Asymptotic front behavior in an $A + B \rightarrow 2A$ reaction under subdiffusion

D. Froemberg, H. H. Schmidt-Martens, and I. M. Sokolov

Institut für Physik, Humboldt-Universität zu Berlin, Newtonstraße 15, D-12489 Berlin, Germany

F. Sagués

Departament de Quimica Fisica, Universitat de Barcelona, Martí i Franqués 1, E-08028 Barcelona, Spain

We discuss the front propagation in the $A + B \rightarrow 2A$ reaction under subdiffusion, which is described by continuous-time random walks with a heavy-tailed power-law waiting-time probability density function. Using a crossover argument, we discuss the two scaling regimes of the front propagation: an intermediate asymptotic regime given by the front solution of the corresponding continuous equation, and the final asymptotics, which is fluctuation dominated and therefore lays out of reach of the continuous scheme. We moreover show that the continuous reaction subdiffusion equation indeed possesses a front solution that decelerates and becomes narrow in the course of time. This continuous description breaks down for larger times when the front gets atomically sharp. We show that the velocity of such fronts decays in time faster than in the continuous regime.

I. INTRODUCTION

Reactions under subdiffusion have attracted much attention in recent years due to their growing relevance for description of processes taking place in porous media such as certain geological formations or gels, in the crowded cell interiors, and in many other strongly inhomogeneous environments including modern drug delivery systems. We focus here on the autocatalytic conversion $A + B \rightarrow 2A$, a reaction that exhibits traveling front solutions if the initial conditions are chosen appropriately, i.e., if A and B are initially separated in space [1,2].

We concentrate on situations when subdiffusion can be modeled within the continuous-time random walks (CTRW) scheme with a waiting-time probability density function (pdf) decaying according to a power law, $\psi(t) \propto t^{-1-\alpha}$. The continuous description of the $A + B \rightarrow 2A$ reaction under subdiffusion, following locally the mass action law corresponding to the Fisher-Kolmogorov-Petrovskii-Piscounov (FKPP) equation, was derived in Ref. [3] and is given by a partial integro-differential equation with a kernel depending on the particle concentrations at all times.

In that preceding work we have shown analytically that the resultant minimal front velocity goes to zero under the assumption of a constant front shape, which was interpreted as propagation failure. In a following paper [4], numerical simulations corroborated this picture, while two different regimes of front propagation were identified. In the fluctuation-dominated regime, pertinent to large reaction rates, the front velocity was found to decay as $v(t) \propto t^{\alpha-1}$, whereas in the regime of small reaction rates, for which the continuous description applies, the front velocity was observed to go as $v(t) \propto t^{\frac{\alpha-1}{2}}$. Longer simulation runs of the continuous case (small reaction rates) revealed that after an intermediate regime that ranged over less than two orders of magnitude in time where $v(t) \propto t^{\frac{\alpha-1}{2}}$ applies, the exponent sets in to decay [5]. Hence the alleged exponent conjectured from the continuous picture was not the final one. Up to now, there has not been any

physically sound interpretation of the front velocities found in these simulations.

In this work we attempt to fill this gap by giving a crossover argument that is used to construct an Ansatz for the solution of the reaction subdiffusion equation at the leading edge. We found that in order to maintain a front velocity that goes as $v(t) \propto t^{\frac{\alpha-1}{2}}$, the additional assumption of the width of the front going as $t^{\frac{\alpha-1}{2}}$ has to be made, so that the front does not maintain a constant form in the course of its propagation. Since the front's width decreases with time, any real (or simulated) subdiffusive FKPP system will sooner or later undergo a change of regime: The front will get atomically narrow, and the continuous scheme breaks down. Physically this has to do with the fact that at large times the jump rate always becomes small compared to the reaction rate, so that the fluctuation-dominated regime sets in. Since the particles react before they are able to leave the site, the front becomes atomically sharp. We suggest that the findings in Ref. [5] (decay of the exponent characterizing the time dependence of the front velocity) can be interpreted in the sense of a transition from the intermediate asymptotics of the reaction described by the continuous reaction-subdiffusion scheme to the final asymptotics corresponding to the fluctuation-dominated regime. We start by presenting simple physical arguments in favor of this picture. We then show that the intermediate asymptotics with $v(t) \propto t^{\frac{\alpha-1}{2}}$ indeed appears as a possible solution of the corresponding integro-differential reaction-subdiffusion equation. Physical arguments show however that this asymptotics cannot be the final one, and that the final regime is fluctuation dominated. We then turn to a numerical investigation of this fluctuation-dominated regime and show that the subdiffusive nature of the motion leads to additional fluctuation effects absent in the normal diffusive case.

II. CROSSOVER ARGUMENTS

Under normal diffusion and with the overall particle concentration $A + B = c$ being locally conserved, the

$A + B \rightarrow 2A$ reaction is described by the FKPP equation

$$\frac{\partial A(x,t)}{\partial t} = D \Delta A(x,t) + k(c - A)A,$$

which has been extensively studied. According to its classical solution [1,2], fronts propagating with velocities $v \geqslant \sqrt{2kcD}$ are possible, and it is moreover known that for steplike initial condition the solution with minimum speed, $v = \sqrt{2kcD}$, is the one that is really achieved at long times.

In order to gain intuition about the front behavior under subdiffusion, we make use of the following idea: For any waiting time pdf ψ with finite mean $\langle t \rangle$, the behavior at very long times $t \gg \langle t \rangle$ corresponds to normal diffusion, so that the behavior pertinent to reaction-diffusion schemes is recovered only if time t is large enough. On the other hand, if the initial domain of the pdf can be approximated by a power law, $\psi(t) \propto t^{-1-\alpha}$ up to some truncation time T, the behavior at short times should correspond to the one in subdiffusion, and there must be a smooth crossover from one regime to the other. We therefore consider the truncated power-law waiting time distribution with truncation parameter T,

$$\psi_T(t) = \frac{(t_0 + T)^\alpha}{(t_0 + T)^\alpha - t_0^\alpha} \frac{\alpha t_0^\alpha}{(t_0 + t)^{1+\alpha}} \Theta(T - t), \qquad (1)$$

with mean value

$$\langle t \rangle = \frac{\alpha T t_0^\alpha + t_0 [t_0^\alpha - (T + t_0)^\alpha]}{(\alpha - 1)[t_0^\alpha - (T + t_0)^\alpha]}. \qquad (2)$$

For $T \gg t_0$, $\langle t \rangle \approx \frac{\alpha}{1-\alpha} t_0^\alpha T^{1-\alpha}$.

For small times $t \ll T$, when the system does not feel the cutoff, the behavior of the velocity will be similar to that in subdiffusion, whereas for large times the behavior will be the classical one with a constant minimal velocity. The crossover between the two regimes must thus take place at some crossover time t_{cr}. We assume that in the anomalous domain $v \simeq vt^\beta$, and that after this a crossover to normal behavior sets in. In the case when the normal behavior is described by the FKPP scheme this corresponds to $v = \text{const.} \sim \sqrt{ckD}$, with $D = a^2/2\langle t \rangle$, where a is the step's length of the corresponding random walk process (an irrelevant microscopical variable), and the time behavior of the velocity in the anomalous regime is given by the equation

$$v t_{cr}^\beta = \left[ck \frac{a^2}{2\langle t(t_{cr}) \rangle} \right]^{1/2}. \qquad (3)$$

In order to determine the crossover time we concentrate on the most basic quantity that is known in the normal as well as in the anomalous case, i.e., the number of performed steps, a measure of mobility, which is given by

$$n_D(t) = \frac{t}{\langle t \rangle} \qquad (4)$$

in the normal regime $t \gg t_{cr}$, and

$$n_{SD}(t) = \frac{t^\alpha}{\Gamma[1 + \alpha] t_0^\alpha} \qquad (5)$$

in the subdiffusive regime $t \ll t_{cr}$.

By enforcing $n_{SD}(t_{cr}) = n_D(t_{cr})$ we find

$$\frac{1 - \alpha}{\alpha} \frac{t_{cr}}{t_0^\alpha T^{1-\alpha}} = \frac{t_{cr}^\alpha}{\Gamma(1 + \alpha) t_0^\alpha}; \qquad (6)$$

and hence $t_{cr} \propto T$ [more precisely $t_{cr}^{1-\alpha} = \frac{\alpha}{\Gamma(1+\alpha)(1-\alpha)} T^{1-\alpha}$]. Obviously, the larger we choose the cutoff parameter T, the larger becomes the crossover time. At the time the crossover takes place, the quantities characterizing the behavior of the system, such as the number of performed steps, the front velocities, etc., have to match for the two regimes. Tuning T we get the respective values of the quantities of interest at t_{cr}, for example, the mean waiting time $\langle t \rangle \propto t_{cr}^{1-\alpha}$ for the normal case in terms of t_{cr}. From Eq. (3) we then get

$$v(t < t_{cr}) \propto t^{\frac{\alpha-1}{2}} \qquad (7)$$

in the subdiffusive regime. Correspondingly we can define other time-dependent effective characteristics in the anomalous regime, e.g., an effective mean waiting time, $\langle t \rangle_{\text{eff}} \propto t^{1-\alpha}$ (the parameter t_{cr} is changed to t), which yields an effective, time-dependent diffusion coefficient $D_{\text{eff}} \propto 1/t^{1-\alpha}$, from which Eq. (7) can be obtained via the classical formula $v = \sqrt{2ckD_{\text{eff}}}$. This discussion elucidates the source of the anomalous front velocity in the regime of small reaction rates, as found numerically in Ref. [4].

We note that even the case for normal diffusion is not simple at all, especially when the one-dimensional situation is considered, the one especially prone to fluctuation effects. To understand the situation we first recall that the FKPP equation, if it holds, has the same form in whatever spatial dimension and provides us not only with the velocity of the front, but also with the front's width. Since in any spatial dimension d the dimensions of the concentration $[c] = L^{-d}$ and that of the reaction rate $[k] = T^{-1}[c]^{-1}$ are connected to each other, so that $[kc]$ always has the dimension of the inverse time, the combination $\sqrt{Dkc}$ always has the dimension of velocity, and the combination $w = \sqrt{D/kc}$ always has the dimension of length. The characteristic width of the front is thus proportional to our parameter w; see Ref. [2] for a quantitative discussion. The velocity of the front and its width w are connected by a simple relation

$$v \sim w/\tau = D/w, \qquad (8)$$

where $\tau = w^2/D$ is of the order of the time that it takes a particle to diffuse through the front's width.

Here it is important to note that the width w is the only relevant parameter of the dimension of length in the continuous theory, but going to the particle picture, another characteristic length, the interparticle distance $l = c^{-1/d}$ emerges, and an additional dimensionless parameter $\Pi = w/l$ appears. The parameter Π gives us the front width measured in the units of the interparticle distance and quantifies the strengths of fluctuation effects in the $A + B \rightarrow 2A$ reaction.

According to the Buckingham's Π theorem [6], the velocity v, $[v] = LT^{-1}$ has to depend on the parameters of the problem as

$$v = \sqrt{kcD} f(\Pi) = \sqrt{kcD} f(\sqrt{D/k} c^{1/d-1/2}),$$

with f being a yet unknown function of a dimensionless parameter, and the prefactor of f reproducing the classical FKPP

behavior of the velocity. The prefactor of f has the same form in any spatial dimension, while the dimensionless argument of the function f has a different form in spaces of different dimension. Evidently, the continuous description works only if $w \gg l$, i.e., in the classical case where $\sqrt{D/ck} \gg c^{-1/d}$: for large concentrations and diffusion coefficients and for small reaction rates. In this case there are many particles within the front region, and the continuous description does hold. For $\Pi \sim 1$ corresponding to the atomically sharp front, the number of particles across the region fluctuates strongly, and therefore front propagation is fluctuation dominated.

Let us now concentrate on the one-dimensional case, as discussed in Refs. [4] and [5]. The fluctuation-dominated regime in one dimension corresponds to $v \propto Dc$ [7], which can be easily understood within Eq. (8) by assuming the width of an atomically sharp front to correspond to the interparticle distance, $w \simeq l = c^{-1}$. Repeating the same crossover arguments, as in the previous case, this kind of behavior under normal diffusion is mirrored onto the form

$$v(t) \propto t^{\alpha - 1} \qquad (9)$$

for the velocity time dependence in the subdiffusive case.

The same crossover arguments as applied to the velocity can be also extended to the width of the front. Since the front width $w \propto D_{\mathrm{eff}}^{1/2}$ is a decaying function of time in the subdiffusive case, the condition for continuous description to hold breaks down for times long enough, and the transition from the intermediate "classical" asymptotics [Eq. (7)] to the final fluctuation-dominated asymptotics [Eq. (9)] inevitably takes place.

In what follows we first show that the "classical" asymptotics [Eq. (7)] indeed appears as a possible solution of the reaction subdiffusion equation, and then we change to investigating the far asymptotic regime, when the reaction-subdiffusion equation breaks down. This is done by use of extensive numerical simulations.

III. CONTINUOUS REACTION-SUBDIFFUSION REGIME

Let us assume the front to behave in accordance with our crossover arguments, namely, to have the velocity and the width going as $t^{\frac{\alpha-1}{2}}$ [i.e., with position $x(t) \propto v_0 t^{\frac{1+\alpha}{2}}$]. The overall form of the front will be assumed exponential at its leading edge $x \to \infty$. Thus, the following Ansatz is made:

$$A(x,t) = A_0 \exp\left[-\lambda_0 t^{\frac{1-\alpha}{2}}\left(x - v_0 t^{\frac{1+\alpha}{2}}\right)\right]$$
$$= A_0 \exp\left[-\lambda_0 t^{\frac{1-\alpha}{2}} z\right], \qquad (10)$$

where $z = x - v_0 t^{\frac{1+\alpha}{2}}$ is the comoving variable. [The exponential Ansatz is due to the fact that we will anyhow linearize the equations at the front's far edge, and we know from elsewhere [8] that the (stationary) solutions of linear reaction-subdiffusion equations are exponentials.]

The equation for the concentration of A particles $A(x,t)$, with c being the overall particle concentration, is (cf. Ref. [3])

$$\frac{\partial A(x,t)}{\partial t} = k[c - A(x,t)]A(x,t) + \frac{a^2}{2}\Delta \int_0^t M(t-t')$$
$$\times \left[A(x,t') - c\right]\exp\left[-\int_{t'}^t kA(x,t'')\,dt''\right]dt', \qquad (11)$$

with the kernel

$$\tilde{M}(u) = \frac{u\tilde{\psi}(u)}{1 - \tilde{\psi}(u)}$$

in Laplace domain [which corresponds to the Riemann-Liouville fractional derivative of order $1 - \alpha$ in the subdiffusive case, $\frac{1}{\Gamma(\alpha)}\frac{d}{dt}\int_0^t \frac{1}{(t-t')^{1-\alpha}}(\cdot)\,dt'$].

We note that $A(x,t)$ becomes small at the leading edge $x \to \infty$, and $\exp[-\int_{t'}^t kA(x,t'')\,dt''] \approx 1$, so that

$$\frac{\partial A(x,t)}{\partial t} = \frac{a^2}{2}\int_0^t \Delta\Big\{M(t-t')(A(x,t')-c)$$
$$\times \exp\left[-k\int_{t'}^t A(x,t'')\,dt''\right]\Big\}dt'$$
$$+ k[c - A(x,t)]A(x,t) \qquad (12)$$
$$\approx \frac{a^2}{2}\int_0^t M(t-t')\Big\{\Delta A(x,t') - 2\nabla A(x,t')$$
$$\times \int_{t'}^t k\nabla A(x,t'')\,dt'' + [c - A(x,t')]$$
$$\times \int_{t'}^t k\Delta A(x,t'')\,dt'' - [c - A(x,t')]$$
$$\times \left[\int_{t'}^t k\nabla A(x,t'')\,dt''\right]^2\Big\}dt'$$
$$+ k[c - A(x,t)]A(x,t). \qquad (13)$$

In particular, with Ansatz (10) and taking into account that the term $t^{-\frac{1+\alpha}{2}}$ is negligible for large t, we have

$$\frac{\partial A(x,t)}{\partial t}$$
$$= A_0 \exp\left[-\lambda_0 t^{\frac{1-\alpha}{2}}\left(x - v_0 t^{\frac{1+\alpha}{2}}\right)\right]$$
$$\times \left[v_0\lambda_0 t^{\frac{1-\alpha}{2}} t^{\frac{\alpha-1}{2}}\frac{\alpha+1}{2} - \lambda_0 t^{-\frac{1+\alpha}{2}}\frac{1-\alpha}{2}\left(x - v_0 t^{\frac{1+\alpha}{2}}\right)\right]$$
$$= A_0 \exp\left[-\lambda_0 t^{\frac{1-\alpha}{2}}\left(x - v_0 t^{\frac{1+\alpha}{2}}\right)\right]$$
$$\times \left(v_0\lambda_0 - \frac{1-\alpha}{2}\lambda_0 x t^{-\frac{1+\alpha}{2}}\right)$$
$$\approx A_0 \exp\left[-\lambda_0 t^{\frac{1-\alpha}{2}}\left(x - v_0 t^{\frac{\alpha+1}{2}}\right)\right]v_0\lambda_0, \qquad (14)$$

$$\nabla A(x,t) = -A_0\lambda_0 t^{\frac{1-\alpha}{2}}\exp\left[-\lambda_0 t^{\frac{1-\alpha}{2}}\left(x - v_0 t^{\frac{1+\alpha}{2}}\right)\right],$$
$$\Delta A(x,t) = A_0\lambda_0^2 t^{1-\alpha}\exp\left[-\lambda_0 t^{\frac{1-\alpha}{2}}\left(x - v_0 t^{\frac{1+\alpha}{2}}\right)\right].$$

Proceeding as in Ref. [3] we have to first order in concentration for the A particles:

$$\frac{\partial A(x,t)}{\partial t}$$
$$\approx \frac{a^2}{2}\int_0^t M(t-t')\Delta A_0 \exp\left[-\lambda_0 t'^{\frac{1-\alpha}{2}}\left(x - v_0 t'^{\frac{\alpha+1}{2}}\right)\right]dt'$$
$$+ \frac{a^2}{2}\int_0^t M(t-t')ck\int_{t'}^t \Delta A_0$$
$$\times \exp\left[-\lambda_0 t''^{\frac{1-\alpha}{2}}\left(x - v_0 t''^{\frac{1+\alpha}{2}}\right)\right]dt''\,dt' + ckA(x,t), \quad (15)$$

i.e.,

$$
A_0 \exp\left[-\lambda_0 t^{\frac{1-\alpha}{2}}\left(x - v_0 t^{\frac{\alpha+1}{2}}\right)\right] v_0 \lambda_0
$$

$$
\approx \frac{a^2}{2}\int_0^t M(t-t')A_0\lambda_0^2 t'^{1-\alpha}\exp\left[-\lambda_0 t'^{\frac{1-\alpha}{2}}\left(x - v_0 t'^{\frac{\alpha+1}{2}}\right)\right]dt'
$$

$$
+\frac{a^2}{2}\int_0^t M(t-t')ckA_0\lambda_0^2\int_{t'}^t t''^{1-\alpha}\exp\left[-\lambda_0 t''^{\frac{1-\alpha}{2}}\right.
$$

$$
\left.\times\left(x - v_0 t''^{\frac{1+\alpha}{2}}\right)\right]dt''\,dt'
$$

$$
+ckA_0\exp\left[-\lambda_0 t^{\frac{1-\alpha}{2}}\left(x - v_0 t^{\frac{\alpha+1}{2}}\right)\right]. \tag{16}
$$

Recall that the kernel is governed by the waiting time probability density function, in Laplace domain $\tilde{M}(u) = \frac{u\tilde{\psi}(u)}{1-\tilde{\psi}(u)}$.

We note that in the following we assume $\psi(t) \propto \tau^\alpha t^{-1-\alpha}$ so that the new parameter τ and the old one t_0 from the original waiting-time distribution $\psi(t) = \frac{\alpha t_0^\alpha}{(t+t_0)^{1+\alpha}}$ [i.e., the ψ we truncated for the crossover argumentation in the preceding section; cf. (1)] turn out to be the same, $\tau = t_0$.

Altogether we have then for $z = x - v_0 t^{\frac{1+\alpha}{2}}$ and t large:

$$
\lambda_0 v_0 \exp\left(-\lambda_0 t^{\frac{1-\alpha}{2}} z\right)
$$

$$
= \exp\left(-\lambda_0 t^{\frac{1-\alpha}{2}} z\right)\left\{\frac{a^2}{2\Gamma(\alpha)\Gamma(1-\alpha)\tau^\alpha}\right.
$$

$$
\left.\times\left[B\lambda_0^2 + \frac{ck\lambda_0}{v_0}(1-B)\right] + ck\right\}, \tag{17}
$$

where B is a constant that originates from the estimation of the involved integrals (see the Appendix), with $B(\alpha, 2-\alpha) \geqslant B \geqslant 0$ and $B(\nu,\mu)$ being the beta-function. This yields the dispersion relation for λ_0:

$$
0 = \lambda_0^2 + \frac{\frac{ckK_\alpha^*}{v_0}(1-B) - v_0}{K_\alpha^* B}\lambda_0 + \frac{ck}{K_\alpha^* B} \tag{18}
$$

with $\frac{a^2}{2\Gamma(\alpha)\Gamma(1-\alpha)\tau^\alpha} = K_\alpha^* = \frac{K_\alpha}{\Gamma(\alpha)}$, where K_α is the generalized diffusion constant. From

$$
\lambda_{0_{1,2}} = -\frac{\frac{ckK_\alpha^*}{v_0}(1-B) - v_0}{2K_\alpha^* B} \pm \sqrt{\frac{\left[\frac{ckK_\alpha^*}{v_0}(1-B) - v_0\right]^2}{4K_\alpha^{*2}B^2} - \frac{ck}{K_\alpha^* B}}, \tag{19}
$$

we find the restriction

$$
\left[\frac{ckK_\alpha^*}{v_0}(1-B) - v_0\right]^2 \geqslant 4ckK_\alpha^* B, \tag{20}
$$

a quartic equation in v_0 that yields

$$
v_0^2 = K_\alpha^* ck(1 + B \pm 2\sqrt{B}). \tag{21}
$$

Note that in the normal case $B = 1$, the minimal front velocity $v_{\min} = \pm 2\sqrt{cDk}$ is reproduced; the other solution is a double one at $v = 0$ for which there is no front. Recall again that $B(\alpha, 2-\alpha) \geqslant B \geqslant 0$; therefore Eq. (21) always has real roots $[B(\alpha, 2-\alpha) > 1$ for all $\alpha < 1]$.

This analysis shows that there exists a set of (nonzero) parameters λ_0 and v_0 for which Ansatz (10) yields a solution to the linearized reaction subdiffusion equation (13), although the integrals appearing in the calculations can be estimated only

approximately. We note that neither an Ansatz taking a front velocity going as $v(t) \propto t^{\alpha-1}$ nor an Ansatz with $v(t) \propto t^{\frac{\alpha-1}{2}}$ and a constant front width yield an asymptotic solution of the reaction-subdiffusion equation, and therefore such types of behavior are impossible within the continuous scheme.

In our previous simulations we were not able to detect the changes in the front shape, presumably due to our averaging procedure over several runs, and hence we did not conjecture any change of regime in Ref. [4]. On the other hand, our simulations were not carried out for long enough times to detect the change of regime in the velocity variable. Since such transitions take place only very slowly, much longer runs of the simulation were really necessary, as the more extensive simulations of Ref. [5] showed. This suggests that indeed the continuous regime as considered above does not describe the final behavior of the front. Now we can interpret the findings of Ref. [5] as the setting in of a slow transition to the fluctuation-dominated regime.

IV. FAILURE OF THE CONTINUOUS DESCRIPTION: ATOMICALLY SHARP FRONTS IN SIMULATIONS FOR LARGE TIMES

Since the subdiffusive front is slowing down and becoming steeper in the course of time, any system will sooner or later enter a regime already discussed in Ref. [4] for subdiffusion and in Refs. [7,9] for normal diffusion. This regime is a fluctuation-dominated one and is no longer described by continuous approaches. Since the integral kernel $M(t)$ of the linearized reaction-subdiffusion equations decays and determines the mean density of steps in time, the waiting times for particles at a site become so large in the course of time that the motion of the front is governed by the first A particle entering a new site. All B particles at the same site have enough time to react with A before the next jump from the site takes place, the reaction rate dependence disappears, and the behavior of the front gets to be the same as in the reaction on the first contact.

Under such a condition the velocity of the front's motion can be estimated using the following argument (adapted from Refs. [10,11] for our sequential updating scheme). Let us consider the front position as fixed by the rightmost A particle(s) and concentrate on the next jump of the front particle. If the A particle is alone at its front position, this next jump takes place with probability $1/2$ by an amount $\pm a$, so that the net front displacement after such a step is zero on average. Conversely, in case of more than one particle sitting at the front position (the probability of which is ac if the concentration is defined as a number of particles per unit length), the front moves by a to the right if the particle makes a step forward (which happens with probability $1/2$). The front does not move if the particle jumps backward, since then there is at least one other particle that keeps the front in the position where it was. Therefore, at a step of a front particle, the front moves on average by a distance $a^2 c/2$. Since the rate at which the particle moves is defined by the time integral of the memory kernel M, the front's velocity is given by

$$
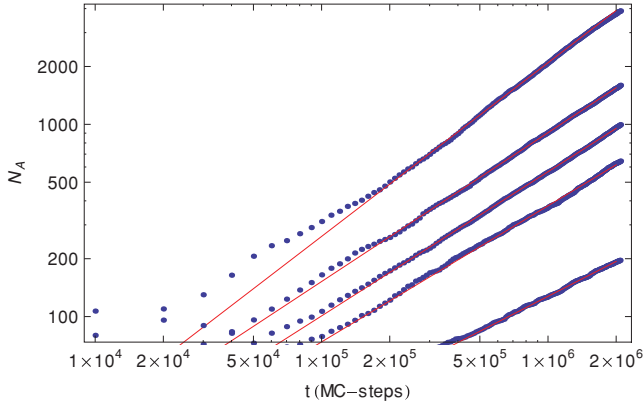v \approx \frac{a^2 c}{2}\int_0^t M(t-t')\,dt'. \tag{22}
$$

FIG. 1. (Color online) Front position for $\alpha = 0.9$, 0.8, 0.75, 0.7, 0.6 (upper to lower graphs), $c = 0.3$. Full (unbroken red) lines denote fits of the large time behavior.

Let us first derive the asymptotic jump rate of the particles. Consider the generic waiting time pdf's with the asymptotic behavior

$$\psi(t) \propto \tau^\alpha t^{-1-\alpha}. \tag{23}$$

The (cumulative) probability to make a step until t, for t large, is then

$$\Psi(t) \simeq 1 - \tau^\alpha t^{-\alpha}; \tag{24}$$

or in Laplace domain, using the Tauberian theorem

$$\tilde{\Psi}(u) \simeq \frac{1}{u} - \Gamma(1-\alpha)\tau^\alpha u^{-1+\alpha}, \tag{25}$$

so that the pdf

$$\tilde{\psi}(u) \simeq 1 - \Gamma(1-\alpha)\tau^\alpha u^\alpha. \tag{26}$$

The rate for a particle to jump is $\int_0^t M(t-t')\,dt'$ or in Laplace domain

$$\frac{\tilde{M}(u)}{u} = \frac{\tilde{\psi}(u)}{1-\tilde{\psi}(u)} \simeq \frac{1}{\tau^\alpha \Gamma(1-\alpha)}u^{-\alpha} \tag{27}$$

for $u \to 0$ so that we have an expression for the velocity in Laplace domain given by

$$\mathcal{L}\{v(t)\} = \frac{ca^2}{2}\frac{1}{\tau^\alpha\Gamma(1-\alpha)}u^{-\alpha}. \tag{28}$$

Transforming back to the time domain yields

$$v(t) = \frac{a^2}{2\Gamma(1-\alpha)\tau^\alpha}\frac{c}{\Gamma(\alpha)}t^{\alpha-1} = K_\alpha\frac{c}{\Gamma(\alpha)}t^{\alpha-1} = cK_\alpha^*t^{\alpha-1}. \tag{29}$$
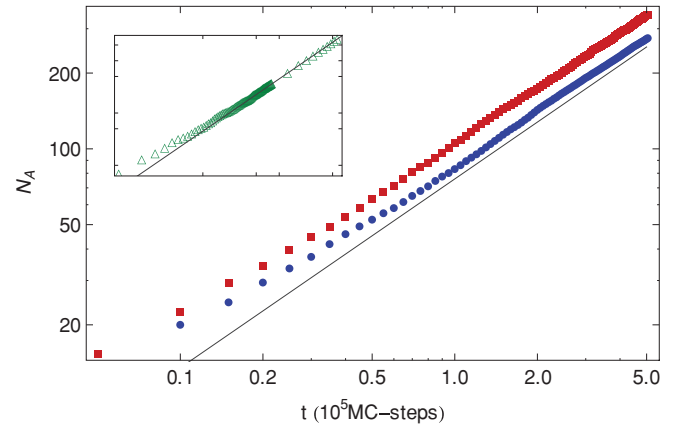

FIG. 2. (Color online) Time dependence of the total amount of A particles N_A for the subdiffusive case (squares) and subdiffusion with randomized particles (circles), $\alpha = 0.75$. The black line denotes the theoretical curve according to (31). The inset shows the situation for an exponential waiting time pdf (with mean 1), t covers the range of 10 to 5×10^4, N_A from 6 to 2000. The black line denotes again the theory, $N_A = Dc^2t$; $c = 0.3$.

With $\frac{1}{\Gamma(\alpha)\Gamma(1-\alpha)} = \frac{\sin(\alpha\pi)}{\pi}$ the front velocity is better expressed as

$$v(t) = \frac{a^2}{\tau^\alpha}\frac{c}{2}\frac{\sin(\alpha\pi)}{\pi}t^{\alpha-1}, \tag{30}$$

which corresponds to the position of the front going as

$$x(t) = \frac{N_A}{c} = \int_0^t v(t)\,dt = \frac{a^2}{2\tau^\alpha}\frac{\sin(\alpha\pi)}{\alpha\pi}ct^\alpha. \tag{31}$$

(N_A is the total amount of A particles.)

Note that the definition of the characteristic waiting time τ adopted here does not allow for simply taking $\alpha = 1$ to perform the limiting transition to normal diffusion, as found, e.g., for the exponential distribution of waiting times, $\psi(t) = \langle t \rangle^{-1}\exp(-t/\langle t \rangle)$. This is due to the presence of the divergent $\Gamma(1-\alpha)$ in Eq. (26): The case $\alpha = 1$ corresponds, strictly speaking, to still (logarithmically) divergent mean waiting times. For the normal case with converging mean Eq. (26) reads $\tilde{\psi}(u) \simeq 1 - \langle t \rangle u$, and, after performing the same steps as above, the front velocity of the normal fluctuation-dominated regime, $v_{\text{fluct}} = cD$, with D being the diffusion constant, is recovered [7]. We performed the numerical simulations of the front propagation using the event-driven algorithm, as described in Ref. [4], applicable when the particles react on contact with probability one. Figure 1 shows the total number of particles in the Monte Carlo (MC) simulation for the fluctuation-dominated regime, i.e., reaction on contact, for a concentration $c = 0.3$. In these simulations we had seven runs for $\alpha = 0.9$, 18 for $\alpha = 0.8$, 41 for $\alpha = 0.75$, 13 for $\alpha = 0.7$, and 18 for $\alpha = 0.6$.

TABLE I. Exponents for the fit $N_A = Ft^\beta$ for different α.

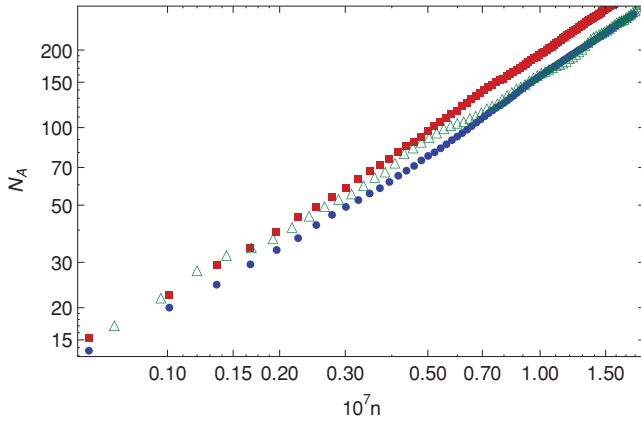| α	0.6	0.7	0.75	0.8	0.9
β	0.603 ± 0.004	0.708 ± 0.004	0.750 ± 0.001	0.775 ± 0.002	0.890 ± 0.009

FIG. 3. (Color online) Total amount of A particles N_A for the normal case (triangles), the subdiffusive case (squares), and subdiffusion with randomized jumps (circles), both $\alpha = 0.75$, depending on the total number of performed steps; $c = 0.3$.

Table I shows the exponents of the long time fits $N_A = Ft^{\beta}$, which coincide well with α.

The values of the prefactor F found from the simulations turned out to be larger, however, than the predicted ones in (31) by around 30%–40%. In order to find out about the origin of this difference, we performed simultaneous simulations of subdiffusion and of subdiffusion with randomized particles, i.e., in the situation when the particles lost their individual memory and were chosen randomly to jump when a jumping time was reached. This variant of the reaction closely mimics the behavior assumed to derive Eq. (22), namely, the assumption that the rate at which the steps of the rightmost A particle are made is equal to the mean jump rate of all particles at time t: We fully disregard the fact that the rightmost A is a very special particle, with its special prehistory.

Figure 2 shows the time dependence of the overall amount of A particles for $\alpha = 0.75$. The theoretical curve (31) lies much closer to the simulation results of subdiffusion with randomized particles. The remaining difference between the simulation of the randomized particles and the theoretical

result is presumably due to the fact that convergence to the asymptotic behavior in subdiffusion is very slow. Apparently, the full subdiffusive picture implies an additional fluctuation effect. For a better interpretation of the results, we also simulated the case of normal diffusion. The inset of the figure shows the situation for an exponential waiting time pdf with mean 1, where the simulated front behavior converges to the predicted behavior indicated by the black line, $N_A = Dc^2t$. We note that Warren *et al.* [10] detected a fluctuation effect in the normal case that occurs at small concentrations. However, as the inset shows, due to the sequential update in our simulations, this effect does not come into play here, and our theoretical approach is sufficient to explain the front behavior in the normal case.

Figure 3 shows the dependence of the overall amount of A particles on the total amount of steps performed for $\alpha = 0.75$. Comparing the two subdiffusive prescriptions (original and randomized) as well as the normal diffusion reveals that the randomized version of subdiffusive front behavior is more akin to the normal diffusive front behavior than the full subdiffusive version: If we interpret the number of steps n as the internal, operational time of the process, the randomized subdiffusive setting and the normal diffusive one have the same asymptotics, whereas the full original subdiffusive front position differs by a certain factor. Figure 4 shows the quotient of the original subdiffusive front position and the randomized one, which can be used to quantify this effect that turns out to be around at least 20%–30%.

Obviously, the additional fluctuation effect of the front behavior is genuinely due to subdiffusion. This effect cannot be explained within the mean-field description of the front behavior but comes into play through the interaction of the particles at the front: The rate at which a front particle performs a jump is higher than the average jump rate of a single particle in the system. If the particle at the edge of the front is subject to a very long waiting time (which happens not often, but occasionally), other particles will outpace that particle and take the lead. Hence, the impact of very long waiting times in single particle dynamics on the front motion is considerably reduced.

V. CONCLUSIONS

We discussed the front motion in the $A + B \rightarrow 2A$ reaction under subdiffusion described by continuous-time random walks where the reaction is governed by the mass action law on a microscopic scale. We have shown that at intermediate times, as long as the process can be described within a continuous picture, the front velocity goes as $v(t) \propto t^{\frac{\alpha-1}{2}}$. The decay of the front velocity goes along with a decay of the width of the front, which at longer times therefore gets atomically sharp. At such times the continuous picture, implied by the description within the reaction-subdiffusion equations scheme, inevitably breaks down. The typical timescale of diffusion becomes very large compared to the typical timescale of reaction, and a crossover to the fluctuation-dominated regime takes place where the front velocity decays faster, $v(t) \propto t^{\alpha-1}$. This fluctuation-dominated regime is the same as in the reaction on the first contact and is characterized by additional fluctuation effects compared to the case of normal diffusion.
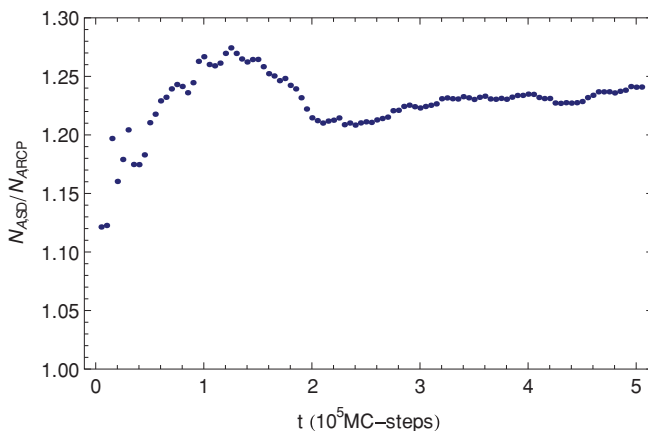

FIG. 4. (Color online) Quotient of total amount of A particles for the subdiffusive case and subdiffusion with randomized particles $\frac{N_{A,SD}}{N_{A,RCP}}$ as a function of time; $\alpha = 0.75$.

APPENDIX: EVALUATION OF INTEGRALS

We investigate the integrals in expression (16) term by term, from left to right and take into account that the constant A_0 cancels:

$$
I_1 = \int_0^t M(t - t')\lambda_0^2 t'^{1-\alpha} \exp\left[-\lambda_0 t'^{\frac{1-\alpha}{2}}\left(x - v_0 t'^{\frac{\alpha+1}{2}}\right)\right] dt'
$$

$$
= \frac{\lambda_0^2}{\Gamma(1-\alpha)\tau^\alpha} \exp\left[-\lambda_0 t^{\frac{1-\alpha}{2}}\left(x - v_0 t^{\frac{1+\alpha}{2}}\right)\right]\frac{1}{\Gamma(\alpha)}\frac{d}{dt}
$$

$$
\times \int_0^t \frac{1}{(t-t')^{1-\alpha}}t'^{1-\alpha} \exp\left[-\lambda_0 t'^{\frac{1-\alpha}{2}}\left(x - v_0 t'^{\frac{1+\alpha}{2}}\right)\right.
$$

$$
\left. + \lambda_0 t^{\frac{1-\alpha}{2}}\left(x - v_0 t^{\frac{1+\alpha}{2}}\right)\right]dt'. \tag{A1}
$$

This expression can be estimated from above since $t' \leqslant t$:

$$
I_1 \leqslant \frac{\lambda_0^2}{\Gamma(1-\alpha)\tau^\alpha} \exp\left[-\lambda_0 t^{\frac{1-\alpha}{2}}\left(x - v_0 t^{\frac{1+\alpha}{2}}\right)\right]
$$

$$
\times \frac{1}{\Gamma(\alpha)}\frac{d}{dt}\int_0^t \frac{1}{(t-t')^{1-\alpha}}t'^{1-\alpha}\,dt'
$$

$$
= \frac{\lambda_0^2}{\Gamma(1-\alpha)\tau^\alpha} \exp\left[-\lambda_0 t^{\frac{1-\alpha}{2}}\left(x - v_0 t^{\frac{1+\alpha}{2}}\right)\right]
$$

$$
\times \frac{1}{\Gamma(\alpha)}\frac{d}{dt}t\int_0^1 \frac{1}{(1-t')^{1-\alpha}}t'^{1-\alpha}\,dt'
$$

$$
= \frac{\lambda_0^2}{\Gamma(1-\alpha)\tau^\alpha} \exp\left[-\lambda_0 t^{\frac{1-\alpha}{2}}\left(x - v_0 t^{\frac{1+\alpha}{2}}\right)\right]\frac{1}{\Gamma(\alpha)}B(\alpha, 2-\alpha). \tag{A2}
$$

The integral in (A1) is monotonic; i.e., it must tend to a constant value $B \leqslant B(\alpha, 2-\alpha)$ for large times ($B = 1$ for the normal diffusive case, in particular). We used here the definition of the beta-function $B(\mu, \nu) = \frac{\Gamma(\mu)\Gamma(\nu)}{\Gamma(\mu+\nu)}$.

The second integral to be evaluated is

$$
I_2 = \int_0^t M(t-t')ck\lambda_0^2 \int_{t'}^t t''^{1-\alpha}
$$

$$
\times \exp\left[-\lambda_0 t''^{\frac{1-\alpha}{2}}\left(x - v_0 t''^{\frac{1+\alpha}{2}}\right)\right]dt''\,dt'. \tag{A3}
$$

At the far edge of the front, our comoving variable $z = x - v_0 t^{\frac{1+\alpha}{2}}$ is very large. The transition to large z can be achieved by introducing a large parameter γ, so that the integral appearing in the integrand of (A3) obtains the form of a Laplace integral, which allows for an asymptotic estimation for $\gamma \to \infty$:

$$
\lim_{\gamma\to\infty}\frac{\lambda_0^2}{\Gamma(1-\alpha)\tau^\alpha}\int_0^t t''^{1-\alpha} \exp\left[-\lambda_0 t''^{\frac{1-\alpha}{2}}\gamma\left(x - v_0 t''^{\frac{1+\alpha}{2}}\right)\right]dt''
$$

$$
= \frac{\lambda_0}{v_0\Gamma(1-\alpha)\tau^\alpha}t^{1-\alpha}\exp\left[-\lambda_0 t^{\frac{1-\alpha}{2}}\left(x - v_0 t^{\frac{1+\alpha}{2}}\right)\right], \tag{A4}
$$

which means that for large γ the value of the above integral is asymptotically determined by the points where the exponent in the integrand attains its maximum; see, e.g., Ref. [12].

Hence, (A3) becomes

$$
\frac{\lambda_0}{v_0}\exp\left[-\lambda_0 t^{\frac{1-\alpha}{2}}\left(x - v_0 t^{\frac{1+\alpha}{2}}\right)\right]\left\{t^{1-\alpha}\int_0^t M(t-t')\,dt' - \int_0^t M(t-t')t'^{1-\alpha}\exp\left[-\lambda_0 t'^{\frac{1-\alpha}{2}}\left(x - v_0 t'^{\frac{1+\alpha}{2}}\right)\right.\right.
$$

$$
\left.\left. + \lambda_0 t^{\frac{1-\alpha}{2}}\left(x - v_0 t^{\frac{1+\alpha}{2}}\right)\right]dt'\right\}
$$

$$
= \frac{\lambda_0}{v_0\Gamma(1-\alpha)\tau^\alpha}\exp\left[-\lambda_0 t^{\frac{1-\alpha}{2}}\left(x - v_0 t^{\frac{1+\alpha}{2}}\right)\right]\left\{t^{1-\alpha}\frac{1}{\Gamma(\alpha)}\frac{d}{dt}\int_0^t \frac{1}{(t-t')^{1-\alpha}}\,dt' - \frac{1}{\Gamma(\alpha)}\frac{d}{dt}\int_0^t \frac{1}{(t-t')^{1-\alpha}}t'^{1-\alpha}\,dt'\right.
$$

$$
\left.\times \exp\left[-\lambda_0 t'^{\frac{1-\alpha}{2}}\left(x - v_0 t'^{\frac{1+\alpha}{2}}\right) + \lambda_0 t^{\frac{1-\alpha}{2}}\left(x - v_0 t^{\frac{1+\alpha}{2}}\right)\right]\right\}
$$

$$
= \frac{\lambda_0}{v_0\Gamma(1-\alpha)\tau^\alpha}\exp\left[-\lambda_0 t^{\frac{1-\alpha}{2}}\left(x - v_0 t^{\frac{1+\alpha}{2}}\right)\right]\times \frac{1}{\Gamma(\alpha)}(1 - B), \tag{A5}
$$

with $B \leqslant B(\alpha, 2-\alpha)$; cf. (A2).

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