Front Propagation in an A+B → 2A Reaction under Subdiffusion

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Abstract: We discuss the front propagation in the A+B → 2A reaction under subdiffusion as described by continuous time random walks with the waiting time probability density $\psi(t) \propto t^{-1-\alpha}$, $0 < \alpha < 1$ and present strong arguments in favor of the following propagation picture. At short times the front propagates at a velocity decaying as $v \propto t^{(\alpha-1)/2}$. This regime can be described within a framework of continuous reaction-subdiffusion equations. At longer time the continuous scheme breaks down, and the propagation velocity shows a faster decay $v \propto t^{\alpha-1}$.

Keywords: subdiffusion, continuous time random walks, front propagation

1. INTRODUCTION

The theory of reactions controlled by subdiffusion attracted much interest in the recent few years both because of practical needs (reactions in porous media and geological formations, and in crowded cellular environments) and because of very unusual mathematical structure of the corresponding equations. In what follows we concentrate on the A+B → 2A autocatalytic reaction leading to a propagation of the pulled front into the unstable B-domain, Ref.(1). Under normal diffusion, the reaction is described by the Fischer-Kolmogorov-Petovskii-Piskunov (FKPP) equation which is mathematically well understood. In the case when all particles where initially B and were distributed in space with the constant concentration B_0 (which will be put to unity in what follows), the equation for the concentration B of B reads

$$\frac{\partial B}{\partial t} = D\Delta B - k(B_0 - B)B. \qquad (1)$$

Here D is the diffusion coefficient of the particles (assumed equal for A and B ones), and k is the reaction rate. The two initial reaction-diffusion equations for A and for B particles are reduced to Eq.(1) by using the conservation law $A + B = B_0$ following from the stoichiometry. The initial condition corresponds to a droplet of A particles introduced at the origin. We concentrate on the reaction front propagating to the right.

Assuming the front to propagate with a constant velocity along the x-direction one changes to a comoving frame thus obtaining an ordinary differential equation for the stable front form. This equation can be linearized close to the leading edge of the front, and the spectrum of possible velocities is obtained by requesting the concentration to be non-negative everywhere. This condition defines then the minimal possible propagation velocity. The fact that this minimal propagation velocity is the one really attained under a sharp initial condition (marginal stability principle) follows from the stability analysis of perturbations.

The minimal propagation velocity in FKPP front is $v = 2\sqrt{DkB_0}$, and the characteristic width of the propagating front is $w \simeq \sqrt{D/kB_0}$. In what follows we confine ourselves to a one-dimensional situation, where the concentrations A, B and B_0 have the dimension of the inverse length L^{-1}, and the reaction rate coefficient k has a dimension of $[k] = \mathrm{LT}^{-1}$.

The case of subdiffusion is much more complicated. First, different types of subdiffusive behaviors are possible, corresponding either to disordered systems (percolation, energetic disorder, etc.) or to systems with slow modes (polymers). Second, even if the model of the subdiffusion is fixed, for example, to be continuous time random walk (CTRW) with the power law probability density function (PDF) of waiting times

$$\psi(t) \simeq \frac{\tau^\alpha}{t^{1+\alpha}} \qquad (2)$$

for $t > \tau$, different reaction-subdiffusion equations emerge when considering situations when the "internal clock" of the particle is reset after the reaction or not, Ref.(3). In what follows we consider the situation when the diffusion on the large scales is hindered, but the small-scale reactions follow the mass action law. The reaction does not reset waiting times, since the last one describe only the large-scale behavior of the system. The simplest case of this situation (the isomerization reaction A → B) was discussed in Ref.(2) and leads to equations where the reaction term is not simply added to a subdiffusion equation like it is the case in Eq.(1) but enters as well the transport operator. The corresponding equation for the A+B → 2A reaction was derived in Ref.(4), where the analysis of the corresponding reaction-subdiffusion equation showed that the minimal propagation velocity is zero, which fact was interpreted as propagation arrest. The situation was clarified in numerical simulations of Ref.(5), where two propagation regimes were identified, both corresponding

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to propagation with the velocity which decays with time. Thus, for small reaction rates and low concentrations the front velocity behaved as $v(t) \propto t^{(\alpha-1)/2}$, where α is the subdiffusion exponent (governing the mean squared displacement of a particle $\langle x^2(t)\rangle \propto t^\alpha$ in the reaction-free case), while for larger concentrations and high reaction rates (a fluctuation-dominated regime which can not be described within continuous reaction-diffusion or reaction subdiffusion equations) the propagation velocity behaves as $v \propto t^{\alpha-1}$.

The longer numerical simulations of Ref.(3) identified the second, but not the first propagation regime, claiming that the first one "is not robust". In what follows we discuss this situation in some detail and present new results on the front propagation in such a system. We show that the continuous description of the reaction-subdiffusion reaction gives hints in favor of propagation of a front with velocity $v(t) \propto t^{(\alpha-1)/2}$. The intermediate asymptotic behavior $v(t) \propto t^{(\alpha-1)/2}$ holds as long as continuous description of the reaction is possible. The front width however decays with time as $w \propto t^{\frac{\alpha-1}{2}}$, and gets of the order of one of the microscopic scales of the problem, so that the continuous description inevitably breaks down at longer time. Then another, final asymptotic behavior ($v \propto t^{\alpha-1}$ for a one-dimensional case) sets in. The present contribution reports on a work in progress, however we are highly confident that the overall physical understanding is reached, although a large amount of computations still has to be performed.

2. MODEL AND EQUATIONS

Let us consider the medium as consisting of compartments of size a. The transport of particles between these compartments is governed by CTRW: the waiting time of a particle in a compartment is given by the PDF, Eq.(2). Within a compartment i the particles react according to classical kinetic law, i.e. the transformation from B to A follows at the rate kA_iB_i where A_i and B_i are the numbers of the particles within the compartment, and k is the properly renormalized reaction rate constant.

Following the same procedure as in Refs. (2; 4) we start from the balance equation for B-particles

$$\dot{B}_i(t) = \frac{1}{2} j^-_{i-1}(t) + \frac{1}{2} j^-_{i+1}(t) - j^-_i(t) - \kappa A_i(t) B_i(t)$$

where $j^-_i(t)$ is the loss flux from the compartment i given by

$$j^-_i(t) = \psi(t) P_s(t,0) B_i(0) + \int_0^t \psi(t-t') P_s(t,t') \left[\dot{B}_i(t') + j^-_i(t') + \kappa A_i(t') B_i(t')\right] dt'$$

and

$$P_s(t,t') = \exp\left[-\kappa \int_{t'}^{t} A_i(t'')dt''\right]$$

is the survival probability of a B-particle. Since the equation for the loss flux only involves the concentrations at one site, it can be easily solved by means of Laplace transform, and the solution can be inserted into the first equation for the concentration. The equation for A follows in a similar way. Afterwards the transition to the continuous limit in space is performed leading to the following equation for B

$$\frac{\partial}{\partial t} B(x,t) = -k[1-B(x,t)]B(x,t) + \frac{a^2}{2}\Delta \int_0^t M(t-t') \times B(x,t') \exp\left[-\int_{t'}^{t} k[1-B(x,t'')]dt''\right] dt', \quad (3)$$

where we used the conservation law $A(x,t) = 1 - B(x,t)$, and with $M(t)$ given by the inverse Laplace transform of $M(u) = u\psi(u)/[1-\psi(u)]$. The equation for A following from the one for B by using the conservation law. For the Markovian process with $\psi(t) = \tau^{-1}\exp(-t/\tau)$ one obtains $M(t)$ to be a δ-function, $M(t) = \tau^{-1}\delta(t)$ and the equations for the concentrations reduce to partial differential equations, the FKPP case. For subdiffusion with waiting time density following Eq.(2), the integral operator with the $M(t)$-kernel is proportional to the Riemann-Liouville fractional derivative of order $1-\alpha$. Thus, in a subdiffusive case the equations for A and B are nonlinear fractional partial differential equations of quite a complex structure.

3. ABSENCE OF THE CONSTANT FRONT VELOCITY

Let us give a short sketch of the calculations done in (4) and leading to the conclusions that no front propagation at a constant velocity is possible. Assuming that $A(x,t)$ is small at the very far edge of the front and linearizing the reaction-subdiffusion equation for $A(x,t)$, one can look for an exponential solution of the form $A = A_0 \exp[-\lambda(x-vt)]$. This solution has to satisfy the equation

$$\lambda v\big(A_0 \exp[-\lambda(x-vt)]\big) = -kA_0 \exp[-\lambda(x-vt)] + \frac{a^2}{2} A_0 \left[-\lambda^2 + \frac{k\lambda}{v}\right] \int_0^t M(t-t') \exp[-\lambda(x-vt')]\, dt' - \frac{a^2}{2}\frac{k\lambda}{v} A_0 \exp[-\lambda(x-vt)] \int_0^t M(t-t')\, dt'. \quad (4)$$

For the Markovian case, the standard expression for the minimal velocity of the stable propagation is reproduced: Taking $M(t) = \tau^{-1}\delta(t)$, introducing a new variable $z = x - vt$, and concentrating on the leading edge of the front ($z \to \infty$), we find the dispersion relation:

$$\frac{a^2}{2\tau}\lambda^2 - v\lambda + k = 0. \quad (5)$$

The quadratic equation (5) has two complex conjugated roots. Since the roots λ corresponding to the propagating front need to stay real (to prevent concentration from taking negative values which are inevitable if the solutions oscillate), the condition $v \geq v_{min} = 2\sqrt{a^2k/2\tau} \equiv 2\sqrt{Dk}$ follows for the propagation velocity, with $D = a^2/2\tau$ being the diffusion coefficient. In this case the two roots

$v = \pm v(\lambda)$ correspond to the two possible directions of the front propagation.

For waiting time PDFs decaying as a power law, $\psi(t) \propto t^{-1-\alpha}$, $0 < \alpha < 1$ for large t, we find with $\hat{t} = t - t'$ that $\int_0^t M(t-t') \exp[\lambda v t']\, dt' = \exp[\lambda v t]\, \tilde{M}(\lambda v)$ and

$$R(t) = \int_0^t M(t-t')\, dt' = \frac{const}{\tau^\alpha} t^{\alpha-1}, \tag{6}$$

so that the last term in (4) vanishes for large t. Note that the integral $R(t)$, Eq.(6) gives the rate of jumps of a particle performing CTRW. Finally, with $z = x - vt$ we get

$$-\lambda v A_0 \exp[-\lambda z] = -k A_0 \exp[-\lambda z]$$
$$+\frac{a^2}{2} A_0 \exp[-\lambda z] \left[(-\lambda^2 + \frac{k\lambda}{v}) \tilde{M}(\lambda v) \right],$$

from which the dispersion relation

$$0 = -\lambda v + k + \frac{a^2}{2}(\lambda^2 - \frac{k\lambda}{v}) \tilde{M}(\lambda v)$$

follows. Taking $\tilde{M}(u) = \tau^{-\alpha} u^{1-\alpha}$ this last one can be put into the form

$$(v\lambda - k)\Big(\frac{a^2}{2\tau^\alpha} \lambda^{2-\alpha} v^{-\alpha} - 1 \Big) = 0$$

and possesses two nonnegative roots for any $v \geq 0$, at variance with the Markovian case, where such roots exist only for $v > v_{min}$. This finding means that the minimal propagation velocity in this case is zero, so that the front velocity tends to zero in the course of time.

4. FRONT MOVING AT A DECAYING VELOCITY

Numerical simulations of Refs. (5) suggest that the front does propagate, but its propagation velocity decays in course of the time. Assuming the constant front form, one could imagine, that the asymptotic solution of the linearized equation could, for example, follow the pattern

$$A(x,t) = A_0 \exp\left[-\lambda_0 \left(x - v_0 t^{\frac{\alpha-1}{2}} \right) \right] = A_0 \exp(-\lambda_0 z) \tag{7}$$

with the constant v_0 indicating now the *subvelocity* of the front. Here $z = x - v_0 t^{\frac{1+\alpha}{2}}$ is the variable defining the comoving frame of the front whose velocity decays as $v \propto t^{(\alpha-1)/2}$. However, substitution of Eq.(7) into Eq.(4) shows that Eq.(7) is not a at all. Thus, the subdiffusion analog of the FKPP equation does not possess a front solution of constant form with the velocity decaying as $v \propto t^{(\alpha-1)/2}$.

Interestingly enough, a different form of the solution is possible, the one with decaying width:

$$A(x,t) = A_0 \exp\left[-\lambda_0 t^{\frac{1-\alpha}{2}} \left(x - v_0 t^{\frac{1+\alpha}{2}} \right) \right], \tag{8}$$

where $\lambda(t) = \lambda_0 t^{\frac{1-\alpha}{2}}$ gives the time-dependent width of the front. Proceeding as in Ref. (4) we have in first order for the A-particles:

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

Evaluating the integrals we get for both $z = x - v_0 t^{\frac{1+\alpha}{2}}$ and t large:

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

where C is a constant (depending on the parameters of the model) for which the inequality $B(\alpha, 2-\alpha) \geq C \geq 0$ holds. The upper bound $B(\alpha, 2-\alpha)$ is the Beta function. This yields the dispersion relation for λ_0:

$$0 = \lambda_0^2 - \frac{kK_\alpha^*(1-C)/v_0 - v_0}{K_\alpha^* C} \lambda_0 + \frac{k}{K_\alpha^* C}$$

with $K_\alpha^* = a^2/2\Gamma(\alpha)\Gamma(1-\alpha)\tau^\alpha = K_\alpha/\Gamma(\alpha)$, where K_α is the generalized diffusion constant. Solving this equation for λ we find a restriction on the values of v_0 for which this λ is real: $(kK_\alpha^*/v_0(1-C) - v_0)^2 \geq 4kK_\alpha^* C$, a quartic equation in v_0 which yields in general four symmetric roots

$$v_0^2 = K_\alpha^* k \left[1 + C \pm 2\sqrt{C} \right]. \tag{9}$$

In the FKPP case pertinent to normal diffusion the value of C is $C = 1$, the minimal front velocity $v_{min} = \pm 2\sqrt{Dk}$ is reproduced; the other solution is a double root $v = 0$, which is a non-physical one and appears due to the overall higher order of the dispersion relation obtained by this method. For any C other than $C = 1$ there exists bounded domain of real roots around zero, $-v_- \leq v_0 \leq v_-$ (the subscript "$-$" corresponds to the minus sign in Eq.(9)) separated by gaps from another domain of real roots $|v_0| > v_+$. The existence of the gap and of the corresponding minimal velocity can be interpreted in favor of propagation of the corresponding front. Of course, such an analysis is still incomplete without looking at the stability of corresponding perturbations. There exists however a strong physical argument in favor of the existence of the propagation mode described above.

5. THE CROSSOVER ARGUMENT

In order to gain intuition about the front's behavior, we make use of the following idea: for any waiting time PDF $\psi(t)$ with finite mean waiting time $\langle t \rangle$, the classical (FKPP) behavior is recovered if only the time t is large

enough, $t \gg \langle t \rangle$. We therefore consider a truncated power-law waiting time distribution

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

with $T \gg \tau$ which possesses a mean

$$\langle t \rangle = \frac{\alpha T \tau + \tau \left(\tau^\alpha - (T-\tau)^\alpha\right)}{(\alpha-1)\left(\tau^\alpha - (T-\tau)^\alpha\right)}.$$

For $T \gg \tau$, $\langle t \rangle \approx \frac{\alpha}{1-\alpha} \tau^\alpha T^{1-\alpha}$. For short times $\tau < t \ll T$, when particles cannot yet feel the cutoff, this distribution is practically a power law, Eq.(2), and the behavior of the front velocity will be similar to that in subdiffusion, whereas for large times the behavior is the classical one with a constant velocity given by the minimal propagation velocity in FKPP. There has to be a crossover at a time t_{cr} between these two regimes. Thus, we assume that in the anomalous domain the velocity is time-dependent, $v_{SD} \propto t^\beta$, and that after a crossover to normal behavior $v_D = const \sim \sqrt{kD(T)}$ sets on. Here $D(T)$ is the final diffusion coefficient, $D(T) = a^2/2\langle t \rangle$ depending on the cutoff time T. The subscripts SD and D indicate the regimes of subdiffusion and of normal diffusion, respectively. The number of performed steps, a measure of mobility, is $n_D(t) = t/\langle t \rangle$ in the normal regime $t \gg t_{cr}$, and $n_{SD}(t) = (\Gamma[1+\alpha]\tau^\alpha)^{-1} t^\alpha$ in the subdiffusive regime $t \ll t_{cr}$. By equating $n_{SD}(t_{cr}) = n_D(t_{cr})$ at the two sides of the crossover we find $t_{cr} \propto T$. The velocities on both sides at the crossover time have to be of the same order of magnitude and therefore $v_{SD}(t_{cr}) \propto t_{cr}^\beta \propto \sqrt{kD(T)}$. Since $t_{cr} \sim T$ and $D(T) \sim T^{\alpha-1}$ we get $\beta = (1-\alpha)/2$ and thus

$$v(t) \propto t^{\frac{\alpha-1}{2}}$$

in the subdiffusive regime $t \ll t_c r$.

The same argument applies to the front's width. The width of the front in the normal FKPP regime is of the order of $w \simeq D/v = \sqrt{D/k}$. Taking the width of the front to behave as $w(t) \propto t^\gamma$ for $t < t_{cr}$ and matching this width with the width of the front in FKPP at t_{cr} we get $w \propto t^{\frac{\alpha-1}{2}}$, in accordance with the previous section.

6. BREAKDOWN OF THE CONTINUOUS DESCRIPTION AND FINAL ASYMPTOTICS

Since the subdiffusive front is not only slowing down but also becomes steeper in the course of time, a Monte-Carlo simulation, if performed long enough, enters a regime where the width of the front is comparable to the one of microscopic scales of the problem, the compartment size a or the interparticle distance $B_0^{-1} = 1$. The first happens at high concentrations, where there are many particles per compartment, the second at low concentrations. Both situations lead to similar behavior of the front's velocity.

Since in continuous time random walks the rate of the particle's jumps $R(t)$ decays in the course of time, at longer time one enters the regime, when the mean time between the two jumps of the particles within the front region gets large compared to the time of the order of kB_0 necessary for full conversion of all particles from B to A in a compartment where at least one A particle is present. Within this picture, the front can be considered as "atomically sharp", and is placed exactly between the last compartment containing A particles and the first A-free compartment. This front moves exactly one a-step forward, when an A-particle from the compartment left from the front makes its jump to the right. Since the rate of these jumps is proportional to the number of the particles in the compartment aB_0 and to $R(t)$, the velocity goes as

$$v \propto a^2 B_0 \left(\frac{t^{\alpha-1}}{\tau^\alpha}\right) \propto B_0 K_\alpha t^{1-\alpha}.$$

This is the situation pertinent to high concentration of particles.

The case of low concentrations (much less then one particle per compartment) needs for a slightly different discussion, parallel to one in Ref. (6). The front is again "atomically sharp": If the A and the B particles meet in the same compartment, they have enough time to react before making a jump, and therefore there are no B particles to the left of the front position and no A particles to the right of it. The front position can be associated with the one of the rightmost A. This one does not change at the average as long as there is a single particle in a compartment (the jumps to the left and to the right are equally probable), but does increase by a with probability 1/2 if another particle is present in the same compartment (the probability of which is of the order of aB_0) since in this case the front cannot jump back. The mean velocity differs from the previous one only in prefactor: $v \propto (a/2) a B_0 t^{\alpha-1}/\tau^\alpha \propto B_0 K_\alpha t^{1-\alpha}$.

The result $v \propto B_0 K_\alpha t^{1-\alpha}$ is exactly what follows immediately from the dimensional analysis, if one assumes that the reaction is infinitely fast on the time scale of jumps and therefore the reaction rate coefficient k cannot play any role.

7. CONCLUSIONS

We discussed the motion of a reaction front in the A+B $\rightarrow$ 2A reaction under subdiffusion in a system where the transport of the particles is described by continuous time random walks but the reaction between them locally follows the mass action law. We show, that the reaction front in such a system moves at intermediate times at a decaying velocity $v \propto t^{(\alpha-1)/2}$, and that this velocity has to cross over to a faster decay $v \propto t^{\alpha-1}$ in the asymptotics of very long times.

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