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Upscaling chemical reactions in multicontinuum systems: When might time fractional equations work?

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A R T I C L E   I N F O

A B S T R A C T

It may often be tempting to take a fractional diffusion equation and simply create a fractional reaction-diffusion equation by including an additional reaction term of the same form as one would include for a standard Fickian system. However, in real systems, fractional diffusion equations typically arise due to complexity and heterogeneity at some unresolved scales. Thus, while transport of a conserved scalar may upscale naturally to a fractional diffusion equation, there is no guarantee that the upscaling procedure in the presence of reactions will also result in a fractional diffusion equation with such a *naive* reaction term added. Here we consider a multicontinuum mobile-immobile system and demonstrate that an effective transport equation for a conserved scalar can be written that is similar to a diffusion equation but with an additional term that convolves a memory function and the time derivative term. When this memory function is a power law, this equation is a time fractional dispersion equation. Including a first-order reaction in the same system, we demonstrate that the effective equation in the presence of reaction is no longer of the same time fractional form. The presence of reaction modifies the nature of the memory function, tempering it at a rate associated with the reaction. Additionally, to arrive at a consistent effective equation the memory function must also act on the reaction term in the upscaled equation. For the case of a bimolecular mixing driven reaction, the process is more complicated and the resulting memory function is no longer stationary in time or homogenous in space. This reflects the fact that memory does not just act on the evolution of the reactant, but also depends strongly on the spatio-temporal evolution and history of the other reactant. The state of mixing in all locations and all times is needed to accurately represent the evolution of reactants. Due to this it seems impossible to write a single effective transport equation in terms of a single effective concentration without having to invoke some approximation, analogous to a closure problem. For both reactive systems simply including a *naive* reactive term in a fractional diffusion equation results in predictions of concentrations that can be orders of magnitude different from what they should be. We demonstrate and verify this through numerical simulations. Thus, we highlight caution is needed in proposing and developing fractional reaction-diffusion equations that are consistent with the system of interest.

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1. Introduction

Anomalous transport, that is, transport where dispersion, as characterized by the spreading of a second centered moment, does not display a scaling consistent with Fickian behavior, has been observed in so many settings that *Eliazar & Klafter* were motivated to write a paper entitled '*Anomalous is Ubiquitous*' [1]. Physical systems where anomalous transport has been observed include electron transport in semiconductors [2,3], flow and transport in porous media [4–6], streams and rivers [7–9], fractured media [10,11], turbulence [12,13], biofilms [14], gels [15] and plasmas [16]; optical media [17]; sediment transport [18–20]; surficial earth processes [21,22]; biology [23,24]; ecology [25,26]; economics [27,28] and many many more. The common thread across all of these systems is that some initial distribution of a scalar within (e.g., tracer concentration in turbulent flow) spreads at sub- or super-diffusive rates, leading to fundamentally different distributions displaying features such as heavy tailing, which are unexpected with conventional Fickian models. These disparities typically occur due to very broad distributions and separation of spatial or temporal scales that arise due to structural complexities associated with the systems of interest (e.g. imperfections in semiconductors, hierarchical structure of eddies in turbulence and

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naturally occurring geologic heterogeneities that give rise to broad distribution of permeabilities in porous media).

The literature on anomalous transport is vast and many different approaches to modeling anomalous behaviors have emerged, including, but in no way limited to, continuous time random walks [29,30], multicontinuum models [31,32], projector formalisms [33,34], Markov chain random walks [4,6,35–38] and fractional dispersion models [5,39,40]. Most of these frameworks share commonalities, are different mathematical conceptualizations of the same problem, or are limit cases of one another. In this paper, we will focus on a form of fractional transport equations, whose application spans many of the aforementioned physical systems (e.g. [24,41–44]), namely a specific form of time fractional dispersion equation [45] that can be rigorously derived as the equation for effective transport for a specific and important microscale model system.

The bulk of work to date has focused on modeling the transport of conserved scalar quantities. However, in almost all of the physical systems mentioned above, chemical reactions or reactive-like processes are also important. These reactions may either be (i) single species or (ii) multispecies interaction-based reactions. For example, in the context of transport through highly heterogeneous porous media (i) degradation reactions are commonly modeled as first-order reactions (e.g. [46]) and (ii) mixing-driven multispecies reactions can occur at the interfaces between two geochemically distinct waters [47–50]. Similar applications of interest occur in cell biology (e.g. [51–53]) and economics (e.g. [54,55]). However, given that any observed anomalous transport typically occurs due to complexity and heterogeneity at some unresolved scale, it is not immediately clear how one should include chemical reactions in anomalous transport models, or at least so we argue here.

In Fickian transport systems it is common to model chemical reactions by simply adding a reaction term r to the governing equation for transport, i.e.

$$\frac{\partial C_i}{\partial t} - D\frac{\partial^2 C_i}{\partial x^2} = -r, \tag{1}$$

where C is concentration and D a dispersion coefficient. For a first-order reaction $i = 1$ and $r = \lambda C_1$ or for a second-order mixing drive reaction $i = 1, 2$ and $r = kC_1C_2$. In this paper we will work with a time-fractional dispersion equation, which was the focus of the work of [45]. For transport of a conserved scalar the governing equation is

$$\frac{\partial C_i}{\partial t} + \beta\frac{\partial^\gamma C_i}{\partial t^\gamma} - D\frac{\partial^2 C_i}{\partial x^2} = 0, \tag{2}$$

where β—the so-called capacity coefficient—is a measure of the ratio of immobile to mobile mass at any moment, and $0 < \gamma < 1$ if the exponent of the fractional time derivative. Thus, given (1) and (2) it may be tempting to look at these equations and simply propose an equation of the exact same form, namely

$$\frac{\partial C_i}{\partial t} + \beta\frac{\partial^\gamma C_i}{\partial t^\gamma} - D\frac{\partial^2 C_i}{\partial x^2} = -r \tag{3}$$

where r takes the exact same form as above. We refer to this as the *naive* approach. Indeed, in the broad and general context of fractional dispersion equations, not only limited to the specific structure of (2), many authors, including us, have done precisely this (e.g. [56–59]). Here we challenge this idea and pose whether it really makes sense to do so at all. It is already known in the literature that in certain instances just plugging in a reaction term r in the same format as for a diffusion equation is not only a bad idea, but can actually lead to unphysical results [60], including predictions of negative concentrations in the context of time-fractional diffusion-reaction equations. In the context of fractional dispersion equations [61] developed a consistent manner of incorporating first order chemical reactions, while in the context of a continuous time

random walk [62] demonstrated how to include mixing driven bimolecular reactions. While such progress is invaluable, open questions still remain. For example, is the upscaled equation unique? Surely different microscale configurations can result in identical upscaled frameworks for conservative transport, but not for reactive systems. Also, some nonlocal model derivations, including that of [62], require an assumption of perfect mixing at a certain scale and without a rigorous upscaling it is not clear if and when such an assumption might be valid. Here we add to this discussion in the goal of ultimately developing more correct and accurate effective anomalous reactive transport models. In particular, we will focus on a physical problem setup where the time-fractional dispersion equation emerges very naturally as the governing equation for the evolution of total concentration for a conservative species [45]. By working within the same framework we then try to derive the appropriate reactive transport equation to see if it still emerges as a fractional dispersion equation with a simple additional r term to represent reactions. Note that for the sake of simplicity we have not included a drift (advection) term in any of the above transport equations, but it is relatively straightforward and does not change the fundamental message we wish to convey here.

2. A system where a time fractional dispersion equation for conservative transport emerges naturally

2.1. Theory - infinite parallel multicontinuum with power law memory

One very natural and practically important way of obtaining a fractional dispersion equation for transport of total concentration was developed by [45] who then applied it to model two distinct hydrologic systems: transport in highly heterogeneous porous media and transport in a mountain stream. By mixing their formalism with some of the ideas developed in [63], we can readily derive a time-fractional dispersion equation from first principles to describe the concentration evolution of a conservative tracer. To begin, consider a multicontinuum system made up of one mobile and a continuum of immobile regions that can exchange mass with the mobile region. Transport of the mobile and immobile components are governed by

$$\frac{\partial C_m}{\partial t} - D\frac{\partial^2 C_m}{\partial x^2} = -\beta\int f(\alpha)\alpha(C_m - C_{im}(\alpha))d\alpha \tag{4}$$

$$\frac{\partial C_{im}(\alpha)}{\partial t} = \alpha(C_m - C_{im}(\alpha)) \quad \forall\alpha \quad 0 \leq \alpha \leq \infty \tag{5}$$

where the density function $f(\alpha)$ describes the volume fraction of immobile regions associated with exchange rate α, and β is the ratio of immobile to mobile volume. C_m is the concentration associated with the mobile phase and $C_{im}(\alpha)$ is the immobile concentration associated with exchange rate α. Without loss of generality here we set $\beta = 1$. Note that in (5) we have also neglected the presence of any advection, which could be present in many real systems. While these are important effects that can influence the exact final outcome, neither of these assumptions affects the central messages of this paper and so for the sake of simplicity we do not consider them as they merely add length, but not content, to the mathematics. Additionally, replicating conditions associated with typical experiments (e.g. [9]), for all situations we consider the initial concentration in the immobile regions to be zero; i.e., $C_{im}(\alpha, t = 0) = 0$. Thus (5) can readily be solved such that

$$C_{im}(\alpha) = \alpha C_m * e^{-\alpha t}, \tag{6}$$

where $*$ represents convolution in time. Taking the time derivative of this and defining the total immobile concentration

$C_{IM} = \int f(\alpha) C_{im}(\alpha) d\alpha$ we can write

$$\frac{\partial C_{IM}}{\partial t} = \int f(\alpha) \frac{\partial C_{im}(\alpha)}{\partial t} d\alpha = g(t) * \frac{\partial C_m}{\partial t} + g(t) C_{m,0} \qquad (7)$$

where $g(t) = \int \alpha f(\alpha) e^{-\alpha t} d\alpha$ is known as the memory function. Combining (4) and (5) we can write

$$\frac{\partial C_m}{\partial t} + g(t) * \frac{\partial C_m}{\partial t} - D \frac{\partial^2 C_m}{\partial x^2} = -g(t) C_{m,0}. \qquad (8)$$

Except for some requirements on the form of $g(t)$, such as monotone decreasing [64], this is a very general formulation. However, by choosing a specific distribution of exchange rates, such that $g(t) = \frac{t^{-\gamma}}{\Gamma(1-\gamma)}$, the second term above is a Caputo fractional derivative and (8) may be written as

$$\frac{\partial C_m}{\partial t} + \frac{\partial^\gamma C_m}{\partial t^\gamma} - D \frac{\partial^2 C_m}{\partial x^2} = -\frac{t^{-\gamma}}{\Gamma(1-\gamma)} C_{m,0}. \qquad (9)$$

Using (7), we can solve for C_m and $\frac{\partial C_m}{\partial t}$ in terms of C_{IM}; combining with (4) and (5) we can also write an equation for the transport of immobile concentration such that

$$\frac{\partial C_{IM}}{\partial t} + \frac{\partial^\gamma C_{IM}}{\partial t^\gamma} - D \frac{\partial^2 C_{IM}}{\partial x^2} = \frac{t^{-\gamma}}{\Gamma(1-\gamma)} C_{m,0}. \qquad (10)$$

Defining total concentration $C_{tot} = C_m + C_{IM}$ and noting that based on our chosen initial condition for immobile concentration $C_{tot}(t = 0) = C_m(t = 0)$, transport for total concentration is governed by

$$\frac{\partial C_{tot}}{\partial t} + \frac{\partial^\gamma C_{tot}}{\partial t^\gamma} - D \frac{\partial^2 C_{tot}}{\partial x^2} = 0. \qquad (11)$$

Thus we have a system where a time fractional dispersion equation emerges naturally as the equation describing transport of a solute in this complex system. This equation, and related, has had great success in replicating observed anomalous transport in diverse systems including subsurface [45] and surface hydrology [65] and surface processes in the earth sciences [41] among many others.

2.2. Numerical example

As an example to visually highlight the rigorous link between Eqs. (4) and (5) and Eq. (11) we present some sample results by solving the two distinct systems numerically. While the theoretical link is rigorous as shown, we develop this numerical capability mainly for later comparison of the systems with chemical reactions. In all cases we consider a finite domain $-5 \leq x \leq 5$ with no flux boundary conditions at $x = -5$ and $x = 5$. For all examples we set $D = 1$. Eqs. (4) and (5) are solved via finite differences with backward differences in time and central differences in space. The continuous density $f(\alpha)$ is approximated by a discrete counterpart following the methods of [66,67] and [68], who in the context of conservative and reactive multicontinuum transport models demonstrated how to generate power-law memory functions over any desired range as the sum of a large number of discrete exponential ones. While they showed that using as few as 20 discrete states was sufficient to obtain excellent results, we chose to use 100 as we found that with this value our results converged for all problems and remained unchanged if we included more (tested against 10^3 and 10^4). By using a finite number, this means that the memory function has some maximum truncation time, which was chosen to be 6 orders of magnitude larger than the largest time scales simulated, meaning that over the time scales of simulation the truncation should play no role. Eq. (11) is also solved by finite differences with the time derivative and diffusion term solved as above. The fractional derivative term is numerically approximated following the finite difference approximations presented by [69].

Fig. 1 shows a comparison of the solution for total concentration obtained by both approaches. Two different initial conditions
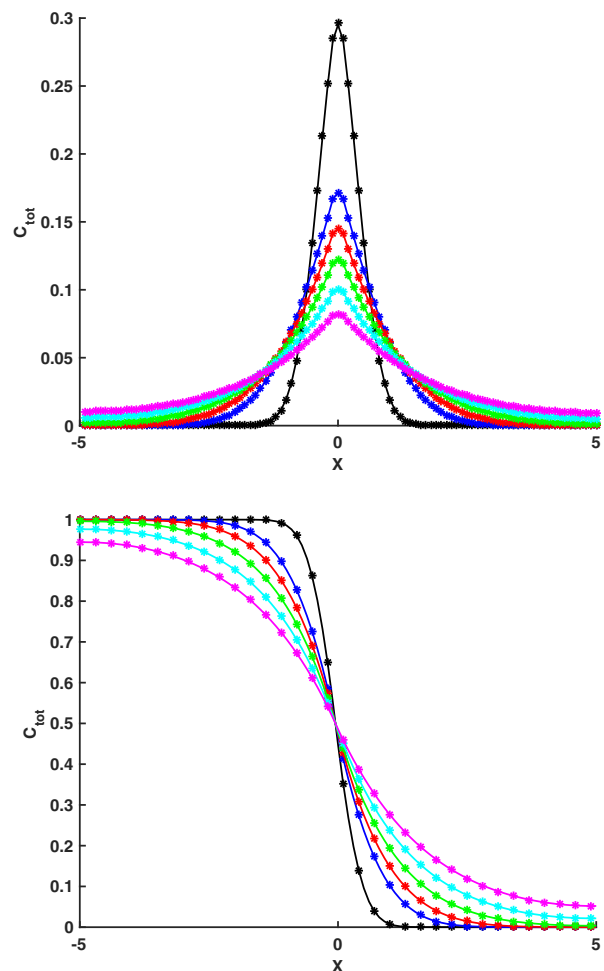

Fig. 1. Numerical Solutions for Conservative Transport corresponding to a narrow pulse (top) and step (bottom) initial condition. The solid lines correspond to the solution of the full system as described in Eqs. (4) and (5) and the dots to the solution of the upscaled fractional dispersion Eq. (11). The different colors correspond to different times $t = 0.1$ (black), 0.5 (blue), 1 (red), 2.5 (green), 10 (cyan) and 50 (magenta). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

are considered, which were chosen as they best highlight some of the features that will be important for the reactive system examples in the following sections. These are a step initial condition where half the domain is filled unit concentration (i.e. $C(x, t = 0) = 1 - \Theta(x)$) and a narrow unit concentration pulse in the center of the domain (i.e. $C(x, t = 0) = \Theta(x + 0.1) - \Theta(x - 0.1)$), where $\Theta(x)$ is the Heaviside step function. In both cases we show results for $\gamma = 0.25$, which will be used in all subsequent examples. Various other values of γ were tested with similar outcomes and this value was chosen as it lies in the heavier tail range enabling certain results to be highlighted visually in a more clear manner. As is clear from the figure, for both initial conditions, the predictions by both models are virtually identical as one would expect given the rigorous link between the two, suggesting our numerical approach is robust.

3. First order reactions

3.1. A naive approach to including first order reactions and why it is wrong

As noted in the introduction, now that we have a governing equation for total concentration like (11), it may be tempting to

simply write that the reactive counterpart for a first-order reaction for this system would be

$$\frac{\partial C_{tot}}{\partial t} + \frac{\partial^\gamma C_{tot}}{\partial t^\gamma} - D\frac{\partial^2 C_{tot}}{\partial x^2} = -\lambda C_{tot}. \tag{12}$$

Before deriving a consistent equation for the total concentration, following the methods in Section 2, let us point out an important potential physical problem with the model in (12). If the system is truly representing a first-order reaction, where concentration degrades at rate λ in all compartments of the multicontinuum, then if we inject a unit of mass into the system, the total mass in the system must decay exponentially at rate λ irrespective of where that mass is located. Integrating (12) over all space, assuming natural boundary conditions at $x = \pm\infty$ or no flux boundary conditions for a finite domain, we can write

$$\frac{\partial M}{\partial t} + \frac{\partial^\gamma M}{\partial t^\gamma} = -\lambda M \qquad M(t=0) = 1 \tag{13}$$

where $M = \int_{-\infty}^{\infty} C_{tot}dx$. Laplace transforming ($t \to s$) we can write a solution

$$\tilde{M} = \frac{1 + s^{\gamma-1}}{s + \lambda + s^\gamma} \neq \frac{1}{s + \lambda}, \tag{14}$$

where the tilde denotes a Laplace transformed variable. Eq. (14) is clearly not the correct exponential decay at rate λ, suggesting that (12) is not a physically consistent equation. In fact, for small s, corresponding to large times, to leading order $\tilde{M} \sim s^{\gamma-1}$, which means that at late time the total mass will decay as a power law in time with scaling $M(t) \sim t^{-\gamma}$, much slower than the expected exponential decay.

3.2. Correct effective equation for total concentration from first principles

Following all the steps for conservative transport in Section 2, we start by writing transport equations for mobile and immobile concentrations assuming a first-order reaction of rate λ in all compartments of the multicontinuum such that

$$\frac{\partial C_m}{\partial t} - D\frac{\partial^2 C_m}{\partial x^2} = -\int f(\alpha)\alpha(C_m - C_{im}(\alpha))d\alpha - \lambda C_m \tag{15}$$

$$\frac{\partial C_{im}(\alpha)}{\partial t} = \alpha(C_m - C_{im}(\alpha)) - \lambda C_{im}(\alpha) \quad \forall \alpha \quad 0 < \alpha < \infty. \tag{16}$$

Solving (16) we can relate immobile and mobile concentrations:

$$\frac{\partial C_{IM}}{\partial t} = \int f(\alpha)\left(\alpha\frac{\partial C_m}{\partial t} * e^{-(\alpha+\lambda)t} + \alpha C_{m,0}e^{-(\alpha+\lambda)t}\right)d\alpha$$

$$= \hat{g}(t) * \frac{\partial C_m}{\partial t} + \hat{g}(t)C_{m,0}, \tag{17}$$

where $\hat{g}(t) = g(t)e^{-\lambda t}$ is now a modified memory function. Combining (15) and (16) and solving for C_m:

$$\frac{\partial C_m}{\partial t} + \hat{g}(t) * \frac{\partial C_m}{\partial t} - D\frac{\partial^2 C_m}{\partial x^2} = -\lambda(C_m + \hat{g}(t) * C_m) - \hat{g}(t)C_{m,0}. \tag{18}$$

As before we can write an equation for the transport of the immobile concentration by solving for C_m in (17) and substituting into (18)

$$\frac{\partial C_{IM}}{\partial t} + \hat{g}(t) * \frac{\partial C_{IM}}{\partial t} - D\frac{\partial^2 C_{IM}}{\partial x^2} = -\lambda(C_{IM} + \hat{g}(t) * C_{IM}) + \hat{g}(t)C_{m,0}. \tag{19}$$

With this, the governing equation for total concentration is

$$\frac{\partial C_{tot}}{\partial t} + \hat{g}(t) * \frac{\partial C_{tot}}{\partial t} - D\frac{\partial^2 C_{tot}}{\partial x^2} = -\lambda(C_{tot} + \hat{g}(t) * C_{tot}). \tag{20}$$

This looks very similar to the time fractional dispersion equation for conservative transport in (11), but a careful look reveals that this not entirely the case. First, the modified memory function $\hat{g}(t)$ is not the conservative memory function $g(t)$, which is what gave rise to the fractional derivative. Rather it is $g(t)e^{-\lambda t}$, which merges a power law and a tempering effect. Physically, this effect arises because after a sufficiently long time, particles are more likely to have reacted than remain trapped in an immobile phase and so will not be released back into the mobile region. Another important feature that is worth noting is that the reactive term on the right hand side is not the *naive* term, discussed in Section 3.1, but a more complicated expression that also includes the new modified memory function. Because it acts on the concentration and not the time derivative of concentration, this is more like a fractional integral than a fractional derivative, although again the exponential tempering must be noted. Now integrating (20) in space and assuming an initial unit mass we can write an equation for total mass, which in Laplace space reads

$$s\tilde{M} - 1 + \tilde{\hat{g}}(s\tilde{M} - 1) = -\lambda(\tilde{M} + \tilde{\hat{g}}\tilde{M}) \Rightarrow \tilde{M} = \frac{1 + \tilde{\hat{g}}}{(s + \tilde{\hat{g}}s + \lambda + \lambda\tilde{\hat{g}})}$$

$$= \frac{1}{s + \lambda} \Rightarrow M(t) = e^{-\lambda t} \tag{21}$$

which is the correct exponential decay that we expect to occur and is consistent with the first order reaction system we proposed.

3.3. Numerical comparison

Using the same numerical methods as described for the conservative transport case, here we present numerical results for a first-order reaction problem. We chose the second initial condition setup, a unit concentration block in the center of the domain (i.e. $C(x, t = 0) = \Theta(x + 0.1) - \Theta(x - 0.1)$) as this best highlights certain features. Three different reaction rates $\lambda = 0.1, 1$, and 10 are chosen. For this comparison we solve three model systems: (i) Eqs. (15) and (16), which represent the full multicontinuum system, (ii) (12), which we argue is the *naive* and incorrect approach to including chemical reactions in this system and (iii) (20), which we argue should be the correct upscaled representation of case (i).

Representative concentration profiles for multiple different reaction rates and at two distinct times are shown in Fig. 2. In all cases except for the very smallest reaction rate at the smallest time, it is abundantly clear that the concentrations predicted with the *naive* approach in (12) do not match those of the full multicontinuum system, while the consistently derived Eq. (20) matches well everywhere. For the largest reaction rate at the largest considered time the mismatch in concentration is on the order of 40 orders of magnitude. It is unsurprising that all three models match reasonably well for the smallest reaction rate at the smallest time, because at that point very little reaction will actually have occurred and transport is still close to conservative and so this agreement needs to be taken with a grain of salt. Fig. 3 shows plots of total mass against time. In these, the mismatches and agreements stand out even more clearly. In particular, in the right-hand figure where mass against time is shown a logarithmic scales, it is immediately clear that for systems (i) and (iii) the total decay in mass is exponential as we had predicted, while for *naive* model (ii) a late time scaling of $t^{-1/4}$, consistent with (14), emerges.

4. Bimolecular reactions

The previous example of a first-order reaction already highlighted significant complications in simply extending fractional transport equations from conservative to reactive transport problems. While we were able to derive a consistent reactive transport
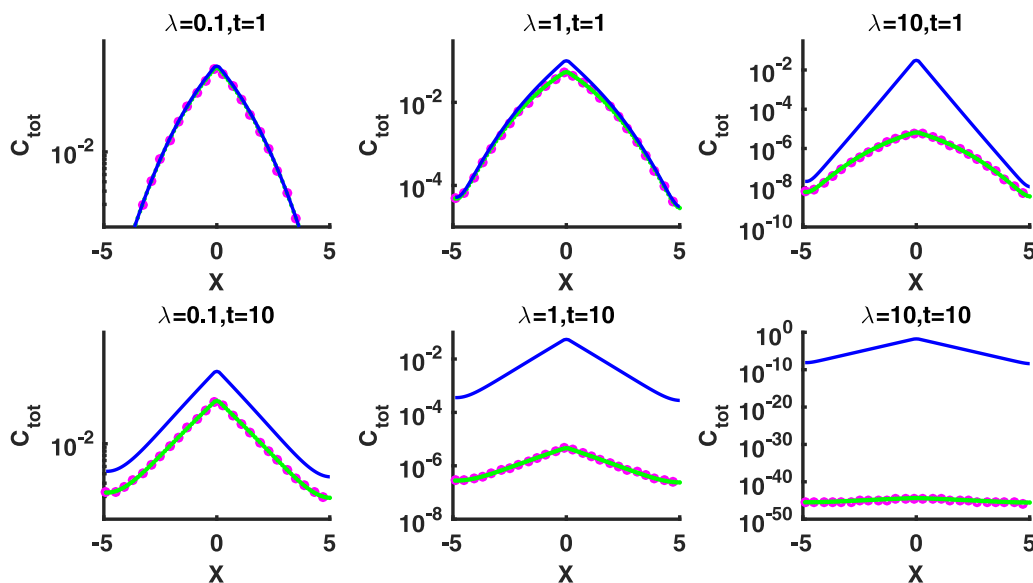
Fig. 2. Numerical Solutions for a first-order reaction with a pulse initial condition. Concentration profiles at two different times $t = 1$ and 10 are shown in the top and bottom rows respectively. Three different rates of reaction $\lambda = 0.1$, 1 and 10 are considered also. The magenta circular dots correspond to the solution of the full system as describe in Eqs. (15) and (16). The blue lines are associated with solving the *naive* incorrect approach equation in (12), while the green line corresponds to the numerical solution of the consistently upscaled Eq. (20). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
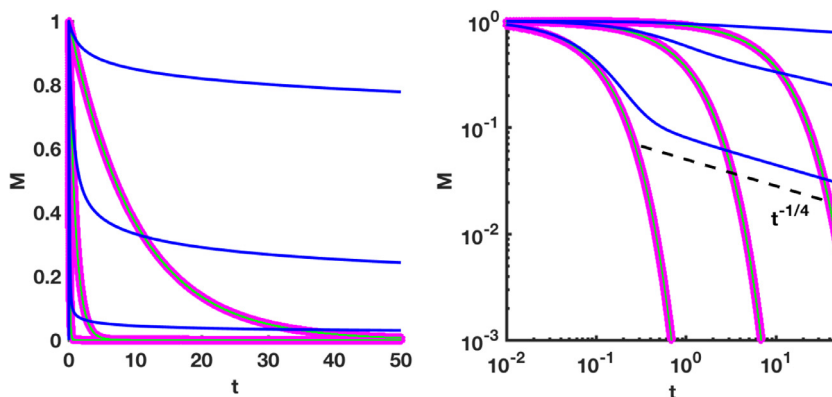
Fig. 3. The evolution of total mass over time for a first-order reaction with the pulse initial condition. (11). The magenta circular dots correspond to the solution of the full system as described in Eqs. (15) and (16). The blue lines is associated with solving the *naive* incorrect approach equation in (12), while the green line corresponds to the numerical solution of the consistently upscaled Eq. (20). The figure on the right is the same as the one on the left, but with logarithmic axes to highlight the late asymptotic time power law scaling of the red lines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

equation and see commonalities with the conservative problem, that system was remarkably simple, given that a first-order reaction system is still linear and so benefits from superposition. In this section, we attempt to extend the approach to a more complex, but important and fundamental reaction: a kinetic irreversible bimolecular reaction $A + B \to C$. We do this to further highlight that great caution must be taken when extending ideas from conservative transport to reactive scenarios. Consider transport equations for species A and B in mobile and immobile regions such that

$$\frac{\partial C_{m,i}}{\partial t} - D\frac{\partial^2 C_{m,i}}{\partial x^2} = -\int f(\alpha)\alpha(C_{m,i} - C_{im,i}(\alpha))d\alpha - kC_{m,A}C_{m,B}$$
$$i = A, B \tag{22}$$

$$\frac{\partial C_{im,i}(\alpha)}{\partial t} = \alpha(C_{m,i} - C_{im,i}(\alpha)) - kC_{im,A}(\alpha)C_{im,B}(\alpha) \quad \forall \alpha$$
$$0 < \alpha < \infty \tag{23}$$

where k is the rate of reaction and the term kC_AC_B represents the rate of reaction following the law of mass action. To proceed as in the previous examples we need a solution for (23), which can

formally be obtained. For example, for $i = A$

$$C_{im,A}(\alpha) = \left(\int \alpha C_{m,A}\exp\left[\int kC_{im,B}(\alpha) + \alpha dt\right]dt\right)$$
$$\times \exp\left[-\int kC_{im,B}(\alpha) + \alpha dt\right]$$
$$= \alpha C_{m,A} * e^{-\alpha t - \int kC_{im,B}(\alpha)dt} \tag{24}$$

but note the resultant expression is complicated and highly coupled to the time-varying concentration of the other species through the integral over time in the exponential term. It is complex and, in principle, requires unknown knowledge, given that the concentration of the other species B will have a very similar solution that depends on the time history of the concentration of species A in this same fashion. Nonetheless, for the sake at attempting completeness, let us continue as we did for the conservative and first-order reaction cases. Taking the time derivative of (24)

$$\frac{\partial C_{im,A}(\alpha)}{\partial t} = \alpha \frac{\partial C_{m,A}}{\partial t} * e^{-\alpha t - \int kC_{im,B}(\alpha)dt} + \alpha C_{m,A,0}e^{-\alpha t - \int kC_{im,B}(\alpha)dt}.$$
$$\tag{25}$$

Multiplying this by $f(\alpha)$ and integrating results in

$$\frac{\partial C_{IM,A}}{\partial t} = \breve{g}(x,t) * \frac{\partial C_{m,A}}{\partial t} + \breve{g}(x,t)C_{m,A,0}. \tag{26}$$

This resembles the solutions for the conservative and first-order reaction systems, but like the first-order reaction system a new modified memory function $\breve{g}(x,t) = \int \alpha f(\alpha)e^{-\alpha t - \int kC_{im,B}(\alpha)dt}d\alpha$ emerges. However, this memory function is much more structurally complex than the previous cases. It depends explicitly on the evolution of the other reactant B throughout all of the immobile zones, which itself is governed by a similarly complicated expression. Recall, the memory function arises in these systems, because of memory effects that integrate time history. Thus it makes sense that for a coupled reactive system, the time history of the other reactant matters also, yielding a function that now also depends on space, due to possible spatial variability of reactant B. In particular, unlike the previous linear examples, it is not unique and very dependent on the specific initial conditions of the problem, meaning that it is perhaps not usefully predictable. Similar complications for upscaling of bimolecular reactions via volume averaging have been noted by [70], who emphasize that for coupled reactive systems *initial condition is everything* [71]. It may be possible, using assumptions and approximations similar to [70], to simplify this memory function and obtain a reasonable approximation. Similarly a perturbation-type solution for small reaction rate, analogous to that in [72], may yield a more manageable and decoupled system and be reasonable for small reaction rates k. However, while possible, neither of these approaches is as universally satisfying as the conservative and first-order reaction case, as they are not exact and would require potentially strong and limiting assumptions (e.g., the approximate models can only be applied over a small and restrictive range of Damkohler or Peclet numbers), which limit applicability (e.g., [73]).

Also developing or proposing such a closure would distract from the central question here, which is whether an effective transport equation with the form of a fractional dispersion equation emerges naturally for this setup, as it did for conservative transport. To this end, recall that the fractional derivative in the transport equation for total concentration arises due to the structure of the memory function. While there may be a fractional-like structure hidden in the new modified memory function $\breve{g}(x,t)$, due to the tight coupling with the spatio-temporal evolution of the other reactant, there is also an additional exponential tempering that is non-homogenous in space and time. Combining (22), (23) and (25) yields

$$\frac{\partial C_m}{\partial t} + \breve{g}(x,t) * \frac{\partial C_m}{\partial t} - D\frac{\partial^2 C_m}{\partial x^2}$$
$$= -k\left(C_{m,A}C_{m,B} - \int f(\alpha)C_{im,A}(\alpha)C_{im,B}(\alpha)d\alpha\right) - \breve{g}(x,t)C_{m,0} \tag{27}$$

and unlike the previous cases it is much more difficult to write an equation for the immobile concentration. Following the procedure from the previous examples, solve for C_m in (26) and substitute into (27), which in Laplace space yields

$$s\tilde{C}_{IM} - \breve{g}(x,s)C_{m,0} + s\breve{g}(x,s)C_{IM} - D\breve{g}(x,s)\frac{\partial^2}{\partial x^2}\frac{\tilde{C}_{IM}}{\breve{g}(x,s)}$$
$$= -k\breve{g}(x,s)\left(\frac{\tilde{C}_{IM,A}}{\breve{g}(x,s)} * \frac{\tilde{C}_{IM,B}}{\breve{g}(x,s)} - \int f(\alpha)\tilde{C}_{im,A}(\alpha) * \tilde{C}_{im,B}(\alpha)d\alpha\right). \tag{28}$$

While one might be able to formally invert the above, one has to question what the utility of this would be and there are some important features to be highlighted. In the previous two cases it was critical to the derivation that the memory functions in the numerator and denominator in the diffusive term canceled out. Since the memory function now depends on space this can no longer be done as it cannot be pulled out of the Laplacian, resulting in a much messier system. Likewise the mobile reactive term, which is a product in real space becomes a convolution in Laplace space and it is not straightforward to get rid of the memory functions there either, or invert back into real space.

Writing the mobile concentration equation in Laplace space

$$s\tilde{C}_m - C_{m,0} + \breve{g}(x,s)(s\tilde{C}_m - C_{m,0}) - D\frac{\partial^2\tilde{C}_m}{\partial x^2}$$
$$= -k\breve{g}(x,s)\left(\tilde{C}_{m,A} * \tilde{C}_{m,B} - \int f(\alpha)\tilde{C}_{im,A}(\alpha) * C_{im,B}(\alpha)d\alpha\right)$$
$$- \breve{g}(x,s)C_{m,0}. \tag{29}$$

Following what we did for the conservative and first-order reactive systems, we would add Eqs. (29) and (28) to obtain a single equation in C_{tot}. Clearly there is no immediately reasonable way of adding these two equations together to yield a single transport equation in terms of C_{tot} alone, and certainly not one that is an obvious time-fractional dispersion equation for total concentration with a reaction term resembling the law of mass action. While perhaps frustrating that we cannot arrive at an elegant solution as we did for our other cases, this is nonetheless important as it highlights that the tightly coupled evolution of species A and B complicates writing an effective equation based on total concentration alone.

Essentially, the total concentration is not a good measure of actual concentrations taking place in the localized reactions. This is very similar to the complications associated with upscaling bimolecular reactions in advective-diffusive systems in the presence of incomplete mixing, an area of active research in many of the fields where anomalous transport models are also popular (e.g. [47,50,57,74–76]). While approximate solutions and improved closure models have enabled the development of improved predictive and numerical models (e.g. [77–79]) a single governing equation in terms of only average/total concentrations still does not, to our knowledge, exist.

Thus for this particular problem that we focus on here, writing a reactive transport equation in terms of only total concentration seems impossible without making some further assumptions or invoking something analogous to a closure argument (e.g. [70,77,78]), which could yield a reasonable approximation, but would still be an approximation, unlike the results derived for the conservative and first-order reactive systems.

4.1. The naive approach and numerical examples

While we have not been able to write a formal equation for the evolution of total concentration in a single equation that only depends on total concentrations, as we were able to in our previous two examples, it is still interesting to consider numerical solutions for the bimolecular reaction case and compare those to what would be obtained if one followed the *naive* approach and simply wrote

$$\frac{\partial C_{tot,i}}{\partial t} + \frac{\partial^\gamma C_{tot,i}}{\partial t^\gamma} - D\frac{\partial^2 C_{tot,i}}{\partial x^2} = -kC_{tot,A}C_{tot,B} \qquad i = A,B. \tag{30}$$

As noted in the introduction, such *naive* approaches, in the general context of anomalous transport models and for fractional dispersion equations, have been taken in the past and it is important to understand what the consequences of such an approach may be, as well as if it might ever be at least a reasonable approximation. Thus, using the same numerical methods as listed previously, we will solve (30) and compare this to the results of the full system, obtained by solving (22) and (23). We consider a step-like initial condition, where half of the domain is filled with unit concentration of A and the other half with unit concentration of B. We consider four reaction rates of $k = 0.1, 1, 10$ and 100.
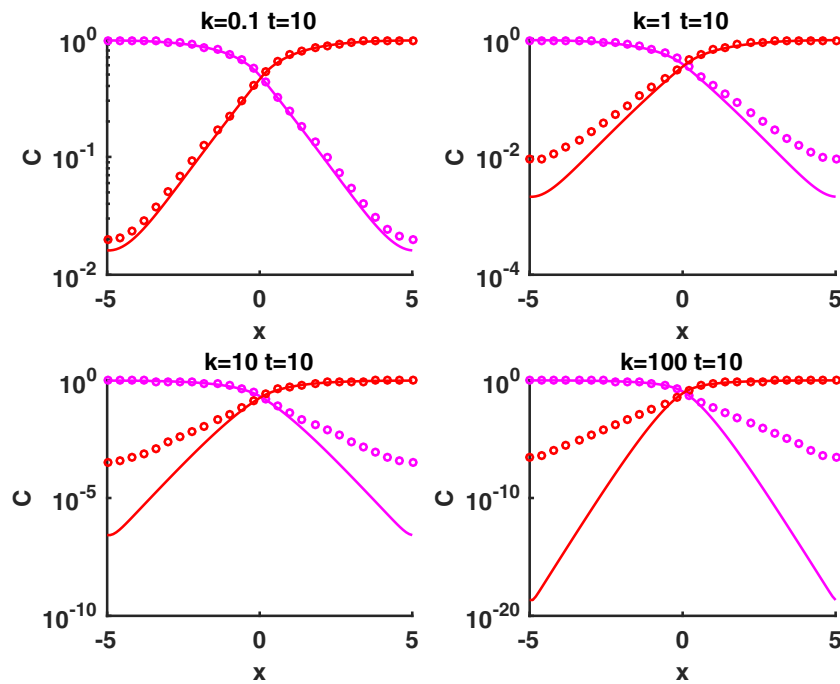
Fig. 4. Numerical solutions for the bimolecular reaction system. Concentration profiles at time $t = 10$ are shown for four different values of reaction rate $k = 0.1$, 1, 10 and 100. Magenta colors correspond to concentrations of species A, while red to species B. The circular dots correspond to the solution of the full multicontinuum set of Eqs. (22) and (23), while the solid lines correspond to the solution of *naive* Eq. (30). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Concentration profiles for the four cases at a single time $t = 10$ are shown in Fig. 4. In all four cases a similar trend is observed. The model built with *naive* equation (30) has much lower concentrations of the species invading into the other half of the domain than the concentrations calculated with the full multicontinuum formulation (i.e. concentration of species A in the right hand side of the domain). As the reaction rate becomes larger this disparity becomes more apparent with deviations in predicted concentrations as large as ten orders of magnitude for the highest reaction rate. Again, for the smallest reaction rate the differences between the two models look relatively minimal, but this is likely due to the limited amount of actual reaction that has actually happened, meaning that the behavior is still *close* to conservative.

Fig. 5 shows the evolution of total mass of the reactants over time for the two models and the results may be somewhat surprising relative to what was just discussed about the concentration profiles. The differences in total amount of mass predicted by the *naive* and full multicontinuum model look smallest for the highest reaction rate system. This is likely because even though concentration differences appear very large for the highest reaction rate system, the concentrations in these tail regions are small and negligible in terms of the total mass in the system and the bulk of reaction is happening at the interface between the two reactants focused around $x = 0$. Once solute passes into the other half of the domain due to dispersion, its likelihood of reaction is very high and so concentrations there are very low. Indeed for the case of infinitely fast chemical reactions for this particular setup, it can be shown that the *naive* and full multicontinuum equation approach are analogous (see Appendix A). This is likely not universally true and initial condition specific. For example, the inclusion of a drift with the exact same initial condition would break the requirements. Additionally in the limit of $k \to \infty$ the entire problem can be recast in terms of solutions to conservative transport equations, for which the connection between the fractional dispersion equation and multicontinuum model have been shown to be rigorous. In Appendix A we explain these details and highlight conditions

that must hold, which again appears to be initial condition and problem specific and thus likely not universal.

5. General discussion - a generic reactive system

The previous examples have already yielded some interesting insights into limitations of extending fractional transport equations for conservative transport to a reactive counterpart, but we have focused on some important, but specific examples. For the sake of a more general discussion, let us consider a generic reactive system, where reactions occur in mobile and immobile parts of the domain. We follow the same procedure as above with the hope of getting an effective equation for transport of total concentration. We denote the reaction in the mobile zone as r_m and $r_{im}(\alpha)$ as that associated with the immobile region with exchange rate α. Given the local nature of reactions, these are assumed to only depend on concentrations in that same zone; i.e. $r_m(C_m)$ and $r_{im}(\alpha, C_{im}(\alpha))$, but their form remains unspecified. Now the governing equations for mobile and immobile concentration are

$$\frac{\partial C_m}{\partial t} - D\frac{\partial^2 C_m}{\partial x^2} = -\int f(\alpha)\alpha(C_m - C_{im}(\alpha))d\alpha - r_m \qquad (31)$$
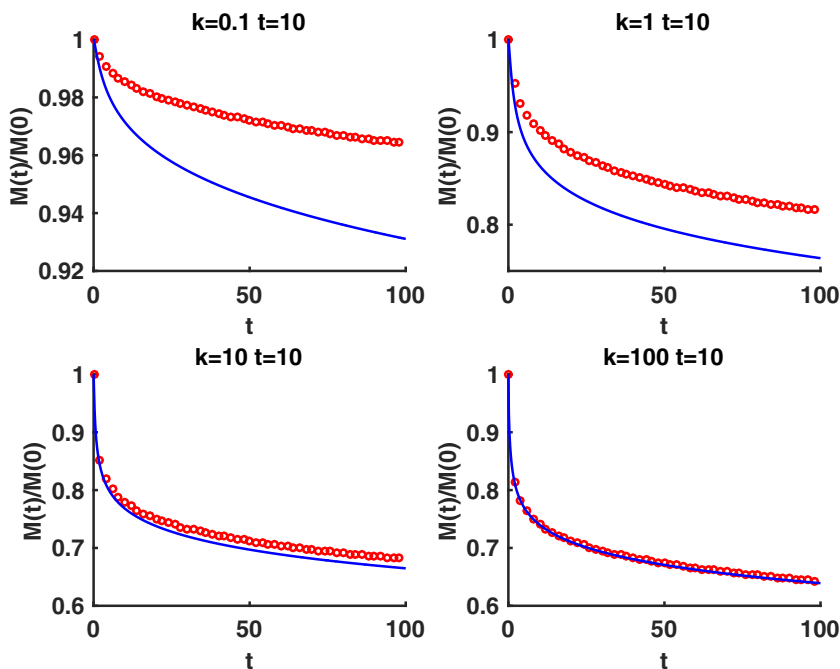
$$\frac{\partial C_{im}(\alpha)}{\partial t} = \alpha(C_m - C_{im}(\alpha)) - r_{im}(\alpha) \quad \forall \alpha \quad 0 \leq \alpha \leq \infty. \qquad (32)$$

Eq. (32) can solved such that

$$C_{im}(\alpha) = \alpha C_m * e^{-\alpha t} - r_{im}(\alpha) * e^{-\alpha t}. \qquad (33)$$

Note that because we have not chosen to specify the form of r_{im} that this may be an implicit solution. Taking the time derivative of (33)

$$\frac{\partial C_{im}(\alpha)}{\partial t} = \alpha\frac{\partial C_m}{\partial t} * e^{-\alpha t} + \alpha C_{m,0}e^{-\alpha t}$$
$$- \frac{\partial r_{im}(\alpha)}{\partial t} * e^{-\alpha t} - r_{im,0}(\alpha)e^{-\alpha t}. \qquad (34)$$

Fig. 5. Evolution of total mass of reactant A from numerical simulation of the bimolecular reaction system. Four different values of reaction rate $k = 0.1$, 1, 10 and 100. The red circular dots correspond to the solution of the full multicontinuum set of Eqs. (22) and (23), while the blue lines correspond to the solution of *naive* Eq. (30). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Since concentration in immobile regions is initially zero, so too is reaction $r_{im,0} = 0$. Multiplying by $f(\alpha)$ and integrating yields

$$\frac{\partial C_{IM}}{\partial t} = g(t) * \frac{\partial C_m}{\partial t} + g(t)C_{m,0} - \int f(\alpha)\frac{\partial r_{im}(\alpha)}{\partial t} * e^{-\alpha t}d\alpha. \quad (35)$$

Combining (31) and (32) it is clear that

$$\frac{\partial C_m}{\partial t} + \frac{\partial C_{IM}}{\partial t} - D\frac{\partial^2 C_m}{\partial x^2} = -r_m - r_{IM} \quad (36)$$

where $r_{IM} = \int f(\alpha)r_{im}(\alpha)d\alpha$. Substituting in (35)

$$\frac{\partial C_m}{\partial t} + g(t) * \frac{\partial C_m}{\partial t} - D\frac{\partial^2 C_m}{\partial x^2} = -r_m - r_{IM} - g(t)C_{m,0}$$

$$+ \int f(\alpha)\frac{\partial r_{im}(\alpha)}{\partial t} * e^{-\alpha t}d\alpha. \quad (37)$$

As before we can write an equation for the transport of the immobile concentration by solving for C_m in (35) and substituting into (36)

$$\frac{\partial C_{IM}}{\partial t} + g(t) * \frac{\partial C_{IM}}{\partial t} - D\frac{\partial^2 C_{IM}}{\partial x^2} = -g(t) * r_m - g(t) * r_{IM} + g(t)C_{m,0}$$

$$- \int f(\alpha)\frac{\partial r_{im}(\alpha)}{\partial t} * e^{-\alpha t}d\alpha + D\frac{\partial^2}{\partial x^2}\left(\int f(\alpha)r_{im}(\alpha) * e^{-\alpha t}d\alpha\right). \quad (38)$$

Combining these last two equations the governing equation for total concentration is

$$\frac{\partial C_{tot}}{\partial t} + g(t) * \frac{\partial C_{tot}}{\partial t} - D\frac{\partial^2 C_{tot}}{\partial x^2} = -r_m - r_{IM}$$

$$- g(t) * r_m - g(t) * r_{IM} + D\frac{\partial^2}{\partial x^2}\left(\int f(\alpha)r_{im}(\alpha) * e^{-\alpha t}d\alpha\right). \quad (39)$$

While the structure of the equations presented for first-order and bimolecular reactions might look different than this, it is straightforward to rearrange those equations to recover something resembling this one. The reason we choose to write the equation this way is that it does show that one can always write an equation for reactive transport that resembles the conservative

fractional dispersion equation for conservative transport, namely a fractional dispersion equation for total concentration, with a slew of additional sources and sinks as seen from the right-hand side. Unless all of these terms on the right-hand side can be combined and written as an expression that exclusively depends on the total concentration, then our objective of writing a fractional dispersion reaction equation that depends on only C_{tot} cannot be met. For the case of a linear first-order reaction, this is relatively straightforward as once we write the solution to (16) we immediately have a simple linear relationship between mobile and immobile concentrations and thus for total concentrations also, meaning that all of the terms on the right hand side can be written straightforwardly in terms C_{tot}. However, for the bimolecular reaction in (24) and indeed the more generic case in (32) the relationship is not as clean, meaning that a straightforward expression for total concentration in terms of just immobile concentration or mobile concentration may not be possible.

Some particularly interesting features of the right-hand side source-and-sink terms stand out and are worthy of discussion:

- One cannot just throw a generic reaction term r_{tot} on the right hand that has the same functional form as r_m. While for a linear reaction it is straightforward to argue that $r_{tot} = r_m + r_{IM}$ will preserve its functional form, it is likely the exception rather than rule for complex coupled and nonlinear reactions. This, as already noted, is directly analogous to upscaling of reactions in incompletely mixed systems.
- As had already been noted for the case of the first-order reaction, the reaction on the right-hand side must also include convolution with the memory function. Memory clearly also influences the reaction process and any effective model that does not account for this is likely incorrect. Unless the reaction rate is proportional to the time derivative of concentration, rather than yielding a fractional derivative, it results in something more closely resembling a fractional integral. Thus the way that memory acts on transport and reaction manifests in a different manner and must be accounted for in the reaction terms, explaining why an ad hoc inclusion of a generic reaction

term is likely to fail. This is consistent with the discussion of [60] who obtain a time fractional dispersion equation by subordinating a diffusion equation, but demonstrate that if one does not take care with how one handles the reaction term, that unphysical negative concentrations can be predicted. In our case, having the memory function convolved with the reaction term on the right-hand side is what ensures consistent conservation of mass. Integrating (39) over all space we can write an equation for total mass

$$\frac{\partial M}{\partial t} + g(t) * \frac{\partial M}{\partial t} = -\int_{-\infty}^{\infty} (r_m + r_{IM} + g(t) * r_m + g(t) * r_{IM})dx \tag{40}$$

which ensures

$$\frac{\partial M}{\partial t} = -\int_{-\infty}^{\infty} (r_m + r_{IM})dx; \tag{41}$$

i.e. that the total change of mass in the system occurs because of all the reactions that are happening in the mobile and immobile regions of the domain. Were the convolution not included, the incorrect amount of mass would be removed as was the case for both of the specific reactive systems considered here.

- While not immediately obvious, the last term on the right-hand side of (39) is the term in the two specific reaction problems that leads to the modification of the structure of the memory function. This can be inferred by looking at (33) and recognizing that when $r_{im}(\alpha)$ was written in terms of $C_{im}(\alpha)$ it could be brought to the left-hand side of the equation, lumped together and then the term that is divided across gives rise to the tempering of the exponential or similar modified effect.

6. Conclusions

In this paper, we set out to show that one must be cautious even in proposing fractional reaction diffusion equations for systems where transport of a conserved scalar can be shown to be governed by a fractional diffusion equation. Typically fractional diffusion equations, or for that matter any anomalous transport model, arises due to complexity and heterogeneity at some small (unresolved) scales and so one has to be careful in simply assuming that the influence on reaction is trivially upscaled.

To this end we consider a simple physical system, where for a conserved scalar one can formally derive a fractional dispersion equation as the consistent effective equation for the evolution of concentration. Leveraging two previous studies, we connect a multicontinuum mobile immobile model system and following [45] rigorously demonstrate that one can derive an effective single transport equation for the evolution of total concentration where all terms depend only on the total concentration. For a specific distribution of exchange rates between the mobile and immobile continua this equation can be written as a time fractional dispersion equation. Next we considered the same setup, but with the addition of reactions. Two specific reaction types were considered, namely a first-order decay reaction and bimolecular kinetic reaction.

For the first-order reaction, following the same procedure in deriving the fractional dispersion equation for conservative transport, we showed that an effective equation can be written for total concentration that only depends on total concentration. However, in going through the procedure a modified memory function arises that tempers the power law that gives rise to the fractional derivative with an exponential whose rate depends on the rate of reaction, thus modifying the structure of the effective equation. Physically this tempering reflects that if a particle remains immobile for too long it is more likely to react that to re-emerge into the mobile continuum. Additionally this memory function acts on the

reaction term. If one were to *naively* write a reaction term without this memory function, one would incorrectly predict the spatial distribution of concentration and rather than obtain an exponential decay in total mass over time, mass would decay much more slowly as a power law $t^{-\gamma}$ in time, where $0 < \gamma < 1$ is the exponent of the time fractional derivative. This was confirmed with numerical simulations. It should be noted that the *naive* approach does not yield an unphysical equation, as was for example the concern of [60]. Indeed it can be shown that it is the correct effective equation, were one to say that a first order reaction happened only in the mobile part of the domain, which for some systems of interest might be the case (e.g.[80]). However, it is not the correct effective equation for the conceptual system which we aimed to represent.

For the case of the bimolecular reaction, going through the same procedure, we demonstrated that there is not a straightforward way of starting from the multicontinuum equations and deriving an effective equation for the evolution of total concentration in terms of only total concentration. In particular, the same procedure results in a new modified memory function, which for one reactant depends explicitly on the time history of the concentration field of the other reactant, which occurs because of the tightly coupled nature of this system. What happens to one reactant depends heavily on what has happened not only to itself, but also to the other reactant; it itself in turn strongly affects the fate of the other. While one can formally write this memory function, it is now nonstationary and dependent on space. This means that many of the required steps to obtain a final equation for total concentration performed in the derivations for the conservative and first-order reaction systems simply do not work. Via numerical simulations we demonstrated again that if one were to simply and *naively* include a reaction term on the right-hand side of a fractional dispersion equation this would result in erroneous predictions of concentration and total amounts of mass, except for some unique infinite reaction rate conditions highlighted in Appendix A.

We conclude by performing the procedure of deriving an effective equation for total concentration on a completely generic reaction system, where the form of the reactive term remains unspecified. We show that while it is possible to always arrive at an effective equation that resembles a fractional dispersion equation, a large number of source-and-sink terms emerge that depend on the specifics of the reactions in the mobile and immobile parts of the domain. Importantly, one of the features that stands out strongly is that any effective equation must have the memory effects act on transport and reaction terms, and not just the transport terms alone. For the case of linear reactions, such as the first-order ones considered here, it is relatively straightforward to combine these into terms that depend only on total reactions, but for more complex coupled and nonlinear reactions this is less straightforward. This problem essentially faces many of the same issues that have been plagued volume averaging and upscaling studies of incomplete mixing effects on chemical reaction, where promising closure approaches exist, but are typically not exact and often carry strong restrictions on regimes of applicability. Thus, we hope that we have made it clear with this work that great caution is needed in proposing fractional reaction dispersion equations, purely on the grounds that conservative transport in a system displays fractional dispersion behaviors. While we focused on one specific form of fractional dispersion equation, our findings likely hold for most all anomalous transport models.

Appendix A. Appendix: Why as $k \to \infty$ does the *naive* approach look more and more correct?

Interestingly as k gets larger and larger the discrepancy between the full system and the *naive* approach becomes smaller. Here we demonstrate that for the unique limit of $k \to \infty$ they do indeed yield the same results. Consider the irreversible reaction $A + B \to C$. The transport equations for species A and B are given by

$$\frac{\partial C_{m,i}}{\partial t} - D \frac{\partial^2 C_{m,i}}{\partial x^2} = -\int f(\alpha) \alpha (C_{m,i} - C_{im,i}(\alpha)) d\alpha + r_m \quad i = A, B \tag{A1}$$

$$\frac{\partial C_{im,i}(\alpha)}{\partial t} = \alpha (C_{m,i} - C_{im,i}(\alpha)) + r_{im}(\alpha) \quad \forall \alpha \quad 0 \le \alpha \le \infty \tag{A2}$$

and for the product C

$$\frac{\partial C_{m,C}}{\partial t} - D \frac{\partial^2 C_{m,C}}{\partial x^2} = -\int f(\alpha) \alpha (C_{m,C} - C_{im,C}(\alpha)) d\alpha - r_m$$
$$i = A, B \tag{A3}$$

$$\frac{\partial C_{im,C}(\alpha)}{\partial t} = \alpha (C_{m,C} - C_{im,C}(\alpha)) - r_{im}(\alpha) \quad \forall \alpha \quad 0 \le \alpha \le \infty \tag{A4}$$

Taking the limit of infinite reaction rate means that nowhere in the domain can the reactants coexist, which is equivalent to

$$C_{m,A} C_{m,B} = 0 \quad C_{im,A}(\alpha) C_{im,B}(\alpha) = 0 \quad \forall \alpha. \tag{A5}$$

Defining conservative components $u_A = C_A + C_C$ and $u_B = C_B + C_C$ then

$$\frac{\partial u_{m,i}}{\partial t} - D \frac{\partial^2 u_{m,i}}{\partial x^2} = -\int f(\alpha) \alpha (u_{m,i} - u_{im,i}(\alpha)) d\alpha \quad i = A, B \tag{A6}$$

$$\frac{\partial u_{im,i}(\alpha)}{\partial t} = \alpha (u_{m,i} - u_{im,i}(\alpha)) \quad \forall \alpha \quad 0 \le \alpha \le \infty. \tag{A7}$$

Now, since A and B cannot coexist it means that everywhere and anywhere in the domain either $C_A = 0$ or $C_B = 0$. Therefore it is always true that $C_C = min(u_A, u_B)$. For conserved quantities we know we can write

$$\frac{\partial u_{tot,i}}{\partial t} + \beta \frac{\partial^\gamma u_{tot,i}}{\partial t^\gamma} - D \frac{\partial^2 u_{tot,i}}{\partial x^2} = 0 \quad i = A, B \tag{A8}$$

We also know that

$$C_{C,tot} = min(u_{A,m}, u_{B,m}) + \int f(\alpha) min(u_{A,im}(\alpha), u_{B,im}(\alpha)) d\alpha \tag{A9}$$

If we can show that the right hand side is the same as $min(u_{A,tot} u_{B,tot})$ then this would be equivalent to showing that in the limit of infinite reaction the *naive* approach works just fine.

For our particular example problem, from symmetry arguments, it is possible to show that $u_A(x) = u_B(-x)$ (we deliberately include no subscript for mobile or immobile as this refers to any u anywhere in our domain and multicontinuum). For our given initial condition at all times $u_A(-x) \ge u_A(x)$ for $x \le 0$ and $u_B(x) \ge u_B(-x)$ for $x \ge 0$. Thus anywhere where $u_{A,m}$ is smaller than $u_{B,m}$ so too $u_{A,im}(\alpha)$ is smaller than $u_{B,m}(\alpha)$, meaning

$$min(u_{A,m}, u_{B,m}) + \int f(\alpha) min(u_{A,im}(\alpha), u_{B,im}(\alpha)) d\alpha$$
$$= min(u_{A,tot}, u_{B,tot}) \tag{A10}$$

To verify this result, we follow the same numerical methods outlined in the main manuscript we conducted. Sample concentration plots are shown in Fig. A.6 and the temporal evolution of mass of reactants over time is shown in Fig. A.7. Both show identical agreement between the system where the full set of multicontinuum equations are solved and the fractional dispersion model, providing some validation of what we have presented in this appendix. Note that this outcome is very specific to this set of initial conditions. It gives rise to the circumstances where these two
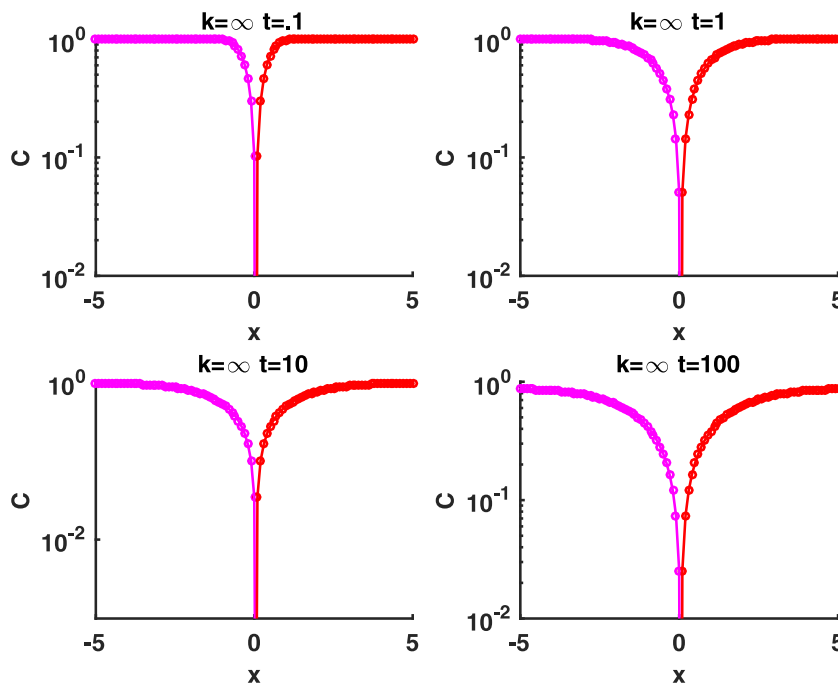
Fig. A6. Numerical solutions for the bimolecular reaction system. Concentration profiles at time $t = 0.1$, 1, 10 and 100 are shown for reaction rate limit $k \to \infty$. Magenta colors correspond to concentrations of species A, while red to species B. The circular dots correspond to the solution of the full multicontinuum set of Eqs. (22) and (23), while the solid lines correspond to the solution of *naive* Eq. (30). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
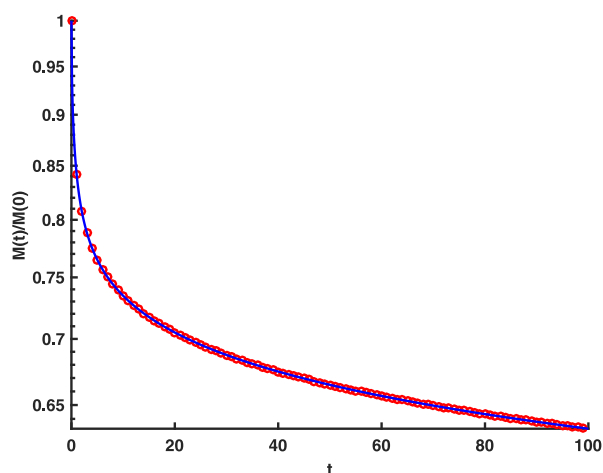
Fig. A7. Evolution of total mass of reactant A from numerical simulation of the bimolecular reaction system for reaction rate limit $k \to \infty$. The red circular dots correspond to the solution of the full multicontinuum set of equations, while the blue lines correspond to the solution of *naive* fractional dispersion equation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

models produce identical results and it is not difficult to conceive of a similar problem where the right set of conditions, such as the symmetry argument, do not hold; e.g. the inclusion of a drift in the mobile region would break the symmetry. Thus the finding of this appendix should only be considered legitimate for this very specific system. We only present it here in this appendix to aid in interpreting the results from Section 4 for the bimolecular reactions in the main manuscript.

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