| \leq k(r)$ in the static limit, i.e. for $D_\alpha \rightarrow 0$. In this limit the exact expression (11) predicts exponential decay of the number of pairs:

$$\hat{N}(s) = [s + k(r_0)]^{-1} \quad \text{and} \quad N(t) = \exp[-k(r_0)t], \quad (13)$$

as expected. The prediction of approximate formula (12), however, is essentially different:

$$\hat{N}_a(s) = [s + k^\alpha(r_0) s^{1-\alpha}]^{-1} \quad \text{and} \quad N_a(t) = E_\alpha[-(k(r_0)t)^\alpha], \quad (14)$$

where $E_\alpha(-x) = (2\pi i)^{-1} \int_{-i\infty}^{i\infty} du e^u (u + x u^{1-\alpha})$ is the Mittag–Leffler function [1]. It is seen that at small times t the approximate reaction kinetics is stretched exponential, $N_a(t) \sim \exp[-(k(r_0)t)^\alpha / \Gamma(1 + \alpha)]$, while at large t it is of inverse power type, $N_a(t) \sim 1/[k(r_0)t]^\alpha$.

Naturally, this drawback of the approximation (12) persists in the case of finite mobilities ($D_\alpha \neq 0$) as well. The deviation of the kinetics $N_a(t)$ from $N(t)$ will be most pronounced at the initial stage of the reaction, determined by $|s| \geq k(r)$ (in this inequality $k(r)$ should be taken at distances r which mainly contribute to the reaction).

Especially strong manifestation of the static behaviour is expected in the case of very fast rates and long-range $k(r)$. This statement can conveniently be clarified with the exponential $k(r)$: $k(r) = k_0 \exp(-\beta r)$. The fact is that for any particular r one can always find large enough k_0 , for which the diffusive displacement during the characteristic reaction time $\tau_r(r) \sim 1/k(r)$, $l(r) \sim \sqrt{D_\alpha \tau_r^\alpha(r)}$, is much smaller than the characteristic size β^{-1} of the function $k(r)$: $l(r) \ll \beta^{-1}$. This inequality implies applicability of the static limit and therefore low accuracy

of approximation (12). The above estimation shows that the r -region of high accuracy of the static approximation and low accuracy of equation (12) increases with the increase of k_0 or increase of the characteristic length $1/\beta$ of the function $k(r)$.

The results and conclusions of general analysis presented above will be illustrated in the next section within some models for $k(r)$.

3. Applications

3.1. Asymptotic kinetics

In this subsection we present a general method for calculating the escape probability when reaction proceeds under dispersive diffusion. The method is a generalization of that formulated to calculate the escape probability in normal diffusion-controlled reactions [24]. The escape probability $\varphi(\vec{r})$ is the probability that a particle starting from a given position \vec{r} , performing a diffusive motion, will escape reaction. It is also convenient to introduce the quantity $\varphi_t(\vec{r}_0)$ by

$$\varphi_t(\vec{r}_0) \equiv \int d\vec{r} \varphi(\vec{r}) \rho(\vec{r}, t|\vec{r}_0), \quad (15)$$

where $\rho(\vec{r}, t|\vec{r}_0)$ satisfies equation (8) with the initial condition $\delta(\vec{r} - \vec{r}_0)$. The function $\varphi_t(\vec{r})$ is finite and $\varphi_{t=0}(\vec{r}_0) = \varphi(\vec{r}_0)$. In the Markovian processes, $\varphi_t(\vec{r})$ is independent of time and is equal to $\varphi(\vec{r})$ for all times [24]. By taking the Laplace transform of the identity,

$$\dot{\varphi}_t(\vec{r}_0) = \int d\vec{r} \varphi(\vec{r}) \dot{\rho}(\vec{r}, t|\vec{r}_0), \quad (16)$$

and substituting equation (4), the above equation is transformed into the equation for $\hat{\varphi}_s(\vec{r}_0) = \int_0^\infty dt \exp(-st) \varphi_t(\vec{r}_0)$ as

$$s\hat{\varphi}_s(\vec{r}_0) - \varphi(\vec{r}_0) = \int d\vec{r} \varphi(\vec{r}) [\lambda^2 (\nabla^2/2) M(s+k(\vec{r})) \hat{\rho}(\vec{r}, s|\vec{r}_0) - k(\vec{r}) \hat{\rho}(\vec{r}, s|\vec{r}_0)] \quad (17)$$

$$= \int d\vec{r} \hat{\rho}(\vec{r}, s|\vec{r}_0) [\lambda^2 M(s+k(\vec{r})) (\nabla^2/2) \varphi(\vec{r}) - k(\vec{r}) \varphi(\vec{r})], \quad (18)$$

where the boundary condition for $\hat{\rho}(\vec{r}, s|\vec{r}_0)$ given in equation (10) is used and the boundary condition for $\varphi(\vec{r})$ is set as

$$\vec{n} \cdot \nabla \varphi(r)|_{r=R} = 0. \quad (19)$$

In the limit of $s \rightarrow 0$, we have $\hat{\varphi}_s(\vec{r}_0) \rightarrow \varphi(\vec{r}_0)/s$ and $\lambda^2 M(s)/2 \simeq D_\alpha s^{1-\alpha}$; the above equation becomes

$$0 = \int d\vec{r} \hat{\rho}(\vec{r}, 0|\vec{r}_0) [k^{1-\alpha}(\vec{r}) D_\alpha \nabla^2 \varphi(\vec{r}) - k(\vec{r}) \varphi(\vec{r})]. \quad (20)$$

Since $\hat{\rho}(\vec{r}, 0|\vec{r}_0)$ is independent of $\varphi(\vec{r})$ for arbitrary initial distance \vec{r}_0 , the escape probability would satisfy

$$D_\alpha \nabla^2 \varphi(\vec{r}) - k^\alpha(\vec{r}) \varphi(\vec{r}) = 0. \quad (21)$$

The relevant boundary conditions are

$$\varphi(\vec{r}) = 1, \quad \text{as } r \rightarrow \infty \quad (22)$$

and equation (19). As a result, the equation for the escape probability under dispersive diffusion is obtained from that under normal diffusion by substitution, $k(\vec{r})/D_1 \rightarrow k^\alpha(\vec{r})/D_\alpha$.

The escape probability is not only important for analysing steady state experiments but also is useful to analyse the asymptotic kinetics of geminate recombination. In the case of normal

diffusion with any model of reactivity, it is known that the asymptotic kinetics of the survival probability $N(t, r_0)$ is expressed as [25], $N(t, r_0) \simeq \varphi(r_0)(1 + \ell_R/\sqrt{\pi D_1 t})$, as long as the reaction radius ℓ_R can be obtained from the asymptotic dependence of the escape probability at large initial separations,

$$\varphi(r_0) \simeq 1 - \ell_R/r_0. \quad (23)$$

The result has been recently generalized to the kinetics under dispersive transport as

$$N(t, r_0) \simeq \varphi(r_0) \left[1 + \frac{\ell_R}{\Gamma(1 - (\alpha/2)) \sqrt{D_\alpha t^\alpha}} \right], \quad (24)$$

for a highly localized reactivity [17, 19]. In the approximation shown by equation (12), the Laplace transform of the survival probability under dispersive transport is obtained by that under normal diffusion by substituting $D_1 \rightarrow s^{1-\alpha} D_\alpha$ and $k(\vec{r}) \rightarrow s^{1-\alpha} k^\alpha(\vec{r})$. By applying such substitution to the Laplace transform of the asymptotic form of the survival probability under normal diffusion, the result after inverse Laplace transformation leads to equation (24). Therefore, the asymptotic kinetics is correctly reproduced by the results of the approximate solution as long as ℓ_R exists. Equation (24) presents the simplest way to calculate the asymptotic kinetics of the survival probability of the geminate pair from the solution of the differential equation for the escape probability (equation (21)) for any initial distance r_0 .

3.2. Square box type reactivity

First, we consider an example for which the analytical solution is possible from equation (8): the square box type reactivity function $k(r)$ without a reflecting boundary [26–29], $k(r) = k_0 \theta(R - r)$ where $\theta(x)$ is the Heaviside theta function. We compare the exact survival probability with the approximate solution by equation (12). The Laplace transform of the exact survival probability obtained from equation (8) in the case of $r_0 < R$ is given by

$$\hat{N}(s) = \frac{1}{s + k_0} \left[1 + \frac{k_0}{s} \frac{(1 + Rq(s)) \sinh[r_0 q(s + k_0)]}{r_0 q(s + k_0) \cosh[Rq(s + k_0)] + r_0 q(s) \sinh[Rq(s + k_0)]} \right], \quad (25)$$

where $q(s) = \sqrt{s^\alpha/D_\alpha}$. The approximate solution of the survival probability in the Laplace domain is obtained from equation (5.10) of Tachiya's result [29] by substituting $D_1 \rightarrow s^{1-\alpha} D_\alpha$ and $k_0 \rightarrow s^{1-\alpha} k_0^\alpha$ as explained below equation (12). In the long-time limit, both results lead to the asymptotic kinetics of equation (24), where the escape probability is given by $\varphi(r_0) = \sinh(r_0 q(k_0))/[r_0 q(k_0) \cosh(Rq(k_0))]$ and the reaction radius is $\ell_R/R = 1 - \tanh(Rq(k_0))/(Rq(k_0))$. The exact and approximate whole time kinetics were obtained by the numerical inversion of the corresponding Laplace transforms of the survival probability through the Stehfest algorithm [30]. Previously, the approximate solution has been compared with the results of numerical simulations for $r_0 = 2R$ [20]. The comparison reveals some discrepancy between these two calculations which is at most 7% of the initial population and is observed at short times. In the present study, the initial condition corresponding to localization of the pair deep inside the region of efficient reaction, $r_0 = 0.1R$, is considered. In the simulation the jump length parameter was assumed as $\lambda = 0.1R$. Other parameters are $\alpha = 0.5$, $k_0(R^2/D_\alpha)^{1/\alpha} = 0.1$ and time is normalized by hopping frequency, γ_t . The CTRW simulation procedure is the same as that used previously [18–20]. Particles react when the reaction time generated from the exponential distribution with the mean value $1/k_0$ is smaller than the detrapping time of the random walk. The trajectory is calculated until the particle either reacts or escapes to a large distance $100R$. The simulation is repeated for at least 10^4 independent trajectories [20]. In figure 1, the analytically obtained value of the escape

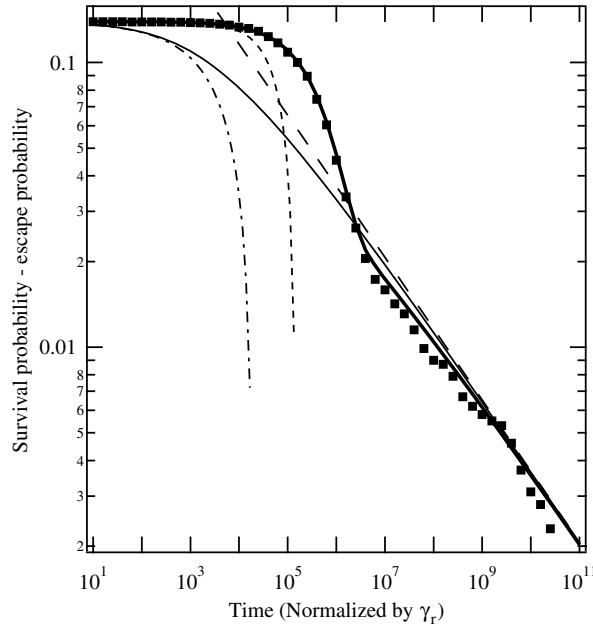


Figure 1. Time dependent part of the survival probability $n_s(t)$ as a function of time for $\alpha = 0.5$ and square box sink. Time is normalized by γ_τ , $r_0/R = 0.1$ and $\lambda/R = 0.1$. $k_0(R^2/D_\alpha)^{1/\alpha} = 0.1$. The thick solid line is the result of Laplace inversion of the exact expression, equation (25). The thin solid line is the approximate solution by equation (12). Dots represent the results of numerical simulations. The long-dashed line is the asymptotic kinetics of equation (24). The short-dashed line is the static result described in the text. The dot-dashed line is the static result of the approximate equation.

probability 0.8608 is subtracted from the analytical solutions of survival probability and the numerical result of the escape probability 0.861 is subtracted from simulation results. As shown in figure 1, the inverse Laplace transformation of equation (25) coincides with the results of numerical simulations as it should. The approximate results deviate at intermediate times. In the asymptotic region, both results converge to the result of equation (24). The initial decay of the exact solution is described by equation (13), while that of the approximate solution is given by equation (14). The behaviour at intermediate times is not reproduced well enough by any approximate solutions.

3.3. Exponentially decreasing reactivity

The case of exponentially decreasing reactivity $k(r) = k_0 \exp(-2\beta r)$ is very important from the point of view of possible applications. For example, the effect of this kind of reactivity is thoroughly discussed in connection with the interpretation of some experiments on geminate recombination [4, 8]. The escape probability under normal diffusion is already known, so that the escape probability under dispersive transport is obtained by substitution, $k(\vec{r})/D_1 \rightarrow k^\alpha(\vec{r})/D_\alpha$ in the expression for the escape probability under normal diffusion as explained below equation (21). In the limit that the radius of the reflecting boundary goes to zero, i.e. $R \rightarrow 0$, the escape probability is obtained from the known result under normal diffusion [31]

$$\varphi(r_0) = \frac{1}{\alpha\beta r_0} \left(K_0(x) - \frac{K_0(x_c)}{I_0(x_c)} I_0(x) \right), \quad (26)$$

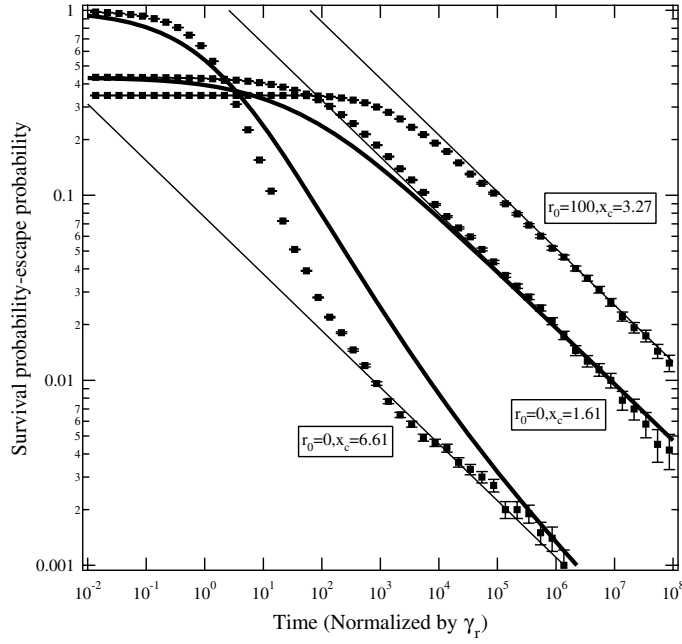


Figure 2. Time dependent part of the survival probability $n_s(t)$ as a function of time for $\alpha = 0.6$ and tunnelling rate $k_0 \exp(-2\beta r)$. Time is normalized by γ_r and the distance is normalized by the jump length parameter λ . $1/\beta = 20$. Three sets of data are presented; they are $r_0 = 0$ and $x_c = 6.61$, $r_0 = 0$ and $x_c = 1.61$, $r_0 = 100$ and $x_c = 3.27$ as shown in the annotation. Dots represent the results of numerical simulations. The thin solid lines are the asymptotic time dependence of equation (24). The thick solid line is the approximate solution by equation (12).

where $x_c \equiv \sqrt{k_0^\alpha/D_\alpha}/(\alpha\beta)$ and $x = x_c \exp(-\alpha\beta r_0)$. If the initial position of the pair is $r_0 = 0$, the escape probability is further simplified to [20], $\varphi(0) = 1/I_0(x_c)$. On the other hand, in the limit of large initial separation the escape probability is written in the form of equation (23) with

$$\ell_R = \frac{1}{\alpha\beta} \left(\gamma + \ln(x_c/2) + \frac{K_0(x_c)}{I_0(x_c)} \right), \quad (27)$$

where $\gamma = 0.57721\dots$ is Euler's constant [32]. The asymptotic kinetics of the survival probability is obtained by substituting equations (26) and (27) into equation (24). In the limit of $x_c \ll 1$, which indicates that the tunnelling rate is smaller than the diffusional escape rate from the region of $r < 1/(\alpha\beta)$, the effective reaction radius is simplified to $\ell_R \simeq (x_c/2)^2$ and the recombination rate reduces to that obtained previously in the case of $r_0 = 0$ [20]. In the opposite limit of $x_c \gg 1$, the result also reduces to that obtained previously [16].

Now let us compare the asymptotic result obtained from equations (24), (26), and (27) with those of numerical simulation. In our Brownian simulation, length is normalized by the jump length λ and the time is normalized by the hopping frequency γ_r . In these units the tunnelling length is taken to be $1/\beta = 20$. In our simulation of 10^4 trajectories we take the dispersive parameter $\alpha = 0.6$, the escape distance 10^4 and the cut-off distance of reaction $50/\beta$. Figure 2 shows the results for the case of initial distance $r_0 = 0$ and $x_c = 1.61$. According to these results, the theoretical and simulation values of the escape probability are 0.567 and 0.566, respectively. The long time behaviour of the kinetics $N(t)$ obtained by simulation proves to be in good agreement with that predicted by equation (24). For the sake of

comparison we also plot $N(t)$ found by approximate solution of equation (12). Some deviation from the simulation results is observed at intermediate times. The deviation increases with the increase of reaction strength corresponding to the increase of x_c . Figure 2 also displays the results of similar calculation for $x_c = 6.61$ with the same initial condition of $r_0 = 0$. The escape probability calculated by simulation, 0.0089, turns out to be close to the theoretical value 0.0085. The reaction strength used in this calculation appears to be large in a sense that the corresponding escape probability is very small. It is seen that for $x_c = 6.61$ the results obtained with the approximate solution deviate from simulation results more significantly than for $x_c = 1.61$, in accordance with explanations presented in the last part of the previous section. It is also clear that for exponential $k(r)$ this deviation is smaller than that for the box model (see in figure 1), because in the case of exponential $k(r)$ the reaction occurs mainly at short distances as compared to those typically contributing to the reaction in the square box model. We also present the results of calculation for the initial distance 100 with $x_c = 3.27$. For this initial distance the escape probability obtained from the simulation, 0.653, is also close to the theoretical value 0.656 calculated with equation (26). Similarly, the prediction of equation (24) agrees well with the simulation results in the asymptotic time range for any initial conditions and reaction strength chosen for simulations.

3.4. The inverse power type reactivity

3.4.1. Escape probability. The model of inverse power type distance dependence of reactivity $k(r) = k_0(R_F/r)^m$ is also very important for applications. The fact is that quite a number of energy transfer processes are described just by this type of $k(r)$. The most well known is the so-called Förster mechanism of energy transfer [33]. In the case of this inverse power type dependence $k(r)$ equation (21) for escape probability should be solved with effective reactivity $k^\alpha(r)$, which is also of inverse power type

$$k^\alpha(r) = k_0^\alpha (R_F/r)^n \quad \text{with } n = m\alpha. \quad (28)$$

For $n \leq 2$ the reaction kinetics is quasistatic [16] and the escape probability is, naturally, equal to zero. When $n > 2$, it is non-zero and is determined by equation (21). Solution of this equation with reflective boundary condition yields⁴

$$\varphi(r) = \sqrt{\frac{R_F}{r}} \frac{2(\nu x_F)^\nu [K_\nu(2\nu x) - C I_\nu(2\nu x)]}{\Gamma(\nu)} \quad \text{with } \nu = 1/(n-2), \quad (29)$$

where $x_F = R_F \sqrt{k_0^\alpha/D_\alpha}$, $x = x_F(R_F/r)^{\frac{1}{2\nu}}$, and the coefficient C is given by

$$C = \frac{K_\nu(2\nu x_R) - x_R K_{\nu+1}(2\nu x_R)}{I_\nu(2\nu x_R) + x_R I_{\nu+1}(2\nu x_R)} \quad (30)$$

with $x_R = x_F(R_F/R)^{\frac{1}{2\nu}}$. Note that in the limit $x_R > 1$, which is realized for $k_0^\alpha > D_\alpha R_F^2$ and $R_F > R$, expression (29) is simplified since $C \simeq 0$. It is of certain interest to consider the escape probability at large initial separations. Expansion of the modified Bessel functions results in [32]

$$\varphi(r) = \begin{cases} 1 - \left(\frac{R_F}{r}\right)^{n-2} \frac{x_F^2}{(3-n)(n-2)} & \text{for } 3 > n > 2, \\ 1 - \frac{R_F}{r} x_F^2 \ln\left(\frac{r}{R_F}\right) & \text{for } n = 3, \\ 1 - \frac{R_F}{r} (\nu x_F)^\nu \left[\frac{\Gamma(1-\nu)}{\Gamma(1+\nu)} + \frac{2C}{\Gamma(\nu+1)\Gamma(\nu)} \right] & \text{for } n > 3. \end{cases} \quad (31)$$

⁴ The eigenfunctions of the problem are found in the textbook of Landau and Lifshitz [34].

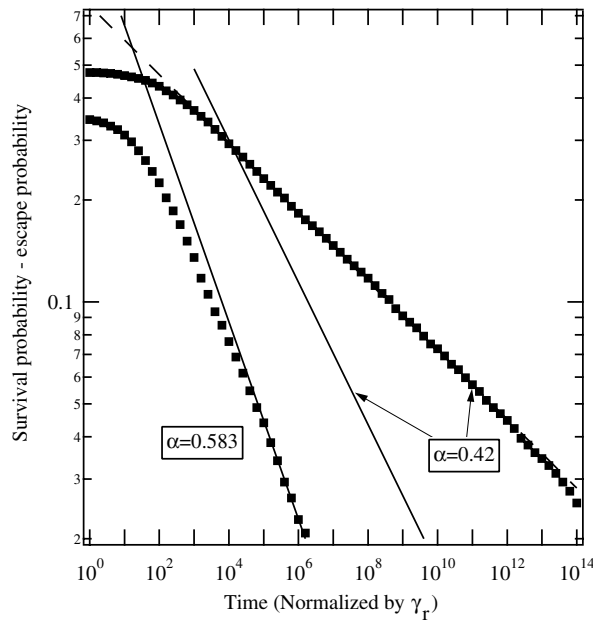


Figure 3. Time dependent part of the survival probability $n_s(t)$ as a function of time for reactivity $k_0(R_F/r)^6$. Time is normalized by γ_r and the distance is normalized by the jump length parameter λ . Other parameters are given in the text. Dots represent the results of numerical simulations. The solid line is the asymptotic time dependence of equation (24) for $\alpha = 0.583$ and the power law $Ct^{-\alpha/2}$ with C being arbitrary chosen for $\alpha = 0.42$. The dashed line is $Ct^{-\mu}$ with $C = 0.75$ and $\mu = 0.102$ obtained by fitting to the numerical results of $\alpha = 0.42$.

It is seen that the conventional $1/r$ -behaviour at large distance, resulting from free diffusive motion outside the region of efficient reaction, is found only for $n > 3$. In the limits of $x_F \gg 1$ or $R \simeq 0$ the parameter $C \simeq 0$ and the expression $\varphi(r)$ is similar to that expected from the results obtained previously for steady state concentration of bulk reactions [16]. In the case of $2 < n \leq 3$, some of the particles can still escape from recombination. However, the distance dependence of the escape probability $\varphi(r)$ strongly deviates from $1/r$ -dependence since the spatial dependence of reactivity $k(r)$ is so long ranged that it disturbs the diffusion fluxes at all distances (even very large). For example, in the case of the Förster mechanism of energy transfer [33], for which $k(r) = k_0(R_F/r)^6$, the escape probability is non-zero at $\alpha > 1/3$, but the conventional $1/r$ -dependence on the initial distance is predicted only for $\alpha > 1/2$.

In order to test the accuracy of the above expressions and analyse the reaction kinetics we also performed Brownian simulation for the rate $k_0(R_F/r)^6$ with $R_F/\lambda = 2$, $x_F = 0.5$, $r_0/\lambda = 2$ and $R = 0$. The simulation method is the same as that for the tunnelling rate except for the cut-off distance of reaction, $3000R_F$. Figure 3 shows the results for $\alpha = 0.583$ ($m\alpha = 3.5$) and $\alpha = 0.42$ ($m\alpha = 2.5$).

The escape probabilities calculated by simulations, 0.63 for $\alpha = 0.583$ and 0.523 for $\alpha = 0.42$, appear to be very close to the corresponding theoretical values 0.615 (for $\alpha = 0.583$) and 0.515 (for $\alpha = 0.42$) obtained with equation (29).

3.4.2. Long time reaction kinetics. The situation with long time kinetics is more complicated.

- (1) In the case $\alpha = 0.583$, for which $n = m\alpha > 3$, the asymptotic kinetics is similar to that predicted for short range reactivity $k(r)$ and is well described by equation (24).

- (2) For smaller values of parameter α which correspond to $2 < n < 3$, the escape probability is not described by equation (23) and the long time behaviour of $N(t)$ is not described by (24). Simulation for $\alpha = 0.42$ shows, however, that the long-time tail of the kinetics seems to be still of power type, $\sim 1/t^\mu$, but with the value of exponent μ differing from the $\alpha/2 = 0.21$ predicted for short-range $k(r)$.

In general, the calculation of reaction kinetics $N(t)$ reduces to solving the complicated Schrödinger-like equation (4), which cannot be solved analytically. Most important specific features of the kinetics can nevertheless be analysed with the use of approximate methods.

For example, for relatively sharp $k(r)$ -dependences, $k(r) \sim r^{-m}$ with $m > 3/\alpha$ (corresponding to $n = m\alpha > 3$), one can apply the approximate theory developed for short-range reactivities [16]. This approximation leads to equation (24), the validity of which is confirmed by numerical results.

Unfortunately, the short range approximation is not applicable in the case $2 < n < 3$. However, it is still possible to solve equation (4) approximately. Below we will outline the method of approximate solution and discuss some results obtained for the problem considered.

The approximate method is based on the observation that for $2 < n < 3$ the long-time tail of reaction kinetics can be evaluated by treating the effect of $k(r)$ perturbatively [34]. This method can be formulated in terms of the Laplace transform of the rate, $\hat{J}(s)$; $\hat{N}(s) = -J(s)$. Evidently, the survival probability is determined by the rate,

$$\hat{N}(s) = [1 - \hat{J}(s)]/s. \tag{32}$$

The general expression for the Laplace transform of the reaction rate $\hat{J}(s)$ is given from equation (4) as

$$\hat{J}(s) = r_0^{-1} \int_0^\infty dr rk(r) (2/\lambda^2) \hat{M}^{-1}(s + k(r)) \hat{g}(r, r_0|s), \tag{33}$$

where $\hat{M}(s) = (2dD_\alpha/\lambda^2)s^{1-\alpha}$ is defined in equation (5) and $\hat{g}(r, r_0|s)$ is the Green's function satisfying equation $[\kappa_\alpha^2(s) + k(r) - d^2/dr^2]g = \delta(r - r_0)$ in which $\kappa_\alpha(s) = \sqrt{s^\alpha/D_\alpha}$.

The main contribution to the term independent of s , $\hat{J}(0)$, comes from the region of r where $k(r)$ is relatively strong (strongly disturbs the PDF $\hat{\rho}(r, s)$) while the first s -dependent term of $J(s)$ is determined by the process at large distances where $k(r)$ is small. Specifically, they are given by the relation between distances $r_s = R_F(k_0/s)^{1/m}$ and $r_\kappa = 1/\kappa_\alpha$. To avoid the analysis of the non-interesting effect term $\hat{J}(0)$ independent of s , hereafter we will assume $k(r)$ to be so weak that $r_\kappa > r_s$ in the region of s corresponding to the timescale of our interest. The solution can be found by expansion of the s -dependent term of $J(s)$ in powers of $k(r)$.

In the lowest order in $k(r)$ the s -dependent part of the rate $\hat{J}(s)$ can be evaluated by equation (33) but with the approximate (free subdiffusion) Green's function $\hat{g}_a(r, r_0|s)$:

$$\hat{g}(r, r_0|s) \simeq \hat{g}_a(r, r_0|s) = (2\kappa_\alpha(s))^{-1} [e^{-\kappa_\alpha(s)|r-r_0|} - e^{-\kappa_\alpha(s)(r+r_0)}] \tag{34}$$

which obeys equation

$$[\kappa_\alpha^2(s) - d^2/dr^2]\hat{g}_a = \delta(r - r_0). \tag{35}$$

The simple approximation (equation (34)) is sufficient for describing quite accurately the behaviour of $\hat{N}(s)$ in the region $s \rightarrow 0$ and predicting asymptotic dependence $N(t)$ at long times. In the expression for $\hat{g}(r, r_0|s)$ the terms depending on r_0 describe the escape probability. Since we are interested in the process at large distances where $k(r)$ is small, equation (34) is further simplified by taking the limit of $r \gg r_0$. In any case for $r \gg r_0$ the escape probability determines only the amplitude of the long time dependence $N(t)$ and does not affect its functional form which is of main interest in our analysis.

Equations (33) and (34) lead to the following expression for $\hat{J}(s)$ at small $s \rightarrow 0$

$$\hat{J}(s) = \hat{J}(0) + \hat{J}_i(s) + \hat{J}_f(s). \quad (36)$$

where

$$\hat{J}_i(s) \sim \int_0^\infty dr r k^\alpha(r) [1 - e^{-\kappa_\alpha(s)r}], \quad (37)$$

$$\hat{J}_f(s) \sim \int_0^\infty dr r \{k^\alpha(r) - k(r)[s + k(r)]^{\alpha-1}\} e^{-\kappa_\alpha(s)r}. \quad (38)$$

When equation (36) is introduced in equation (32), the term $1 - \hat{J}(0)$, is shown to equal to $\varphi(r_0)$, which is not interesting for our further discussions. Formulae (36)–(38) prove to be very useful for analysis of the time dependent part of the survival probability. At very small s , estimation of $\hat{N}(s) - \varphi(r_0)/s \simeq \hat{J}_f(s)/s \sim s^{(n-2)/m-1} \int_0^\infty dx x^{2/m} [x^{\alpha-1} - (1+x)^{\alpha-1}] \sim s^{(n-2)/m-1}$ indicates that

$$N(t) \simeq \varphi(r_0) + x_F^2 (k_0 t)^{-\mu_f} \quad \text{where } \mu_f = (n-2)/m. \quad (39)$$

μ_f can conveniently be represented as

$$(2/\alpha)\mu_f = 2(n-2)/n. \quad (40)$$

The rigorous analytical expressions are obtained for equations (37) and (38). By analysing the analytical expression it can be shown that equation (39) is indeed the long-time asymptote.

The proposed approach allows one to obtain the exact expression for the exponent μ_f in the final asymptotic behaviour of $N(t)$ (given in equation (39)). It is clear that the final asymptotic dependence (39) seems to exist for values of $4 > n > 2$, though the corresponding contribution is expected to decrease with the increase of n . In terms of results of the above analysis the conventional asymptotic behaviour $N(t) \sim t^{-\alpha/2}$ found for $4 > n > 3$ is, actually, intermediate since $\mu_f < \alpha/2$ in the case of $4 > n$. The final asymptotic dependence $n_f(t)$ is still given by equation (39) though the difference in the powers as well as the amplitude of the part of the kinetics is small.

To test the above prediction we performed simulations for a few values of α in the region $1/3 < \alpha \leq 0.5$, which correspond to $2 < n < 3$. In order to make the errors in the escape probability less than 2% of those estimated from equation (29), the simulations were performed for 2×10^4 independent trajectories with the cut-off distance of reaction, $5000R_F$. Other values of parameters are $R_F/\lambda = 2.0$, $x_F = 0.2$, $r_0/\lambda = 2.0$ and $R = 0$. In figure 4, we present the dependence of $2\mu/\alpha$ on n for $2 < n < 3$, where μ is the exponent determined by fitting numerical data to the dependence $C_\mu t^{-\mu}$ for each value of α . The obtained values of $2\mu/\alpha$ correlate with the theoretical line based on equation (40) as seen from figure 4. $(2/\alpha)\mu_f$ depends only on n regardless of the exponent m . In order to check this relation for m different from 6, we also performed simulations of dispersive diffusion under dipole–quadrupole energy transfer, $k(r) = k_0(R_F/r)^8$. As shown in figure 4, μ is independent of m for the same set of α and $n = m\alpha$.

It is worth noting that in the simulation we had to take a large value of the cut-off distance of reaction: $5000R_F$. Such a choice of the cut-off distance is essential to obtain reliably the exponents of asymptotic decay of $N(t)$ for the case $2 < n < 3$, in which the reaction disturbs the distribution of particles at any (even large) distances. In addition, in this simulation the value of x_F is taken to be small, $x_F = 0.2$, in order to reduce the initial quasistatic stage of the reaction. For this value of x_F the escape probability (estimated with equation (29)) is fairly large: $\varphi \simeq 0.9$. The large value of φ allowed us to evaluate the exponents μ accurately enough to reliably distinguish the systematic change of μ with the change of α .

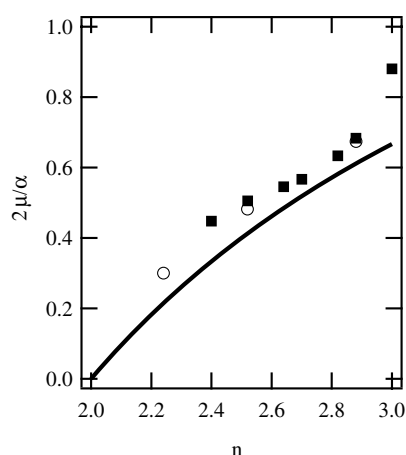


Figure 4. $2\mu/\alpha$ against n for reactivity $k_0(R_F/r)^m$ with $m = 6$ or 8 , where μ is the exponent obtained by fitting the numerical data to $C_\mu t^{-\mu}$. Dots and circles represent $m = 6$ and 8 , respectively. The solid line is $2\mu_f/\alpha = 2(n-2)/n$.

4. Summary and conclusions

In this paper the kinetics of geminate reactions assisted by dispersive (subdiffusive) relative motion of reacting particles is thoroughly analysed. The analysis is made with the use of analytical solutions of the corresponding non-Markovian master equation and numerical simulation of the process. The main goal of our work is to study the specific features of interference of anomalous (dispersive) stochastic relative motion with long-range reactivity which is modelled by the first order decay with the rate $k(r)$ depending on the interparticle distance r . In the analysis we have considered three models for $k(r)$: the square box model, exponential model $k(r) \sim \exp(-2\beta r)$, and inverse power model $k(r) \sim 1/r^m$. The interference is demonstrated to strongly manifest itself in some anomalous properties of the reaction kinetics. The effects of interference are found both for static characteristics and time dependence. In a wide region of parameters of the model the striking difference in the kinetics is observed for reactions assisted by normal diffusion and by subdiffusion. Moreover, the deviation of the reaction kinetics from that for normal diffusion is mainly determined by the anomaly parameter α (which characterizes (anomalous) long-time behaviour of the mean square displacement: $\langle r^2(t) \rangle \sim t^\alpha$, $\alpha < 1$).

To demonstrate the appropriateness of the treatments based on the non-Markovian master equation and numerical simulation, we have analysed the reaction modelled with reactivity $k(r)$ of square box form. This model allows for exact analytical solution. The results of both calculations prove to agree completely. This analysis revealed, in addition, some important general features of the reaction kinetics: for large amplitude and range of $k(r)$, as well as for initial distances deeply in the region of non-zero $k(r)$, the kinetics, i.e., the number $N(t)$ of surviving pairs, is mainly quasistatic (exponential), while in the opposite case the long tail of the kinetics is of inverse power type $n_s(t) = N(t) - \varphi(r_0) \sim 1/t^{\alpha/2}$ with anomalous exponent.

In the case of more realistic reactivity $k(r)$ (exponential and of inverse power type) the non-Markovian master equation cannot be solved exactly. However, some important anomalous properties of the kinetics $N(t)$ under study are obtained by approximate analysis of its asymptotic behaviour at long times.

In particular, some peculiarities of the subdiffusion-assisted reaction kinetics are very clearly demonstrated by means of static observables (escape and reaction probabilities, rate

constants etc). For example, it is shown that the dependence of reaction probability $\varphi_r(r_0)$ on the initial separation r_0 changes very significantly with the change of anomaly parameter α . This is especially true for reactions with reactivity $k(r)$ of inverse-power type, $k(r) \sim 1/r^m$: for $n = \alpha m > 3$ the result $\varphi_r(r_0) \sim 1/r_0$ coincides with that predicted in the normal diffusion approach, while for $3 > n > 2$ it changes to the markedly weaker dependence $\varphi_r(r_0) \sim 1/r_0^{n-2}$.

In parallel with the change-over in the dependence of $\varphi_r(r_0)$ on r_0 the asymptotic behaviour of reaction kinetics, $N(t)$ also significantly changes as $n = \alpha m$ is changed. For $n > 3$ the long time part of the kinetics $n_s(t) = N(t) - \varphi(r_0)$ is similar to that obtained in the case of normal diffusion but with t replaced by t^α , i.e. $n_s(t) \sim 1/t^{\alpha/2}$. For $3 > n > 2$, it becomes more dispersive, though remaining of inverse-power type: $n_s(t) \sim 1/t^{\alpha(1-2/n)}$. Strictly speaking, such power law decay persists in the case of $4 > n > 3$. The difference between the powers, $\alpha(1 - 2/n)$ and $\alpha/2$, is too small to distinguish between them by the numerical simulations in this work.

In this paper we have confined ourselves to pure theoretical discussion of the anomalous kinetics of subdiffusion-assisted geminate reaction. The obtained results should, however, be important for various applications. As one of them the geminate recombination of photoinduced charge carriers in glasses has already been discussed in the literature [4, 5]. This reaction is described by the exponentially decreasing reactivity $k(r)$. The case of $k(r)$ of inverse power type is also quite important from the point of view of possible applications to excitation transfer processes [8] as has already been mentioned in section 3.4. In connection with possible application of the results, it is worth noting that as mentioned above (in section 3.4) when discussing the accuracy of simulation data serious requirements on the accuracy of possible experimental measurements have to be satisfied in order to observe some predicted anomalous features of long-time asymptotic kinetics of subdiffusion assisted geminate reactions (for $3 > n > 2$).

In this work we have concentrated on the analysis of the kinetics of geminate reactions. However, the kinetics of geminate reactions is known to be closely related to that of bulk reactions [8]. The correspondence between them is well established for reactions assisted by normal diffusion. As for subdiffusion-assisted processes, there are still some problems to solve [16], especially in the case $3 > n > 2$ in which anomalous geminate kinetics is observed.

Acknowledgments

We would like to thank Professor J Klafter for useful discussions. This work is supported by the COE development program of the Ministry of Education, Culture, Sports, Science and Technology (MEXT) and Russian Foundation for Basic Research.

Appendix. Derivation of equation (4)

As before [20], the problem is formulated on the basis of a discrete model on a periodic lattice of dimension d and then take the continuous limit in space. We denote the vector characterizing a jump to the nearest neighbour site j by \vec{b}_j . In the presence of both jump processes and reaction the waiting time distribution of making a jump and that of reaction are given by [35] $\psi_{\text{rw}}(\vec{r}, t) = \psi(t) \exp(-k(\vec{r})t)$ and $\psi_{\text{rc}}(\vec{r}, t) = k(\vec{r}) \exp[-k(\vec{r})t] \int_t^\infty dt_1 \psi(t_1)$, respectively. The equation for the probability $\eta(\vec{r}_i, t) dt$ of just arriving at site \vec{r}_i in the time interval between t and $t + dt$ is written as

$$\eta(\vec{r}_i, t) = \frac{1}{2d} \sum_{j=1}^{2d} \int_0^t dt_1 \psi_{\text{rw}}(\vec{r}_i - \vec{b}_j, t - t_1) \eta(\vec{r}_i - \vec{b}_j, t_1) + \delta_{\vec{r}_i, \vec{r}_0}. \quad (\text{A.1})$$

By subtracting $\int_0^t dt_1 \psi_{\text{rw}}(\vec{r}_i, t - t_1) \eta(\vec{r}_i, t_1)$ from both sides of equation (A.1), we obtain in the small- λ limit

$$\left[1 - \hat{\psi}_{\text{rw}}(\vec{r}, s)\right] \hat{\eta}(\vec{r}, s) = \lambda^2 \left[\nabla^2 / (2d)\right] \hat{\psi}_{\text{rw}}(\vec{r}, s) \hat{\eta}(\vec{r}, s) + \delta(\vec{r} - \vec{r}_0), \quad (\text{A.2})$$

where the Laplace transform is introduced, i.e. $\hat{\eta}(\vec{r}, s) = \int_0^\infty dt \exp(-st) \eta(\vec{r}, t)$. The density $\rho(\vec{r}, t)$ is given in terms of the probability of remaining at a site, $\phi(\vec{r}, t) \equiv \int_t^\infty dt_1 [\psi_{\text{rc}}(\vec{r}, t_1) + \psi_{\text{rw}}(\vec{r}, t_1)]$, as $\rho(\vec{r}, t) = \int_0^t dt_1 \phi(\vec{r}, t - t_1) \eta(\vec{r}, t_1)$. By noticing $\hat{\phi}(\vec{r}, s) = [1 - \hat{\psi}_{\text{rw}}(\vec{r}, s) - \hat{\psi}_{\text{rc}}(\vec{r}, s)]/s$ we obtain equation (4).

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