Front propagation in a one-dimensional autocatalytic reaction-subdiffusion system

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We study numerically the autocatalytic irreversible reaction $A+B\rightarrow 2A$ on a one-dimensional lattice for the case of subdiffusive reactants performing symmetric continuous-time random walks with the power-law waiting time density function $\psi(t)\propto t^{-1-\alpha}$ with $0<\alpha<1$ in a large range of other relevant parameters. We show that the propagation failure previously found by the same authors [Phys. Rev. E **78**, 011128 (2008)] essentially corresponds to a propagation of a front of a stable form at a velocity which decays with time.

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Reaction-subdiffusion phenomena have attracted much attention in the last few years both because of the experimental relevance for reactions taking place in porous media, complex biological structures, and geological formations, as well as due to theoretical and mathematical challenges posed by the description of such phenomena. Several recent works were dedicated to the theoretical description of Turing patterns and of fronts in such systems [1–7]. Depending on the special assumptions on the reaction and on the behavior of the corresponding waiting times after the elementary act of reaction the behavior of systems under subdiffusion might either resemble the case of normal diffusion or strongly differ from it. The theoretical discussion of a special model of Ref. [3] has shown, for example, that the latter is the case for the irreversible autocatalytic reaction $A+B\rightarrow 2A$, which under normal diffusion is described by the Fisher-Kolmogorov-Petrovsky-Piskunov (FKPP) equation [8,9]. $A+B\rightarrow 2A$ is the simplest autocatalytic reaction scheme and is an important building block of several more complicated multistep reactions. It was introduced in 1937 to describe the propagation of a favorable gene in a population and is known (under a broad class of initial conditions) to lead to a propagation of a stable pulled front keeping its form and sweeping through the system at a constant velocity equal to the minimal velocity of the stable front's propagation [10,11]. Reference [3] showed that the minimal velocity of a front's propagation under subdiffusion is zero, which fact was interpreted as a propagation failure. The important question however is what does the absence of the stable front propagating at a constant velocity really mean. Here several scenarios can come in mind. For example, a front may always exist and even possess a constant form, but decelerate or accelerate as it is the case in the superdiffusive situation of Ref. [12], or the front does not possess any constant limiting form and, for example, flattens and fills the whole system. The aim of the present work is to understand what happens with such a front with the help of numerical simulations of the corresponding system.

In what follows we simulate numerically the irreversible $A+B\rightarrow 2A$ reaction on a one-dimensional (1D) lattice (chain of sites) of length L with lattice spacing $a=1$. Initially, the B particles are distributed homogeneously on the sites of the lattice with concentration (average number of particles per site) c. At the first step of simulations a single A particle is introduced at the left end of the lattice, being the seed of the transformation.

All particles perform unbiased continuous-time random walks (CTRWs) with the waiting times at a site following the probability density function (pdf),

$$\psi(t)=\frac{\alpha}{(1+t)^{1+\alpha}} \tag{1}$$

with $0<\alpha<1$. A particle arriving at lattice site i at some instance of time stays there for a sojourn time t given by Eq. (1) and then makes a jump to the neighboring site to the left or to the right with equal probabilities. The pdf [Eq. (1)] does not possess the first moment and therefore leads to the subdiffusion of particles. The particles are phantom in the sense that they do not possess any excluded volume. The particles of the same type do not interact at all; the particles of different types may react according to the $A+B\rightarrow 2A$ reaction scheme when encountered at the same site.

We consider two different situations with respect to the probability of such reaction:

(1) A simpler one: when an A particle encounters B particles at site i, the reaction takes place immediately, i.e., the B particles present at site i are immediately converted into A.

(2) A generic one: reaction with a constant rate. The reaction attempts take place at constant intervals of time $\Delta t_r=1$, the transformation of B into A at a site i takes place with probability $pN_A(i)N_B(i)$ per attempt with $N_A(i)$ being the number of A particles at site i and $N_B(i)$ the number of B particles at site i, respectively. If such a reaction takes place a B particle at a site (if more than one) is chosen at random and transformed into A. This model corresponds to a system discussed in Ref. [3] which at smaller scales consists of compartments (here represented by lattice sites) in which the reaction follows the usual kinetic laws. The classical reaction rate would be $k=p/\Delta t_r$, i.e., equals p in the units system adopted here.

The first case considered here corresponds to the situation simulated in Ref. [13] for normal diffusion; much of the discussions carried out in that work for the normal case can be immediately transferred to the case of anomalous diffu-

sion as well. The second case corresponds to the situation theoretically considered in Ref. [3]. We note that A and B particles are considered the same in all respects except for their chemical nature, and that the fact of changing this nature does not influence the waiting time of a particle at a site.

Let us first recover the results for the Markovian case of normal diffusion [14]. Here two different limiting cases of the front propagation can be considered, which are essentially the limits of very high and of very low concentrations. Let us consider the reaction taking place in a one-dimensional system (e.g., in a very thin capillary), with given *one-dimensional* concentration c of reactants, $[c]=[L^{-1}]$. The classical FKPP theory of the $A+B\rightarrow 2A$ reaction would then predict the propagation of a stationary front of width $w\propto\sqrt{D/kc}$ moving at a constant velocity $v=2\sqrt{Dkc}$ (here k is the one-dimensional reaction rate, $[k]=[L/T]$). The width of the front has to be compared to the typical interparticle distance $l=c^{-1}$. The classical theory is applicable if $w\gg l$, i.e., for $c\gg k/D$. In the opposite case, when the predicted front's width gets smaller than the typical interparticle distance, the mean-field FKPP theory breaks down. In this case one has to do with fluctuation-dominated regime. In the case of large enough k (or small enough concentrations) the velocity of the front gets to be $v\simeq cD$, i.e., is considerably slower than in the classical picture [13]. Thus the classical result is correct for high concentrations or/and small reaction rates [14] ($c\rightarrow\infty$ and $k\rightarrow 0$). This fact was theoretically explained in Ref. [15] (see Ref. [11] for a review).

Let us now turn to the case of anomalous diffusion. The CTRWs with the waiting time pdf lacking the first moment are nonstationary and nonergodic [16]. This fact needs to be taken into account in the simulations and makes it impossible to use effective algorithms of the Gillespie type based on the Markovian property of normal diffusion. To implement a multiparticle CTRW process we proceed as follows. We first label all particles (independent on their A or B nature) and generate a sequence of jumping times for each of them by adding up the waiting times for jumps following from Eq. (1) (one takes care, of course, that the maximal jumping time for each particle exceeds the overall time of simulation). Then, all jumping times are sorted and stored. For the reaction with probability one an event-driven algorithm can be used: we check what is the next particle to jump, let it jump on the chain, and rename the particles according to the reaction scheme if A and B particles occur at the same site. For the case of the reaction with finite rate we check for reactions at time intervals $\Delta t_r=1$ at each site parallel to the jumps of the particles.

Let us now turn to the results of our simulations. The reaction-on-contact model gives us the simplest situation which, due to the possibility to use the event-driven algorithm, can be simulated relatively fast. In our simulations of the reaction-on-contact model, we set up a chain of length $L=10\,000$ sites with concentration $c=0.2$.

Since the overall concentration of particles in reaction stays constant, the position of the reaction front can be defined by the total number of A particles $N_A(t)$ produced in the reaction: $x=N_A(t)/c$. This quantity is shown in Fig. 1 for different values of parameters α in the pdf [Eq. (1)], as well as for the exponential waiting time distribution

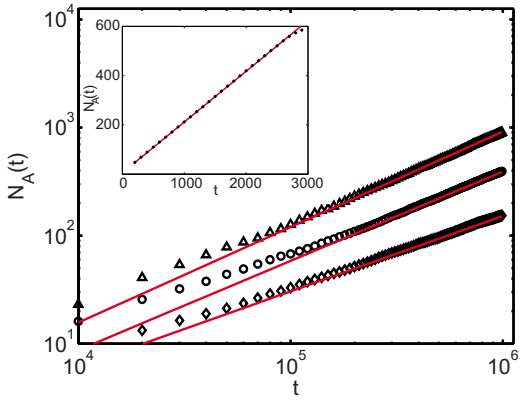

FIG. 1. (Color online) Number of A particles as a function of time in the reaction-on-contact model with subdiffusive motion for different values of $\alpha=0.9(\triangle)$, 0.8 ($\bigcirc$), and $0.7(\diamond)$ (see the text for details). Note the double-logarithmic scales. The lines correspond to the power-law fits [Eq. (2)] with the values of β listed in the text. The inset corresponds to the case of normal diffusion (exponential waiting time distribution with $1/\tau=1$).

$\psi(t)=\tau^{-1}\exp(-t/\tau)$ (the Markovian case) formally corresponding to $\alpha=1$. Plotting $N_A(t)$ as a function of time on double-logarithmic scales we readily infer that the $N_A(t)$ follows the power law

$$N_A(t)\propto t^{\beta}. \tag{2}$$

In Fig. 1, it can be observed that the estimated values of β are all smaller than one, i.e., that $N_A(t)$ does not grow at a constant rate. The estimated values of β following from the least-squares fit are $\alpha=0.9(\triangle):\beta=0.88\pm 0.01$, $\alpha=0.8(\bigcirc):\beta=0.82\pm 0.02$, and $\alpha=0.7(\diamond):\beta=0.70\pm 0.02$.

The Markovian setting (see the inset of the figure) is the only case where $N_A(t)$ grows linearly in t, i.e., the only case where constant front velocities are observed. This situation can also serve as the test of our algorithm since all findings of Ref. [13] (e.g., the linear concentration dependence of the front velocity and its linear dependence on $1/\tau$) are reproduced: the line in the inset corresponds to the fit $N_A(t)=a+bt$ with $a=5.8$ and $b=0.206$. In all other cases the behavior is consistent with the assumption $N_A(t)\propto t^{\alpha}$, which means that the velocity of the front is decaying with time as $v\propto t^{\alpha-1}$. Thus, no stable front propagation with a constant velocity occurs. We recall however that the one-dimensional reaction where the reaction takes place with probability of 1 on contact is not the case that is described by the FKPP equation even in the Markovian case since this regime is fluctuation dominated.

Let us now turn to the case when reaction takes place with low probability $p<1$ per unit time. The position of the front shows again a power-law dependence on time t with an exponent that corresponds to the waiting time parameter α. The results for $L=10\,000$, $c=0.3$, and reaction probability $p=0.1$ are given in Fig. 2. Again, the pure power-law fit [Eq. (2)] adequately describes the data; the fitting procedure returns the following estimated values of β for different values of α: $\alpha=0.9(\bigcirc):\beta=0.874\pm 0.002$,

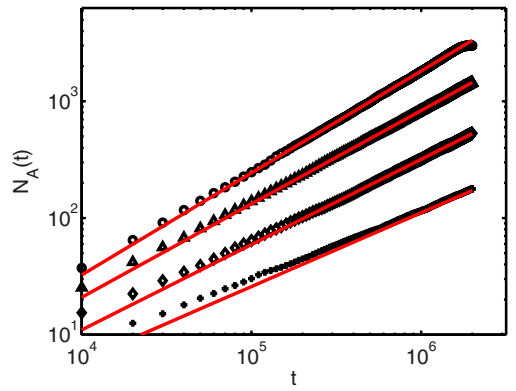

FIG. 2. (Color online) Number of A particles depending on time (logarithmic scale) for the reaction with probability $p=0.1$ per unit time. The motion of particles is subdiffusive, which is reflected by the power-law waiting time pdf (1). The results correspond to different values of $\alpha=0.9(\bigcirc)$, 0.8 $(\triangle)$, 0.7 $(\diamond)$, and 0.6(+). The lines represent the power-law fits [Eq. (2)].

$\alpha=0.8(\triangle):\beta=0.800\pm0.003$, $\alpha=0.7(\diamond):\beta=0.73\pm0.01$, and $\alpha=0.6(+):\beta=0.63\pm0.02$.

The results presented in the figure show that $\alpha\simeq\beta$ and hence the velocity of the front again goes as $v\propto t^{\alpha-1}$. The values of the concentration c and of the reaction probability p used in Fig. 2 lie however in the domain where considerable differences from the classical FKPP kinetics in 1D are still observed in the Markovian case due to fluctuation effects and to low dimensionality of the system.

To check whether the propagation failure still occurs in the "classical" regime with subdiffusive motion we chose the values of parameters $c=10$ and $p=0.006$, for which the behavior for the Markovian system is well described by classical FKPP results. Figure 3 represents the results obtained by examining the number of A particles $N_A(t)$. The slowing down of the front corresponding to the propagation failure can be observed from the least-squares fits in the last decade of data represented. These fits are shown by solid lines. Again, the estimated values β for the different values of $\alpha=0.8,0.7,0.6$ are all significantly smaller than 1: $\alpha=0.8(\triangle):\beta=0.906\pm0.002$, $\alpha=0.7(\diamond):\beta=0.849\pm0.001$, and $\alpha=0.6(\bigcirc):\beta=0.776\pm0.001$. Thus, in the subdiffusion

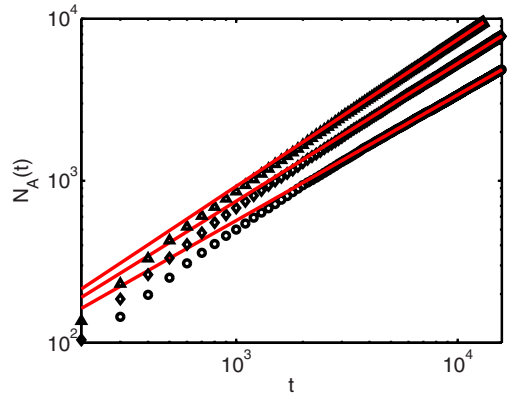

FIG. 3. (Color online) $N_A(t)$ in the classical regime with $c=10$ and $p=0.006$ for different $\alpha=0.8(\triangle)$, 0.7 $(\diamond)$, and 0.6 $(\bigcirc)$. The solid lines represent the fits (see text for details).

case the reaction front in the irreversible $A+B\rightarrow 2A$ reaction also slows down, and the velocity of its propagation tends to zero, in accordance with the analytical findings of Ref. [3]. Looking at the exponents in this case we readily infer that all of them are very close to the value of $\beta=1/2+\alpha/2$. This means that the front's velocity decays as a function of time, namely, approximately as $v(t)\propto t^{(\alpha-1)/2}$.

Both our findings, the one for the fluctuation-dominated regime and the one for the classical one, have therefore a very simple interpretation within the old-fashioned mean-fieldlike picture (advocated by Batchelor in case of turbulent diffusion) describing the corresponding complex transport process via a mean time-dependent diffusion coefficient $D(t)$. For a continuous-time random walk with the waiting time distribution characterized by the exponent α, the mean-squared displacement of a single particle goes as $\langle x^2(t)\rangle\propto t^{\alpha}$, i.e., behaves as if it could be described as a diffusive process with the diffusion coefficient $D(t)\propto t^{\alpha-1}$. The behavior of the corresponding front velocities follows this behavior of the diffusion coefficient, i.e., $v(t)\propto D(t)\propto t^{\alpha-1}$ in the fluctuation-dominated regime of small concentrations and high reaction rates and $v(t)\propto\sqrt{D(t)}\propto t^{(\alpha-1)/2}$ in the opposite classical limiting case.

Let us now turn to the shape of the front. For the reaction on contact the definition of the front's position and "shape" does not pose any problems, because the front is sharp and is essentially situated between the rightmost A and the leftmost B particle and its form is essentially given by the probability distribution of the distance between these particles [13]. For $p<1$ this is no more the case, and the definition of the front's form poses a much more subtle task since it involves the operational definition of a comoving frame [14].

Let us first recall some results for the Markovian regime. The problem with calculating the front's profile is that for each realization of the front the position at a given time t is different due to statistical Gaussian fluctuations of its velocity. By just averaging over different realizations (i.e., defining the comoving frame as the one moving with the mean velocity of the front), one gets a front form which is an error function with the width growing with time and which is much broader than the profile in each single realization. The way leading to a correct form (tending to a FKPP one in the case when the equation is valid) corresponds to a definition of a comoving frame for each separate realization and then averaging the results. As such a frame, the position of the rightmost A particle can serve. This is exactly the approach we use here.

Thus, in each realization the relative particles' positions with respect to the rightmost A particle are calculated at a given time, and then the densities in such realigned fronts are averaged over different realizations. In Fig. 4 two front profiles are shown. The dashed lines, each averaged over 400 processes, correspond to front forms at different times $t=1600,1700,\ldots,1900$ (the system is running until $t=2000$) for the subdiffsive case with $\alpha=0.6$, $c=10$, and $p=0.006$. The solid lines give the front forms for the same model ($c=10$, $p=0.006$) with $\alpha=0.9$ at times $t=900,\ldots,1900$. In the inset figure the Markovian reaction-diffusion case, corresponding to the exponential waiting time pdf $\psi(t)=(1/\tau)\exp(-t/\tau)$ for $1/\tau=1$, $c=10$, and $p=0.006$ at the same

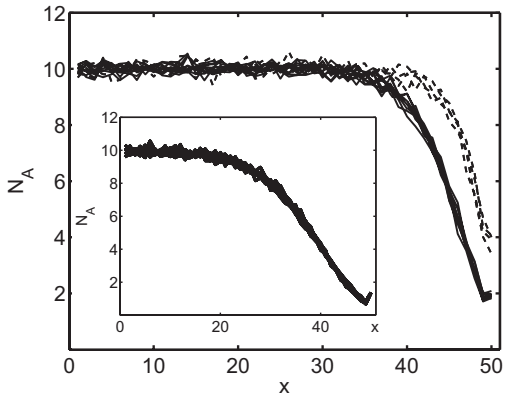

FIG. 4. Front form for $\alpha=0.9$ (solid lines) at times $t=900,1000,\ldots,1900$ and for $\alpha=0.6$ (dashed lines) at times $t=1600,\ldots,1900$. The inset figure shows fronts observed from a system with exponential waiting time pdf $(1/\tau=1)$ at times $t=900,1000,\ldots,1900$.

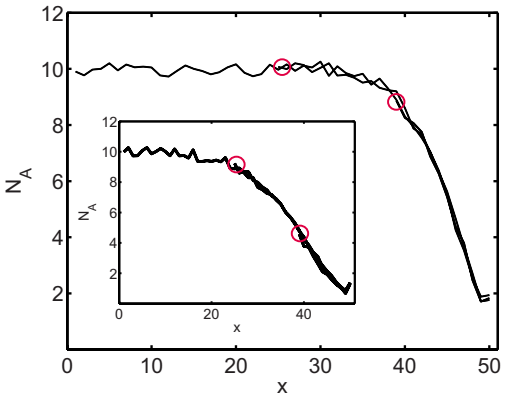

FIG. 5. (Color online) Realigned front form at different times $t=200,500,1000$ with $\alpha=0.9$, $c=10$, $p=0.006$, and $L=1000$. The circles (from left to right) show the end of the front at $t=500$ and $t=200$. The inset shows the same behavior for the case of Markovian diffusion.

times, each line averaged over 297 processes (the value of τ is chosen to have the fronts of approximately the same overall width) is shown. The results of the reaction-diffusion system were plotted in a separate frame, since the two situations are not comparable. The reason for this is the fundamental difference in the waiting time distributions.

In all cases the front forms do not show visible changes with time, i.e., the overall situation corresponds to a propagation of the essentially stationary front at a velocity which is constant in the Markovian diffusion situation and is decaying with time for subdiffusion. The fact that the front profile does not change with time has also been confirmed for lower concentrations c and higher rates p, i.e., in the regime when the FKPP does not work, and its subdiffusive analog may also break down.

It is also interesting to discuss the behavior of the front's forms at shorter times, still far from any stationary propagation regime. In Fig. 5 the front profile of the subdiffusive case with $\alpha=0.9$, $c=10$, and $p=0.006$ is given for $t=200$, 500, and 1000. The fronts, specifically the one at $t=200$, are not yet well developed. Still when realigned, they show the same form of their leading edge. The circles show the position of the origin (left-hand end of the system) after such realignement: right circle shows the end of the front at $t=200$ and left circle the end of the front at $t=500$. One readily infers that the foremost zone of the front develops practically immediately in its final form and does not show any considerable changes during the further evolution. We stress that the same behavior is observed also in the case of normal Markovian diffusion (see the inset).

Let us summarize our findings. We carried out numerical simulations of an irreversible $A+B\rightarrow 2A$ reaction under subdiffusion in different domains of parameters. The results of the simulations show that the propagation failure in a subdiffusive system found theoretically in our previous work does not correspond to the arrest or to spreading out of the front. On the contrary, the reaction front attains a constant form and propagates through the system. However, the velocity of the propagating front decays with time. The corresponding decay can be qualitatively described by assuming the effective time-dependent diffusion coefficient $D(t)\propto t^{\alpha-1}$ in the corresponding expressions for the velocity.

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