Anomalous subdiffusion with multi-species linear reaction dynamics

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We have introduced a set of coupled fractional reaction-diffusion equations to model a multi-species system undergoing anomalous subdiffusion with linear reaction dynamics. The model equations are derived from a mesoscopic continuous time random walk formulation of anomalously diffusing species with linear mean field reaction kinetics. The effect of reactions is manifest in reaction modified spatio-temporal diffusion operators as well as in additive mean field reaction terms. One consequence of the non-separability of reaction and subdiffusion terms is that the governing evolution equation for the concentration of one particular species may include both reactive and diffusive contributions from other species. The general solution is derived for the multi-species system and some particular special cases involving both irreversible and reversible reaction dynamics are analyzed in detail. We have carried out Monte Carlo simulations corresponding to these special cases and we find excellent agreement with theory.

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I. INTRODUCTION

In recent years numerous physical and biological systems have been reported in which the diffusion rates of species cannot be characterized by the single parameter of the diffusion constant. Instead, the (anomalous) diffusion is characterized by a scaling parameter γ as well as a diffusion coefficient $D(\gamma)$ and the mean square displacement of diffusing species $\langle r^2(t) \rangle$ scales as a nonlinear power law in time, i.e., $\langle r^2(t) \rangle \sim t^\gamma$ [1]. The case of subdiffusion $0 < \gamma < 1$ is particularly prevalent in biological systems [2–10] and is generic in media with obstacles [11, 12] or binding sites [13].

Anomalous subdiffusion has been successfully modelled mesoscopically using Continuous Time Random Walks (CTRWs) [14, 15], or Generalised Master Equations (GMEs), with a long-tailed waiting-time density [1]. This leads to a macroscopic formulation as a fractional subdiffusion equation (see e.g., [1, 16, 17]) with a temporal fractional order derivative acting on the spatial Laplacian operator. Fractional variants of the Fokker-Planck equation have also been derived in the case of anomalous subdiffusion in an externally applied force field [16, 18–20].

A fundamental question that has arisen in recent years is how to incorporate reaction terms correctly when the particles involved are undergoing anomalous subdiffusion. Earlier model formulations utilized fractional reaction-diffusion equations where a temporal fractional

derivative operated either solely on the spatial Laplacian term [21–25], or upon both the Laplacian and the reaction terms [26–30]. However, in the simple case of linear reaction dynamics, it was shown [25] that the equation

$$\frac{\partial n}{\partial t} = D_\gamma \frac{\partial^{1-\gamma}}{\partial t^{1-\gamma}} \frac{\partial^2 n}{\partial x^2} - kn \qquad (1)$$

breaks down to give physically unrealistic negative solutions, and the equation

$$\frac{\partial n}{\partial t} = D_\gamma \frac{\partial^{1-\gamma}}{\partial t^{1-\gamma}} \frac{\partial^2 n}{\partial x^2} - \frac{\partial^{1-\gamma}}{\partial t^{1-\gamma}} kn \qquad (2)$$

only applies to subdiffusion with instantaneous removals. In the above equations $\frac{\partial^{1-\gamma}}{\partial t^{1-\gamma}}$ is a Riemann-Liouville fractional derivative [31]. Neither of the above equations describes subdiffusion with a constant (in time) per capita removal of species. Proceeding from a mesoscopic CTRW description with a long tailed waiting-time density and with a reduction in particle concentration driven by constant per capita linear reaction dynamics, it has been shown that the appropriate fractional reaction-diffusion equation to model this process is [25]

$$\frac{\partial n}{\partial t} = D_\gamma e^{-kt} \frac{\partial^{1-\gamma}}{\partial t^{1-\gamma}} \left(e^{kt} \frac{\partial^2 n}{\partial x^2} \right) - kn. \qquad (3)$$

The effect of linear reactions is thus manifest in a reaction modified spatio-temporal diffusion operator as well as in the additive mean field reaction term. An equivalent result, using a slightly different formalism, has also been derived by balancing reaction and diffusion fluxes in a CTRW description [32] and this result has been generalized to two species with irreversible linear reaction kinetics [32, 33]. An example is the two-species system in which the concentration of one species, A, decays at

a constant per capita rate and the concentration of another species, B, increases at the same rate (i.e., $A \to B$) [32, 33]. The governing evolution equations for the concentrations can be written as

$$\frac{\partial a}{\partial t} = D_\gamma e^{-kt} \frac{\partial^{1-\gamma}}{\partial t^{1-\gamma}} \left(e^{kt} \frac{\partial^2 a}{\partial x^2} \right) - ka \qquad (4)$$

$$\frac{\partial b}{\partial t} = \frac{\partial^{1-\gamma}}{\partial t^{1-\gamma}} \frac{\partial^2 b}{\partial x^2} + ka$$
$$+ \left[\frac{\partial^{1-\gamma}}{\partial t^{1-\gamma}} - e^{-kt} \frac{\partial^{1-\gamma}}{\partial t^{1-\gamma}} \left(e^{kt} \right) \right] \frac{\partial^2 a}{\partial x^2} \qquad (5)$$

where a and b denote the concentration of species A and B.

The evolution equation for species A is identical to Eq. (3) but the evolution equation for species B involves a linear combination of both pure fractional diffusive terms as well as reaction modified fractional diffusive terms involving species A. A CTRW formulation of two-species reversible reactions with heavy tailed waiting-time densities was also provided in [33] but no corresponding formulation as a fractional reaction-diffusion equation was obtained for this case. In related work, a set of integro-differential equations has been introduced to model a multi-species system with anomalous subdiffusion and nonlinear reaction dynamics [34, 35]. This set of equations, which was derived from a CTRW formulation with aged walkers, also has coupling between the diffusive terms and the reaction terms. However in contrast to the evolution equations reported in [32, 33] and those derived below, there is no coupling between diffusive terms from different species,

In this paper we have derived a set of coupled fractional reaction-diffusion equations to describe the evolution in the concentrations of n species undergoing anomalous subdiffusion with reactions described by the linear mean-field reaction equations

$$\frac{\partial \mathbf{n}}{\partial t} = R\mathbf{n} \qquad (6)$$

where R is a constant reaction rate matrix and $\mathbf{n}$ is a vector of species concentrations. Starting with a mesoscopic CTRW description and assuming that the walkers composing each species are governed by the same step-length densities and the same waiting-time densities we derive the following balance equation

$$\frac{\partial \mathbf{n}}{\partial t} = D_\gamma e^{Rt} \frac{\partial^{1-\gamma}}{\partial t^{1-\gamma}} \left(e^{-Rt} \frac{\partial^2 \mathbf{n}}{\partial x^2} \right) + R\mathbf{n}, \qquad (7)$$

which is a generalization of Eq. (3) for multi-species. In the above equation e^{Rt} is a matrix exponential. This system of equations includes the possibility of diffusive contributions between species and thus differs from the evolution equations of [34, 35] (when restricted to linear reaction dynamics).

The remainder of this paper is organized as follows. In Section II we present the mesoscopic CTRW formulation for a multi-species system undergoing anomalous subdiffusion with linear mean field reaction dynamics. The macroscopic fractional reaction-diffusion equations for this model system, Eq.(7), are derived in Section III. The general solution is also obtained in this section. In Section IV we analyze examples involving two-species with irreversible and reversible reactions. The results are compared with Monte Carlo simulations. In Section V we describe a generalization of the formalism allowing for species whose jumps are governed by different waiting-time densities. The CTRW formulation in this case does not reduce, in general, to a system of fractional reaction-diffusion equations. Finally the models and results are discussed in Section VI.

II. CONTINUOUS TIME RANDOM WALK FORMULATION

Here we consider n reacting particle species satisfying the linear mean-field reaction equation in Eq. (6) where each species undergoes anomalous subdiffusion with the same waiting-time, $\psi(t)$, and jump-length, $\lambda(x)$, probability densities. In the following we use the CTRW approach of [25, 33] with decoupled jump-length and waiting-time densities. The master equation for the probability, $\mathbf{q}(x,t)$, that the particle arrives at the position x at time t taking into account Eq. (6) is

$$\mathbf{q}(x,t) = \delta(t) \mathbf{q}(x,0) + \int_{-\infty}^{\infty} \lambda(x - x^{'})$$
$$\int_0^t \psi(t - t^{'})e^{R(t-t^{'})}\mathbf{q}(x^{'},t^{'}) \, dt^{'} \, dx^{'}. \quad (8)$$

To find the corresponding probability, $\mathbf{n}(x,t)$, of being at x at some time t we use the convolution as in [25]

$$\mathbf{n}(x,t) = \int_0^t \Phi(t - t^{'})e^{R(t-t^{'})}\mathbf{q}(x,t^{'}) \, dt^{'}. \qquad (9)$$

Here the change in concentrations due to reactions is taken into account through the matrix exponential, which operates on those walkers that have arrived at earlier times $t^{'}$ and then survived without jumping for a time $t-t^{'}$ according to the survival probability $\Phi\left(t - t^{'}\right)$. The survival probability is defined by

$$\Phi(t) = 1 - \int_0^t \psi(t^{'}) \, dt^{'}. \qquad (10)$$

Equation (8) and Eq. (9) can be combined by first multiplying both equations by e^{-Rt} to find

$$e^{-Rt}\mathbf{q}(x,t) = e^{-Rt}\delta(t)\mathbf{q}(x,0) + \int_{-\infty}^{\infty} \lambda(x - x^{'})$$
$$\int_0^t \psi(t - t^{'})e^{-Rt^{'}}\mathbf{q}(x^{'},t^{'}) \, dt^{'} \, dx^{'} \quad (11)$$

and

$$e^{-Rt}\mathbf{n}\left(x,t\right) = \int_0^t \Phi(t-t^{'})e^{-Rt^{'}}\mathbf{q}(x,t^{'})\,dt^{'} \quad (12)$$

where we have used the identity [36]

$$e^{-Rt}e^{R(t-t^{'})} = e^{-Rt^{'}}. \quad (13)$$

Now using Laplace transforms, as in [25], we obtain

$$e^{-Rt}\mathbf{n}\left(x,t\right) = \Phi\left(t\right)\mathbf{n}\left(x,0\right) + \int_{-\infty}^{\infty} \lambda(x-x^{'})$$
$$\int_0^t \psi(t-t^{'})e^{-Rt^{'}}\mathbf{n}(x^{'},t^{'})\,dt^{'}\,dx^{'} \quad (14)$$

or by multiplying by e^{Rt} we yield the master equation

$$\mathbf{n}\left(x,t\right) = \Phi\left(t\right)e^{Rt}\mathbf{n}\left(x,0\right) + \int_{-\infty}^{\infty} \lambda(x-x^{'})$$
$$\int_0^t \psi(t-t^{'})e^{R(t-t^{'})}\mathbf{n}(x^{'},t^{'})\,dt^{'}\,dx^{'}. \quad (15)$$

We note that the above equation can be rewritten using a Caputo fractional deriviative (see [37]) if a Mittag-Leffler density is used for $\psi(t)$ [38, 39] but there is no advantage to do so in this case.

The two species system considered in [33] with (I) irreversible linear reactions $(A \rightarrow B)$ and (II) reversible linear reactions $(A \rightleftharpoons B)$ corresponds to a two-species reduction of Eq. (15) with the mean field reaction matrices

$$R_I = \begin{bmatrix} -k & 0 \\ k & 0 \end{bmatrix} \quad \text{and} \quad R_{II} = \begin{bmatrix} -k_1 & k_2 \\ k_1 & -k_2 \end{bmatrix} \quad (16)$$

respectively. The reaction matrices are diagonalisable in these examples. In the next section we show that with the introduction of a long-tailed waiting-time density, $\psi(t)$, we can simplify Eq. (15) to a general system of fractional reaction-diffusion equations.

III. FRACTIONAL REACTION-DIFFUSION EQUATION

To find the corresponding system of fractional reaction-diffusion equations we first multiply Eq. (15) by e^{-Rt} to give

$$e^{-Rt}\mathbf{n}(x,t) = \Phi(t)\mathbf{n}(x,0) + \int_{-\infty}^{\infty} \lambda\left(x-x^{'}\right)$$
$$\int_0^t \psi\left(t-t^{'}\right)e^{-Rt}e^{R\left(t-t^{'}\right)}\mathbf{n}(x^{'},t^{'})\,dt^{'}\,dx^{'}. \quad (17)$$

Now upon setting

$$\mathbf{y}(x,t) = e^{-Rt}\mathbf{n}(x,t), \quad (18)$$

noting $\mathbf{n}(x,0) = \mathbf{y}(x,0)$, and using Eq. (13), we have that Eq. (17) simplifies to

$$\mathbf{y}(x,t) = \Phi(t)\mathbf{y}(x,0) +$$
$$\int_{-\infty}^{\infty} \lambda\left(x-x^{'}\right)\int_0^t \psi\left(t-t^{'}\right)\mathbf{y}(x^{'},t^{'})\,dt^{'}\,dx^{'}. \quad (19)$$

If $\psi(t)$ is a long-tailed waiting-time density then Eq.(19) is a multi-species representation of the well known CTRW master equation for anomalous subdiffusion which leads to the macroscopic fractional subdiffusion equation [1], now written in vector form,

$$\frac{\partial\mathbf{y}}{\partial t} = D_\gamma \frac{\partial^{1-\gamma}}{\partial t^{1-\gamma}}\frac{\partial^2\mathbf{y}}{\partial x^2}. \quad (20)$$

The governing evolution equation for the concentrations $\mathbf{n}$ is now obtained by combining Eq. (18) and Eq. (20). Explicitly, after substituting Eq. (18) into Eq. (20), evaluating the first order time derivative, and rearranging, we find

$$\frac{\partial\mathbf{n}}{\partial t} = e^{Rt}Re^{-Rt}\mathbf{n} + e^{Rt}D_\gamma\frac{\partial^{1-\gamma}}{\partial t^{1-\gamma}}\left(e^{-Rt}\frac{\partial^2\mathbf{n}}{\partial x^2}\right). \quad (21)$$

The final form of the fractional reaction diffusion equation is then

$$\frac{\partial\mathbf{n}}{\partial t} = R\mathbf{n} + e^{Rt}D_\gamma\frac{\partial^{1-\gamma}}{\partial t^{1-\gamma}}\left(e^{-Rt}\frac{\partial^2\mathbf{n}}{\partial x^2}\right). \quad (22)$$

where we have used the identity [40]

$$e^{Rt}R = Re^{Rt}. \quad (23)$$

Equation (22) is the main result of this paper. It is clear from this equation that the reaction terms and diffusion terms are coupled when the particles are undergoing anomalous subdiffusion (see also [33]). Note too that as a consequence of the matrix multiplication in this equation, the governing evolution equation for the concentration of one species will in general involve not only diffusive terms for this species but also diffusive terms corresponding to other particle species. In the Markovian case, $\gamma = 1$, the system Eq. (22) reduces to the familiar form

$$\frac{\partial\mathbf{n}}{\partial t} = R\mathbf{n} + D_1\frac{\partial^2\mathbf{n}}{\partial x^2}, \quad (24)$$

and, in contrast to the anomalous subdiffusion case, the reaction and diffusive terms are no longer coupled.

The solution to the system in Eq. (22) can readily be found from the equivalent coupled system described by Eq. (18) and Eq. (19). The general solution to the initial value problem is given by

$$\mathbf{n}(x,t) = \frac{1}{\sqrt{4\pi D_\gamma t^\gamma}}\int_{-\infty}^{\infty} G_\gamma(x^{'},t)\,e^{tR}\mathbf{n}(x^{'},0)\,dx^{'} \quad (25)$$

where $G_\gamma(x,t)$ is the Green's solution of the fractional subdiffusion equation [1]. Explicitly,

$$G_\gamma(x,t) = \frac{1}{\sqrt{4\pi D_\gamma t^\gamma}} H_{1,2}^{2,0}\left[\frac{x^2}{4D_\gamma t^\gamma} \left| \begin{array}{c} \left(1-\frac{\gamma}{2},\gamma\right) \\ (0,1)\left(\frac{1}{2},1\right) \end{array}\right.\right],$$ (26)

where H is a Fox function [31, 37] which can be evaluated using the method in [1] if γ is a rational number.

The multi-species fractional reaction diffusion system, Eq. (22), can be simplified further in special cases. First note that if all particles are initially located at the origin then $\mathbf{n}(x,0) = \delta(x)\,\mathbf{n}_o$ and the convolution in Eq. (25) yields the solution

$$\mathbf{n}(x,t) = G_\gamma(x,t)e^{tR}\mathbf{n}_o.$$ (27)

Secondly note that if the matrix R can be diagonalised Eq. (22) can be transformed into a system of linearly independent subdiffusion-reaction equations by setting

$$\mathbf{w}(x,t) = P\mathbf{n}$$ (28)

where P is matrix whose columns are eigenvectors corresponding to the eigenvalues of R [41]. The governing system of evolution equations in this case decouples to

$$\frac{\partial \mathbf{w}}{\partial t} = D\mathbf{w} + e^{Dt}D_\gamma \frac{\partial^{1-\gamma}}{\partial t^{1-\gamma}}\left(e^{-Dt}\frac{\partial^2 \mathbf{w}}{\partial x^2}\right).$$ (29)

where D is a diagonal matrix composed of the eigenvalues of R.

IV.   TWO-SPECIES FRACTIONAL REACTION DIFFUSION EXAMPLES

In this section we present explicit forms and solutions of Eq. (22) for two-particle systems with linear reaction systems described by the coefficient matrices in Eq. (16) and we compare the analytic solutions with Monte Carlo simulations. A brief description of the Monte Carlo simulations is given in the appendix. The cases that we consider were considered previously by [33] using a different formulation and here we demonstrate how our general multi-species system, Eq. (22), encompasses these special cases. For ease of notation we denote the concentrations of the two species by A and B. In these illustrative examples the reaction coefficient matrix, R, is diagonalisable but the general system described by Eq. (22) can be applied to anomalous subdiffusion with any linear mean-field reaction kinetics.

A.   Irreversible reaction $A \rightarrow B$

The reaction coefficient matrix in this case is given by R_I in Eq. (16). The matrix exponential in Eq. (22) can readily be evaluated resulting in

$$\frac{\partial a}{\partial t} = e^{-kt}D_\gamma\frac{\partial^{1-\gamma}}{\partial t^{1-\gamma}}\left(e^{kt}\frac{\partial^2 a}{\partial x^2}\right) - ka,$$ (30)

for species A (similar to the single species case described by Eq. (3)), and

$$\frac{\partial b}{\partial t} = D_\gamma\frac{\partial^{1-\gamma}}{\partial t^{1-\gamma}}\frac{\partial^2\,(a+b)}{\partial x^2} + ka$$
$$- e^{-kt}D_\gamma\frac{\partial^{1-\gamma}}{\partial t^{1-\gamma}}\left(e^{kt}\frac{\partial^2 a}{\partial x^2}\right) \quad (31)$$

for species B. In this case we recover the fractional reaction diffusion equations derived in [32, 33]. Diffusive terms corresponding to both species appear in the evolution equation for species B. The solutions of Eq. (30) and Eq. (31) with initial conditions $a(x,0) = a_o\delta(x)$ and $b(x,0) = b_o\delta(x)$, can be obtained from Eq. (27), yielding

$$a(x,t) = a_o e^{-kt}G_\gamma(x,t),$$ (32)

and

$$b(x,t) = \left(b_o + a_o\left(1 - e^{-kt}\right)\right)G_\gamma(x,t),$$ (33)

similar to [32].

Solutions for the two-species irreversible reactions with anomalous subdiffusion are compared with the results of Monte Carlo simulations in Fig. 1 for parameter values $a_o = b_o = 1/2$, $k = 0.1$, $\gamma = 1/2$, and $D_\gamma = 0.892$. The analytic solutions are in excellent agreement with the Monte Carlo simulations at times $t = 1$ and $t = 2$, for both species A and B. The Monte Carlo simulations do not match as closely at shorter times $t = 0.01$, but there are two reasons for this. Firstly, the analytic results are for a delta function initial condition that is infinite at $t = 0$ whereas the Monte Carlo simulations necessarily use a finite initial condition at $t = 0$. Secondly our Monte Carlo simulations employ a Pareto Law for the waiting-time density and the macroscopic fractional subdiffusion equation Eq. (22) was only derived from CTRWs in the long-time asymptotic limit [1, 25] for this density.
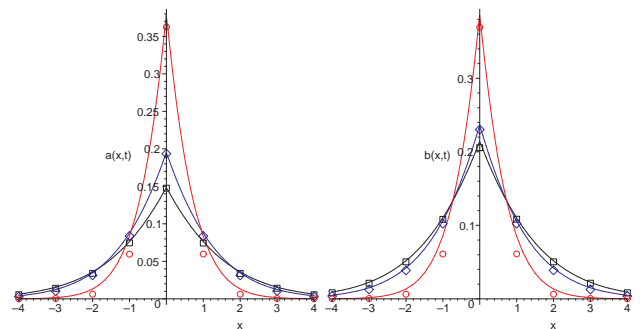

FIG. 1: (Color online) Comparison of the Green's function solution (solid lines) and the Monte Carlo simulations (symbols) for species A (left) and B (right) with two-species irreversible reactions (Eqs. (30) and (31)) at the times $t = 0.1$ (red $\circ$), $t = 1.0$ (blue $\diamond$), and $t = 2.0$ (black $\square$) with the parameters $k = 0.1$ and $\tau = 0.1$. The Monte Carlo results were obtained from an ensemble average over 50 simulations.

B. Reversible reaction $A \rightleftharpoons B$

The reaction coefficient matrix in this case is given by R_{II} in Eq. (16) and the resulting evolution equations are

$$\frac{\partial a}{\partial t} = \rho_2 D_\gamma \frac{\partial^{1-\gamma}}{\partial t^{1-\gamma}} \frac{\partial^2 (a+b)}{\partial x^2} - k_1 a + k_2 b$$
$$+ e^{-k^* t} D_\gamma \frac{\partial^{1-\gamma}}{\partial t^{1-\gamma}} \left(e^{k^* t} \frac{\partial^2 (\rho_1 a - \rho_2 b)}{\partial x^2} \right), \quad (34)$$

and

$$\frac{\partial b}{\partial t} = \rho_1 D_\gamma \frac{\partial^{1-\gamma}}{\partial t^{1-\gamma}} \frac{\partial^2 (a+b)}{\partial x^2} + k_1 a - k_2 b$$
$$- e^{-k^* t} D_\gamma \frac{\partial^{1-\gamma}}{\partial t^{1-\gamma}} \left(e^{k^* t} \frac{\partial^2 (\rho_1 a - \rho_2 b)}{\partial x^2} \right) \quad (35)$$

where $k^* = k_1 + k_2$, $\rho_1 = k_1/k^*$, and $\rho_2 = k_2/k^*$. We observe here, due to the albeit linear interaction between the two species, that both equations have subdiffusive (standard fractional and reaction modified fractional) contributions for both species.

As an aside we note that the above two equations can be written in the form

$$\frac{\partial (a+b)}{\partial t} = D_\gamma \frac{\partial^{1-\gamma}}{\partial t^{1-\gamma}} \frac{\partial^2 (a+b)}{\partial x^2} \quad (36)$$

for $a + b$ and

$$\frac{\partial (\rho_1 a - \rho_2 b)}{\partial t} = -k^* (\rho_1 a - \rho_2 b)$$
$$+ e^{-k^* t} D_\gamma \frac{\partial^{1-\gamma}}{\partial t^{1-\gamma}} \left(e^{k^* t} \frac{\partial^2 (\rho_1 a - \rho_2 b)}{\partial x^2} \right) \quad (37)$$

for $\rho_1 a - \rho_2 b$.

The solution of Eqs (34) and (35) again with the initial conditions $a(x,0) = a_o \delta(x)$ and $b(x,0) = b_o \delta(x)$, are

$$a(x,t) = a_o (\rho_2 + \rho_1 e^{-k^* t}) G_\gamma(x,t)$$
$$+ b_o \rho_2 (1 - e^{-k^* t}) G_\gamma(x,t) \quad (38)$$

$$b(x,t) = a_o \rho_1 (1 - e^{-k^* t}) G_\gamma(x,t)$$
$$+ b_o (\rho_1 + \rho_2 e^{-k^* t}) G_\gamma(x,t). \quad (39)$$

These solutions are compared with the results of Monte Carlo simulations in Figure 2 and again there is excellent agreement. The parameter values used in the simulations were as follows; $a_o = 1$, $b_o = 0$, $k_1 = k_2 = 0.1$, $\gamma = 1/2$ and $D_\gamma = 0.892$.

V. DIFFERENT WAITING-TIME DENSITIES

In the previous examples and in the CTRW formulation leading to Eq. (22) we assumed that the waiting-time
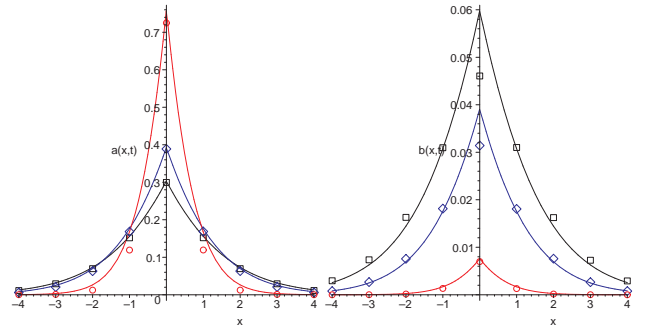

FIG. 2: (Color online) Comparison of the Green's function solution (solid lines) and the Monte Carlo simulations (symbols) for species A (left) and B (right) for the two-species reversible reaction (Eqs. (38) and (39)) at the times $t = 0.1$ (red ○), $t = 1.0$ (blue ◇), and $t = 2.0$ (black □). The parameters are $k_1 = 0.1$, $k_2 = 0.1$, and $\tau = 0.1$. The Monte Carlo results were obtained from an ensemble average over 50 simulations.

densities are the same for each species. Here we consider the possibility in which the subdiffusion of each species is governed by a different waiting time density. We have not developed a general theory for this case but we have obtained interesting results in the case of two species irreversible reactions $A \rightarrow B$, with the anomalous exponent for species A set to $\gamma_a = 1/2$ and standard diffusion for species B, (i.e., $\gamma_b = 1$), that point the way to a more general theory. Here we do not expect the results for species A to change compared with the previous irreversible simulations, as its concentration is not coupled to B in Eq. (6) with $R = R_I$. However since particles of type A are transformed into particles of type B and the waiting-time densities differ, we expect a change in the behaviour of the concentration of species B.

A possible generalization of the above is to write Eqs. (8) and (9) as

$$\mathbf{q}(x,t) = \delta(t) \mathbf{n}(x,0) + \int_{-\infty}^{\infty} \lambda(x - x')$$
$$\int_0^t e^{R(t-t')} \Psi(t - t') \mathbf{q}(x',t') \, dt' \, dx' \quad (40)$$

and

$$\mathbf{n}(x,t) = \int_0^t e^{R(t-t')} \Theta(t - t') \mathbf{q}(x,t') \, dt' \quad (41)$$

where

$$\Psi(t) = \begin{bmatrix} \psi_1(t) & 0 \\ 0 & \psi_2(t) \end{bmatrix} \text{ and } \Theta(t) = \begin{bmatrix} \phi_1(t) & 0 \\ 0 & \phi_2(t) \end{bmatrix}. \quad (42)$$

Unfortunately it is not possible to reduce these equations into the form of Eq. (15) except in special cases such as when the waiting times are identical $\psi_1(t) = \psi_2(t)$ or the reaction coefficient matrix R is diagonal. However the equations can, in this case, be reduced to a system of

fractional reaction-diffusion equations. The equation for the concentration of particles of type A is again given by Eq. (30), and its solution by Eq. (32), but now with γ_a and D_{γ_a} replacing γ and D_γ. The equation for particles of type B is

$$\frac{\partial b}{\partial t} = D_{\gamma_b} \frac{\partial^{1-\gamma_b}}{\partial t^{1-\gamma_b}} \frac{\partial^2 (a+b)}{\partial x^2} + ka$$
$$- D_{\gamma_b} \frac{\partial^{\gamma_a - \gamma_b}}{\partial t^{\gamma_a - \gamma_b}} \left[e^{-kt} \frac{\partial^{1-\gamma_a}}{\partial t^{1-\gamma_a}} \left(e^{kt} \frac{\partial^2 a}{\partial x^2} \right) \right] \quad (43)$$

which differs from Eq. (31) mainly due to the presence of the fractional derivative, $\frac{\partial^{\gamma_a - \gamma_b}}{\partial t^{\gamma_a - \gamma_b}}$, operating on the second term. The solution of this equation can be shown to be

$$b(x,t) = \left(a_o \left(1 - e^{-kt} \right) + b_o \right) G_{\gamma_b}(x,t) + \frac{a_o e^{-kt}}{\sqrt{4\pi D_{\gamma_b} t^{\gamma_b}}} \sum_{l=1}^{\infty} \sum_{m=1}^{\infty} \frac{(kt)^l}{l!} \left[\frac{D_{\gamma_a} t^{\gamma_a}}{D_{\gamma_b} t^{\gamma_b}} \right]^m$$
$$\left\{ H_{2,3}^{3,0} \left[\frac{x^2}{4D_{\gamma_b} t^{\gamma_b}} \, \middle| \, \begin{matrix} \left(1 - \frac{\gamma_b}{2} + l + (\gamma_a - \gamma_b) m, \gamma_b \right) \left(1 - \frac{\gamma_b}{2} - \gamma_b m, \gamma_b \right) \\ (0,1) \left(\frac{1}{2}, 1 \right) \left(l + 1 - \frac{\gamma_b}{2} - \gamma_b m, \gamma_b \right) \end{matrix} \right] - \frac{D_{\gamma_b} t^{\gamma_b}}{D_{\gamma_a} t^{\gamma_a}} \right.$$
$$\left. H_{2,3}^{3,0} \left[\frac{x^2}{4D_{\gamma_b} t^{\gamma_b}} \, \middle| \, \begin{matrix} \left(1 - \frac{\gamma_b}{2} + l + (\gamma_a - \gamma_b)(m-1), \gamma_b \right) \left(1 - \frac{\gamma_b}{2} - \gamma_b + \gamma_a - \gamma_b m, \gamma_b \right) \\ (0,1) \left(\frac{1}{2}, 1 \right) \left(l + 1 - \frac{\gamma_b}{2} - \gamma_b + \gamma_a - \gamma_b m, \gamma_b \right) \end{matrix} \right] \right\}. \quad (44)$$

The solution reduces to the solution in Eq. (33) when $\gamma_a = \gamma_b = \gamma$ and $D_{\gamma_a} = D_{\gamma_a} = D_\gamma$.

We have compared the above solutions with Monte Carlo simulations in Fig. 3 and we find excellent agreement except in the short time behaviour of species B ($t = 0.1$). Again this may be due to the approximate delta function initial conditions that we used in the simulations, as Eq. (44) matches the simulations extraordinarily well at later times. However it is also possible that Eq. (44) has the same long-time asymptotic behaviour as the correct solution, but the short-time behaviour is not correct.
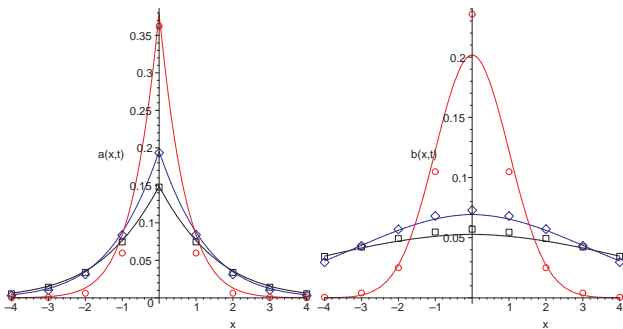

FIG. 3: (Color online) Comparison of the Green's function solution (solid lines) and the Monte Carlo simulations (symbols) for the two-species irreversible reaction (Eqs. (32) and (44)) at the times $t = 0.1$ (red $\circ$), $t = 1.0$ (blue $\diamond$), and $t = 2.0$ (black $\square$) with the parameters $k = 0.1$, $\tau = 0.1$, $\gamma_a = 0.5$, and $\gamma_b = 1$. The Monte Carlo results were obtained from an ensemble average over 50 simulations.

VI. SUMMARY AND DISCUSSION

In this paper we have considered a general multi-species system undergoing anomalous subdiffusion with linear reaction dynamics. Starting from a mesoscopic CTRW model formulation with the same waiting-time and jump-length densities for each species we have derived a system of fractional reaction-diffusion equations for linear reactions described by a general reaction coefficient matrix. The resulting system of equations in vector form is similar to the analogous single particle case [25] but with a matrix exponential replacing the exponential in the modified fractional derivative temporal operator. This work extends the one and two particle results of [25, 32, 33] to the n particle case.

One of the consequences of anomalous subdiffusion on the form of the fractional equations is that reaction term and diffusion terms are no longer independent but are instead coupled as in the single species case. Further, due to the presence of the matrix exponential the governing equation for one species may involve diffusive contributions from other species. This differs from the work of [34, 35] where the diffusive contributions are restricted to the one species. The reason behind the extra diffusive terms, as mentioned in [33], is linked to the non-Markovian nature of anomalous subdiffusion. In essence, the newly created particles remember the diffusive behaviour of their reactant ancestors because of the waiting-time probability density function. The coupling of concentrations in the mean-field reaction equations then results in the additional diffusive contributions due to other species. However, no extra contributions will arise if there is no coupling to the other species.

We assessed the validity of our fractional reaction-diffusion equations by comparing solutions with Monte Carlo simulations and we found excellent agreement for the cases tested except at very short times. We also investigated the possibility of different waiting-time densities for different species. Here the CTRW formulation could not be reduced to a system of fractional reaction-diffusion equations except in certain special cases. We carried out Monte Carlo simulations and found that the concentrations of species with different waiting-time densities could be represented as a linear combination of the Green's functions of the relevant fractional subdiffusion equations.

The results of this paper provide a useful platform for developing robust models for multi-species systems undergoing anomalous subdiffusion with nonlinear reactions. In the case of linear reaction dynamics it was shown that the formulation of the appropriate fractional reaction-diffusion equations requires careful consideration of the reaction dynamics and how they effect diffusive contributions for a given species. We expect that these considerations will be even more delicate with nonlinear reactions. With the numbers of reports of biological systems displaying anomalous subdiffusion rapidly increasing, this remains an important area for future research.

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APPENDIX: MONTE CARLO SIMULATIONS

The Monte Carlo simulations were conducted on a one-dimensional discrete grid with periodic boundaries where the particles performed jumps to their nearest neighbours in an unbiased manner after waiting a random amount of time.

For our purposes, we used the Pareto law used by [28]

$$\psi\left(t\right) = \frac{\gamma/\tau}{\left(1 + t/\tau\right)^{1+\gamma}} \qquad (A.1)$$

to generate the random waiting-times. The parameters γ and τ are the anomalous exponent and the characteristic time respectively. This probability density function was chosen for ease of calculation and because it has the required long-time asymptotic scaling

$$\psi\left(t\right) \sim \frac{\gamma}{\tau}\left(\frac{t}{\tau}\right)^{-1-\gamma} \qquad (A.2)$$

needed by the CTRW theory.

For comparison of analytic and Monte Carlo simulations we require an estimate of the diffusion coefficient. Using the appropriate jump-length density for nearest-neighbour jumps and the waiting-time density, Eq. (A.1), it can be shown that the diffusion coefficient is given by

$$D_\gamma = \frac{\Delta x^2}{2\tau^\gamma \Gamma\left(1 - \gamma\right)} \qquad (A.3)$$

where Δx is the grid-spacing. Note, in the case of the Mittag-Leffler density [39], or when $\gamma = 1$, the term $\Gamma\left(1 - \gamma\right)$ does not appear in this expression. We note a method for evaluating Mittag-Leffler distributed deviates using two uniform random numbers is available in [42, 43] but was not used in this paper.

In general, the outline of the simulation process is given in the following. Each simulation run begins with assigning the initial position for every particle and their corresponding jump-times. Initially the jump times are simply the random times generated using Eq. (A.1) as described in [44].

After the initial set-up, the simulation then cycles through the following steps. First the particle with minimum jump-time is found and the elapsed time, T, since the last jump is evaluated. The reaction probability for both species is then evaluated. For example, in the reversible reaction simulation runs, the reaction probability is $(1 - \exp(-k_1 T))$ for species A and $(1 - \exp(-k_2 T))$ for species B. Analogous probabilities for the irreversible reaction case are found for both species by setting $k_1 = k$ and $k_2 = 0$. Every particle of each species is then tested for deletion by comparing a random number against the relevant reaction probability. If the test for particle deletion is successful, then the particle in question is deleted. A corresponding particle of the other species is created to replace the deleted particle at the same grid point. If the jumping particle is not deleted, then the particle is moved one lattice site to the left or right (a jump) and a new jump-time for the particle is obtained by adding a random waiting-time to the jumping particle's current jump-time. The process then repeats through the previous steps until the total time for the simulation run is exceeded.

Output is saved at regular time intervals of the simulation run and used to average over a number of simulation runs.

For each figure in this paper, unless otherwise stated, simulation runs began with 100,000 particles of type A and of type B released from the origin to mimic a delta function initial condition. The characteristic time of the waiting-time density, $\psi(t)$, were set to $\tau = 0.1$ and the exponent, $\gamma = 0.5$. The results given were averaged over 50 simulation runs.