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Subdiffusion-assisted reaction kinetics in disordered media

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Abstract

We present a theory for describing the reaction process occurring in disordered media with energetically disordered trapping sites and spatial constraints. The theory is based on a generalized fractional reaction–diffusion equation, which describes the time evolution of the mean distribution of a particle performing a continuous time random walk on a fractal network. The motion of a particle is subdiffusive because of the spatial constraints and/or the random detrapping times described by a waiting time distribution given by $\psi(t) \sim t^{-(1+\alpha)}$ with $0 < \alpha < 1$. Assuming that the reaction occurs at a separation of contact, the reaction and transport processes are decoupled and the kinetic information for the reaction is expressed in terms of the reaction-free Green's function obtained with the reflecting boundary condition at the separation of contact. The survival probability of a reactant pair is shown to decay asymptotically as $\tau^{-\alpha|d_s/2-1|}$, where d_s is the fracton dimension of the fractal network under consideration. We also check the validity of the analytical results by comparison with Monte Carlo simulation results.

1. Introduction

Kinetics of reactions occurring in disordered media, such as glasses, amorphous semiconductors, lipid bilayers and living cells, often display anomalous behaviour and have attracted much attention [1–3]. A main cause of the observed peculiarities in reaction kinetics is the dispersive transport of reactant particles due either to spatial constraints on jump paths or to the presence of energetically disordered trapping sites with diverging mean detrapping time below some threshold temperature.

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The tool most widely used to describe the anomalous dynamics is the continuous time random walk (CTRW) model [1, 4, 5]. In this model the random walker makes a jump between lattice points after a certain waiting time that is chosen randomly from a distribution function $\psi(t)$. In the presence of energetic disorder, the waiting time distribution may behave as $\psi(t) \sim t^{-(1+\alpha)}$ with $0 < \alpha < 1$ at long times [6]. Hence, the mean detrapping time diverges and the mean squared displacement (MSD) increases sublinearly with time; $\langle r^2(t)\rangle \sim t^{\alpha}$. On the other hand, spatially disordered media are frequently modelled by fractal lattices [1–3]. Due to the constraints on jump paths, particle transport on fractals becomes subdiffusive even when the mean detrapping time at a lattice site is finite. The MSD is given by $\langle r^2(t)\rangle \sim t^{2/d_{\mathrm{w}}}$ with the walk dimension d_{w} larger than 2 in most cases [3, 7].

Most previous works dealing with subdiffusion-assisted reaction kinetics focused upon either one of the two causes of subdiffusion. Reaction kinetics in fractal media have been studied based on the random walk models [1, 3, 8] or by using a generalized diffusion equation approach [9, 10]. Blumen *et al* used random walk models to study the trapping and target problems as well as bimolecular cases, $\mathrm{A} + \mathrm{A} \rightarrow 0$ and $\mathrm{A} + \mathrm{B} \rightarrow 0$ [1, 8]. It was shown that expressions for survival probability obtained for regular lattices in the Euclidean dimension d could be used in analysing the computer simulation results obtained for fractal lattices with the replacement of d by the fracton dimension d_{s}. This idea was extended further in investigating the reversible recombination reaction by the use of a generalized diffusion equation defined in d_{s}-dimensional space [10]. However, by using a scaling argument Sheu *et al* showed that for the bimolecular $\mathrm{A} + \mathrm{B} \rightarrow 0$ reaction, the asymptotic kinetic behaviour depends not only on d_{s} but also on the fractal dimension d_{f} [11].

The anomalous slowing down of reaction rates due to diverging mean residence time of reactant molecules at lattice sites has been extensively investigated by using CTRW approaches [1, 12]. Recently, however, alternative approaches based on the fractional diffusion equation (FDE) have become increasingly popular [13, 14]. The FDE itself can be derived from the CTRW model [13, 15], but the major advantage of FDE-based approaches is that the solution of the FDE can be obtained by using similar mathematical techniques that have been used for solving the standard diffusion equation. In addition, the influence of external fields and the effects of excluded volumes of reactants can be incorporated in a more straightforward manner. Yuste and Lindenberg used the FDE approach to investigate the dynamics of single-species coagulation reactions in one dimension [16]. To take into account the excluded volume effects on the geminate pair reaction and the pseudo-first-order target problem in subdiffusive media, Sung *et al* introduced the delta-function reaction sink together with the reflecting boundary at the separation of contact of reactants to construct the reaction–diffusion equation [17]. Subsequently, Seki *et al* elaborated on the construction of a proper boundary condition for use with the FDE [18, 19]. It was shown that the reaction term must include a memory effect because the escape from a non-reactive encounter is delayed in conformity with a waiting time distribution which can be related to that governing the subdiffusive motion in the bulk. In a related work, Sung and Silbey considered the one-dimensional CTRW with arbitrary reaction rate and waiting time distributions at the boundary, and obtained a formally exact solution in the continuum limit without recourse to a reaction–diffusion equation [20]. Hence their approach enables one to find an appropriate reaction term in the generalized reaction–diffusion equation. Very recently, Shushin used another approach based on the non-Markovian stochastic Liouville equation to tackle the problems involving long-range coordinate-dependent reactivity [21].

In this work, we consider the kinetics of reactions in subdiffusive media involving both spatial constraints and energetically disordered trapping sites. Blumen *et al* addressed the pseudo-first-order $\mathrm{A} + \mathrm{B} \rightarrow 0$ case for this general situation by using the CTRW

approach [1, 22]. However, to include the detailed microscopic features of the reaction event, such as the excluded volume effect and the distance-dependent reactivity, it is preferable to use a generalized FDE approach. As an initial attempt along this line, we will study the reaction kinetics of a geminate pair which performs CTRW on the fractal lattice.

In section 2, an appropriate form of the generalized reaction–diffusion equation is established. In section 3, a Laplace-transform expression for the survival probability of the reactant pair is obtained in terms of a reaction-free Green's function. The effects of various reaction parameters, such as the sink size and the initial separation of the geminate pair, and of transport properties, such as the dimensional parameters of the fractal lattice and the waiting time exponent α, can be predicted from the analytical expression of survival probability. In particular, it is shown that the survival probability decays asymptotically as $\tau^{-\alpha|d_s/2-1|}$. In section 4, the accuracy of the analytical results is checked against Monte Carlo simulation results. The theoretical results are in good agreement with CTRW simulations on a Sierpinski gasket. Section 5 concludes the present work.

2. Generalized reaction–diffusion equation

Let us first consider the subdiffusive motion of a particle performing CTRW on a fractal lattice in the absence of a reaction. The probability density $P(r, t)$ of the particle starting from the origin and travelling a distance r in time t can be expressed in the Laplace domain as [3]

$$\hat{P}(r, s) = \sum_{n=0}^{\infty} P_n(r)\hat{\psi}(s)^n[1 - \hat{\psi}(s)]/s. \tag{1}$$

Here, $\hat{f}(s)$ denotes the Laplace transform of a function $f(t)$. $P_n(r)$ is the probability of being at the distance r after n steps, and $\psi(t)$ is the waiting time distribution at a lattice site. For a fractal lattice, lacking translational invariance, $P_n(r)$ must be averaged over all pairs of the lattice sites separated by the distance r.

It is known that anomalous dynamic features associated with fractals can be incorporated into an intrinsic metric, defined by the relation $y = r^\beta/\beta$ with $\beta = d_w/2 = d_f/d_s$ [23, 24]. In the intrinsic metric space, which we will simply call the y-space, many dynamic relations for fractals reduce to the familiar forms known for regular lattices in Euclidean space. For example, an approximate expression for $P_n(r)$ is given in y-space as

$$P_n(y) = \frac{1}{(4\pi D_{sp} n)^{d_s/2}} \exp\left(-\frac{y^2}{4D_{sp}n}\right), \tag{2}$$

where D_{sp} is the diffusion coefficient defined in terms of the step number n rather than time. As can be noted in equation (2), the fracton dimension d_s plays the role of the mass scaling exponent in y-space. Although equation (2) deviates from the universal asymptotic scaling behaviour $P_n(y) \sim n^{-d_s/2} \exp[-c(y^2/n)^{1/(d_w-1)}]$ for $n \ll (r/b)^{d_w}$, where c is a constant and b is the lattice spacing, it becomes accurate for large n compared to $(r/b)^{d_w}$ [25, 26]. Since we are interested in intermediate to long time events, we will adopt the simpler expression for $P_n(y)$ in equation (2).

Applying the fractional radial Fourier transformation [27],

$$\tilde{f}(k) = (2\pi)^{d_s/2} k^{1-d_s/2} \int_0^\infty \mathrm{d}y\, y^{d_s/2} J_{d_s/2-1}(ky) f(y), \tag{3}$$

where $J_\nu(x)$ is the νth-order Bessel function of the first kind, equation (1) becomes

$$\hat{\tilde{P}}(k, s) = \frac{1 - \hat{\psi}(s)}{s[1 - \hat{\psi}(s)\mathrm{e}^{-D_{sp}k^2}]}. \tag{4}$$

Taking the diffusion approximation (small k) and carrying out the inverse fractional radial Fourier transformation, we obtain the time-nonlocal generalized diffusion equation in y-space as

$$s\hat{P}(y,s) - \frac{\delta(y)}{\gamma_{d_s} y^{d_s-1}} = \frac{s\hat{\psi}(s)}{1-\hat{\psi}(s)} D_{\rm sp} \mathcal{L}_{d_s}(y) \hat{P}(y,s), \tag{5}$$

where γ_{d_s} is the metric factor given by $\gamma_{d_s} = 2\pi^{d_s/2}/\Gamma(d_s/2)$ and $\mathcal{L}_{d_s}(y)$ is the generalized radial Laplacian in y-space,

$$\mathcal{L}_{d_s}(y) = y^{1-d_s}(\partial/\partial y) y^{d_s-1}(\partial/\partial y). \tag{6}$$

In r-space, $\mathcal{L}_{d_s}$ is just the generalized diffusion operator proposed by O'Shaughnessy and Procaccia [28],

$$\mathcal{D}_{\rm OP}(r) = r^{1-d_f}(\partial/\partial r)(r^{d_f-1}/r^{d_w-2})(\partial/\partial r). \tag{7}$$

Now we consider the irreversible reaction between a geminate pair of reactant molecules. For simplicity, we assume that one of the reactants, say A, is immobile and located at the origin. The other reactant, say B, is initially located at a distance r_0, and subsequently performs a CTRW on the lattice embedded in d-dimensional Euclidean space. The reaction then occurs at a distance σ smaller than r_0. More precisely, we consider a reaction zone which is defined as the d-dimensional spherical shell with the inner and outer radii given by $\sigma - \frac{1}{2}b$ and $\sigma + \frac{1}{2}b$, respectively. When B arrives in this reaction zone, it either reacts or escapes from the zone in the outward direction. It is not allowed to penetrate inside the reaction zone.

Let $\phi_\sigma(t)$ and $\psi^{\rm nr}_\sigma(t)$ be the reaction and the escape time distributions at the reaction zone, respectively, which are normalized as $\int_0^\infty {\rm d}t' \, [\phi_\sigma(t') + \psi^{\rm nr}_\sigma(t')] = 1$. In terms of these distribution functions, we can obtain a formal expression for the probability that B has not undergone reaction until time t. The time dependence of this survival probability, denoted as $S(t|r_0)$, can be expressed in the Laplace domain as [20]

$$\begin{aligned}\hat{\tilde{S}}(s|r_0) &= -\hat{\phi}_\sigma(s) \left\{ \sum_{m=0}^{\infty} [\hat{h}_\sigma(s|\sigma+b)\hat{\psi}^{\rm nr}_\sigma(s)]^m \right\} \hat{h}_\sigma(s|r_0) \\ &= -\frac{\hat{\phi}_\sigma(s)\hat{h}_\sigma(s|r_0)}{1-\hat{\psi}^{\rm nr}_\sigma(s)\hat{h}_\sigma(s|\sigma+b)} \qquad (r_0 \neq \sigma),\end{aligned} \tag{8}$$

where $\hat{\tilde{S}}(s|r_0)$ denotes the Laplace transform of $\partial S(t|r_0)/\partial t$. $h_\sigma(t|r_0)\,{\rm d}t$ is the probability that B arrives at σ for the first time between times t and $t + {\rm d}t$, given that it was initially at r_0. Note that the mth term in the first line of equation (8), $\{-\hat{\phi}_\sigma(s)[\hat{h}_\sigma(s|\sigma+b)\hat{\psi}^{\rm nr}_\sigma(s)]^m \hat{h}_\sigma(s|r_0)\}$, represents the contribution from the reaction event at the $(m+1)$th visit to the reaction zone. The position $\sigma + b$ represents the lattice sites off the reaction zone which can be reached at a single jump from the reaction zone.

The first passage time distribution $h_\sigma(t|r_0)$ is related to the probability $G^*_\sigma(t|r_0)$ that B is found at σ at time t *in the absence of reaction* given that it was initially located at r_0,

$$\hat{G}^*_\sigma(s|r_0) = \frac{1-\hat{\psi}^*_\sigma(s)}{s}\delta_{\sigma r_0} + \hat{G}^*_\sigma(s|\sigma)\hat{h}_\sigma(s|r_0). \tag{9}$$

Here, $\psi^*_\sigma(t)\,{\rm d}t$ is the probability that B escapes from the reaction zone between times t and $t + {\rm d}t$ after the arrival at the reaction zone at time 0 *in the absence of reaction*. We will later discuss the relation between $\psi^*_\sigma(t)$ and $\psi^{\rm nr}_\sigma(t)$. When $r_0 \neq \sigma$, we have

$$\hat{G}^*_\sigma(s|r_0) = \frac{1-\hat{\psi}^*_\sigma(s)}{s}\left\{\sum_{m=0}^{\infty}[\hat{h}_\sigma(s|\sigma+b)\hat{\psi}^*_\sigma(s)]^m\right\}\hat{h}_\sigma(s|r_0)$$
$$= \frac{1-\hat{\psi}^*_\sigma(s)}{s}\cdot\frac{\hat{h}_\sigma(s|r_0)}{1-\hat{h}_\sigma(s|\sigma+b)\hat{\psi}^*_\sigma(s)} \qquad (r_0 \neq \sigma). \tag{10}$$

Similarly, we have

$$\hat{G}^*_\sigma(s|\sigma) = \frac{1-\hat{\psi}^*_\sigma(s)}{s}\left\{\sum_{m=0}^{\infty}[\hat{h}_\sigma(s|\sigma+b)\hat{\psi}^*_\sigma(s)]^m\right\}$$
$$= \frac{1-\hat{\psi}^*_\sigma(s)}{s}\cdot\frac{1}{1-\hat{h}_\sigma(s|\sigma+b)\hat{\psi}^*_\sigma(s)} = \frac{1-\hat{\psi}^*_\sigma(s)}{s} + \hat{\psi}^*_\sigma(s)\hat{G}^*_\sigma(s|\sigma+b). \tag{11}$$

From equations (9)–(11), $\hat{h}_\sigma(s|r_0)$ can be rewritten as

$$\hat{h}_\sigma(s|r_0) = \frac{\hat{G}^*_\sigma(s|r_0)}{s^{-1}[1-\hat{\psi}^*_\sigma(s)] + \hat{\psi}^*_\sigma(s)\hat{G}^*_\sigma(s|\sigma+b)} \qquad (r_0 \neq \sigma). \tag{12}$$

Note that $\hat{h}_\sigma(s|r_0)$ is independent of the boundary condition.

Substituting equation (12) into (8) we can show that

$$\hat{S}(s|r_0) = \frac{1}{s}\left[1 - \frac{\hat{F}(s,r_0)}{1+\hat{F}(s,\sigma+b)}\right], \tag{13}$$

where $\hat{F}(s,r_0)$ is given by

$$\hat{F}(s,r_0) = \frac{\hat{\phi}_\sigma(s)\hat{G}^*_\sigma(s|r_0)}{s^{-1}[1-\hat{\psi}^*_\sigma(s)] + [\hat{\psi}^*_\sigma(s) - \hat{\psi}_\sigma(s)]\hat{G}^*_\sigma(s|\sigma+b)} \tag{14}$$

with

$$\hat{\psi}_\sigma(s) = \hat{\phi}_\sigma(s) + \hat{\psi}^{\mathrm{nr}}_\sigma(s). \tag{15}$$

Equations (13)–(15) generalize the results of reference [20] obtained for one-dimensional CTRW reaction dynamics to the case of arbitrary fractal dimension. In the long time limit ($s \to 0$), the second term in the denominator of $\hat{F}(s,r_0)$ in equation (14), which results from the coupling between transport and reaction at the boundary, becomes negligible compared to the first term. On the other hand, in the continuum limit ($b \to 0$), $\hat{G}^*_\sigma(s|r_0)$ should be replaced with $(\gamma_{d_\mathrm{f}}\sigma^{d_\mathrm{f}-1}b)\hat{G}^*(\sigma,s|r_0)$, where $\gamma_{d_\mathrm{f}} = 2\pi^{d_\mathrm{f}/2}/\Gamma(d_\mathrm{f}/2)$ and $\hat{G}^*(\sigma,s|r_0)$ is the reaction-free Green's function which satisfies the time-nonlocal generalized diffusion equation in (5),

$$s\hat{G}^*(r,s|r_0) - \frac{\delta(r-r_0)}{\gamma_{d_\mathrm{f}} r_0^{d_\mathrm{f}-1}} = \frac{s\,\hat{\psi}(s)}{1-\hat{\psi}(s)} D_{\mathrm{sp}}\mathcal{D}_{\mathrm{OP}}(r)\hat{G}^*(r,s|r_0). \tag{16}$$

$\hat{G}^*(\sigma,s|r_0)$ satisfies the boundary conditions $\partial G^*(r,t|r_0)/\partial r|_{r=\sigma} = 0$ and $\lim_{r\to\infty} G^*(r,t|r_0) = 0$.

Finally, we can show that the generalized reaction–diffusion equation which is consistent with the survival probability expression in equation (13) is given by

$$s\hat{G}(r,s|r_0) - G(r,0|r_0) = \frac{s\,\hat{\psi}(s)}{1-\hat{\psi}(s)} D_{\mathrm{sp}}\mathcal{D}_{\mathrm{OP}}(r)\hat{G}(r,s|r_0) - \frac{s\hat{\phi}_\sigma(s)}{1-\hat{\psi}^*_\sigma(s)} b\delta(r-\sigma)\hat{G}(r,s|r_0), \tag{17}$$

with $G(r,t|r_0)$ denoting the full Green's function for reaction–diffusion.

To go further, we need an explicit expression for $\psi(t)$, the waiting time distribution at the lattice sites off the boundary of the reaction zone. An interesting model for dispersive transport, which leads to a power-law waiting time distribution, was presented by Jakobs and Kehr [6]. According to their model, the release of B from a lattice site is assumed to be an activated process, and thus the release rate is given by

$$\gamma_r(E) = \gamma_h \exp(-E/k_B T), \tag{18}$$

where E is the energy barrier at a given site, k_B is the Boltzmann constant and T is the absolute temperature. It is then assumed that the energy barrier distribution $f(E)$ has the form,

$$f(E) = \frac{1}{k_B T_c} \exp(-E/k_B T_c), \tag{19}$$

with $k_B T_c$ being a characteristic energy defining the distribution. Hence, the probability that B is released from the site at time t is given by

$$\psi(t) = \int_0^\infty \mathrm{d}E f(E)\gamma_r(E) \exp[-\gamma_r(E)t] = \alpha\gamma_h \frac{\gamma(1+\alpha, \gamma_h t)}{(\gamma_h t)^{1+\alpha}}, \tag{20}$$

where $\alpha = T/T_c$ and γ is the incomplete gamma function $\gamma(a, z) = \int_0^z \mathrm{d}p\, \mathrm{e}^{-p} p^{a-1}$ [29]. The waiting time distribution function $\psi(t)$ is normalized [$\int_0^\infty \mathrm{d}t\, \psi(t) = 1$], and for $\gamma_h t \gg 1$ it becomes [30].

$$\psi(t) \cong \alpha\gamma_h \frac{\Gamma(1+\alpha)}{(\gamma_h t)^{1+\alpha}}, \tag{21}$$

where $\Gamma(z)$ is the gamma function [29]. The Laplace transform of $\psi(t)$ is given in terms of the hypergeometric function, and its large and small s-limits are [19]

$$\hat{\psi}(s) = 1 - {}_2F_1[1, \alpha, \alpha+1, -\gamma_h/s] \sim \begin{cases} 1 - \dfrac{\pi\alpha}{\sin\pi\alpha}\left(\dfrac{s}{\gamma_h}\right)^\alpha & \text{for } \dfrac{s}{\gamma_h} \ll 1, \\ \dfrac{\alpha}{\alpha+1} \cdot \dfrac{\gamma_h}{s} & \text{for } \dfrac{s}{\gamma_h} \gg 1. \end{cases} \tag{22}$$

The distribution $\psi_\sigma^*(t)$ of escape times from the reaction zone *in the absence of reaction* can be related to $\psi(t)$ as follows. We suppose that the waiting time distribution at a site in the reaction zone is also given by $\psi(t)$, but the probability that the jump at the reaction zone occurs in the outward direction (therefore leading to escape) is p, which is less than unity. Since B cannot penetrate inside σ, it should remain at the boundary after an unsuccessful jump until the next trial. Therefore we can write

$$\hat{\psi}_\sigma^*(s) = p\hat{\psi}(s)\left[1 + (1-p)\hat{\psi}(s) + (1-p)\hat{\psi}(s)(1-p)\hat{\psi}(s) + \cdots\right] = \frac{p\hat{\psi}(s)}{1-(1-p)\hat{\psi}(s)}. \tag{23}$$

We then have to introduce an appropriate reaction model. For simplicity, we assume that the reaction process is a Poisson process so that the reaction time distribution is given by

$$\phi_\sigma^*(t) = \gamma_r \mathrm{e}^{-\gamma_r t}, \tag{24}$$

where γ_r is the first-order rate constant for reaction at the reaction zone. Note that $\phi_\sigma^*(t)\,\mathrm{d}t$ is the probability that the reaction takes place between times t and $t + \mathrm{d}t$ *in the absence of any jumps leading to the escape from the reaction zone*.

The reaction and escape time distributions, $\phi_\sigma(t)$ and $\psi_\sigma^{\mathrm{nr}}(t)$, introduced earlier, are the working distributions in the presence of coupling between the CTRW and reaction. These are related to $\phi_\sigma^*(t)$ and $\psi_\sigma^*(t)$ as $\phi_\sigma(t) = \phi_\sigma^*(t)\int_t^\infty \mathrm{d}\tau\psi_\sigma^*(\tau)$ and $\psi_\sigma^{\mathrm{nr}}(t) =$

$\psi^*_\sigma(t)\int_t^\infty \mathrm{d}\tau\phi^*_\sigma(\tau)$ [20], and are normalized as $\int_0^\infty \mathrm{d}\tau[\phi_\sigma(\tau)+\psi^{\mathrm{nr}}_\sigma(\tau)]=1$. For the Poisson reaction process, for which $\phi^*_\sigma(t)$ is given by equation (24), we have

$$\hat{\psi}^{\mathrm{nr}}_\sigma(s)=\hat{\psi}^*_\sigma(s+\gamma_r) \tag{25}$$

$$\hat{\phi}_\sigma(s)=\frac{\gamma_r}{s+\gamma_r}[1-\hat{\psi}^*_\sigma(s+\gamma_r)]. \tag{26}$$

Substituting the small s-limit expressions for $\hat{\psi}(s)$, $\hat{\psi}^*_\sigma(s)$, and $\hat{\phi}_\sigma(s)$ into equation (17) and then taking the inverse Laplace transformation of the resulting equation, we can obtain the following reaction–diffusion equation that is valid for the intermediate to long time regime,

$$\frac{\partial G(r,t|r_0)}{\partial t}={}_0D_t^{1-\alpha}\left[D_{\alpha f}\mathcal{D}_{\mathrm{OP}}(r)G(r,t|r_0)-\kappa_{\alpha f}\frac{\delta(r-\sigma)}{\gamma_{d_{\mathrm{f}}}\sigma^{d_{\mathrm{f}}-1}}G(r,t|r_0)\right]. \tag{27}$$

Here, ${}_0D_t^{1-\alpha}$ is the fractional differential operator defined by

$${}_0D_t^{1-\alpha}f(t)=\frac{1}{\Gamma(\alpha)}\frac{\partial}{\partial t}\int_0^t \mathrm{d}\tau\frac{f(\tau)}{(t-\tau)^{1-\alpha}}\qquad \text{for } 0<\alpha<1, \tag{28}$$

and the generalized diffusion coefficient $D_{\alpha f}$ is given by

$$D_{\alpha f}=\frac{\sin\pi\alpha}{\pi\alpha}\gamma_h^\alpha D_{\mathrm{sp}}. \tag{29}$$

In this expression for $D_{\alpha f}$ the characteristics of the waiting time distribution are carried by the factor $(\sin\pi\alpha/\pi\alpha)\gamma_h^\alpha$, while the feature of spatial constraints associated with the fractal lattice is represented by D_{sp}. For a regular lattice in d-dimensional space, $D_{\mathrm{sp}}=b^2/2d$. For the Sierpinski gasket embedded in d-dimensional space, D_{sp} is given by [28]

$$D_{\mathrm{sp}}=\frac{b^{d_{\mathrm{w}}}}{(d+1)d_{\mathrm{f}}(d_{\mathrm{w}}-d_{\mathrm{f}})}. \tag{30}$$

In equation (27), the intrinsic rate coefficient $\kappa_{\alpha f}$ is given by

$$\kappa_{\alpha f}=\gamma_{d_{\mathrm{f}}}\sigma^{d_{\mathrm{f}}-1}\frac{\sin\pi\alpha}{\pi\alpha}\gamma_h^\alpha pb\hat{\phi}_\sigma(0). \tag{31}$$

$\hat{\phi}_\sigma(0)$ is the cumulative probability that a B molecule undergoes reaction after arrival at the reaction zone rather than escaping from it. Limiting expressions for $\hat{\phi}_\sigma(0)$ can be obtained from equations (22), (23), and (26):

$$\hat{\phi}_\sigma(0)\sim\begin{cases}\dfrac{\pi\alpha}{p\sin\pi\alpha}\left(\dfrac{\gamma_r}{\gamma_h}\right)^\alpha & \text{for } \dfrac{\gamma_r}{\gamma_h}\ll 1,\\[2ex] 1-\dfrac{p\,\alpha}{(1+\alpha)}\dfrac{\gamma_h}{\gamma_r} & \text{for } \dfrac{\gamma_r}{\gamma_h}\gg 1.\end{cases} \tag{32}$$

In order for the reaction–diffusion equation in (27) to produce results that are consistent with simulation results for CTRW on a fractal lattice with finite lattice spacing b_0, the generalized diffusion coefficient $D_{\alpha f}$, given by equations (29) and (30), must have an invariant value in taking the continuum limit ($b\to 0$). Since $D_{\mathrm{sp}}\propto b^{d_{\mathrm{w}}}$, this requires γ_h to scale as $\gamma_h=\gamma_h^0(b_0/b)^{d_{\mathrm{w}}/\alpha}$, where γ_h^0 is the parameter used for the CTRW simulation. For the Sierpinski gasket, we thus have

$$D_{\alpha f}=\frac{\sin\pi\alpha}{\pi\alpha}\frac{(\gamma_h^0)^\alpha b_0^{d_{\mathrm{w}}}}{(d+1)d_{\mathrm{f}}(d_{\mathrm{w}}-d_{\mathrm{f}})}. \tag{33}$$

Then, equations (31) and (32) show that in the limit when $\gamma_r\gg\gamma_h$, $\kappa_{\alpha f}\propto b^{1-d_{\mathrm{w}}}\to\infty$ as $b\to 0$. This situation corresponds to the case where the absorbing boundary condition has to be applied in modelling the reaction event. On the other hand, when $\gamma_r\ll\gamma_h$, $\kappa_{\alpha f}$ can be kept finite with γ_r scaled as $\gamma_r=\gamma_r^0(b_0/b)^{1/\alpha}$, where γ_r^0 is the reaction frequency parameter used in the simulation. In this latter case, we have

$$\kappa_{\alpha f}=\gamma_{d_{\mathrm{f}}}\sigma^{d_{\mathrm{f}}-1}b_0(\gamma_r^0)^\alpha. \tag{34}$$

3. Green's function and survival probability

A key kinetic observable of interest is the survival probability, $S(t|r_0) = \int \mathrm{d}V\, G(r, t|r_0)$. From equation (27), we can obtain the following expression for the survival probability in the Laplace domain,

$$\hat{S}(s|r_0) = \frac{1}{s} - \frac{\kappa_{\alpha f} s^{1-\alpha} \hat{G}^*(\sigma, s|r_0)}{s[1 + \kappa_{\alpha f} s^{1-\alpha} \hat{G}^*(\sigma, s|\sigma)]}. \tag{35}$$

The Laplace-transformed expression for the *reaction-free* Green's function, $\hat{G}^*(r, s|r_0)$, can be obtained by solving the equation,

$$[s - s^{1-\alpha} D_{\alpha f} \mathcal{D}_{\mathrm{OP}}(r)]\, \hat{G}^*(r, s|r_0) = \delta(r - r_0)/\gamma_{d_\mathrm{f}} r_0^{d_\mathrm{f}-1}, \tag{36}$$

which is derived from equation (16) with (22) in the small-s limit. By changing the variable as $y = r^\beta/\beta$ and using the relation $\delta[h(q)] = \sum_i \delta(q - q_i)/|h'(q_i)|$, with q_i being the root of $h(q)$, we obtain

$$\hat{G}^*(x, z|x_0) = \frac{1}{k_D} \frac{z^{\alpha-1} K_\nu(z^{\alpha/2} x^\beta) K_\nu(z^{\alpha/2} x_0^\beta)}{(x x_0)^{\beta\nu}} \left[\frac{I_\nu(z^{\alpha/2} x_<^\beta)}{K_\nu(z^{\alpha/2} x_<^\beta)} + \frac{I_{\nu+1}(z^{\alpha/2})}{K_{\nu+1}(z^{\alpha/2})} \right], \tag{37}$$

where $x = r/\sigma$, $x_0 = r_0/\sigma$ and $z = s t_D$ with $t_D = (\sigma^{2\beta}/D_{\alpha f}\beta^2)^{1/\alpha}$. $k_D = \gamma_{d_\mathrm{f}} \sigma^{d_\mathrm{f}}/t_D \beta$ and it reduces to the well known Smoluchowski expression for the diffusion-controlled rate constant in the case of ordinary diffusion on regular lattices. $I_\nu(q)$ and $K_\nu(q)$ with $\nu = d_\mathrm{s}/2 - 1$ are modified Bessel functions of the first and the second kind, respectively [29], and $x_< = \min(x, x_0)$.

From equations (35) and (37), we obtain an expression for the survival probability in the reduced length and timescales as

$$\hat{S}(z|x_0) = \frac{1}{z} - \frac{\boldsymbol{k}_F \hat{\mathcal{G}}(1, z^\alpha|x_0)}{z[1 + \boldsymbol{k}_F \hat{\mathcal{G}}(1, z^\alpha|1)]}, \tag{38}$$

where $\hat{\mathcal{G}}(x, z^\alpha|x_0)$ is the Laplace transform of the reduced reaction-free Green's function $\gamma_{d_\mathrm{f}}^{-1} k_D \hat{G}^*(x, z|x_0)$. We note that $\hat{\mathcal{G}}(x, z|x_0)$ satisfies the fractal diffusion equation

$$[z - \beta^{-2} \mathcal{D}_{\mathrm{OP}}(x)] \hat{\mathcal{G}}(x, z|x_0) = \beta^{-1} \delta(x - x_0)/\gamma_{d_\mathrm{f}} x_0^{d_\mathrm{f}-1}. \tag{39}$$

Therefore, the dynamic influence of temporal disorder in waiting times characterized by $\psi(t)$ can be counted just by replacing z with z^α in $\hat{\mathcal{G}}(x, z|x_0)$. $\boldsymbol{k}_F$ is a reduced intrinsic rate coefficient defined as $\boldsymbol{k}_F = \gamma_{d_\mathrm{f}} \kappa_{\alpha f}/k_D t_D^{1-\alpha}$. From equations (33) and (34), we have

$$\boldsymbol{k}_F = \frac{\gamma_{d_\mathrm{f}} (d + 1) d_\mathrm{f} (d_\mathrm{w} - d_\mathrm{f})}{\beta} \left(\frac{\sigma}{b_0} \right)^{d_\mathrm{w}-1} \frac{\pi\alpha}{\sin \pi\alpha} \left(\frac{\gamma_r^0}{\gamma_h^0} \right)^\alpha. \tag{40}$$

From equations (37) and (38) with the use of the recurrence relation for the Bessel functions, $K_\nu(q) = (q/2\nu)[K_{\nu+1}(q) - K_{\nu-1}(q)]$, we can obtain the asymptotic expression for the survival probability in the time domain as

$$S(\tau|x_0) \cong \left[1 - \frac{1}{x_0^{2\beta\nu}(1 + 2\nu/k_F)} \right] \left[1 + \frac{\Gamma(1 - \nu)}{\Gamma(1 + \nu)\Gamma(1 - \alpha\nu)} \left(\frac{1}{1 + 2\nu/k_F} \right) \left(\frac{1}{4\tau^\alpha} \right)^\nu \right] \quad (2 < d_\mathrm{s} < 4) \tag{41}$$

$$S(\tau|x_0) \cong \left(\frac{2}{k_F} + 2 \ln x_0^\beta \right) \left\{ \frac{1}{\ln(4\tau^\alpha) - 2\gamma + 2/k_F} - \frac{\alpha\gamma}{[\ln(4\tau^\alpha) - 2\gamma + 2/k_F]^2} \right\} \quad (d_\mathrm{s} = 2) \tag{42}$$

$$S(\tau|x_0) \cong \left[\frac{1}{k_F} + \frac{1}{2\nu} \left(1 - \frac{1}{x_0^{2\beta\nu}} \right) \right] \frac{2\Gamma(1 + \nu)}{\Gamma(|\nu|)\Gamma(1 + \alpha\nu)} \left(\frac{1}{4\tau^\alpha} \right)^{|\nu|} \quad (0 < d_\mathrm{s} < 2). \tag{43}$$

Here $\tau = t/t_D$, $k_F = \boldsymbol{k}_F/\gamma_{d_f}$, and $\gamma = 0.577\,215\,66\cdots$ is the Euler–Mascheroni constant. For the case with regular lattices in three dimensions, $d_f = d_s = 3$, $\beta = d_f/d_s = 1$ and $\nu = 1/2$. Hence equation (41) reduces to equation (5.4) of [19]. On the other hand, for the case of the simple random walk on fractal lattices, $\alpha = 1$ and equations (41)–(43) with $x_0 = 1$ reduce to equations (7) and (8) of [10].

We see that the survival probability $S(\tau|x_0)$ decays as $\sim 1/\tau^{\alpha|d_s/2-1|}$ at long times except for the case with $d_s = 2$. Seki *et al* [19] showed that for the case with regular lattices in three dimensions $S(\tau|x_0)$ decays as $\sim 1/\tau^{\alpha/2}$, while Sung *et al* [10] showed that for the case of the simple random walk on fractal lattices it decays as $\sim 1/\tau^{|d_s/2-1|}$. Hence, the asymptotic power-law decay of $S(\tau|x_0)$ as $\sim 1/\tau^{\alpha|d_s/2-1|}$ could have been inferred from the assumption that the temporal constraint due to energetic disorder and the spatial constraint are uncorrelated.

4. Comparison with computer simulation results

In this section we examine the range of applicability of the present theoretical results by comparison with the Monte Carlo (MC) simulation results. We have simulated the CTRW and reaction dynamics occurring on the Sierpinski gasket embedded in two-dimensional Euclidean space, for which $d_f = (\ln 3)/(\ln 2) = 1.58$, $d_w = (\ln 5)/(\ln 2) = 2.32$ and $d_s = 2d_f/d_w = 1.36$.

4.1. Validity of the generalized FDE in equation (36)

We will first check the validity of the proposed FDE *in the absence of reaction*. By taking the limit of equation (37) as $r_0 \to 0$, we can obtain the time-domain expression for the particle displacement distribution function as

$$G^*(r,t|0) = \frac{\beta}{\gamma_{df}\Gamma(d_s/2)r^{d_f}} H_{12}^{20}\left(\frac{r^\beta}{2\beta}\frac{1}{\sqrt{D_{\alpha f}t^\alpha}}\,\middle|\,\begin{matrix}(1,1/2)\\(d_s/2,1/2)\quad(1,1/2)\end{matrix}\right), \tag{44}$$

where H_{pq}^{mn} is the Fox H-function defined as the Mellin–Barnes type path integral [31]

$$H_{pq}^{mn}\left(z\,\middle|\,\begin{matrix}(a_p,A_p)\\(b_q,B_q)\end{matrix}\right) = H_{pq}^{mn}\left(z\,\middle|\,\begin{matrix}(a_1,A_1),(a_2,A_2),\ldots,(a_p,A_p)\\(b_1,B_1),(b_2,B_2),\ldots,(b_q,B_q)\end{matrix}\right) = \frac{1}{2\pi\mathrm{i}}\int_L \mathrm{d}s\,\chi(s)z^s$$

with the integral density

$$\chi(s) = \frac{\prod_1^m \Gamma(b_j - B_j s)\prod_1^n \Gamma(1-a_j+A_j s)}{\prod_{m+1}^q \Gamma(1-b_j+B_j s)\prod_{n+1}^p \Gamma(a_j - A_j s)}.$$

The expression for the mean squared displacement (MSD) can be obtained as

$$\begin{aligned}\langle r^2(t)\rangle &= \int_0^\infty \mathrm{d}r\,\gamma_{df} r^{d_f-1} r^2 G^*(r,t|0)\\ &= \frac{\Gamma((d_s/2)+(1/\beta))\Gamma(1+(1/\beta))}{\Gamma(d_s/2)\Gamma(1+(\alpha/\beta))}\left(4\beta^2 D_{\alpha f}\right)^{1/\beta} t^{\alpha/\beta}.\end{aligned} \tag{45}$$

We compare the predictions of equations (44) and (45) with the MC simulation results for a particle performing a CTRW on the Sierpinski gasket. For each MC trajectory the initial position is chosen randomly. To generate the waiting times in conformity with the distribution in equation (20), we first generate the trap energy E according to the exponential distribution in equation (19) with $k_B T_c = 10$. For this randomly chosen energy barrier, the value of the release rate $\gamma_r(E)$ is calculated from equation (18) with $k_B T = \alpha k_B T_c$; we carry out two sets of simulations with $\alpha = 0.5$ and 0.7. The waiting time is then obtained by multiplying $1/\gamma_r(E)$ to an exponentially distributed, positive, random deviate of unit mean [32].

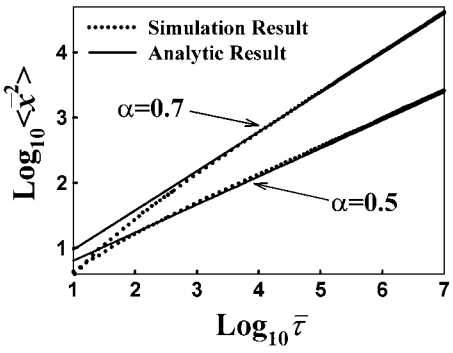

Figure 1. The mean squared displacement $\langle \bar{x}^2 \rangle$ as a function of time $\bar{\tau}$ on a Sierpinski gasket.

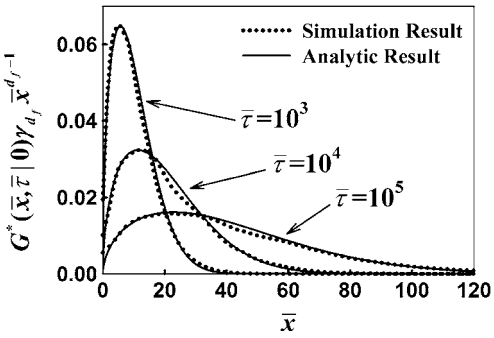

Figure 2. Particle distributions $G^*(\bar{x}, \bar{\tau}|0)\gamma_{d_f}\bar{x}^{d_f-1}$ for CTRW on a Sierpinski gasket. The waiting time distribution exponent α is set to 0.7.

For the CTRW on the Sierpinski gasket, the particle may jump to any one of the four nearest neighbouring sites with equal probability of 1/4. After landing on a site at time t, the waiting time Δt at the site is generated as described above, and upon moving to the neighbouring site time advances to $t + \Delta t$. To avoid the system size effect, we use a very large lattice whose side length is $2^{22}b_0$. By comparing the simulation results with those obtained for the lattice with side length of $2^{21}b_0$, we have checked that the size effect is absent.

In figure 1, MC simulation results for MSD are compared with the analytical results from equation (45). We use the following reduced variables: $\bar{x} = r/b_0$ and $\bar{\tau} = t/(b_0^{2\beta}/D_{\alpha f}\beta^2)^{1/\alpha}$. The solid lines represent the analytical results, while the dotted curves are the simulation results obtained from 20 000 trajectories. The upper curves are for the case with $\alpha = 0.7$, while the lower curves are for the case with $\alpha = 0.5$. It is seen that the analytical results are in good agreement with simulations for $\bar{\tau} > 3$. Since the generalized diffusion coefficient $D_{\alpha f}$ is determined from equation (33) without any adjustable variables, the agreement between the MC simulations and equation (45) requires the correctness of the amplitude factor as well as the time exponent.

In figure 2, MC simulation results for particle distribution $G^*(\bar{x}, \bar{\tau}\,|0)\gamma_{d_f}\bar{x}^{d_f-1}$ calculated from 70 000 trajectories are compared with the results obtained from the analytical expression in equation (44). The Fox H-function is evaluated by using the series expression [33],

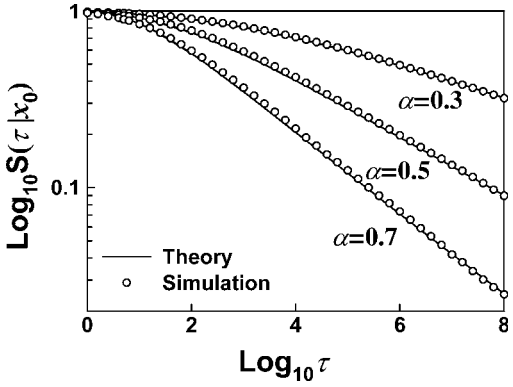

Figure 3. Comparison of the survival probability curves calculated from the theory and MC simulations for the geminate pair reaction on a Sierpinski gasket. The CTRW parameter α is varied as marked on the figure with $\sigma = b_0$, $r_0 = 4b_0$ and $\gamma_r^0/\gamma_h^0 = 1$.

$$H_{pq}^{mn}(z) = \sum_{h=1}^{m}\sum_{\nu=0}^{\infty}\left[\frac{\Pi_{j=1,j\neq h}^{m}\Gamma(b_j - B_j(b_h+\nu)/B_h)}{\Pi_{j=m+1}^{q}\Gamma(1-b_j+B_j(b_h+\nu)/B_h)} \times \frac{\Pi_{j=1}^{n}\Gamma(1-a_j+A_j(b_h+\nu)/B_h)}{\Pi_{j=n+1}^{p}\Gamma(a_j-A_j(b_h+\nu)/B_h)}\frac{(-1)^{\nu}z^{(b_h+\nu)/\mathrm{B}_h}}{\nu!B_h}\right]. \tag{46}$$

The plots are given for several values of $\bar{\tau}$ with $\alpha = 0.7$. The agreements between theory and simulations are excellent.

4.2. CTRW and reaction dynamics on a Sierpinski gasket

To avoid the artefactual effects due to finite system size, we use a very large lattice whose side length is $2^{22}b_0$. To get the survival probability $S(\tau|x_0)$ that is appropriately averaged over the initial configurations, the centre of the reaction sink (the position of fixed particle A) is randomly chosen for each trajectory and then the starting position of the random walker (particle B) is randomly chosen among the lattice sites located between the circles of radius $(r_0 - \frac{1}{2}b_0)$ and $(r_0 + \frac{1}{2}b_0)$, concentric with the sink.

The particle B moves around the lattice sites until it reacts with A. When B falls into the reaction zone with $\sigma - \frac{1}{2}b_0 < r < \sigma + \frac{1}{2}b_0$, the time at which reaction or escape from the reaction zone will occur is calculated as follows. We first generate the detrapping time t_n and the reaction time t_r from $\psi(t)$ in equation (20) and $\phi_\sigma^*(t)$ in equation (24), respectively. When $t_r < t_n$, we take that the reaction occurs at time t_r after the arrival at the reaction zone. The trajectory is terminated and the total time of survival is recorded. On the other hand, if $t_n < t_r$, B makes a jump to a randomly selected nearest neighbouring site and time advances by t_n. However, if B has attempted to jump to a site inside the inner reaction zone boundary $(\sigma - \frac{1}{2}b_0)$, the movement is withdrawn although time has advanced by t_n. We take B to just arrive at the same site in the reaction zone where it has been trapped.

In figures 3–6, we compare the simulation results against theory. In figure 3, we vary the CTRW parameter α with $\sigma = b_0$, $r_0 = 4b_0$ and $\gamma_r^0/\gamma_h^0 = 1$. In figure 4, we vary the reaction radius σ with $\alpha = 0.7$, $r_0 = \sigma + 3b_0$ and $\gamma_r^0/\gamma_h^0 = 1$. In figure 5, we vary the initial location r_0 of B with $\alpha = 0.7$, $\sigma = b_0$ and $\gamma_r^0/\gamma_h^0 = 1$. In figure 6, we vary the inherent reaction rate parameter γ_r^0/γ_h^0 with $\alpha = 0.7$, $\sigma = b_0$ and $r_0 = 4b_0$. Note that the simulation timescale is set

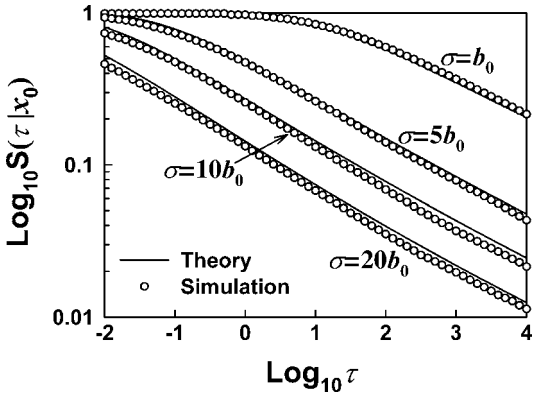

Figure 4. Comparison of the survival probability curves calculated from the theory and MC simulations for the geminate pair reaction on a Sierpinski gasket. The reaction radius σ is varied as marked on the figure with $\alpha = 0.7$, $r_0 = \sigma + 3b_0$ and $\gamma_r^0/\gamma_h^0 = 1$.

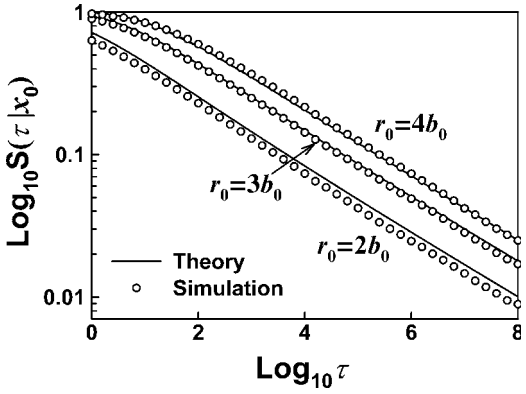

Figure 5. Comparison of the survival probability curves calculated from the theory and MC simulations for the geminate pair reaction on a Sierpinski gasket. The initial location r_0 of B is varied as marked on the figure with $\alpha = 0.7$, $\sigma = b_0$ and $\gamma_r^0/\gamma_h^0 = 1$.

by the inverse of the jump frequency parameter γ_h^0. Hence the actual value of γ_h^0 is immaterial as long as the data are represented by the reduced variables, x_0 and τ.

For each set of simulation parameters, at least 40 000 trajectories have been generated to calculate the time-dependent survival probability $S(\tau|x_0)$. The simulation results are plotted as open circles and compared with the theoretical results (solid curves) calculated from equations (37) and (38) by numerical inverse Laplace transformation. The generalized diffusion coefficient $D_{\alpha f}$ can be calculated from equation (33), and the intrinsic rate coefficient $\kappa_{\alpha f}$ is given by equation (34). There are no adjustable parameters involved in the calculation.

Figures 3–6 show that the theoretical results are in good agreement with the simulation results. However, some deviations are noticeable. The reaction–diffusion equation in equation (27) involves coarse-graining of the detailed structure of fractal lattices. Hence it may not give an accurate description of reaction dynamics occurring at short distances. Indeed, when the initial location of B is too close to the reaction radius σ, we observe a slight deviation of the theoretical result from simulation (see figure 5). Also, when the inherent reactivity is

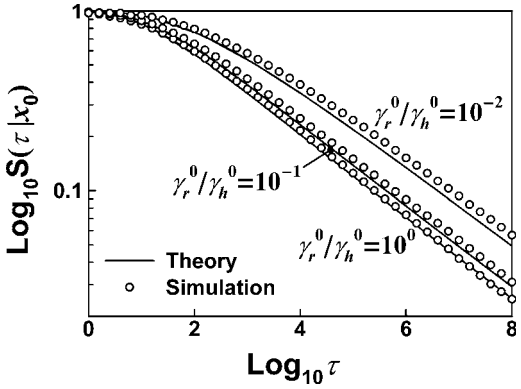

Figure 6. Comparison of the survival probability curves calculated from the theory and MC simulations for the geminate pair reaction on a Sierpinski gasket. The inherent reaction rate parameter γ_r^0/γ_h^0 is varied as marked on the figure with $\alpha = 0.7$, $\sigma = b_0$ and $r_0 = 4b_0$.

small (that is, for small values of γ_r^0/γ_h^0), the B particle can visit the reaction zone repeatedly before undergoing reaction and thus a more accurate description of reaction dynamics at short distances is required. Figure 6 shows that the theory deviates a little from simulation for small values of γ_r^0/γ_h^0. Although we have not presented the results for the case with $\gamma_r^0/\gamma_h^0 > 1$, both theoretical and simulation results converge to a single curve for $\gamma_r^0/\gamma_h^0 > 10$. The curve presented in figure 6 for the case with $\gamma_r^0/\gamma_h^0 = 1$ is already very close to the limiting curve.

5. Concluding remarks

In this work we presented a generalized fractional reaction–diffusion equation to describe the non-classical kinetics of reactions occurring in disordered media, which involve dual origins of subdiffusive transport, that is, energetically disordered trapping sites and spatial constraints on the jump paths. In deriving the reaction–diffusion equation, we considered the reaction model in which reactant particles perform CTRW on fractal lattices and react with each other at the separation of contact.

As an application of the proposed reaction–diffusion equation, we considered the reaction between a geminate pair. We obtained an exact analytical expression for the survival probability of the reactant pair in the Laplace domain. The survival probability depends on various reaction and transport parameters. In particular, it was shown that the survival probability decays asymptotically as $\sim 1/\tau^{\alpha|d_s/2-1|}$ with α and d_s denoting the waiting time exponent for CTRW and the fracton dimension of the fractal lattice, respectively.

We also carried out Monte Carlo simulations to evaluate the accuracy of the theoretical results. For the geminate reaction occurring on the Sierpinski gasket, the analytical results are in good agreement with simulation results, indicating that both transport and reaction events are properly modelled by the proposed reaction–diffusion equation.

Acknowledgment

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