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Reaction-subdiffusion equations for the $A \rightleftharpoons B$ reaction

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We consider a linear reversible isomerization reaction $A \rightleftharpoons B$ under subdiffusion described by continuous time random walks (CTRW). The reactants' transformations take place independently on the motion and are described by constant rates. We show that the form of the ensuing system of mesoscopic reaction-subdiffusion equations is unusual: the equation for time derivative of say $A(x,t)$ contains the terms depending not only on ΔA, but also on ΔB. This mirrors the fact that in subdiffusion the flux of particles at time t is defined by the distributions of the particles' concentrations at all previous times. Since the particles which jump as A at time t could previously be both A or B, this flux depends on both A and B concentrations.

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Many phenomena in systems out of equilibrium can be described within a framework of reaction-diffusion equations. Examples can be found in various disciplines ranging from chemistry and physics to biology. Both reaction-diffusion systems with normal and anomalous diffusion have been extensively studied over the past decades. However, for the latter, a general theoretical framework which would hold for all kinds of reactions is still absent. The reasons for subdiffusion and therefore its properties can be different in systems of different kinds; we concentrate here on the situations when such subdiffusion can be adequately described by continuous-time random walks (CTRWs). In CTRWs the overall particle's motion can be considered as a sequence of jumps interrupted by waiting times, the case pertinent to many systems where the transport is slowed down by obstacles or by binding sites. In the case of anomalous diffusion these times are distributed according to a power law lacking the mean. The case of exponential distribution, on the other hand, corresponds to a normal diffusion. On the microscopic level of particles' encounter the consideration of subdiffusion does not seem to be problematic, although it has posed several interesting questions [1–5]. However, these microscopic approaches cannot be immediately adopted for description of spatially inhomogeneous systems, which, in the case of normal diffusion, are successfully described within the framework of reaction-diffusion equations. To discuss such behavior under subdiffusion many authors used the kind of description where the customary reaction term was added to a subdiffusion equation for concentrations to describe such phenomena as a reaction front propagation or Turing instability [6–11].

The results of these works were jeopardized after it was shown in Ref. [12] that these procedures do not lead to a correct description even of a simple irreversible isomerization reaction $A \rightarrow B$. The transport operator describing the subdiffusion is explicitly dependent on the properties of reaction, which stems from an essentially very simple observation that only those particles jump (as A) which survive (as A).

The properties of the reaction depend strongly on whether the reaction takes place only with the step of the particle, or independently on the particles' steps, and moreover, whether the newborn particle retains the rest of its previous waiting time or is assigned a new one [13,14]. Here we consider in detail the following situation: The $A \rightleftharpoons B$ transformations take place independently on the particles' jumps; the waiting time of a particle on a site is not changed by the reaction, both for the forward and for the backward transformation. An example for such a situation is the reaction as taking place in an aqueous solution which soaks a porous medium (say a sponge or some geophysical formation). If sojourn times in each pore are distributed according to the power law, the diffusion on the larger scales is anomalous; on the other hand, the reaction within each pore follows usual kinetics. We start by putting a droplet containing, say, only A particles somewhere within the system and follow the spread and reaction by measuring the local A and B concentrations.

Stoichiometry of the chemical reaction implies the existence of a conservation law. In the case of $A \rightleftharpoons B$ it is evident that the overall number of particles is conserved. If the isomerization takes place independently on the particle's motion, then the evolution of the overall concentration $C(x,t) = A(x,t) + B(x,t)$, where $A(x,t)$ and $B(x,t)$ are the local concentrations of A and B particles, respectively, is not influenced by the reaction, and has to follow the simple subdiffusion equation

$$\dot{C}(x,t) = K_\alpha \, {}_0D_t^{1-\alpha} \Delta C.$$

On the other hand, neither the result of the treatment in Ref. [15] nor the result of Ref. [16] reproduce this behavior which

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is a consequence of the fundamental stoichiometry. In the work [15] (where two of the authors of the present Brief Report were involved) it was implicitly assumed that the back reaction can only take place on a step of a particle, without discussing this assumption. The more general approach of Ref. [16], definitely correct for irreversible reactions, also fails to reproduce this local conservation law and thus is inappropriate for the description of reversible reactions under the conditions discussed. According to Ref. [14] the approach of Ref. [16] implies that the waiting time after each reaction is assigned anew, which makes a large difference in the reversible case.

Considering the reaction $A \rightleftharpoons B$ taking place independently on the particles' steps we show that the form of the corresponding equations is somewhat unusual, which emphasizes the role of coupling between the reaction and transport in reaction-subdiffusion kinetics. Following the approach of Ref. [12,15] we describe the behavior of concentrations in the discrete scheme by the following equations:

$$\dot{A}_i(t) = -I_i(t) + \frac{1}{2}I_{i-1}(t) + \frac{1}{2}I_{i+1}(t) - k_1A_i(t) + k_2B_i(t),$$

$$\dot{B}_i(t) = -J_i(t) + \frac{1}{2}J_{i-1}(t) + \frac{1}{2}J_{i+1}(t) + k_1A_i(t) - k_2B_i(t),$$

where $I_i(t)$ is the loss flux of A particles on site i and $J_i(t)$ is the corresponding loss flux for B particles at site i. In the continuous limit the equations read as

$$\dot{A}(x,t) = \frac{a^2}{2}\Delta I(x,t) - k_1A(x,t) + k_2B(x,t), \tag{1}$$

$$\dot{B}(x,t) = \frac{a^2}{2}\Delta J(x,t) + k_1A(x,t) - k_2B(x,t). \tag{2}$$

We now use the conservation laws for A and B particles to obtain the equations for the corresponding fluxes. The equations for the particles' fluxes on a given site in time domain (the index i or the coordinate x is omitted) are

$$\begin{aligned} I(t) = {} & \psi(t)P_{AA}(t)A(0) \\ & + \int_0^t \psi(t-t')P_{AA}(t-t')[I(t') + k_1A(t') - k_2B(t') \\ & + \dot{A}(t')]dt' + \psi(t)P_{BA}(t)B(0) \\ & + \int_0^t \psi(t-t')P_{BA}(t-t')[J(t') - k_1A(t') \\ & + k_2B(t') + \dot{B}(t')]dt' \end{aligned} \tag{3}$$

for A particles and

$$\begin{aligned} J(t) = {} & \psi(t)P_{BB}(t)B(0) \\ & + \int_0^t \psi(t-t')P_{BB}(t-t')[J(t') - k_1A(t') + k_2B(t') \\ & + \dot{B}(t')]dt' + \psi(t)P_{AB}(t)A(0) \\ & + \int_0^t \psi(t-t')P_{AB}(t-t')[J(t') + k_1A(t') \\ & - k_2B(t') + \dot{A}(t')]dt' \end{aligned}$$

for B particles.

The explanation of the form of, e.g., Eq. (3) is as follows: An A particle which jumps from a given site at time t either was there as A from the very beginning, and jumps as A probably having changed its nature several time in between, or came later as A and jumps as A, or was there from the very beginning as B and leaves the site as A, etc. Here P_{AA}, P_{AB}, P_{BA}, and P_{BB} are the survival or transformation probabilities, i.e., the probability that a particle which was A at $t=0$ (when it came to the site) is also A at time t (when it leaves the site), probably having changed its nature from A to B and back in between, the probability that a particle which was A at $t=0$ is B at time t, the probability that a particle which was B at $t=0$ is A at time t, and the probability that a particle which was B at $t=0$ is B at time t:

$$P_{AA}(t) = \frac{k_2}{k_1+k_2} + \frac{k_1}{k_1+k_2}e^{-(k_1+k_2)t},$$

$$P_{BA}(t) = \frac{k_2}{k_1+k_2} - \frac{k_2}{k_1+k_2}e^{-(k_1+k_2)t},$$

$$P_{BB}(t) = \frac{k_1}{k_1+k_2} + \frac{k_2}{k_1+k_2}e^{-(k_1+k_2)t},$$

$$P_{AB}(t) = \frac{k_1}{k_1+k_2} - \frac{k_1}{k_1+k_2}e^{-(k_1+k_2)t}. \tag{4}$$

These are given by the solution of the classical reaction kinetic equations

$$\dot{A}(t) = -k_1A(t) + k_2B(t),$$

$$\dot{B}(t) = k_1A(t) - k_2B(t). \tag{5}$$

The values of P_{AA}, P_{AB} are given by the solutions $P_{AA}(t)=A(t)$ and $P_{AB}(t)=B(t)$ under initial conditions $A(0)=1$, $B(0)=0$, and the values of P_{BA} and P_{BB} are given by $P_{BA}(t)=A(t)$ and $P_{BB}(t)=B(t)$ under initial conditions $A(0)=0$, $B(0)=1$.

In the Laplace domain we get

$$\begin{aligned} I(u) = {} & \psi_1(u)[I(u) + k_1A(u) - k_2B(u) + uA(u)] \\ & + \psi_2(u)[J(u) - k_1A(u) + k_2B(u) + uB(u)], \end{aligned}$$

$$\begin{aligned} J(u) = {} & \psi_3(u)[J(u) - k_1A(u) + k_2B(u) + uB(u)] \\ & + \psi_4(u)[I(u) + k_1A(u) - k_2B(u) + uA(u)], \end{aligned} \tag{6}$$

where $\psi_1(u)$, $\psi_2(u)$, $\psi_3(u)$, and $\psi_4(u)$ are the Laplace transforms of $\psi_1(t)=\psi(t)P_{AA}(t)$, $\psi_2(t)=\psi(t)P_{BA}(t)$, $\psi_3(t)=\psi(t)P_{BB}(t)$, and $\psi_4(t)=\psi(t)P_{AB}(t)$, respectively.

Using shift theorem we can get the representations of ψ_i in the Laplace domain. They read

$$\psi_1(u) = \frac{k_2}{k_1 + k_2}\psi(u) + \frac{k_1}{k_1 + k_2}\psi(u + k_1 + k_2),$$

$$\psi_2(u) = \frac{k_2}{k_1 + k_2}\psi(u) - \frac{k_2}{k_1 + k_2}\psi(u + k_1 + k_2),$$

$$\psi_3(u) = \frac{k_1}{k_1 + k_2}\psi(u) + \frac{k_2}{k_1 + k_2}\psi(u + k_1 + k_2),$$

$$\psi_4(u) = \frac{k_1}{k_1 + k_2}\psi(u) - \frac{k_1}{k_1 + k_2}\psi(u + k_1 + k_2). \qquad (7)$$

The system of linear equations for the currents, Eqs. (6), then has the solution

$$I(u) = a_{11}(u)A(u) + a_{12}(u)B(u),$$

$$J(u) = a_{21}(u)A(u) + a_{22}(u)B(u)$$

with the following values for the coefficients:

$$a_{11} = \frac{1}{k_1 + k_2}\frac{1}{1 + \phi\psi - \psi - \phi}\{- \phi\psi[k_1k_2 + u(k_1 + k_2) + k_1^2] + \phi k_1(u + k_1 + k_2) + \psi k_2 u\},$$

$$a_{21} = \frac{k_1}{k_1 + k_2}\frac{1}{1 + \phi\psi - \psi - \phi}[\phi\psi(k_1 + k_2) + (\psi - \phi)u - (k_1 + k_2)\phi],$$

and with the two other coefficients, a_{12} and a_{22} differing from a_{21} and a_{11} by interchanging k_1 and k_2. Here $\psi \equiv \psi(u)$ and $\phi \equiv \psi(u+k_1+k_2)$.

For the exponential waiting time density $\psi(t) = \tau^{-1}\exp(-t/\tau)$ the corresponding values are

$$a_{11} = a_{22} = 1/\tau,$$

$$a_{12} = a_{21} = 0,$$

and the system of equations for the concentrations in the continuous limit, Eqs. (2), reduces to the customary system of reaction-diffusion equations. For the case of the power-law distributions $\psi(t) \simeq t^{-1-\alpha}$ the Laplace transform of the waiting time PDF is $\psi(u) \simeq 1 - cu^{\alpha}$ for small u, with $c = \tau^{\alpha}\Gamma(1-\alpha)$, so that

$$a_{11} = \frac{c^{-1}}{k_1 + k_2}[k_2u^{1-\alpha} + k_1(u + k_1 + k_2)^{1-\alpha} - ck_1(k_1 + k_2) - cu(k_1 + k_2)],$$

$$a_{22} = \frac{c^{-1}}{k_1 + k_2}[k_1u^{1-\alpha} + k_2(u + k_1 + k_2)^{1-\alpha} - ck_2(k_1 + k_2) - cu(k_1 + k_2)],$$

$$a_{21} = \frac{c^{-1}}{k_1 + k_2}[k_1u^{1-\alpha} - k_1(u + k_1 + k_2)^{1-\alpha} + ck_1(k_1 + k_2)],$$

$$a_{12} = \frac{c^{-1}}{k_1 + k_2}[k_2u^{1-\alpha} - k_2(u + k_1 + k_2)^{1-\alpha} + ck_2(k_1 + k_2)].$$

Now we turn to the case of long times and relatively slow reactions, so that all parameters, u, k_1, and k_2, can be considered as small. In this case, for $\alpha < 1$, the leading terms in all these parameters are the first two terms in each of the four equations, and the other terms can be neglected. In the time domain the operator corresponding to $u^{1-\alpha}$ is one of the fractional derivative ${}_0D_t^{1-\alpha}$, and the operator corresponding to $(u+k_1+k_2)^{1-\alpha}$ is the transport operator of Ref. [15], ${}_0\mathcal{T}_t^{1-\alpha}(k_1+k_2)$ with ${}_0\mathcal{T}_t^{1-\alpha}(k) = e^{-kt}\,{}_0D_t^{1-\alpha}e^{kt}$. Introducing the corresponding equations for the currents into the balance equations for the particle concentrations we get

$$\dot{A}(x,t) = K_{\alpha}\left[\frac{k_2}{k_1 + k_2}{}_0D_t^{1-\alpha} + \frac{k_1}{k_1 + k_2}{}_0\mathcal{T}_t^{1-\alpha}(k_1 + k_2)\right]\Delta A(x,t) + K_{\alpha}\left[\frac{k_2}{k_1 + k_2}{}_0D_t^{1-\alpha} - \frac{k_2}{k_1 + k_2}{}_0\mathcal{T}_t^{1-\alpha}(k_1 + k_2)\right]\Delta B(x,t) - k_1A(x,t) + k_2B(x,t), \qquad (8)$$

$$\dot{B}(x,t) = K_{\alpha}\left[\frac{k_1}{k_1 + k_2}{}_0D_t^{1-\alpha} - \frac{k_1}{k_1 + k_2}{}_0\mathcal{T}_t^{1-\alpha}(k_1 + k_2)\right]\Delta A(x,t) + K_{\alpha}\left[\frac{k_1}{k_1 + k_2}{}_0D_t^{1-\alpha} + \frac{k_2}{k_1 + k_2}{}_0\mathcal{T}_t^{1-\alpha}(k_1 + k_2)\right]\Delta B(x,t) + k_1A(x,t) - k_2B(x,t). \qquad (9)$$

Note also that the equation for $C(x,t) = A(x,t) + B(x,t)$ following from summing up Eqs. (8) and (9) is a simple subdiffusion equation,

$$\dot{C}(x,t) = K_{\alpha}\,{}_0D_t^{1-\alpha}\Delta C,$$

as it should be. On the other hand, neither the result of the treatment in Ref. [15] nor the result of Ref. [16] reproduce this behavior which is a consequence of the fundamental conservation law prescribed by the stoichiometry of reaction.

Note that this system still holds for $\alpha = 1$ when both the fractional derivative ${}_0D_t^{1-\alpha}$ and the transport operator ${}_0\mathcal{T}_t^{1-\alpha}(k_1+k_2)$ are unit operators. In this case the usual system of reaction-diffusion equations is restored:

$$\dot{A}(x,t) = K\Delta A(x,t) - k_1A(x,t) + k_2B(x,t),$$

$$\dot{B}(x,t) = K\Delta B(x,t) + k_1A(x,t) - k_2B(x,t).$$

The physical explanation of the additional terms (with the Laplacians of the concentrations of particles of other sort) in the case of subdiffusion has to do with its nonlocality in time. The flux of A particles at time t is defined by the distributions of the particles' concentrations at all previous times. Since the particles which jump as A at time t could be both A and B at the previous instants of time, this flux depends both on the (gradients of) A and B concentrations. The dependence on the concentration of a particle of the opposite sort disappears only in the case where no memory on the past conditions is present, i.e., in the case of normal diffusion.

Let us summarize our findings. We considered the system of mesoscopic (reaction-subdiffusion) equations describing the kinetics of a reversible isomerization $A \rightleftharpoons B$ taking place in a subdiffusive medium. When the waiting times of the particles are not assigned anew after their transformations (i.e., when the overall concentration of reactants is governed by the simple subdiffusion equation), this reaction is described by a rather unusual system of reaction-subdiffusion equations having a form which was up to our knowledge not discussed before: Each of the equations, giving the temporal changes of the corresponding concentrations, depends on the Laplacians of *both* concentrations, A and B (not only on the same one, as in the case of normal diffusion). This is a rather unexpected situation especially taking into account the fact that our reaction is practically decoupled from the transport of particles. The form reduces to a usual reaction-diffusion form for normal diffusion (due to cancellations). It is important to note that the physical reason of the appearance of such a form is the possibility of several transformations $A \to B \to A \to B \cdots$ during one waiting period, and that such possibilities have to be taken into account also for more complex reactions including reversible stages. In the present Brief Report we concentrated on a simplest case of a reversible reaction, namely on one with linear kinetics (just as it was done in Ref. [12] for an irreversible one), for which the solution to the problem can be found without explicitly putting down reaction-subdiffusion equations and evidently reads $A(x,t)=C(x,t)P_{AA}(t)$, $B(x,t)=C(x,t)P_{AB}(t)$. This solution satisfies our final system of equations, so that neither simulations nor other independent proofs are necessary. The situation for more complex reactions might be more involved, but the emergence of the Laplacians of concentrations of several reactants (not only the one for which the corresponding equation is put down) is quite general.

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[1] R. Metzler and J. Klafter, Chem. Phys. Lett. **321**, 238 (2000).
[2] J. Sung, E. Barkai, R. J. Silbey, and S. Lee, J. Chem. Phys. **116**, 2338 (2002); J. Sung and R. J. Silbey, Phys. Rev. Lett. **91**, 160601 (2003).
[3] K. Seki, M. Wojcik, and M. Tachiya, J. Chem. Phys. **119**, 2165 (2003); **119**, 7525 (2003).
[4] S. B. Yuste and K. Lindenberg, Phys. Rev. Lett. **87**, 118301 (2001).
[5] S. B. Yuste and K. Lindenberg, Phys. Rev. E **72**, 061103 (2005).
[6] S. Fedotov and V. Méndez, Phys. Rev. E **66** 030102(R) (2002).
[7] V. Méndez, V. Ortega-Cejas, and J. Casas-Vásques, Eur. Phys. J. B **53**, 503 (2006).
[8] B. I. Henry and S. L. Wearne, Physica A **276**, 448 (2000).
[9] B. I. Henry and S. L. Wearne, SIAM (Soc. Ind. Appl. Math.) J. Appl. Math. **62**, 870 (2002).
[10] B. I. Henry, T. A. M. Langlands, and S. L. Wearne, Phys. Rev. E **72**, 026101 (2005).
[11] T. A. M. Langlands, B. I. Henry, and S. L. Wearne, J. Phys.: Condens. Matter **19**, 065115 (2007).
[12] I. M. Sokolov, M. G. W. Schmidt, and F. Sagués, Phys. Rev. E **73**, 031102 (2006).
[13] B. I. Henry, T. A. M. Langlands, and S. L. Wearne, Phys. Rev. E **74**, 031116 (2006).
[14] Y. Nec and A. A. Nepomnyashchy, J. Phys. A: Math. Theor. **40**, 14687 (2007).
[15] M. G. W. Schmidt, F. Sagués, and I. M. Sokolov, J. Phys.: Condens. Matter **19**, 06511 (2007).
[16] A. Yadav and W. Horsthemke, Phys. Rev. E **74**, 066118 (2006).