Stationary Fronts in an $A + B \to 0$ Reaction under Subdiffusion

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We consider stationary profiles of reactants' concentrations and of reaction zones of an $A + B \to 0$ reaction in a flat subdiffusive medium fed by reactants of both types on both sides. The structures formed under such conditions differ strikingly from those in simple diffusion and exhibit accumulation and depletion zones close to the boundaries and nonmonotonic behavior of the reaction intensity with respect to the reactants' concentrations at the boundaries. These findings are connected to an effectively nonlinear character of transport in subdiffusive systems under reactions.

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Many phenomena in systems out of equilibrium correspond to reactions between diffusing species and can be described by reaction-diffusion equations. Examples range from chemistry and physics (e.g., recombination of charge carriers) to predator-prey relations in ecology. Various systems however exhibit anomalous, non-Fickian diffusion [1,2]. Recent findings on subdiffusive motion in gels [3], in bacterial cytoplasm [4], and actin filament networks [5] make investigations of reactions under subdiffusion especially interesting. The corresponding subdiffusion can be modeled by continuous time random walks (CTRW) with a heavy-tailed waiting time density $\psi(t) \propto t^{-1-\alpha}$, yielding a fractional subdiffusion equation instead of a Fickian one. The microscopic approach to reactions under subdiffusion is discussed, e.g., in [6,7]; however, it can hardly be used for studying spatial structures. Reaction-subdiffusion equations of different types have been proposed on phenomenological basis [8–11]. References [12,13] showed, however, that the reaction-subdiffusion equations do not follow by simply changing a diffusion operator for a subdiffusion one. A rather general approach to reaction-subdiffusion was proposed in Ref. [14]; applied to Turing instability it revealed only quantitative differences with reaction-diffusion.

In the present Letter we show that stationary structures formed under subdiffusion differ vastly from those in reaction-diffusion or may be absent under the conditions when their reaction-diffusion analogs exist. We concentrate on the irreversible $A + B \to 0$ reaction, which is known to correspond to the simplest structure-building reaction, and was experimentally realized in [15–17] both in gel and in gel-free experiments. The situation discussed below can be experimentally realized in a subdiffusive gel reactor (the system of Ref. [3]) or in a porous medium in contact with two well-mixed reservoirs on both sides. Here we confine ourselves to an effectively one-dimensional situation, and assume the concentrations to depend only on the x coordinate.

We first give the derivation of equations for stationary reaction-subdiffusion conditions by generalizing the scheme of Ref. [12]. In a CTRW a particle arriving at a site i at time t' stays there for a sojourn time t drawn according to the probability density function $\psi(t)$. Leaving the site it makes a step with probability $1/2$ in either direction. The generalized reaction-diffusion equations are based on two balance conditions for occupation numbers $A_i(t)$ and $B_i(t)$. The balance equation for A particles at each site reads

$$\dot{A}_i(t) = j_i^+(t) - j_i^-(t) + R_i\{A, B\} \tag{1}$$

$$= \tfrac{1}{2} j_{i-1}^-(t) + \tfrac{1}{2} j_{i+1}^-(t) - j_i^-(t) + R_i\{A, B\}. \tag{2}$$

where $j_i^-(t)$ is the loss flux of A-particles at site i, i.e., the probability for an A particle to leave i per unit time, $j_i^+(t)$ is the gain flux at the site, and $R_i\{A, B\} = -kA_iB_i$ is a reaction term. The equations for A and B particles are symmetric so that we concentrate only on A_i. A reaction-subdiffusion equation is a combination of Eq. (2) and of the equation for the loss fluxes $j^-(t)$ following from the distribution of sojourn times $\psi(t)$ and survival probability $P(t, t_0)$.

The particles leaving site i at time t either were at i from the very beginning (and survived), or arrived at some $t' < t$ and survived until t. The probability density to make a step at time t, having arrived at t', is given by $\psi(t - t')$. We have then $j_i^-(t) = \psi(t)P_i(t, 0)A_i(0) + \int_0^t \psi(t - t')P_i(t, t')j_i^+(t')dt'$, which, by using Eq. (1), can be rewritten in the form

$$j_i^-(t) = \psi(t)P_i(t, 0)A_i(0) + \int_0^t \psi(t - t')P_i(t, t') \times [\dot{A}_i(t') + j_i^-(t') + kA_i(t')B_i(t')]dt'. \tag{3}$$

The survival probability of A at i is given by the classical kinetic equation $\frac{d}{dt}P_i(t) = -kB_i(t)P_i(t)$ and depends on $B(t)$ via

$$P_i(t, t_0) = \exp\left(-k \int_{t_0}^t B_i(t')dt'\right). \tag{4}$$

At this stage we assume the relative change in the concentrations between two neighboring sites to be small which allows for changing to a continuous coordinate $x = ai$, with a being the lattice spacing:

$$\dot{A}(x, t) = \frac{a^2}{2}\Delta j^-(x, t) - kA(x, t)B(x, t). \tag{5}$$

Equation (5) together with Eqs. (3) and (4) and their counterparts for B give the full system of equations for time-dependent concentrations. We note that the integral form in time of Eq. (5) can be transformed to a special case of equations of Ref. [14].

Up to now we considered an initial-condition problem, with A particles introduced into the system at $t = 0$. In the case of normal diffusion the steady state (achieved if the concentration of the particles at the boundaries of the system are fixed by external sources) is described by the same reaction-diffusion equations, with time derivatives at the left-hand side put to zero. For the case of subdiffusion the situation is more involved.

Let us assume that in the course of time the system achieves a steady state with time-independent $A(x)$ and $B(x)$. This state is maintained through the sources at the boundaries of the system, with no particle sources in the interior. Let us label the particles according to the time t_0 they were introduced into the system, so that, e.g., $A(x, t|t_0)dt_0$ is the concentration at point x at time t of A particles introduced between t_0 and $t_0 + dt_0$ (a partial concentration of A). The partial concentration $A(x, t_0|t_0)$ of newly introduced particles is zero everywhere in the interior of the system. The overall concentration of A particles at site x is given by the integral

$$A(x) = \int_{-\infty}^{t} A(x, t|t_0)dt_0. \tag{6}$$

In a steady-state $A(x, t|t_0)$ can only be a function of the difference of the time arguments, i.e., of the elapsed time $t_e = t - t_0$ so that $A(x, t|t_0) = A(x, t - t_0)$ and $A(x) = \int_0^\infty A(x, t_e)dt_e$. Since $A(x)$ and $B(x)$ are time independent, the survival probabilities $P_A(x, t, t')$ and $P_B(x, t, t')$ in reaction-subdiffusion equations are the functions of the differences of their time arguments so that $P_A(x, t, t') = \exp[-kB(x)(t - t')]$. The integral in the equation for the flux now takes the form of a convolution

$$\begin{aligned} j^-(x, t|t_0) = {}& \psi(t)P_A(x, t - t_0)A(x, t_0|t_0) \\ &+ \int_{t_0}^{t} \psi(t - t')P_A(x, t - t') \\ &\times [\dot{A}(x, t'|t_0) + j^-(x, t'|t_0) \\ &+ kA(x, t'|t_0)B(x)]dt', \end{aligned} \tag{7}$$

where $j^-(x, t'|t_0)$ are the loss fluxes for those A particles which were introduced into the system at time t_0. We now pass to the Laplace domain with respect to t_e and denote $\tilde{A}(x, u) = \int_{t_0}^\infty A(x, t|t_0)\exp[-u(t - t_0)]dt$. The Laplace transform of the product $\Psi(t, x) = \psi(t)\exp[-kB(x)t]$ is given by the shift theorem and is equal to $\tilde{\Psi}(u, x) = \tilde{\psi}[u + kB(x)]$, so that

$$\tilde{j}^-(x, u) = \frac{[u + kB(x)]\tilde{\psi}[u + kB(x)]}{1 - \tilde{\psi}[u + kB(x)]}\tilde{A}(x, u). \tag{8}$$

Inserting this into the equations for the partial concentrations $A(x, t_e)$ in a steady state given by Eqs. (5) with t changed to t_e and $B(x, t)$ replaced by $B(x)$, we get in the Laplace domain

$$\begin{aligned} u\tilde{A}(x, u) - A(x, t_0|t_0) = {}& \frac{a^2}{2}\Delta\frac{[u + kB(x)]\tilde{\psi}[u + kB(x)]}{1 - \tilde{\psi}[u + kB(x)]} \\ &\times \tilde{A}(x, u) - k\tilde{A}(x, u)B(x), \end{aligned} \tag{9}$$

where $A(x, t_0|t_0)$ differs from zero only at the boundaries. With $A(x) = \tilde{A}(x, 0)$ the stationary concentration $A(x)$ in the interior of the system is given by

$$\frac{a^2}{2}\Delta\frac{kB(x)\tilde{\psi}[kB(x)]}{1 - \tilde{\psi}[kB(x)]}A(x) - kA(x)B(x) = 0, \tag{10}$$

with the boundary conditions corresponding to the given concentrations on the boundaries. For a Markovian case of regular diffusion, corresponding to $\psi(t) = \tau^{-1}\exp(-t/\tau)$, one has $\tilde{\psi}(u) = 1/(1 + u\tau)$ so that this equation reduces to $(a^2/2\tau)\Delta A(x) - kA(x)B(x) = 0$, a usual stationary reaction-diffusion equation. In the non-Markovian case, corresponding to subdiffusion, the waiting time distribution in the Laplace domain can be approximated by $\tilde{\psi}(u) \simeq 1 - (\tau u)^\alpha\Gamma(1 - \alpha)$ for small u. This implies $\kappa B(x)\tau \ll 1$, as is taken to hold in further computations. Equation (10) now reads

$$\frac{a^2}{2}\frac{1}{\tau^\alpha\Gamma(1 - \alpha)}\Delta B(x)^{1-\alpha}A(x) - k^\alpha A(x)B(x) = 0. \tag{11}$$

It is easy to see that the Markovian equation is a special case of Eq. (11) for $\alpha = 1$. The combination $D_\alpha = a^2/2\tau^\alpha\Gamma(1 - \alpha)$ stands for a (generalized) diffusion coefficient. The full system of steady-state equations is given by Eq. (10) and the corresponding equation for B. It is interesting to stress that the system of equations with additional *linear* temporal operator acting on the Laplacian in the case of initial-condition problem turns to a system of reaction-diffusion equations with a *nonlinear* diffusion term for a stationary state.

Turning to a proposed experiment with a gel reactor let us consider a system on an interval (0,1) with given reactants' concentrations on the boundaries. Our reactor is in contact with two well-mixed reservoirs containing reacting mixtures at different concentrations on both sides. We fix $A(0) = B(1) = 1$. For the sake of simplicity we consider here a symmetric situation with $A(0) = B(1)$ and $A(1) = B(0)$. We take $A(0) \geq A(1)$ and refer to the medium to the left of the reactor as to the major source of A and to the one to the right as to the minor source [except for the case $A(1) = B(0) = 1$]. Because of symmetry we always have

$B(x) = A(1 - x)$. In Fig. 1 we show numerical results for the steady-state Eqs. (11) obtained by a semi-implicit relaxation algorithm [18].

The results for subdiffusion ($\alpha = 0.9$) are compared to the ones for normal diffusion ($\alpha = 1$). The parameters are: $k = 0.01$, $D_\alpha = 1/2\Gamma(1 - \alpha)$ for $\alpha = 0.9$ and $D_\alpha = 1/2$ for $\alpha = 1$. The $A(0) = B(1)$ concentration is fixed to be $A(0) = 1$, the other concentration varies from $B(0) = A(1) = 1$ (symmetric case, when the CTRW-reactor separates two stoichiometric reacting mixtures) to $B(0) = A(1) = 10^{-4}$. The rather high value of $\alpha = 0.9$ was taken in order to be able to place all curves on the same scale; the results for smaller α are similar in form but strongly differ in their absolute values.

In the symmetric case the behavior of reactants' concentrations in reaction-diffusion and in reaction-subdiffusion situations is very similar, with maximal concentrations achieved close to the boundaries (sources). For asymmetric conditions the behaviors of concentrations in the two cases differ strongly. One of the most marked differences corresponds to accumulation of A particles in the interior of the subdiffusive medium close to the major source. Its counterpart is a depletion zone on the other side of the system, corresponding to the symmetric accumulation zone for B. The dependence of the height of the accumulation peak on the strength of the minor source is nonmonotonic: The reduction of the minor source strength $A(1) = B(0)$ leads first to its growth, and then to its motion closer to the boundary accompanied by decay. This behavior can be explained as follows. For equally strong $A(0)$ and $B(0)$ sources A-particles react in vicinity of the boundary before they could travel a considerable distance. For weaker minor source some of A-particles can travel without reaction and accumulate inside the system leading to the formation of the peak. Since the effective mobility of subdiffusing species decays in the course of time (the number of steps per unit time goes as $t^{\alpha-1}$), the effective diffusion is caused by the reaction itself just as in the case of immobile reactants [19,20]. For very weak minor sources this effective diffusivity gets so small that the peak moves closer to the boundary and eventually disappears.

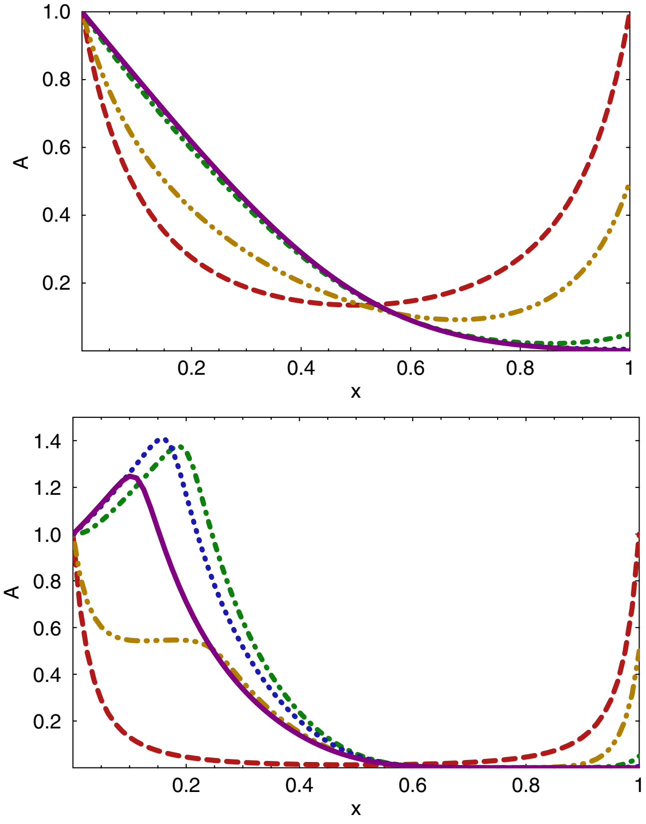

FIG. 1 (color online). Stationary particle concentration profile $A(x)$ for $\alpha = 1$ (upper panel) and for $\alpha = 0.9$ (lower panel); $A(1) = 1$ (dashed line), 0.5 (dash-dot-dot line), 5×10^{-2} (dash-dot line), 5×10^{-3} (dotted line), and 1×10^{-4} (solid line), see text for details. Note the peak's displacement and the nonmonotonic behavior of its height with decreasing minor source strength for the subdiffusive case; the behavior of the particle concentration profile in regular diffusion is monotonic with respect to the strength of the minor source and tends to a limiting form for $A(1) \to 0$.

The smaller is the α, the more pronounced get the peak and the depletion zone. To examine the dependence of the effects on α we performed calculations for $k = 0.001$ and $A(1) = 0.05$, a pair of parameters where pronounced peaks exist for a wide range of α. The peaks' maximal heights and their positions are 3.49×10^4 at 0.238 for $\alpha = 0.5$, 7.98 at 0.225 for $\alpha = 0.6$, 1.60 at 0.188 for $\alpha = 0.7$, 1.01 at 0.100 for $\alpha = 0.8$, and for $\alpha = 0.9$ no local maximum exists. The minima and their positions are 6.82×10^{-12} at 0.763 for $\alpha = 0.5$, 3.69×10^{-5} at 0.736 for $\alpha = 0.6$, 1.17×10^{-3} at 0.775 for $\alpha = 0.7$, 4.71×10^{-3} at 0.80 for $\alpha = 0.8$ and 6.99×10^{-3} at 0.813 for $\alpha = 0.9$.

Let us now turn to reaction intensities, Fig. 2. For the symmetric case the reaction takes place mostly close to the boundaries of the system. For smaller $A(1)$ the reaction zone starts to form in the middle of the system. However, also here striking differences between the reaction-diffusion and the reaction-subdiffusion cases are seen. In the reaction-diffusion case the dependence of the form of the reaction zone on $A(1)$ is weak for small $A(1)$, and there exists a clear limiting form for $A(1) = 0$. This behavior is known and is used in the time-scale separation approach of Refs. [21,22] based on the quasistatic approximation. For reaction-subdiffusion the behavior of the reaction zone with respect to its height is nonmonotonic. When lowering $A(1)$, the maximum of reaction intensity first gets higher and then starts to lower, and the distribution as a whole broadens. The reason for this is quite evident. The stationary reaction zone exists only if it is fed by A- and B-reactants on the corresponding sides. Both in the diffusion and in the subdiffusion case the reaction zone is the higher and the narrower the larger is the particles' inflow into the reaction area. This inflow is governed by the effective diffusion coefficient of the corresponding reac-

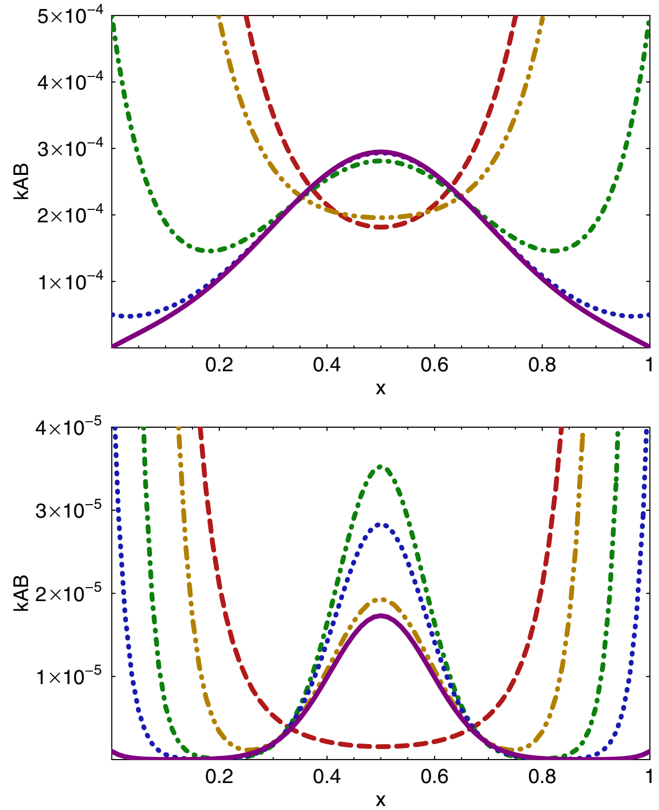

FIG. 2 (color online). Stationary reaction intensity profile $kA(x)B(x)$ for $\alpha = 1$ (upper panel) and for $\alpha = 0.9$ (lower panel). The parameters are the same as in Fig. 1, namely: $A(1) = 1$ (dashed line), 0.5 (dash-dot-dot line), 5×10^{-2} (dash-dot line), 5×10^{-3} (dotted line), and 1×10^{-4} (solid line). In the diffusive case the stationary reaction intensity profile approaches a limiting form under decreasing minor source strength. For subdiffusion reaction the height of the profile shows nonmonotonic behavior with respect to this parameter. Note the difference in vertical scales.

tants, which, in the subdiffusive case, depends on the concentration of the reacting counterpart. For $A(1) = B(0) = 0$ the effective diffusion coefficient vanishes on the corresponding side of the system preventing the inflow of reactants from their major sources into the interior of the system. The reaction zone blurs and fades out. In this case no stationary front exists. This effect is also clearly seen when considering the time evolution of concentrations which can be done by discussing the properties of the inverse Laplace transform of Eq. (9). This means that the adiabatic approximation of Refs. [21,22] fails in subdiffusion, and the analysis of the front's motion in this case has to be done anew.

Let us summarize our findings. We discussed the stationary form of reactants' concentrations and of reaction zones in the $A + B \longrightarrow 0$ reaction in a subdiffusive medium fed by reactants on both sides. We show that the behavior of the concentration and of the reaction intensity profiles in subdiffusion differs strikingly from those in simple diffusion. The non-Markovian character of subdiffusive motion leads to an effectively nonlinear transport. This leads to the formation of accumulation and depletion zones close to the boundaries, and to nonmonotonic behavior of the reaction intensity with respect to the strength of the minor source in the anomalous case.

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[18] One first changes to new variables $A^*(x) = B^{1-\alpha}(x)A(x)$ and $B^*(x) = A^{1-\alpha}(x)B(x)$. They are then considered as being formally dependent on a new time variable ζ. Then we integrate numerically the equation $(\partial/\partial\zeta)A^* = D_\alpha \Delta A^* - \kappa^\alpha (A^* B^*)^{1/(2-\alpha)}$ (with $B^*(1-x, \zeta) = A^*(x, \zeta)$) from the initial-condition $A(x, 0) = (A(1, 0) - 1)x + 1$ using the Crank-Nicholson algorithm until the solution reaches stationarity.
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