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Reaction-subdiffusion equations

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To analyze possible generalizations of reaction-diffusion schemes for the case of subdiffusion we discuss a simple monomolecular conversion $A \to B$. We derive the corresponding kinetic equations for the local A and B concentrations. Their form is rather unusual: The parameters of the reaction influence the diffusion term in the equation for a component A, a consequence of the non-Markovian nature of subdiffusion. The equation for the product contains a term which depends on the concentration of A at all previous times. Our discussion shows that reaction-subdiffusion equations may not resemble the corresponding reaction-diffusion ones and are not obtained by a trivial change of the diffusion operator for a subdiffusion one.

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Many phenomena in systems out of equilibrium can be described using a picture of reactions. Apart from chemistry, the examples are exciton quenching, recombination of charge carriers or radiation defects in solids, predator-pray relationships in ecology, etc. Reactions in homogeneous media are often described by formal kinetic schemes. Thus, the concentrations $C_i(t)$ of the components follow the first-order differential equations $dC_i(t)/dt = f_i\{C_1(t), \ldots, C_N(t)\}$ where the reaction terms typically have a form $f_i\{C_1, \ldots, C_N\} = \pm \kappa_i C_1^{n_1} C_2^{n_2}, \ldots, C_1^{n_N}$, with the powers n_j depending on the stoichiometry of the reaction, and the κ_i denote the corresponding reaction rates. In inhomogeneous situations (layered systems, fronts, etc.) a mesoscopic approach based on reaction-diffusion equations for the position-dependent concentrations $C_i(\mathbf{r},t)$ is often the appropriate way of description. In case of normal diffusion such equations are obtained by adding a diffusive term to classical reaction schemes

$$\frac{\partial C_i(\mathbf{r},t)}{\partial t} = K_i \Delta C_i(\mathbf{r},t) + f_i, \tag{1}$$

with $f_i = f_i\{C_1(\mathbf{r},t), \ldots, C_N(\mathbf{r},t)\}$ and K_i being the diffusivity of the component i. This approach is applicable whenever characteristic scales of spatial inhomogeneities are much larger than mean interparticle distances and particles' mean free paths (see, e.g., [1]). As we proceed to show, the possibility to put down such schemes is due to the Markovian nature of normal diffusion.

In many cases, however, the diffusion is anomalous [2]. Although reactions under anomalous diffusion conditions are under extensive investigation since the late 1970s (when the works appeared following the splash of interest to fractal systems), a general theoretical approach going beyond simplest models and scaling considerations is still absent. Some important steps to adequately describe the situation were done quite recently. One is pertinent to situations described within the continuous-time random walk (CTRW) scheme [3]. In this case the subdiffusive nature of motion stems from the fact that particles get trapped and have to wait for a time t [distributed according to a power-law probability density function $\psi(t) \propto t^{-1-\alpha}$] until the next step can be performed [4–7]. The microscopic approach of these works aims on the understanding of the situation when the particles performing CTRW react on encounter (and do not react as long as they do not move). Such a situation is pertinent to exciton quenching in solids, or to transport in ion channels [8].

In many cases, however, a mesoscopic approach is desirable. Such an approach was adopted in the case of reactions under Lévy flights, Refs. [9,10], where the transport process involved is Markovian. The case of subdiffusion is much more subtle due to the non-Markovian character of subdiffusive transport [11]. Here two different situations can be encountered. Thus, the reaction at small scales can be also subdiffusion controlled (like in the models discussed above) or the reaction locally follows normal, classical kinetics. This last case, that we address here, adequately describes reactions in porous media, a situation of extreme importance in hydrology, where the transport in catchments is hindered by trapping in stagnant regions of the flow, caves, and pores on all scales. The transport at long times and large scales is well described by CTRW [12]. However, the particles trapped in stagnant regions can still react. A mesoscopic approach to such a case was adopted in [13] within a probabilistic scheme, while [14] tackle this problem by using equations of the same form as our Eq. (1) where the diffusion operator is changed for a subdiffusion one, containing an additional fractional derivative in time [3,15]

$$\frac{\partial C_i(\mathbf{r},t)}{\partial t} = {}_0D_t^{1-\alpha_i} K_{i,\alpha_i} \Delta C_i(\mathbf{r},t) + f_i. \tag{2}$$

In this equation α_i is the exponent of the anomalous diffusion for the component i, ${}_0D_t^{1-\alpha_i}$ is the operator of fractional (Riemann-Liouville) derivative, and K_{i,α_i} is the corresponding anomalous diffusion coefficient. Such equations with decoupled transport and reaction term were postulated based on the analogy with Eq. (1) and look quite plausible. In some cases also a reaction term has to be modified by applying a fractional derivative as suggested by a microscopic model in [5].

In what follows we derive the reaction-subdiffusion equations for the simplest reaction scheme (monomolecular conversion $A \to B$) corresponding, e.g., to radioactive decay of isotope A which is introduced into the ground water at some place at time $t=0$ and is transported according to anomalous diffusion. We show that the corresponding equations *do not* follow a pattern of Eq. (2), so that the reaction and diffusion terms do not decouple.

Let us assume for the time being that all properties of A and B particles are the same, so that the reaction corresponds to a relabeling of A into B taking place at a rate κ. In what follows we will use one-dimensional notation, the generalization to higher dimensions is trivial. Equations (1) for this case read

$$\frac{\partial A}{\partial t} = K\Delta A - \kappa A, \quad \frac{\partial B}{\partial t} = K\Delta B + \kappa A, \tag{3}$$

with K being the normal diffusion constant. Let $C(x,t) = A(x,t) + B(x,t)$ be the sum of concentrations. It evolves according to a diffusion equation

$$\frac{\partial C}{\partial t} = K\Delta C. \tag{4}$$

Both concentrations A and B follow

$$A(x,t) = e^{-\kappa t} C(x,t), \quad B(x,t) = [1 - e^{-\kappa t}] C(x,t). \tag{5}$$

To see this apply Laplace transform to Eqs. (3). Note that the solution for $A(x,t)$ in the Laplace domain is $\tilde{A}(x,u) = \tilde{C}(x,u+\kappa)$. Equation (5) reflects the fact, that the conversion is independent of the motion of particles, so that concentrations of As and of Bs are proportional to the overall concentration multiplied by the probability for a particle to survive as A or to become B. The same argument leads to the conclusion that Eq. (5) also holds in anomalous diffusion, whatever the evolution equation for C is. For subdiffusion

$$\frac{\partial C(x,t)}{\partial t} = K_\alpha \, {}_0D_t^{1-\alpha} \Delta C(x,t), \tag{6}$$

so that in Fourier-Laplace domain for the initial condition $C(x,0) = \delta(x)$ one has $\tilde{C}(k,u) = (u + u^{1-\alpha} k^2 K_\alpha)^{-1}$ so that, for instance

$$\tilde{A}(k,u) = \frac{1}{(u+\kappa) + (u+\kappa)^{1-\alpha} k^2 K_\alpha}. \tag{7}$$

However, neither the solution of Eq. (2) nor the solution of the fractional equation with the modified reaction term [5] reproduce this result: the simple reaction-subdiffusion schemes do not describe the conversion reaction correctly.

Let us now turn to the derivation of correct reaction-diffusion equations for our case. We will follow the way of the derivation of the generalized master equation for CTRW used in Ref. [16] based on the ideas of [17]. We start from a discrete scheme and consider particles occupying sites of a one-dimensional lattice. The generalized reaction (sub-)diffusion equations follows from the balance conditions for particle numbers. A balance condition for the mean number A_i of particles A on site i of the system reads

$$\frac{dA_i(t)}{dt} = \Gamma_i^+(t) - \Gamma_i^-(t) - \kappa A_i(t), \tag{8}$$

where $\Gamma_i^-(t)$ is the loss per unit time due to the particles' departure from the site (loss flux) at site i, $\Gamma_i^+(t)$ is the gain flux, and κA_i is the loss due to conversion. Particles' conservation for transitions between the two neighboring sites corresponds to

$$\Gamma_i^+(t) = w_{i-1,i} \Gamma_{i-1}^-(t) + w_{i+1,i} \Gamma_{i+1}^-(t), \tag{9}$$

where $w_{i,j}$ is a probability to jump to site j when leaving i. For unbiased walks one has $w_{i-1,i} = w_{i+1,i} = 1/2$. Thus

$$\frac{dA_i(t)}{dt} = \frac{1}{2}\Gamma_{i-1}^-(t) + \frac{1}{2}\Gamma_{i+1}^-(t) - \Gamma_i^-(t) - \kappa A_i(t). \tag{10}$$

We now combine this continuity equation with the equation for $\Gamma_i^-(t)$ following from the assumption about the distribution of sojourn times. The loss flux at time t is connected to the gain flux at the site in the past: the particles which leave the site i at time t either were at i from the very beginning (and survived without being converted into B), or arrived at i at some later time $t' < t$ (and survived). A probability density that a particle making a step at time t arrived at its present position at time t' is given by the waiting time distribution $\psi(t-t')$, the survival probability being $p(t) = e^{-\kappa t}$. Thus

$$\Gamma_i^-(t) = \psi(t) e^{-\kappa t} A_i(0) + \int_0^t \psi(t-t') e^{-\kappa(t-t')} \Gamma_i^+(t') dt'. \tag{11}$$

Applying Eq. (8) we get

$$\Gamma_i^-(t) = \psi_s(t) A_i(0) + \int_0^t \psi_s(t-t') \left[\frac{A_i(t')}{dt'} + \kappa A_i(t') + \Gamma_i^-(t') \right] dt', \tag{12}$$

where $\psi_s(t) = \psi(t) e^{-\kappa t}$ is the nonproper waiting time density for the actually made new step provided the particle survived. This approach can also be generalized to bimolecular reactions though leading to equations with a more involved structure than in the present case. Changing to the Laplace domain and noting that $\tilde{\psi}_s(u) = \tilde{\psi}(u+\kappa)$ we get

$$\tilde{\Gamma}_i^-(u) = \tilde{\Phi}_\kappa(u) \tilde{A}_i(u), \tag{13}$$

with $\tilde{\Phi}_\kappa(u)$ given by

$$\tilde{\Phi}_\kappa(u) = \frac{(u+\kappa)\tilde{\psi}(u+\kappa)}{1 - \tilde{\psi}(u+\kappa)}. \tag{14}$$

Returning to the time-domain we thus get

$$\Gamma_i^-(t) = \int_0^t \Phi_\kappa(t-t') A_i(t') dt'. \tag{15}$$

Note that $\Phi_\kappa(t)$ given by the inverse Laplace transform of $\tilde{\Phi}_\kappa(u)$ corresponds to $\Phi_\kappa(t) = \Phi_0(t) e^{-\kappa t}$ where $\Phi_0(t)$ obtained by taking $\kappa=0$ is the usual memory kernel of the generalized master equation for the CTRW.

Combining Eq. (15) with Eqs.(8) and (9) we get

$$\frac{dA_i(t)}{dt} = \int_0^t \Phi_\kappa(t-t')\left[\frac{A_{i-1}(t')}{2} + \frac{A_{i+1}(t')}{2} - A_i(t')\right]dt' - \kappa A_i(t). \tag{16}$$

Transition to a continuum in space ($x=ai$) gives

$$\begin{aligned}\frac{\partial A(x,t)}{\partial t} &= \frac{a^2}{2}\int_0^t \Phi_\kappa(t-t')\Delta A(x,t')dt' - \kappa A(x,t)\\ &= \frac{a^2}{2}\int_0^t \Phi_0(t-t')e^{-\kappa(t-t')}\Delta A(x,t')dt' - \kappa A(x,t),\end{aligned} \tag{17}$$

a rather unexpected form, where the reaction rate explicitly affects the transport term.

For the exponential waiting time distribution $\psi(t)=e^{-\lambda t}$ corresponding to $\tilde{\psi}(u)=\lambda/(u+\lambda)$ the kernel reads $\Phi_0(t) = \lambda\delta(t)$, and the existence of an additional exponential multiplier does not play any role: The reaction diffusion equation is perfectly exact.

In the case of slowly decaying $\Phi_0(t)$ the exponential cutoff introduced by the reaction is crucial. For power-law waiting time distributions and for $\kappa=0$ the integral operator $\int_0^t \Phi_0(t-t')f(t')dt'$ is the operator of the fractional derivative: For such distributions $\tilde{\psi}(u) \simeq 1-(\tau u)^\alpha\Gamma(1-\alpha)$ (where τ is the appropriate time scale) we have (for $u \to 0$) $\tilde{\Phi}_0(u) \simeq [1/\tau^\alpha\Gamma(1-\alpha)]u^{1-\alpha}$ which is proportional to the operator of the Riemann-Liouville derivative of the order α: $(a^2/2)\int_0^t \Phi_0(t-t')f(t')dt' = K_\alpha\, {}_0D_t^{1-\alpha}f$ for sufficiently regular functions f. The generalized diffusion coefficient reads $K_\alpha = a^2[2\tau^\alpha\Gamma(1-\alpha)]^{-1}$. For $\kappa > 0$ however the reaction affects the diffusion part of the equation: the Laplace transform of the integral kernel $\Phi_\kappa(t)$ reads

$$\tilde{\Phi}_\kappa(u) \simeq \frac{1}{\tau^\alpha\Gamma(1-\alpha)}(u+\kappa)^{1-\alpha} \tag{18}$$

and is no more a fractional derivative. The integral operator $\hat{T}_t(1-\alpha,\kappa)f = \tau^\alpha\Gamma(1-\alpha)\int_0^t \Phi_\kappa(t-t')f(t')dt'$ corresponds in time domain to

$$\hat{T}_t(1-\alpha,\kappa)f = \left(\frac{d}{dt}\int_0^t \frac{e^{-\kappa(t-t')}}{(t-t')^{1-\alpha}}f(t')dt' + \kappa\int_0^t \frac{e^{-\kappa(t-t')}}{(t-t')^{1-\alpha}}f(t')dt'\right), \tag{19}$$

turning to be a fractional derivative only for $\kappa=0$. The equation for the A concentration thus finally reads

$$\frac{\partial A(x,t)}{\partial t} = K_\alpha \hat{T}_t(1-\alpha,\kappa)\Delta A(x,t) - \kappa A(x,t). \tag{20}$$

Although our reaction does not depend on the particles' motion, the parameters of the reaction explicitly enter the transport operator $\hat{T}$ of the equation.

Analogously we will now derive an equation for the B particles. As for A one has a balance condition for the mean particle number B_i of B particles on site i

$$\frac{dB_i(t)}{dt} = J_i^+(t) - J_i^-(t) + \kappa A_i(t), \tag{21}$$

where J_i^+ denotes the gain flux and J_i^+ the loss flux of particles B at site i. The continuity equation reads

$$\frac{dB_i(t)}{dt} = \frac{1}{2}J_{i-1}^-(t) + \frac{1}{2}J_{i+1}^-(t) - J_i^-(t) + \kappa A_i(t). \tag{22}$$

A B particle that leaves the site i at time t either has come there as a B particle at some prior time or was converted from an A particle that either was at site i from the very beginning or arrived there later, at $t' > 0$. Thus

$$J_i^-(t) = \int_0^t \psi(t-t')J_i^+(t')dt' + A_i(0)\psi(t)[1-e^{-\kappa t}] + \int_0^t \psi(t-t')[1-e^{-\kappa(t-t')}]I_i^+(t')dt'. \tag{23}$$

We then use the local balance equation (21), apply Laplace transform, solve for $\tilde{J}_i^-(u)$ and use the initial condition $B_i(0)=0$ as well as Eq. (13) for $\tilde{I}_i^-$. We get

$$\tilde{J}_i^-(u) = \tilde{\Phi}_0(u)\tilde{B}_i(u) + [\tilde{\Phi}_0(u) - \tilde{\Phi}_\kappa(u)]\tilde{A}_i(u). \tag{24}$$

We now substitute the inverse Laplace transform of this into the continuity equation (22) and perform the transition to a continuum

$$\frac{\partial B(x,t)}{\partial t} = \frac{a^2}{2}\int_0^t \Phi_0(t-t')\Delta B(x,t')dt' + \kappa A(x,t) + \frac{a^2}{2}\int_0^t \Phi_0(t-t')[1-e^{-\kappa(t-t')}]\Delta A(x,t')dt'. \tag{25}$$

For the exponential waiting time density for which $\Phi_0(t) = \lambda\delta(t)$ the third term in Eq. (25) vanishes and a normal reaction-diffusion equation arises. For a power law waiting time distribution Eq. (25) can be written in terms of fractional derivatives and the operator $\hat{T}_t(1-\alpha,\kappa)$, Eq. (19)

$$\frac{\partial B(x,t)}{\partial t} = K_{\alpha 0}D_t^{1-\alpha}\Delta B(x,t) + \kappa A(x,t) + K_\alpha[{}_0D_t^{1-\alpha} - \hat{T}_t(1-\alpha,\kappa)]\Delta A(x,t). \tag{26}$$

Note that the equation for the product contains a term depending on the concentration of the component A at all previous times. This term has to do with the fact that the products are introduced into the system later on in course of the reaction, and their motion therefore is described not by the normal CTRW (and the corresponding fractional diffusion equation) but by the aged one [18]. Note also that the sum of Eqs. (20) and (26) always yields the "normal" subdiffusion equation for the overall concentration $C(x,t)$, Eq. (6). More-

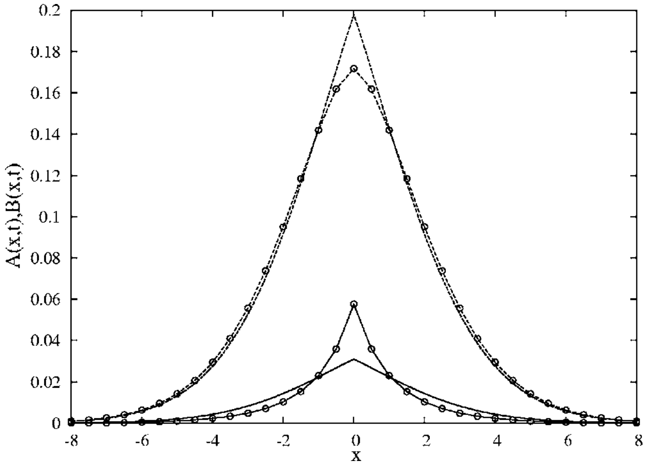

FIG. 1. Shown are the exact solution for independent subdiffusion and conversion for A particles (solid line) and B particles (dashed line) and the numerical solution of Eq. (2) for A particles (solid line with dots) and B particles (dashed line with dots). The parameters are: $\alpha=0.75$, $\kappa=0.001$, $K_\alpha \simeq 7.76 \times 10^{-3}$, $t=2000$.

over the solutions of Eqs. (20) and (26) satisfy Eq. (5).

In order to elucidate the difference between the correct scheme and the simple reaction-diffusion approach we compare the exact result with the numerical solution of Eq. (2) with decoupled transport and reaction term for the initial condition $A(x,0)=\delta(x)$, $B(x,0)\equiv 0$. The exact solution for $C(x,t)=A(x,t)+B(x,t)$ is known as the Fox's H function [3]

$$C(x,t) = \frac{1}{4K_\alpha t^\alpha} H^{1,0}_{1,1}\left[\frac{|x|}{\sqrt{K_\alpha t^\alpha}} \middle| \begin{matrix} (1-\alpha/2,\alpha/2) \\ (0,1) \end{matrix} \right], \tag{27}$$

from which $A(x,t)=e^{-\kappa t}C(x,t)$ and $B(x,t)=[1-e^{-\kappa t}]C(x,t)$ follow. Equation (2) is solved numerically using a numerical scheme recently proposed by Yuste *et al.* [19]. The results are shown in Fig. 1. The qualitative differences between the forms of the concentration profiles are quite evident.

In summary, we derived here the equations describing the time evolution for the local A and B concentrations in a simple monomolecular conversion reaction $A \to B$ taking place at a constant rate κ and under subdiffusion conditions. These equations do not have a usual form of reaction-diffusion equations with the transport term independent on the reaction one. This fact is due to the non-Markovian property of the subdiffusion process, and will persist for more complex reaction schemes as well. The reaction-diffusion scheme with decoupled transport and reaction term fails even qualitatively to describe the situation.

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