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Mixing-driven equilibrium reactions in multidimensional fractional advection–dispersion systems

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ABSTRACT

We study instantaneous, mixing-driven, bimolecular equilibrium reactions in a system where transport is governed by a multidimensional space fractional dispersion equation. The superdiffusive, nonlocal nature of the system causes the location and magnitude of reactions that take place to change significantly from a classical Fickian diffusion model. In particular, regions where reaction rates would be zero for the Fickian case become regions where the maximum reaction rate occurs when anomalous dispersion operates. We also study a global metric of mixing in the system, the scalar dissipation rate and compute its asymptotic scaling rates analytically. The scalar dissipation rate scales asymptotically as $t^{-(d+\alpha)/\alpha}$, where d is the number of spatial dimensions and α is the fractional derivative exponent.

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1. Introduction

Despite the name, anomalous transport that does not follow Fick's law of diffusion is ubiquitous. The systems of interest to physicists that display non-Fickian transport include turbulent flows [1,2], diffusion and flow in porous media [3–5], fractured media [6,7], plasmas [8], gels [9], optical media [10], sediment transport [11] and biological cells [12] to mention a few. In all of these examples, a passive tracer plume can spread at a sub- or superdiffusive rate, and significant plume concentrations may be present at much earlier and/or later times relative to a Fickian system.

The underlying cause of anomalous transport is not always evident [13,14], but a broad range of modeling approaches have emerged to capture these anomalous behaviors, including but not limited to projector formalisms [15], continuous time random walks (CTRW) [16], delayed diffusion [17] and time and/or space fractional advection–dispersion equations (fADE) [18,19]. These models aim to describe mass transfer over large distances and with a wide range of transfer times. This manifests as spatial and/or temporal nonlocality in the governing equations. To date, the majority of these models have focused on transport in a single dimension, although some multidimensional examples exist [20,21].

Here we focus on transport governed by the multidimensional space fADE, which is nonlocal in space, and models the transfer of mass over large distances. This is one of potentially many spatially nonlocal equations; we use it because it is the continuum governing equation of the probability density of a multidimensional Lévy motion. Lévy type motion is common in many physical systems [22] and is appealing because it is analytically tractable and has elegant and physically useful solutions, which provide valuable insight into the general effects of spatial nonlocality on transport. It also represents the

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limit process toward which heavy-tailed random walks converge, in the same way that a multi-Gaussian is the limit process for finite-variance random walks in several dimensions [20]. This provides a solid basis for interpretation of observations at a range of scales. From [20] the multidimensional space fADE for conservative transport can be written as:

$$\frac{\partial c(\mathbf{x}, t)}{\partial t} + \mathbf{v} \cdot \nabla c(\mathbf{x}, t) = D_\alpha \mathbb{D}_M^\alpha c(\mathbf{x}, t), \quad (1)$$

where $c(\mathbf{x}, t)$ is concentration of a passive tracer, $1 < \alpha \leq 2$, and D_α is the generalized dispersion coefficient with units $[L^\alpha T^{-1}]$. The mixing measure $M = M(d\theta)$ reflects the probability of moving in any direction in d -dimensions by the random direction vector θ with probability measure $M(d\theta)$ on the unit sphere. From a practical perspective the mixing measure can be chosen to physically represent transport through a fracture network (e.g. Ref. [23]). It can also potentially vary in space (e.g. Refs. [24–26]), although in this study we will focus on cases where it does not. The fractional Laplace operator $\mathbb{D}_M^\alpha f(\mathbf{x}, t)$ may be defined by its Fourier transform, which is

$$\mathbb{F}(\mathbb{D}_M^\alpha f(\mathbf{x})) = \left[\int_{\|\theta\|=1} (i\mathbf{k} \cdot \theta)^\alpha M(d\theta) \right] \hat{f}(\mathbf{k}), \quad (2)$$

where $\hat{f}(\mathbf{k})$ is the Fourier transform of $f(\mathbf{x})$, $\mathbb{F}$ denotes the Fourier transform $\mathbb{F}(f) = \int_{\mathbb{R}^d} f(\mathbf{x}) e^{-i\mathbf{k} \cdot \mathbf{x}} d\mathbf{x}$, with inverse $\mathbb{F}^{-1}(\hat{f}) = f = \frac{1}{(2\pi)^d} \int_{\mathbb{R}^d} \hat{f}(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{x}} d\mathbf{k}$, d is the number of spatial dimensions, and $M(d\theta)$ is the probability distribution of unit vectors θ on the unit sphere. For example, the Riesz fractional derivative in 2- d specifies a Uniform continuous distribution $M(d\theta) = (1/2\pi) d\theta$. The fADE in (1) governs the macroscopic ensemble average of a microscopic particle model with power law jumps [27, Section 6.5].

Let us also define the vector-valued fractional gradient $\nabla_M^\alpha f(\mathbf{x})$ as the function with Fourier transform

$$\int_{\|\theta\|=1} \theta (i\mathbf{k} \cdot \theta)^\alpha \hat{f}(\mathbf{k}) M(d\theta).$$

Recall that the directional derivative

$$\mathbb{D}_\theta^1 f(\mathbf{x}) = \theta \cdot \nabla f(\mathbf{x}) = \left. \frac{d}{ds} f(\mathbf{x} + \theta s) \right|_{s=0}$$

has Fourier transform $(i\mathbf{k} \cdot \theta) \hat{f}(\mathbf{k})$. The fractional directional derivative can be defined by

$$\mathbb{D}_\theta^\alpha f(\mathbf{x}) = \mathbb{D}_s^\alpha f(\mathbf{x} + \theta s) \Big|_{s=0}$$

where $\mathbb{D}_t^\alpha$ denotes the Riemann–Liouville fractional derivative in one variable and s reflects an arclength. Then it is not hard to check that $\mathbb{D}_\theta^\alpha f(\mathbf{x})$ has Fourier transform $(i\mathbf{k} \cdot \theta)^\alpha \hat{f}(\mathbf{k})$. Then we can also write

$$\mathbb{D}_M^\alpha f(\mathbf{x}) = \int_{\|\theta\|=1} \mathbb{D}_\theta^\alpha f(\mathbf{x}) M(d\theta).$$

Similarly

$$\nabla_M^\alpha f(\mathbf{x}) = \int_{\|\theta\|=1} \theta \mathbb{D}_\theta^\alpha f(\mathbf{x}) M(d\theta).$$

Then a quick check using Fourier transforms shows that (e.g. Ref. [28])

$$\nabla_M^{\alpha-1} \cdot \nabla f(\mathbf{x}) = \nabla \cdot \nabla_M^{\alpha-1} f(\mathbf{x}) = \mathbb{D}_M^\alpha f(\mathbf{x}) \quad (3)$$

so that we can also write

$$\frac{\partial c}{\partial t} = -\mathbf{v} \cdot \nabla c + D_\alpha \nabla_M^{\alpha-1} \cdot \nabla c = -\mathbf{v} \cdot \nabla c + D_\alpha \nabla \cdot \nabla_M^{\alpha-1} c, \quad (4)$$

in which the dispersive term is the fractional divergence of the concentration gradient, or the divergence of the fractional gradient. For more details on this see Ref. [28].

1.1. Reactive transport

The study of anomalous transport of conservative (non-reactive) tracers has been extensive. However, many problems of practical interest do not deal with conservative components, and being able to model the additional effect of chemical reaction is important. Several experimental and numerical observations suggest that, in systems where anomalous conservative transport is observed, one can also anticipate anomalous effects to emerge in terms of reactions. This is unsurprising because mixing, which is strongly driven by (classical and anomalous) dispersion, is what bring reactants into contact with one another. Therefore, anomalous dispersion can induce anomalous mixing [29–32], which in turn can induce anomalous reactions [33,34].

The influence of fractional dispersion on reactions has received considerable attention (e.g. Refs. [35,36]). In this context, there has been much interest in the propagation of fronts in nonlinear single species systems (e.g. Refs. [37–42]). The effect of large motion deviations on the propagation speed and shape of reaction/diffusion fronts is often surprising and/or counterintuitive; for example superdiffusion appears able to slow rather than enhance reactive front propagation (e.g. Refs. [37,38]). Works [35–42] assume that the reaction rate is a known function of respective concentration c and is part of the governing equation. However, reactions come in a broad range of categories (e.g., single species, multispecies, kinetic, instantaneous) and we consider a multispecies case here. It is worth noting in general that for multispecies reactions when the systems is nonlocal in time it is not Markovian in time and special care has to be taken with the memory of particles undergoing reaction; otherwise particles that are not physically collocated at the same point in space and time may artificially and non-physically react with one another (e.g. Refs. [43–45]). However for the spatially nonlocal case such a problem does not arise.

In this particular work, we focus our attention on a mixing driven instantaneous equilibrium precipitation *bimolecular* reaction with a strong emphasis on the role of mixing. This particular reaction is of broad interest for chemical reactions in porous media (e.g. Ref. [46]). The effects of spatially and temporally nonlocal transport on this type of reaction have received some attention in the one-dimensional case [47,33]. The influence of temporal nonlocality using a multi-rate mass transfer model was explored by Ref. [47]. Similarly, the role of spatial nonlocality using a single dimension space fADE was studied by Ref. [33]. These works illustrate that the influence of nonlocality (whether in space or time) is to modify the global rate of mixing that occurs, accelerating or decelerating it relative to a Fickian system. More importantly, the nonlocal nature of these systems allows reactions to occur in regions that would be precluded in a Fickian system. In some cases, the region of minimum reaction for a system with Fickian transport can become the region of maximum reaction for the anomalous systems [33].

To the best of our knowledge, such reactive systems with nonlocal transport have not been studied in multiple spatial dimensions. It is well known that the spatial dimensionality of a system plays an important role on mixing and reaction characteristics (e.g. Refs. [48,49]). In this paper we focus exclusively on the role of spatial nonlocality and extend the work of Ref. [33] to a system with transport governed by a multidimensional space fADE. We do so by combining and extending the fractional calculus methods developed in Refs. [50,28,27].

2. Spatial fractional advection–dispersion reaction system

2.1. Model description

We consider a mixing-limited chemical reaction of two solutes of concentrations c_1 and c_2 that react and precipitate to form c_3 with local chemical equilibrium conditions [46]. In incompressible flow, the velocity is divergence-free, and c_1 and c_2 are assumed here to be transported by space-fractional dispersion,

$$\frac{\partial c_i(\mathbf{x}, t)}{\partial t} + \mathbf{v} \cdot \nabla c_i(\mathbf{x}, t) - D_\alpha \mathbb{D}_M^\alpha c_i(\mathbf{x}, t) = -r(\mathbf{x}, t) \quad i = 1, 2 \quad (5)$$

while c_3 is immobile

$$\frac{\partial c_3(\mathbf{x}, t)}{\partial t} = +r(\mathbf{x}, t). \quad (6)$$

The two species c_1 and c_2 are in local equilibrium so that

$$c_1(\mathbf{x}, t)c_2(\mathbf{x}, t) = K \quad (7)$$

with K the equilibrium constant. It is well known, and can be shown by the principle of Galilean invariance, that the constant drift term $\mathbf{v}$ has no role on mixing or mixing-driven reaction rates other than to shift the location of reaction. Therefore we consider only the case of $\mathbf{v} = 0$. In all instances in this work we consider an unbounded system with natural boundary conditions.

2.2. Nondimensional model

Let us introduce the following dimensionless variables

$$c_i = c_i^* \sqrt{K} \quad t = t^* \left[\frac{L^\alpha}{D} \right]^{\frac{1}{1-\alpha}} \quad \mathbf{x} = \mathbf{x}^* L \quad (8)$$

where L is some characteristic length scale of the system of interest. Our governing equations can now be written as

$$\frac{\partial c_i^*(\mathbf{x}^*, t^*)}{\partial t^*} - \mathbb{D}_M^\alpha c_i^*(\mathbf{x}^*, t^*) = -r^*(\mathbf{x}^*, t^*) \quad i = 1, 2 \quad (9)$$

$$\frac{\partial c_3^*(\mathbf{x}^*, t^*)}{\partial t^*} = r^*(\mathbf{x}^*, t^*) \quad (10)$$

and the equilibrium condition becomes

$$c_1^*(\mathbf{x}^*, t^*)c_2^*(\mathbf{x}^*, t^*) = 1. \quad (11)$$

From here on we drop the stars and unless explicitly noted, all quantities are taken as dimensionless.

2.3. Mapping to conservative component

Let us define a component

$$u(\mathbf{x}, t) = c_1(\mathbf{x}, t) - c_2(\mathbf{x}, t). \quad (12)$$

Subtracting (9) for $i = 2$ from (9) for $i = 1$ we note that $u(\mathbf{x}, t)$ is conservative and its transport is governed by the conservative fractional dispersion equation

$$\frac{\partial u(\mathbf{x}, t)}{\partial t} - \mathbb{D}_M^\alpha u(\mathbf{x}, t) = 0 \quad (13)$$

which is linear and therefore can be solved for arbitrary initial conditions using the Greens' function for this equation. Using the equilibrium condition in (11) and the definition of $u(\mathbf{x}, t)$ the concentrations of the reactive species can be related to $u(\mathbf{x}, t)$ as

$$c_{1,2}(\mathbf{x}, t) = \pm \frac{u(\mathbf{x}, t)}{2} + \sqrt{\frac{u(\mathbf{x}, t)^2}{4} + 1}. \quad (14)$$

Therefore, given a solution to the conservative transport problem for $u(\mathbf{x}, t)$, we can calculate the distributions of the non-conservative species $c_1(\mathbf{x}, t)$ and $c_2(\mathbf{x}, t)$ and subsequently deduce the reaction rate.

2.4. Calculation of local reaction rate

Substituting (14) into (9), then simplifying using (13) results in reaction rate

$$r(\mathbf{x}, t) = -\frac{\partial}{\partial t} \left(\sqrt{\frac{u(\mathbf{x}, t)^2}{4} + 1} \right) + \mathbb{D}_M^\alpha \left(\sqrt{\frac{u(\mathbf{x}, t)^2}{4} + 1} \right). \quad (15)$$

The nonlinear nature of r can be seen using the rules of fractional vector calculus outlined in Refs. [50,28,27]. Reaction rate $r(\mathbf{x}, t)$ can be written as (see Appendix A for details)

$$\begin{aligned} r(\mathbf{x}, t) &= -\frac{dc}{du} \mathbb{D}_M^\alpha u + \int_{\|\theta\|=1} \sum_{j=0}^{\infty} \binom{\alpha-1}{j} \mathbb{D}_\theta^j \left(\frac{dc}{du} \right) \mathbb{D}_\theta^{\alpha-j} u M(d\theta) \\ &= \int_{\|\theta\|=1} \sum_{j=1}^{\infty} \binom{\alpha-1}{j} \mathbb{D}_\theta^j \left(\frac{dc}{du} \right) \mathbb{D}_\theta^{\alpha-j} u M(d\theta). \end{aligned} \quad (16)$$

For the Fickian dispersion case where $\alpha = 2$, all terms for $j > 1$ in the binomial series vanish, and we recover the expression derived by Ref. [46]. Estimating reactions in a system where transport is governed by the multidimensional FADE is not as simple as the Fickian case. In particular, it is worth noting that $r(\mathbf{x}, t)$ for the Fickian case depends only on the first spatial derivative of u , while for the superdiffusive case it depends on many higher order derivatives and antiderivatives. Using the *generator form* of the vector fractional derivative [27, Example 6.29]

$$\mathbb{D}_M^\alpha f(\mathbf{x}) = \int_{\|\theta\|=1} \int_0^\infty (f(\mathbf{x} - r\theta) - f(\mathbf{x}) + r\theta \cdot \nabla f(\mathbf{x})) \frac{\alpha(\alpha-1)}{\Gamma(2-\alpha)} r^{\alpha-1} dr M(d\theta) \quad (17)$$

in the case $1 < \alpha < 2$, it follows from (9) that the dependence of r on c is nonlocal when $\alpha < 2$, since the vector fractional derivative at any given location depends on values of concentration over the entire domain, with influence that falls off as a power law of the radial distance between locations.

To demonstrate how this nonlocality affects the reaction rate, consider a pulse initial condition $u(\mathbf{x}, 0) = \delta(\mathbf{x}) + u_\infty$, which represents a perturbation to equilibrium, where u_∞ is constant, by adding one component at time $t = 0$ at location $\mathbf{x} = 0$. Consider the mixing measure $M(d\theta) = \frac{1}{2}(\delta(\theta) + \delta(\theta - \pi/2))d\theta$, representing transport in a fracture system with fractures oriented along the positive x and y axes [23]. Consider the Fickian case $\alpha = 2$ as well as three anomalous cases with $\alpha = 1.9, 1.5$, and 1.3 .

Eq. (15) for this setup can be solved by a finite difference scheme [51,52] on a bounded domain, yielding the reaction rate. The bounded domain is chosen large enough that no significant concentrations approach the boundary. This numerical approximation assumes that $\sqrt{u^2/4 + 1} \approx 0$ outside the domain. But $u(\mathbf{x}, t) \rightarrow u_\infty$ as $|\mathbf{x}| \rightarrow \infty$ for any solution to (13)

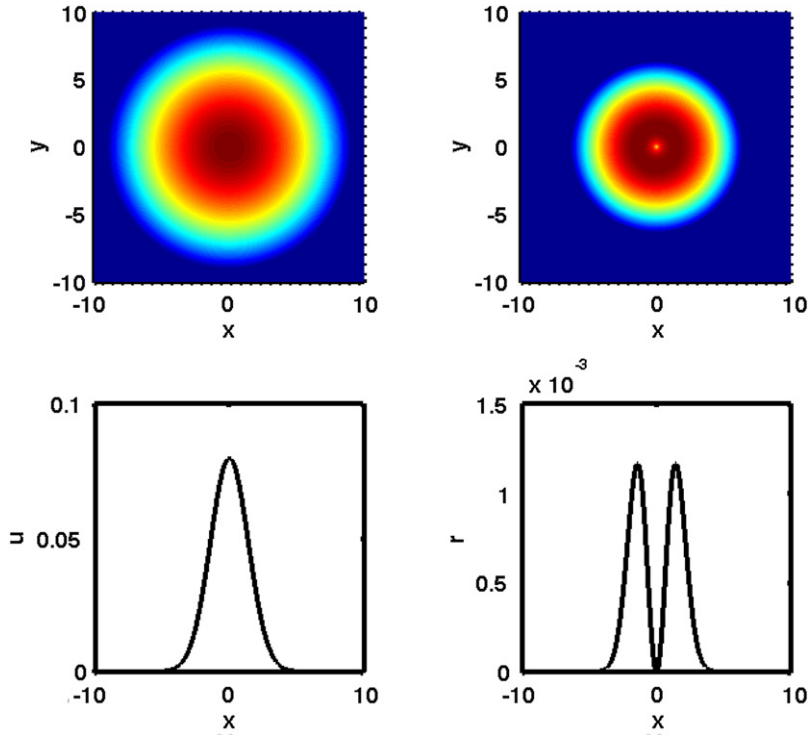


Fig. 1. (Color online) Plots of concentration field u (left) and reaction rate r (right) for the Fickian case $\alpha = 2$ and $u_\infty = 0$. The top row gives a surface view over a large area while the bottom is a transect for $y = 0$. Note that the region of maximum concentration, i.e. the origin, corresponds to zero reaction. The plot is for $t = 1$.

with a compactly supported initial concentration, and hence the term $\sqrt{(u^2/4) + 1} \rightarrow \sqrt{(u_\infty^2/4) + 1}$ as $|\mathbf{x}| \rightarrow \infty$. To obtain a computationally tractable formula, note that $\frac{\partial}{\partial t} \sqrt{u_\infty^2/4 + 1} = 0$, and also that $\mathbb{D}_M^\alpha \sqrt{u_\infty^2/4 + 1} = 0$, which follows since we are using the *generator form* of the vector fractional derivative as shown in (17). Then the reaction rate can be computed by substituting $c_i - \sqrt{u_\infty^2/4 + 1}$ into (9) instead of c_i , which leads to

$$r(\mathbf{x}, t) = -\frac{\partial}{\partial t} \left(\sqrt{\frac{u(\mathbf{x}, t)^2}{4} + 1} \right) + \mathbb{D}_M^\alpha \left(\sqrt{\frac{u(\mathbf{x}, t)^2}{4} + 1} - \sqrt{u_\infty^2/4 + 1} \right). \quad (18)$$

Now a finite difference scheme can be applied to compute the reaction rate. Solutions to (13), and hence (18), can also be obtained via FFT inversion. For certain special cases of the mixing measure, analytical solutions are available, which can be explicitly computed using widely available codes for the one dimensional stable density, see Ref. [27, Examples 6.4, 6.22, 6.30, 6.54].

Fig. 1 depicts the distribution of u and r at a time $t = 1$ for the Fickian case $\alpha = 2$. For u we obtain the classical multidimensional Gaussian distribution. Note that the reaction rate r is equal to zero at $x = 0$, the region where u is maximum. This is because the region of maximum u corresponds to the region where the gradient of u is zero, and by Eq. (16), this means that the rate of reaction there will also be zero. Physically, at the maximum, the concentration graph is flat, so there is no local variation in concentration to drive the reaction. The region of maximum reaction corresponds to the region of maximum gradient resulting in a *double-hump* distribution for r .

Surface plots for equivalent conservative component and reaction rate for the anomalous transport cases are shown in Figs. 2 and 3. Fig. 2 provides a larger view with axes that span a greater spatial range in order to highlight tails, while Fig. 3 focuses on the origin for better comparison with the Fickian case in Fig. 1. It is clear (Fig. 2) that the distribution of u is very different from the Fickian case, with a strong predominant transport along the coordinate axes, the directions weighted by the mixing measure. The symmetry of the Fickian case is completely broken. The reaction rate r follows a relatively similar trend to u , perhaps even more strongly pinned to the principal axes than u (Fig. 2). More importantly, the region of maximum u and zero gradient no longer corresponds to zero r . In fact, as the system becomes more anomalous (i.e., as α decreases), this becomes the point of greatest reaction (Fig. 3).

To amplify this point, transects of the conservative component along the x -axis and reaction rate for $\alpha = 1.9, 1.7, 1.5$ and 1.3 are shown in Fig. 4. The least anomalous cases of $\alpha = 1.9$ and 1.7 still display some remnants of the *double hump*, while

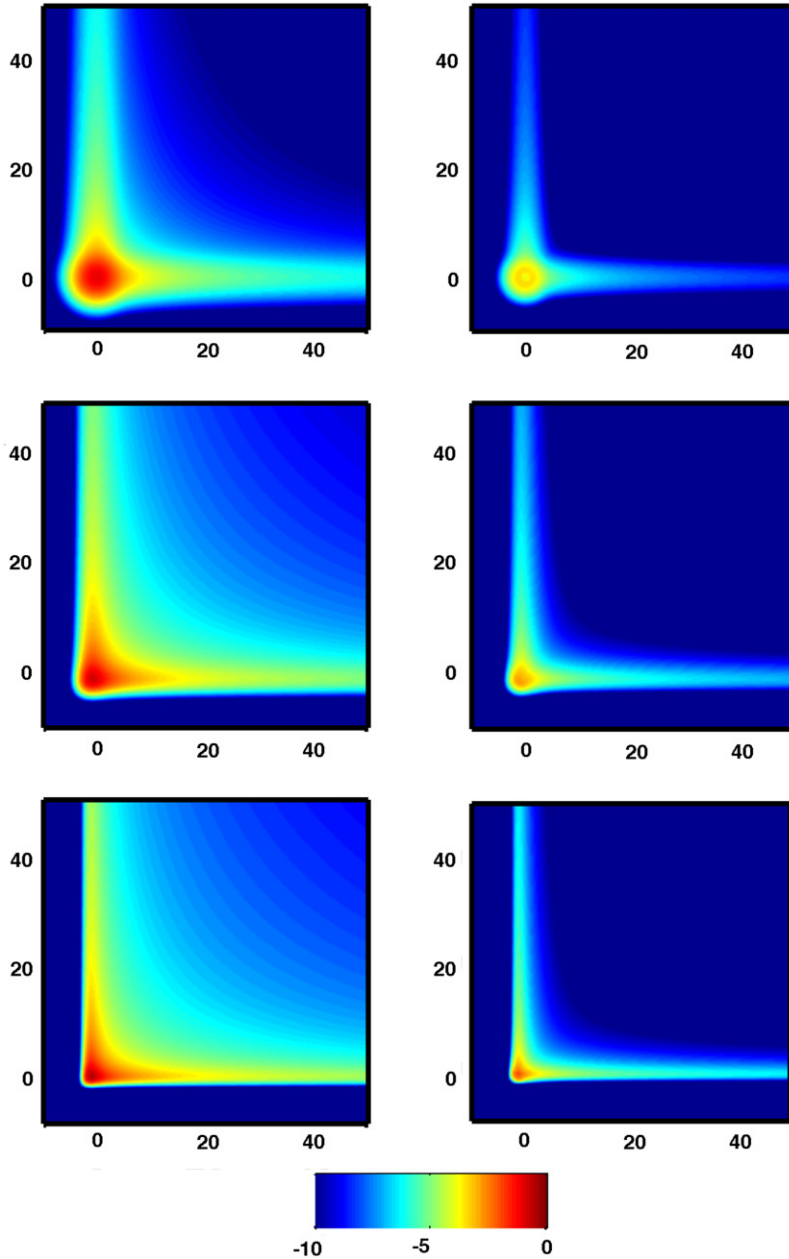


Fig. 2. (Color online) Plots of concentration field $\log_{10}(u)$ (left) and reaction rate $\log_{10}(r)$ (right) for $\alpha = 1.9$ (top), $\alpha = 1.5$ (middle) and $\alpha = 1.3$ (bottom). In all cases the mixing measure $M(d\theta)$ is pinned on the x and y axes, i.e. $M(d\theta) = \frac{1}{2}(\delta(\theta) + \delta(\theta - \pi/2))d\theta$ and $u_\infty = 0$.

for the more anomalous cases of $\alpha = 1.5$ and 1.3 , no trace of this remains, and the region of zero gradient in u coincides with the maximum in r . This clearly illustrates the nonlocal dependence of reaction rate on u .

2.5. Global measures of mixing and reaction

Often global metrics of reaction are just as useful as local ones. By global we mean integrated measures of reaction that reflect some sort of average behavior. Let us define a global reaction rate as

$$R_T(t) = \int_{\mathbb{R}^d} r(\mathbf{x}, t) d\mathbf{x}, \quad (19)$$

where $R_T(t)$ measures the total amount of reaction taking place in the domain at any given time. Starting with (9), let $c = c_i$ for $i = 1$ or $i = 2$, use the one variable chain rule, apply (13), and then (3) to see that

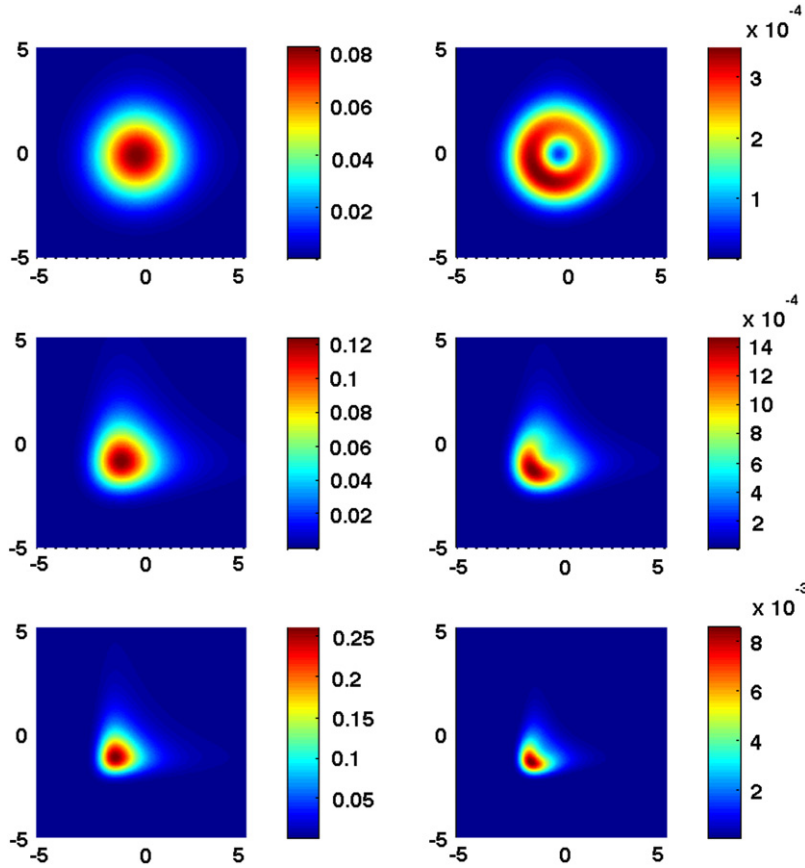


Fig. 3. (Color online) Zoomed plots with focus on origin of concentration field u (left) and reaction rate r (right) for $\alpha = 1.9$ (top), $\alpha = 1.5$ (middle) and $\alpha = 1.3$ (bottom). In all cases the mixing measure $M(d\theta)$ is pinned on the x and y axes, i.e. $M(d\theta) = \frac{1}{2}(\delta(\theta) + \delta(\theta - \pi/2))d\theta$ and $u_\infty = 0$.

$$\begin{aligned} r(\mathbf{x}, t) &= -\frac{\partial c}{\partial t} + \mathbb{D}_M^\alpha c = -\frac{dc}{du} \frac{\partial u}{\partial t} + \mathbb{D}_M^\alpha c \\ &= -\frac{dc}{du} \mathbb{D}_M^\alpha u + \mathbb{D}_M^\alpha c = -\frac{dc}{du} \nabla \cdot \nabla_M^{\alpha-1} u + \nabla \cdot \nabla_M^{\alpha-1} c. \end{aligned} \quad (20)$$

A general property is that, if $f(\mathbf{x})$ is scalar-valued and $G(\mathbf{x})$ has values in $\mathbb{R}^d$, then $\nabla \cdot (fG) = \nabla f \cdot G + f \nabla \cdot G$. Apply this along with the one variable chain rule to see that

$$\nabla \cdot \left[\left(\frac{dc}{du} \right) \nabla_M^{\alpha-1} u \right] = \left(\frac{d^2 c}{du^2} \right) \nabla u \cdot \nabla_M^{\alpha-1} u + \left(\frac{dc}{du} \right) \nabla \cdot \nabla_M^{\alpha-1} u.$$

Then

$$\left(\frac{dc}{du} \right) \nabla \cdot \nabla_M^{\alpha-1} u = \nabla \cdot \left[\left(\frac{dc}{du} \right) \nabla_M^{\alpha-1} u \right] - \left(\frac{d^2 c}{du^2} \right) \nabla u \cdot \nabla_M^{\alpha-1} u \quad (21)$$

and so from (20) we can see that

$$r(\mathbf{x}, t) = -\nabla \cdot \left[\left(\frac{dc}{du} \right) \nabla_M^{\alpha-1} u \right] + \left(\frac{d^2 c}{du^2} \right) \nabla u \cdot \nabla_M^{\alpha-1} u + \nabla \cdot \nabla_M^{\alpha-1} c.$$

Using the divergence theorem, it can be shown that as $\|\mathbf{x}\| \rightarrow \infty$ (see Appendix B),

$$\int_{\mathbb{R}^d} \nabla \cdot \nabla_M^{\alpha-1} c \, d\mathbf{x} = 0 = \int_{\mathbb{R}^d} \nabla \cdot \left[\left(\frac{dc}{du} \right) \nabla_M^{\alpha-1} u \right] d\mathbf{x}.$$

Therefore

$$R_T(t) = \int_{\mathbb{R}^d} r(\mathbf{x}, t) d\mathbf{x} = \int_{\mathbb{R}^d} \left(\frac{d^2 c}{du^2} \right) (\nabla u \cdot \nabla_M^{\alpha-1} u) d\mathbf{x}. \quad (22)$$

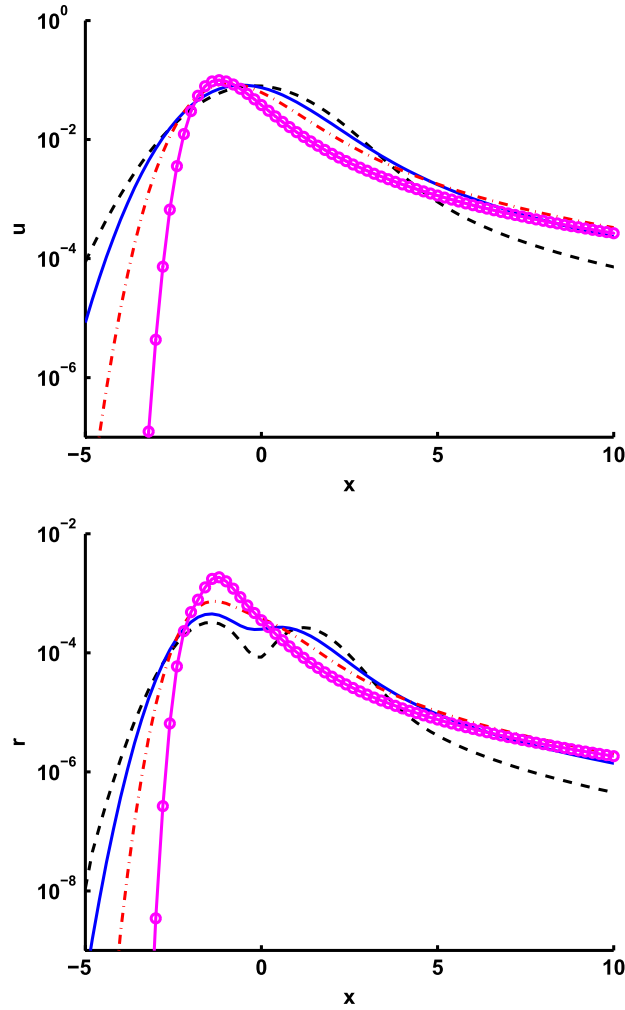


Fig. 4. (Color online) Concentration field u (top) and reaction rate r (bottom) at $t = 1$ along the x -axis for $\alpha = 1.9$ (black $---$), $\alpha = 1.7$ (blue $-$), $\alpha = 1.5$ (red $- \cdot -$) and $\alpha = 1.3$ (purple $- \cdot \cdot -$). In all cases the mixing measure $M(d\theta)$ is pinned on the x and y axes, i.e. $M(d\theta) = \frac{1}{2}(\delta(\theta) + \delta(\theta - \pi/2))d\theta$ and $u_\infty = 0$.

The integrand is made up of two distinct factors. The first factor, d^2c/du^2 , depends solely on the chemistry of the problem, and is called the speciation term. The second term, $\nabla u \cdot \nabla_M^{\alpha-1} u$, is a manifestation of mixing, or dispersion. The fractional derivative in the mixing term reflects the nonlocal nature of mixing in the case of anomalous dispersion ($\alpha < 2$). Eq. (22) decomposes the problem of chemical reaction and mixing into its two components: (i) mixing of a conservative scalar; and (ii) speciation. A Taylor series expansion about $u = u_\infty$ shows that

$$\frac{dc}{du} = \frac{1}{2} + \frac{u_\infty}{\sqrt{u_\infty^2/4 + 1}} + \frac{2}{(u_\infty^2 + 4)^{3/2}}(u - u_\infty) + \dots \quad (23)$$

and hence for u close to equilibrium u_∞ it is reasonable to approximate the speciation term by a constant: $d^2c/du^2 \approx 2/(u_\infty^2 + 4)^{3/2}$. Then $R_T(t) \approx \frac{2}{(u_\infty^2 + 4)^{3/2}} M_T(t)$, where

$$M_T(t) = \int_{\mathbb{R}^d} \nabla u \cdot \nabla_M^{\alpha-1} u \, d\mathbf{x} \quad (24)$$

is a global measure of mixing. In the Fickian case, $M_T(t)$ is often called the scalar dissipation rate (e.g. Refs. [53,30,54].) An argument similar to (21) shows that

$$\nabla u \cdot \nabla_M^{\alpha-1} u = \nabla \cdot [u \nabla_M^{\alpha-1} u] - u \nabla \cdot \nabla_M^{\alpha-1} u$$

and then it follows from (24) that

$$M_T(t) = \int_{\mathbb{R}^d} \nabla \cdot [u \nabla_M^{\alpha-1} u] \, d\mathbf{x} - \int_{\mathbb{R}^d} u \nabla \cdot \nabla_M^{\alpha-1} u \, d\mathbf{x}.$$

Apply the divergence theorem as before

$$M_T(t) = - \int_{\mathbb{R}^d} u \nabla \cdot \nabla_M^{\alpha-1} u \, d\mathbf{x}, \quad (25)$$

use the one variable chain rule, apply (13), and then (3) to see that

$$\frac{\partial u^2}{\partial t} = 2u \frac{\partial u}{\partial t} = 2u \mathbb{D}_M^\alpha u = 2u \nabla \cdot \nabla_M^{\alpha-1} u,$$

and substitute into (25) to arrive at

$$M_T(t) = - \frac{1}{2} \frac{\partial}{\partial t} \int_{\mathbb{R}^d} u^2(\mathbf{x}, t) \, d\mathbf{x}, \quad (26)$$

which is an alternative definition of the scalar dissipation rate [53,30,54].

2.5.1. Arbitrary initial condition

Next we will apply the Fourier transform to compute the global reaction rate. For an arbitrary initial condition $u(\mathbf{x}, t) = u_0(\mathbf{x})$ that is nonnegative and integrable, the Fourier transform of $u(\mathbf{x}, t)$ is given by

$$\hat{u}(\mathbf{k}, t) = \hat{u}_0(\mathbf{k}) \exp \left[t \int_{\|\theta\|=1} (i\mathbf{k} \cdot \theta)^\alpha M(d\theta) \right]. \quad (27)$$

Therefore, using the Plancherel Theorem [55], M_T can be written as

$$\begin{aligned} M_T &= - \frac{1}{2} \frac{\partial}{\partial t} \int_{\mathbb{R}^d} u^2(\mathbf{x}, t) \, d\mathbf{x} \\ &= - \frac{1}{2} \frac{d}{dt} \frac{1}{(2\pi)^d} \int_{\mathbb{R}^d} \hat{u}(\mathbf{k}, t) \overline{\hat{u}(\mathbf{k}, t)} \, d\mathbf{k} \\ &= - \frac{1}{2} \frac{d}{dt} \frac{1}{(2\pi)^d} \int_{\mathbb{R}^d} \hat{u}(\mathbf{k}, t) \hat{u}(-\mathbf{k}, t) \, d\mathbf{k} \\ &= - \frac{1}{2} \frac{d}{dt} \frac{1}{(2\pi)^d} \int_{\mathbb{R}^d} \hat{u}_0(\mathbf{k}) \hat{u}_0(-\mathbf{k}) \exp \left[t(i^\alpha + (-i)^\alpha) \int_{\|\theta\|=1} (\mathbf{k} \cdot \theta)^\alpha M(d\theta) \right] \, d\mathbf{k} \end{aligned} \quad (28)$$

where $(\pm i)^\alpha = \exp(\pm i\pi/2) = \cos(\pi\alpha/2) \pm i \sin(\pi\alpha/2)$. Then $i^\alpha + (-i)^\alpha = 2 \cos(\pi\alpha/2)$, and a change of variables $\mathbf{k}' = t^{1/\alpha} \mathbf{k}$ leads to

$$M_T = - \frac{1}{2} \frac{d}{dt} \left(t^{-d/\alpha} (2\pi)^{-d} \int_{\mathbb{R}^d} \hat{u}_0(t^{-1/\alpha} \mathbf{k}) \hat{u}_0(-t^{-1/\alpha} \mathbf{k}) \exp \left[2 \cos(\pi\alpha/2) \int_{\|\theta\|=1} (\mathbf{k} \cdot \theta)^\alpha M(d\theta) \right] \, d\mathbf{k} \right). \quad (29)$$

The integral over $\mathbb{R}^d$ is not independent of time, but since we have $\hat{u}_0(t^{-1/\alpha} \mathbf{k}) \rightarrow \hat{u}_0(0) = \int u_0(\mathbf{x}) \, d\mathbf{x}$ as $t \rightarrow \infty$, it follows that at late times

$$M_T = Ct^{-(\alpha+d)/\alpha}, \quad (30)$$

where

$$C = \frac{d}{2\alpha(2\pi)^d} \int_{\mathbb{R}^d} \hat{u}_0(0)^2 \exp \left[2 \cos(\pi\alpha/2) \int_{\|\theta\|=1} (\mathbf{k} \cdot \theta)^\alpha M(d\theta) \right] \, d\mathbf{k}. \quad (31)$$

Thus the global reaction rate diminishes as a power law in time, the scaling of which depends only on the fractional derivative exponent α and the dimension. The mixing measure, which controls finer details of the dispersion, is reflected in the constant C as is the structure of the initial condition $\hat{u}_0(0)$. A figure comparing the global reaction rate R_T calculated with the finite difference method and the scalar dissipation approximation $1/4M_T$ from (24) for the example cases considered in Figs. 2 and 3 is shown in Fig. 5. The approximation $R_T = 1/4M_T$ works well at late times as shown by the close agreement. At early times, particularly for the more anomalous cases, the approximation is not good. At small times larger values of u exist that make the Taylor expansion approximation in (23) poor. With regard to mixing, at early times systems with smaller α , i.e., more anomalous transport, display greater mixing as quantified by M_T , while at late times systems with larger α have greater mixing. This is very similar to the one dimensional case and physically represents the fact that enhanced early time mixing must lead to better mixed late time states. For the Fickian case, we recover the well-known scaling $t^{-d/2-1}$, e.g., see Ref. [30]. Note that for a delta pulse initial condition (i.e. $u(\mathbf{x}, t = 0) = \delta(\mathbf{x})$) the scaling (30) emerges immediately and holds at all times.

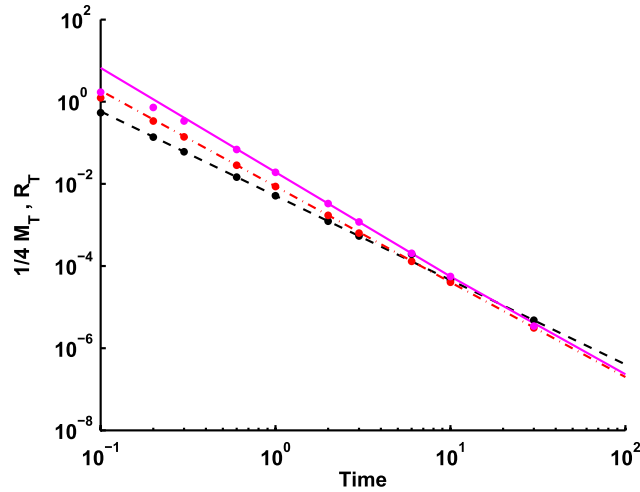


Fig. 5. (Color online) A comparison between global reaction rate R_T and the scalar dissipation rate approximation $M_T/4$. The lines represent $M_T/4$ for $\alpha = 1.9$ (black —), $\alpha = 1.5$ (red —) and $\alpha = 1.3$ (purple —). The equivalent dots correspond to R_T measured from the finite difference calculations. In all cases the mixing measure $M(d\theta)$ is pinned on the x and y axes, i.e. $M(d\theta) = \frac{1}{2}(\delta(\theta) + \delta(\theta - \pi/2))d\theta$ and $u_\infty = 0$.

3. Conclusion

We have studied mixing processes and mixing-driven instantaneous equilibrium reactions in a multidimensional system where transport is governed by the space fractional dispersion equation, which reflects mass transfer over large distances. Our conclusions can be summarized as

- (i) The reactive system considered in this work can be fully understood by modeling the transport of an equivalent conservative component $u = c_1 - c_2$.
- (ii) The reaction rate r for a system with fractional dispersion is nonlocal in nature, as reactants can move long distances over short periods of time in such a system.
- (iii) Reactions in systems governed by the fADE can take place in regions where they would be precluded from occurring in the Fickian case. Regions of zero reaction in the Fickian case can become regions of maximum reaction for anomalous systems. This has been observed in previous research [33] for the one dimensional case, but appears to occur to an even greater extent in the multidimensional case.
- (iv) Global metrics of reaction and mixing indicate that fractional dispersion changes how quickly mixing and mixing-driven reactions occur. The scalar dissipation rate $M_T(t)$, a measure of mixing over time, scales as $t^{-\frac{d+\alpha}{\alpha}}$, which clearly depends on the value α of the fractional dispersion exponent.

It is important to note that some of the results here are specific to the particular form of chemical reaction chosen, which would be true regardless of chemical reaction. We choose this reaction, because it is one that has been deemed important and relevant to porous media, which also happens to be a field where fractional dispersion models have been popular and had great success. There are however some general take away messages that may apply to other forms of chemical reactions, including the fact that reactions in fractional dispersion systems can take place in locations precluded by traditional models. Additionally the conclusions based on mixing, which is the fundamental driver of many chemical reactions are more general.

4. Future work

It would be interesting to develop a microscopic particle model for the space-fractional reaction–diffusion system (4) and (5). The space-fractional advection–dispersion Eq. (1) governs a random walk of dispersive particle motions $X_1 + \dots + X_n$ with polar decomposition $X = R\theta$, where the jump length distribution is given by $P(R > r) = Cr^{-\alpha}$ and the jump direction distribution follows $P(\theta \in U) = M(U)$, with $M(d\theta)$ the mixing measure from (2). Then we have $D = C\Gamma(2 - \alpha)/(1 - \alpha)$ [27, Theorem 6.21]. In order to construct the corresponding particle model for (4) and (5), one has to consider a similar model with particles of three types, and allow particles of types 1 and 2 to combine into particles of type 3 under certain probabilistic conditions. A related model in one spatial dimension was recently considered in Ref. [56] for the case of Fickian dispersion.

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Appendix A. Local reaction rate

Using (3), the reaction rate (9) can be calculated as

$$r(\mathbf{x}, t) = -\frac{dc}{du} \frac{\partial u}{\partial t} + \nabla_M^{\alpha-1} \cdot \left[\frac{dc}{du} \nabla u \right]. \quad (32)$$

Now write

$$\nabla c = \frac{dc}{du} \nabla u$$

and $\mathbf{x} = (x_1, \dots, x_d)'$ so that

$$\begin{aligned} \mathbb{D}_M^\alpha c &= \nabla_M^{\alpha-1} \cdot \nabla c \\ &= \nabla_M^{\alpha-1} \cdot \left(\frac{dc}{du} \nabla u \right) \\ &= \int_{\|\theta\|=1} \mathbb{D}_\theta^\alpha \left[\left(\frac{dc}{du} \right) \theta \cdot \nabla u \right] M(d\theta) \\ &= \int_{\|\theta\|=1} \mathbb{D}_\theta^\alpha \left[\left(\frac{dc}{du} \right) \sum_{i=1}^d \theta_i \frac{\partial u}{\partial x_i} \right] M(d\theta) \\ &= \sum_{i=1}^d \int_{\|\theta\|=1} \theta_i \mathbb{D}_\theta^\alpha \left[\frac{dc}{du} \frac{\partial u}{\partial x_i} \right] M(d\theta). \end{aligned}$$

Apply the generalized Leibnitz product rule for multidimensional fractional calculus, Theorem 3.1 in Ref. [50], to see that

$$\begin{aligned} \mathbb{D}_M^\alpha c &= \sum_{i=1}^d \int_{\|\theta\|=1} \theta_i \sum_{j=0}^{\infty} \binom{\alpha-1}{j} \mathbb{D}_\theta^j \left(\frac{dc}{du} \right) \mathbb{D}_\theta^{\alpha-1-j} \left(\frac{\partial u}{\partial x_i} \right) M(d\theta) \\ &= \int_{\|\theta\|=1} \sum_{j=0}^{\infty} \binom{\alpha-1}{j} \mathbb{D}_\theta^j \left(\frac{dc}{du} \right) \mathbb{D}_\theta^{\alpha-1-j} \sum_{i=1}^d \theta_i \left(\frac{\partial u}{\partial x_i} \right) M(d\theta) \\ &= \int_{\|\theta\|=1} \sum_{j=0}^{\infty} \binom{\alpha-1}{j} \mathbb{D}_\theta^j \left(\frac{dc}{du} \right) (\theta \cdot \nabla)^{\alpha-1-j} (\theta \cdot \nabla) u M(d\theta) \\ &= \int_{\|\theta\|=1} \sum_{j=0}^{\infty} \binom{\alpha-1}{j} \mathbb{D}_\theta^j \left(\frac{dc}{du} \right) (\theta \cdot \nabla)^{\alpha-j} u M(d\theta). \end{aligned}$$

Then it follows from (32) that

$$\begin{aligned} r(\mathbf{x}, t) &= -\frac{dc}{du} \mathbb{D}_M^\alpha u + \int_{\|\theta\|=1} \sum_{j=0}^{\infty} \binom{\alpha-1}{j} \mathbb{D}_\theta^j \left(\frac{dc}{du} \right) \mathbb{D}_\theta^{\alpha-j} u M(d\theta) \\ &= \int_{\|\theta\|=1} \sum_{j=1}^{\infty} \binom{\alpha-1}{j} \mathbb{D}_\theta^j \left(\frac{dc}{du} \right) \mathbb{D}_\theta^{\alpha-j} u M(d\theta). \end{aligned} \quad (33)$$

Appendix B. Divergence theorem for global reaction rate R_T

To demonstrate that

$$\int_{\mathbb{R}^d} \nabla \cdot \nabla_M^{\alpha-1} c \, d\mathbf{x} = 0$$

note,

$$\int_{\mathbb{R}^d} \nabla \cdot \nabla_M^{\alpha-1} c \, d\mathbf{x} = \int_{\mathbb{R}^d} \int_{\mathbb{R}^d} \left[\int_{\|\theta\|=1} (i\mathbf{k} \cdot \theta)^\alpha M(d\theta) \right] \hat{c}(\mathbf{k}) \frac{e^{-i\mathbf{k}\mathbf{x}}}{(2\pi)^d} d\mathbf{k} d\mathbf{x}. \quad (34)$$

Executing the integral over $\mathbf{x}$

$$\int_{\mathbb{R}^d} \nabla \cdot \nabla_M^{\alpha-1} c \, d\mathbf{x} = \int_{\mathbb{R}^d} \left[\int_{\|\theta\|=1} (i\mathbf{k} \cdot \theta)^\alpha M(d\theta) \right] \hat{c}(\mathbf{k}) \delta(\mathbf{k}) d\mathbf{k} \quad (35)$$

which as long as $\hat{c}(0)$ is finite, which for any reasonable system should be zero.

To demonstrate

$$\int_{\mathbb{R}^d} \nabla \cdot \left[\left(\frac{dc}{du} \right) \nabla_M^{\alpha-1} u \right] d\mathbf{x} = 0$$

note that

$$\int_{\mathbb{R}^d} \nabla \cdot \left[\left(\frac{dc}{du} \right) \nabla_M^{\alpha-1} u \right] d\mathbf{x} = \oint_{\mathbb{S}^d} \left[\left(\frac{dc}{du} \right) \nabla_M^{\alpha-1} u \right] \cdot d\mathbf{n}. \quad (36)$$

For a very large radius, we know that $u \rightarrow u_\infty$ and as such the Taylor leading approximation for $\frac{dc}{du} = \frac{1}{2} + \frac{u_\infty}{\sqrt{u_\infty^2/4+1}}$ becomes an excellent approximation such that

$$\begin{aligned} \lim_{r \rightarrow \infty} \oint_{\mathbb{S}^d} \left[\left(\frac{dc}{du} \right) \nabla_M^{\alpha-1} u \right] \cdot d\mathbf{n} &= \oint_{\mathbb{S}^d} \left[\left(\frac{1}{2} + \frac{u_\infty}{\sqrt{u_\infty^2/4+1}} \right) \nabla_M^{\alpha-1} u \right] \cdot d\mathbf{n} \\ &= \left(\frac{1}{2} + \frac{u_\infty}{\sqrt{u_\infty^2/4+1}} \right) \int_{\mathbb{R}^d} \nabla \cdot \left[\nabla_M^{\alpha-1} u \right] d\mathbf{x}. \end{aligned}$$

Now a similar argument to (35) shows that this is always zero.

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