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Key Points:

- We propose a novel Lagrangian method for reactive transport
- The method removes a resolution inherent to previous methods
- We demonstrate consistency with classical numerical approaches

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A particle number conserving Lagrangian method for mixing-driven reactive transport

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Abstract The purely Lagrangian algorithm for chemical reactions introduced by *Benson and Meerschaert* (2008) suffers from a low-concentration resolution problem. We alleviate the problem by redefining the probabilistic collision/reaction (birth/death) stochastic process as a mass-reduction operation. Theoretically, this corresponds to replacing an on/off particle with a large number of "subparticles" and tracking the number fraction. The new particle reaction process maintains the original particle numbers but adjusts each particle's mass upon reaction. Several simulations show the veracity as well as the gains in low-concentration resolution offered by the algorithm. We also compare the results to those obtained by a traditional finite difference model with suitably defined initial condition, demonstrating that the Lagrangian models match these.

1. Introduction

Chemical reactions play an important role in the evolution of many hydrologic systems (see the review by *Dentz et al*. [2011]). It is important to recognize that reactants must physically come into contact for reactions to occur; mixing is the process that enables this. Reactions will occur in well-mixed systems at a rate determined purely by thermodynamics. However, when incomplete mixing of reactants occurs, the observed rate of reaction can be significantly less than this. Such incomplete mixing can occur in porous media as exemplified in experiments in a homogeneous glass bead pack by *Gramling et al*. [2002] and a heterogeneous porous medium [*Oates*, 2007]. Many traditional models such as the advection-dispersion-reaction equation (ADRE) assume perfect mixing at some scale and overpredict the amount of reaction that actually occurs. Theoretical studies, based on volume averaging and homogenization [*Battiato et al*., 2009; *Battiato and Tartakovsky*, 2011; *Chiogna and Bellin*, 2013], demonstrate how the mixing assumptions inherent to such models can break down and result in incorrect predictions.

A number of techniques have emerged to address the impact of incomplete mixing on overall reaction progress. These include concentration perturbation expansions [*Luo et al*., 2008; *Tartakovsky et al*., 2012], modifications of nonlocal continuous time random walks [*Edery et al*., 2009; *Hansen and Berkowitz*, 2015; *Zhang et al*., 2014], memory effect models [*Donado et al*., 2009], ADRE models with time-varying kinetic rate parameters [*Sanchez-Vila et al*., 2010], higher-order volume-averaging closures [*Porta et al*., 2013], concentration probability density methods [*Chiogna and Bellin*, 2013], modified spatial Gillespie algorithms [*De Anna et al*., 2011], time-subordination of the Markovian well-mixed reaction [*Benson et al*., 2013], and Lagrangian random walk and reaction models [*Benson and Meerschaert*, 2008]. While all have had some success in reproducing experimental observations, in this note we focus specifically on the random walk methods.

Particle-based random walk methods are popular for use in hydrologic systems, particularly for conservative solute transport, as they are straightforward to implement in heterogeneous velocity fields and, for sufficiently smooth velocity fields, do not suffer from numerical diffusion. Due to their discrete nature, the particle methods impart noise (whether user-defined or not) on concentration fields. If desired, this noise can be smoothed via spatial or temporal interpolation kernels [*Fernàndez-Garcia and Sanchez-Vila*, 2011; *Pedretti and Fernàndez-Garcia*, 2013]. Comprehensive discussions on the benefits and shortcomings of random walk methods (as well as others) are given in *Salamon et al*. [2006] and *Boso et al*. [2013]. An important point that should be stressed regarding particle-based random walk methods is that the numerical particles do not have a physical volume, or size; they are points that carry mass that can move through space and time. This is in contrast to an alternative family of Lagrangian models, Smoothed Particle Hydrodynamics (SPH), which can also be used to model reactive transport. A comprehensive discussion on SPH is also included in *Boso et al*. [2013].

While random walks have also often been used to model reactive transport, in many cases, particle positions are reinterpolated on to an Eulerian grid and reaction rates calculated in an Eulerian manner [*Tompson and Dougherty*, 1992], which may remove some of the inherent benefits of random walks. To avoid this reinterpolation step, *Benson and Meerschaert* [2008] proposed a novel random collision method for reactive transport. *Paster et al*. [2013] theoretically demonstrated the equivalence of this method and a diffusion-reaction equation in the limit of infinitesimal time step. Using this method, described in detail below, *Benson and Meerschaert* [2008] studied the simple reaction $A+B \rightarrow C$ in a one-dimensional system where particles are initially uniformly, but randomly, distributed in the domain of interest with equal mean initial concentrations of both reactant species. If the system is well-mixed, the mean concentration in the domain evolves at late time as $C \sim t^{-1}$. However, with their method, *Benson and Meerschaert* [2008] show that at late times the concentrations actually evolve as $t^{-1/4}$ in one dimension. This late time scaling emerges due to incomplete mixing of the reactants and the result is consistent with predictions by physicists working on related problems [*Toussaint and Wilczek*, 1983; *Kang and Redner*, 1985; *Zumofen et al*., 1996; *De Anna et al*., 2011]. *Paster et al*. [2014] generalized the method to two and three dimensions and demonstrated that the results are consistent with those obtained by a moment method closure [*Tartakovsky et al*., 2012]. In particular, these studies all show that the time-of-onset of the anomalous reaction rate (i.e., $t^{-1/4}$ in the one-dimensional case) depends on the size of the domain, the number of particles used, the rate of reaction, and the magnitude of diffusion coefficient, all of which can be combined into a single dimensionless Damkohler number. Because the particle-based solution depends on the initial number of particles, it would appear that the solution is discretization-dependent, since the chosen number of particles discretizes the total mass of the system. This problem was addressed by *Paster et al*. [2014], who showed that the finite number of particles naturally encodes an autocorrelated stochastic initial condition, which is responsible for the transition to an incomplete mixing regime at late times. Hence, the initial particle number and initial particle masses are not an arbitrary modeling choice. Using this argument, *Ding et al*. [2013] were able to use this method to reproduce the experimental observations of reactive transport in a column, where they independently estimated the required number of particles from the concentration images presented by *Gramling et al*. [2002].

While the analytical methods of *Tartakovsky et al*. [2012] and *Paster et al*. [2014] can explain these particle-number-dependent behaviors, they are based on closures that make some strong assumptions that require further validation; e.g., the assumption that third and higher-order moments in concentration are negligible and the assumption of highly idealized initial conditions for auto and cross correlations of the species concentration fields that make the problem analytically tractable. Additionally, the algorithm of *Benson and Meerschaert* [2008] simply removes particles upon species conversion, which naturally imposes a resolution with which concentration can be measured (i.e., the mass of a single particle). As we show in detail in this work, this restriction results in poor convergence of this particle tracking algorithm at late times. In this note we propose a modification to the algorithm of *Benson and Meerschaert* [2008], which circumvents the removal of particles and allows for resolution of smaller concentrations as needed. We also compare the original and modified method to the results of a highly resolved finite-difference-based solution, but with an equivalent stochastic initial condition, to demonstrate that these methods are indeed solving the reactive transport problem correctly. Additionally, we show the convergence of the proposed algorithm to the diffusion-reaction equation in the limit of infinitesimal time step.

2. Problem Setup

Consider a one-dimensional domain of length L. The domain is initially filled with solutes A and B of concentrations $C_A(x,t)$ and $C_B(x,t)$ $[ML^{-1}]$, which evolve by the reaction diffusion equation

$$\frac{\partial C_i}{\partial t} = D\frac{\partial^2 C_i}{\partial x^2} - kC_AC_B, \qquad i=A,B, \tag{1}$$

where D $[L^2T^{-1}]$ is the diffusion coefficient, assumed to be the same for both A and B and k $[LM^{-1}T^{-1}]$ is the thermodynamic reaction rate. The initial mass of each reactant in the domain is the same such that the average concentration C_0 of each is the same. The 1:1 stoichiometry of the reaction implies that the mean concentration of each will be the same at all times. The initial concentration in the domain is defined by discretizing the total mass of reactant into N_0 particles and distributing these particles by assigning a position to each particle drawn from a uniform distribution $U(0, L)$. The mean distance between each particle is then given by $l=L/N_0$. This distance encodes the autocorrelation scale of noise in the initial condition [*Paster et al.*, 2014]. Boundary conditions at $x=0$ and L are considered periodic.

Defining nondimensional variables $t^*=tkC_0$, $x^*=x/l$, and $C^*=C/C_0$ the governing equation can be written in dimensionless form

$$\frac{\partial C_i^*}{\partial t^*}=\frac{1}{Da}\frac{\partial^2 C_i^*}{\partial x^{*2}}-C_A^* C_B^*, \qquad i=A, B, \tag{2}$$

where $Da=kC_0 l^2/D$ is the Damkohler number that quantifies the ratio of how quickly the species react to how quickly they diffuse.

2.1. Particle Tracking: The *Benson and Meerschaert* [2008] Algorithm

Particles in this algorithm go through a two-step process during each time step. First their positions are updated following a standard Langevin equation

$$\mathbf{x}_i^*(t^*+\Delta t^*)=\mathbf{x}_i^*(t^*)+\sqrt{\frac{2\Delta t^*}{Da}}\xi_i, \qquad i=A, B, \tag{3}$$

where $\mathbf{x}^*$ is the vector of dimensionless particle locations and ξ is a vector of the same length with independent normally distributed variables with zero mean and unit variance. Next, to assess reaction, each A, B particle pair is compared. We cycle through each A particle and compare to all B particles. For each pair the probability of reaction is calculated as

$$P_{react}=P_{col}P_{react|col}, \tag{4}$$

where the probability density function (for Fickian diffusion) of colocation $v^*(s^*)=dP_{col}/dx^*=\frac{1}{\sqrt{8\pi\Delta t^*/Da}} e^{\frac{-s^{*2}}{8\Delta t^*/Da}}$ depends on the separation distance $s^*=|x_A^*-x_B^*|$. In dimensionless units, the probability of reaction is calculated by $P_{react}=\Delta t^* v^*(s^*)$. For a dimensional form of this expression we refer the interested reader to the original work by *Benson and Meerschaert* [2008].

The probability of reaction P_{react} is compared to a uniform random number $U(0, 1)$ and if $P_{react} > U$ the reaction occurs and both particles are removed from the system. In this specific work we are not interested in tracking the evolution of the reaction product C, but if we were, a new C particle would be created [e.g., *Ding and Benson*, 2015]. Otherwise, if the reaction does not occur, both particles survive and we move on to the next particle pair until all have been exhausted. Then we move to the next time step and begin the process again. For practical reasons we only actually compare particle pairs that are closer than a distance $a\sqrt{2\Delta t^*/Da}$, where $a=3$, as the probability of reactions for particles at distances greater than this is negligible and this significantly speeds up calculations (for details, see *Paster et al.* [2014]).

2.2. Particle Tracking: Number Preserving

Here we propose a modification to the above algorithm. In this method each particle is characterized by (i) its location $x^*(t^*)$ and (ii) the amount of mass that it carries which we denote by $m^*(t^*)$, both of which evolve in time. In the same way as before, during each time step particle locations are updated via a random walk as in equation (3). Again, as above, we cycle through all particle pairs in the system, but rather than calculating the probability that a reaction occurs we note that the probability density for a particle location starting at a point x_0^* at the beginning of a time step, after a time step Δt^* is given by

$$p^*(x^*, \Delta t^*|x_0^*)=\frac{1}{\sqrt{4\pi\Delta t^*/Da}} e^{\frac{-(x^*-x_0^*)^2}{4\Delta t^*/Da}}, \tag{5}$$

which is the fundamental solution to the diffusion equation for a pulse initial condition at $x^*=x_0^*$ after time step Δt^*.

Now we propose that the rate of reaction between an A particle and a B particle will reduce the mass of each particle. Heuristically, the mass of each particle spreads according to the Gaussian, and we may integrate the local reactions that follow the law of mass action such that

$$\begin{aligned}-\frac{\Delta m^*_{A,B}}{\Delta t^*}=\int_\Omega r dx=&\int_\Omega \frac{m^*_A}{\sqrt{4\pi\Delta t^*/Da}}\, e^{\frac{-(x^*-x^*_{A0})^2}{4\Delta t^*/Da}}\times\frac{m^*_B}{\sqrt{4\pi\Delta t^*/Da}} e^{\frac{-(x^*_{B0}-x^*)^2}{4\Delta t^*/Da}}dx^*\\ &=\frac{m^*_A m^*_B}{\sqrt{8\pi\Delta t^*/Da}} e^{\frac{-(x^*_{A0}-x^*_{B0})^2}{8\Delta t/Da}}=m^*_A m^*_B v^*(s^*).\end{aligned} \tag{6}$$

An argument making the heuristics more rigorous is presented in Appendix A and again for the interested reader, equation (6) is presented in dimensional form in equation (A1).

The mass of each particle is updated following (6) and then we move on to the next particle pair until all have been exhausted. Note that in the method above, the change of mass of a particle depends only on the distance between particles and the Damkohler number. Again, for efficiency only particles within a distance $a\sqrt{2\Delta t^*/Da}$ are considered. With this algorithm no particle is ever destroyed, but the mass that it carries continuously decreases over time. Similar to the procedure of *Paster et al*. [2013] we show that the modified algorithm converges to the ADRE at the limit $\Delta t^* \to 0$ (see Appendix B).

2.3. Finite Differences

We also solve equation (2) using a first-order explicit in time, central in space finite difference method

$$\frac{C^*_i(x^*,t^*+\Delta t^*)-C^*_i(x^*,t^*)}{\Delta t^*}=\frac{1}{Da}\frac{C^*_i(x^*+\Delta x^*,t^*)-2C^*_i(x^*,t^*)+C^*_i(x^*-\Delta x^*,t^*)}{(\Delta x^*)^2}-C^*_A(x^*,t^*)C^*_B(x^*,t^*). \tag{7}$$

The discretization in space $\Delta x^*=1/N$ is chosen so as to resolve the noisy initial condition, which is set by counting the number of initial particles n in each bin and assigning a concentration $\frac{n}{N\Delta x^*}$. Time steps are chosen to ensure stability of the numerical simulation $\Delta t^*=bDa(\Delta x^*)^2$, where $b=0.1$, less than the required value of 0.5 [*Pozrikidis*, 1998]. Note that for the smallest Da numbers this restriction can result in an extremely small and restrictive time step.

3. Results

We ran the above described algorithms for four test cases. As the only dimensionless parameter describing the behavior of this system is Da, we vary it over several orders of magnitude such that $Da=10^{-3}, 10^{-2}, 10^{-1}, 1$. In all cases, 1000 particles were used to calculate the solutions (or in the case of the finite difference method to generate the initial condition). In Figure 1, we plot the evolution of mean concentration against time for the three numerical models proposed above and we also include the solution to the well-mixed problem $C^*_{wm}=\frac{1}{1+t^*}$. In all cases the ensemble average mean concentration over 10 realizations is shown.

For the larger $Da=1$ case we clearly observe the emergence of the anomalous $t^{-1/4}$ scaling, while for the smallest $Da=10^{-3}$, mixing is dominant enough that this behavior is never observed. The intermediate cases show the anomalous time scale as well as a deviation associated with a finite size effect. Due the finite size of the domain the system eventually rehomogenizes (i.e., segregated regions of reactants, or so-called "islands" of a single species become large in comparison to the size of the domain and begin to overlap in a well-mixed manner). Note that while the existence of this finite size effect has been identified and discussed in previous studies [*Bolster et al*., 2012; *Paster et al*., 2014, 2015], the return of the system to the well-mixed scaling of $C\sim t^{-1}$ has not, mainly due to a resolution issue, discussed in further detail below.

The match between all three methods is excellent, particularly for larger concentrations. For smaller dimensionless concentrations, of order 10^{-3}, the finite difference method and the particle number preserving random walk method we propose here continue to match quite well, while the particle destroying method does not, which is not surprising given that with 1000 particles the best resolution that this method can achieve is $\mathcal{O}(1/1000=10^{-3})$.

It should be noted that this issue of resolution can be readily addressed by using more particles; obviously this comes at additional computational cost, which when done naively scales as $\mathcal{O}(N^2)$, but when done

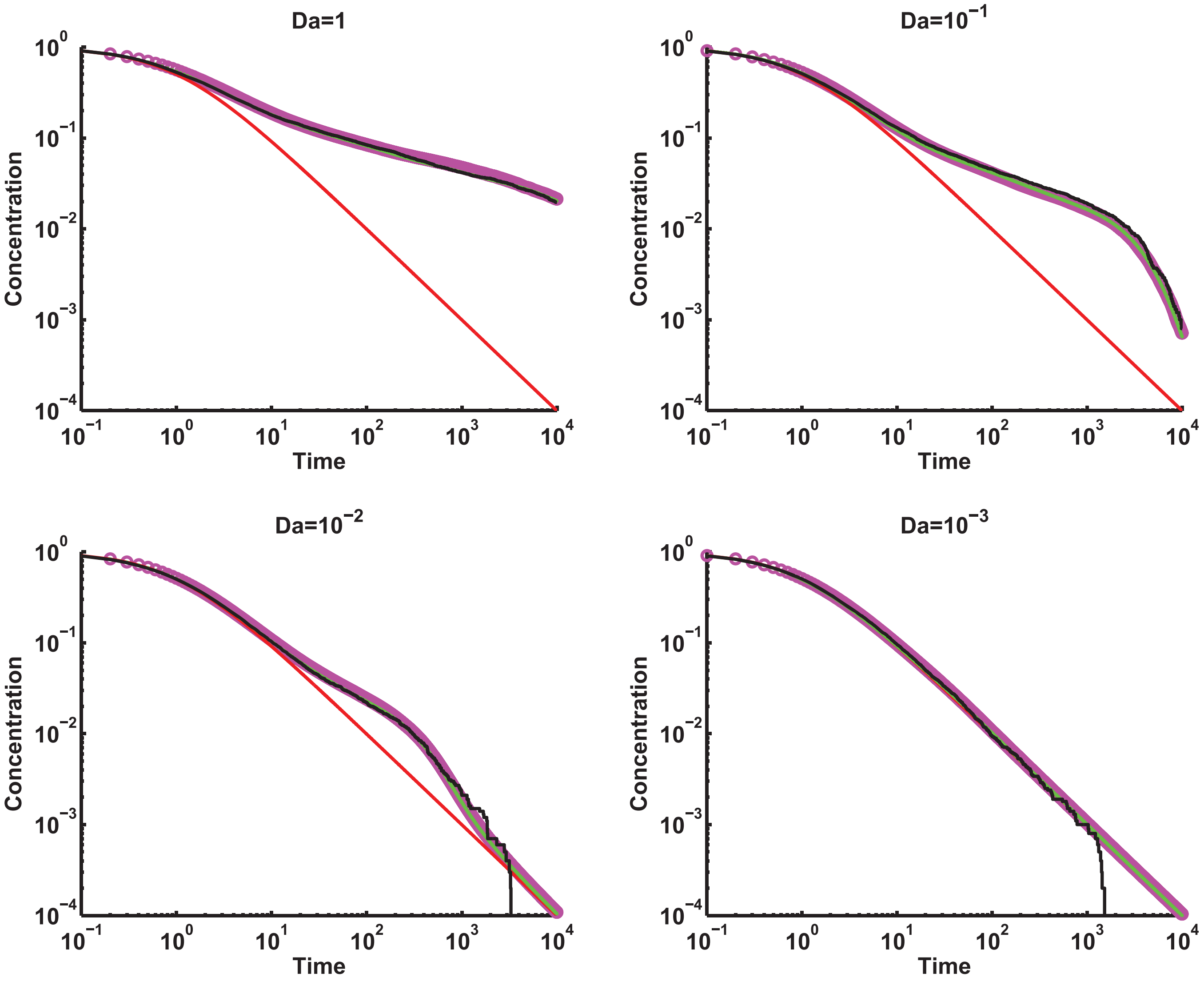

Figure 1. Comparison of the three numerical methods. Average concentrations plotted against time for the well-mixed case (red line), *Benson and Meerschaert*'s original particle method (black line), our modified particle method (purple circles), and the finite difference solution (green line).

efficiently can be reduced to $\mathcal{O}(N\ln N)$ [*Paster et al.*, 2014]. To demonstrate that the same problem can be solved with greater resolution, we also ran the same four sets of simulations, using *Benson and Meerschaert*'s original particle tracking algorithm, but increased the number of particles by a factor of 10 ($N=10^4$). To ensure that we still consider the same initial condition as before, 10^3 particles of each species are distributed randomly and uniformly through the domain and then an additional nine particles of the same kind are placed at each of these locations. In all cases we obtain an improved match with the other numerical solutions over one more order-of-magnitude of concentration (Figure 2). For context the solution that would be obtained if the 10^4 particles were randomly but uniformly distributed throughout the entire domain is also shown, clearly yielding a different (better mixed) result. For clarity, in the comparison only the results of the finite difference solution are shown in Figure 2. If we increase the number of particles, in the same manner, to 10^5 (not shown here) the solution also matches well at all plotted times. Again this validates the fact that the solution to the imperfectly mixed problem is entirely dependent on the spatial correlation structure associated with the initial condition and is not a numerical error associated with a finite number of particles.

These results emphasize that any particle-based method will inherently have a noise associated with it, meaning that representing a perfectly uniform initial concentration is more difficult to encode. A recent paper by *Rahbaralam et al.* [2015] applies a kernel density estimator method to smooth the concentration

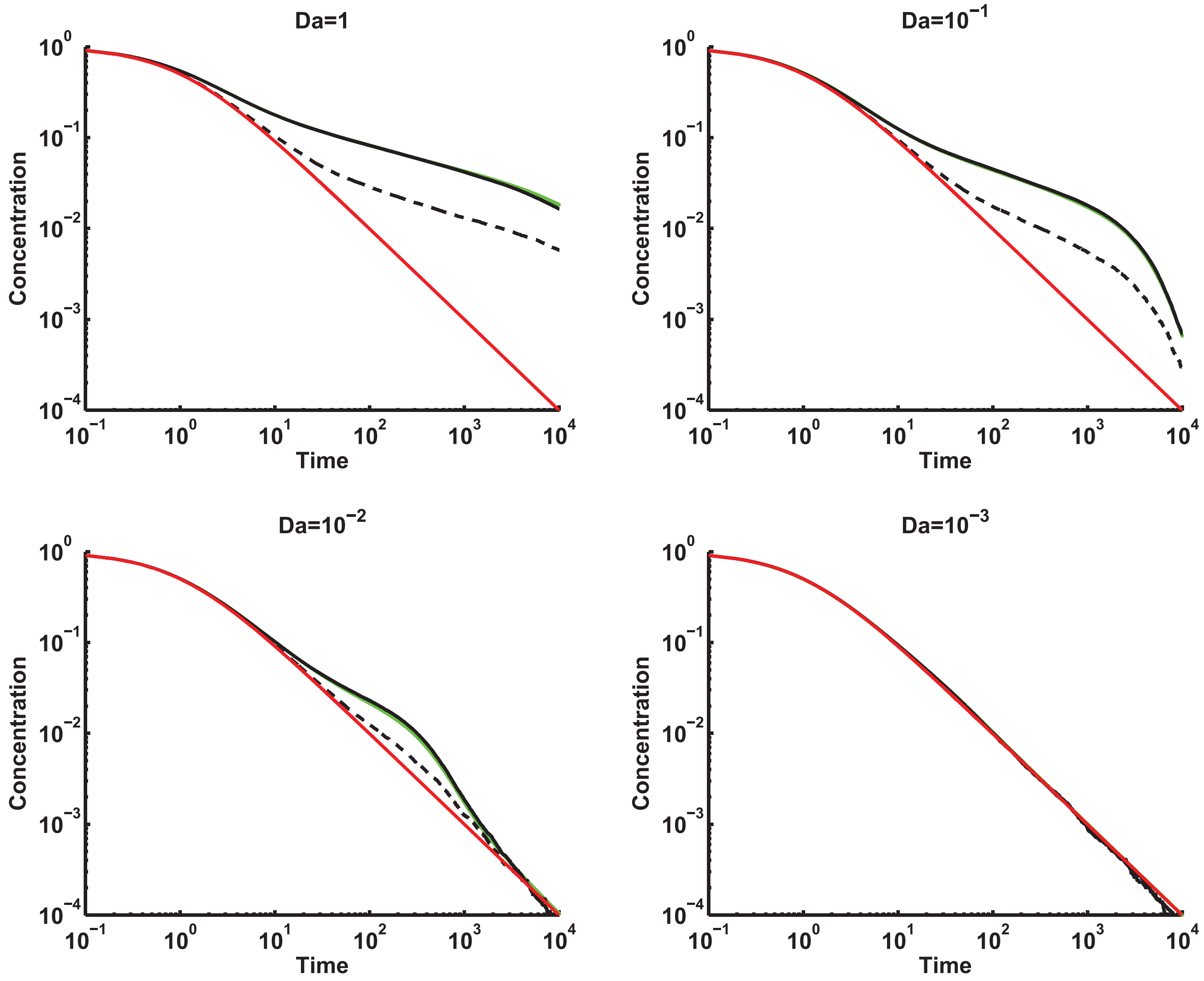

Figure 2. Average concentrations plotted against time for *Benson and Meerschaert*'s particle method with 10 times as many particles as in Figure 1, but an identical initial condition (black line) and the finite difference solution (green line). For context the solution that would be obtained if the 10 times as many particles were randomly but uniformly distributed throughout the domain is also shown (dashed black line). The red line corresponds to the well-mixed solution. Note how compared to Figure 1 the solutions match better at lower concentrations up to concentrations of O(10^{-4}), whereupon resolution effects again become an issue for Benson and Meerschaert's method.

field from the particles, thus suppressing incomplete mixing effects and allowing well-mixed reaction calculations with a relatively small number of particles. On the other hand, incorporating the noisy initial condition can be beneficial as it can represent the incomplete mixing effects that arise in natural systems [e.g., *Ding et al*., 2013], but the link between concentration statistical structure and particle numbers is something that a user must be aware of. The two approaches are important and indeed kernel-based approaches need not damp out all noise and could be designed to generate more complex initial conditions, while maintaining a tractable number of particles.

4. Conclusions

In this note we have proposed a modification to *Benson and Meerschaert*'s reactive random walk method, where we preserve the number of particles in the system at all times, but allow the mass of each particle to change over time, rather than fixing it at a given value and either allowing a particle to survive or be destroyed. We apply the method to a classical problem, a bimolecular reaction in a finite periodic domain, where the initial mean concentrations of both species are the same and solutes move by diffusion. The emergent behavior is controlled by the dimensionless Damkohler number, which quantifies how quickly reaction happens relative to diffusive mixing. We solve our example problem for four test cases, spanning 4 orders of magnitude in *Da*, ranging from a system where incomplete mixing effects dominate to one where they are completely suppressed. Additionally, we solve the problem using a well-established and classical finite difference method, encoding the same noisy initial conditions inherent to the particle tracking algorithms. In all cases we demonstrate good agreement between all three methods although *Benson and Meerschaert*'s original algorithm fails to match the other two correctly at concentrations smaller than $\mathcal{O}(1/N)$ where N is the number of particles used, which in their method sets a scale for the smallest resolvable concentration. Our modification to this method does not suffer from this resolution issue as any particle can take on any arbitrarily small mass. We demonstrate that the resolution problem associated with *Benson and Meerschaert*'s algorithm can be rectified by using more particles, but preserving the desired initial condition. The consistency of the modeled mean concentrations across all methods verifies that the slow-down of reactions that occurs is indeed associated with a noisy initial condition, as suggested theoretically by previous works [*Paster et al.*, 2014; *Bolster et al.*, 2012; *Tartakovsky et al.*, 2012], but relying on strong closure assumptions. This clearly shows how important characterizing initial conditions can be for reactive systems. While in conservative transport cases, noise and specific details associated with the initial condition can smear out over time, for the case of reactive transport strong and controlling signatures can remain for all times. Although in this work we focus on a one-dimensional problem, all the above can readily be extended to two and three dimensions, following for example the work of *Paster et al*. [2014].

While we have shown that this modified approach does not suffer from the aforementioned resolution issue that *Benson and Meerschaert*'s original algorithm does, we have only applied it to a relatively simple reaction system. This novel approach remains to be fully tested in more complex reaction systems, with multiple species and reversible reactions. In this context the original method recently has been extended with an application to mixing-limited Michaelis-Menton-type bioremediation reactions [*Ding and Benson*, 2015].

Appendix A: Making Heuristics in Equation (6) Rigorous

Equation (6) for the reduction of the mass of each particle in our modified algorithm is presented heuristically in this note. The heuristics are made rigorous by defining a particle as a collection of many "subparticles" at the same location, and defining the changing mass of a particle of species i as $m_i = \lim_{N\to\infty} \frac{n_i}{N} m_0$, where n_i is the number of subparticles at time t, and m_0 is the initial mass of one macroparticle. To elucidate certain physical features all variables in this appendix are presented in dimensional form and the resulting expressions are only made nondimensional, as in the main text, in the final step. At $t=0$, by which we mean the beginning of a time step, $n_i = N$, i.e., all subparticles are present. Focusing on the change in mass of an A "macroparticle" when reacting with one other B "macroparticle," we may write

$$\frac{dm_A}{dt} = \lim_{N\to\infty} \lim_{\Delta t\to 0} \frac{(n_A+\Delta n_A)-n_A}{N\Delta t} m_0 = \lim_{N\to\infty} \lim_{\Delta t\to 0} \frac{\Delta n_A}{N\Delta t} m_0. \tag{A1}$$

To calculate the number of subparticles reacted, consider the probabilities of the sequence of reactions starting with the first A subparticle and first B subparticle $P_{1,1}(react) \equiv P_{1,1} = m_p \Delta t k v(s)$, where the mass of each microparticle $m_p = m_A/n_A = m_0/N$. The reaction with the next B subparticle factors in the survival probability from the previous reaction, so $P_{1,2} = m_p \Delta t k v(s)(1-P_{1,1})$, and the nth B subparticle has $P_{1,n_B} = m_p \Delta t k v(s)(1+\sum_{m=1}^{n_B-1} (-P_{1,1})^m)$. Because $m_p = m_0/N$, the higher-order terms are negligible for small Δt and large N so that $P_{1,n_B} \approx P_{1,1} = m_p \Delta t k v(s)$. A similar argument extends to the other A subparticles. By definition, for $N \to \infty$, the proportion of subparticles that react is the total number of possible reactions times the probability of each: $\Delta n_A = -\sum_{i=1}^{n_A} \sum_{j=1}^{n_B} P_{i,j} = -n_A n_B P_{1,1}$, so

$$\frac{dm_A}{dt} = \lim_{N\to\infty} \lim_{\Delta t\to 0} \frac{-n_A n_B k \Delta t m_p v(s)}{N\Delta t} m_0 = -n_A n_B \frac{m_0}{N} \frac{m_0}{N} k v(s) = -m_A m_B k v(s). \tag{A2}$$

Returning to dimensionless quantities, where $m_i^* = m_i/(C_0 l)$ and $v(s) = (1/l) v^*(s^*)$,

$$\frac{dm_A^*}{dt^*} = -m_A^* m_B^* v(s^*). \tag{A3}$$

Appendix B: Convergence to ADRE

In the revised algorithm, in each time step, the particles move by random walk and then react. For species *A*, and similarly for species *B*, this can be formally written as

$$x^*_{Aj}(t^*+\Delta t^*)=x^*_{Aj}(t)+\sqrt{2\Delta t^*/Da}\,\xi_j, \tag{B1}$$

$$m^*_{Aj}(t^*+\Delta t^*)=m^*_{Aj}(t^*)+\Delta m^*_{Aj}(t^*), \tag{B2}$$

where $j=1,\ldots,N_A$ is the *A* particle index, and

$$\Delta m^*_{Aj}=-m^*_{Aj}\sum_{k=1}^{N_B} m^*_{Bk}(t^*)v^*\left(x^*_{Aj}(t^*)-x^*_{Bk}(t^*)\right)\Delta t^* \tag{B3}$$

is the reduction in its mass.

Our method is in essence an operator splitting approach, and the convergence of the random walk process to the diffusion equation (without reaction) is well known. What remains to be proven is that the change of the mass of the particles, as described by equations (B2) and (B3) is a correct analogy of the reaction operator $\frac{\partial C^*_i}{\partial t^*}=-C^*_A C^*_B$. Thus, our goal here is to show that the modified reaction step we propose indeed converges to this expression.

Now consider an infinitesimal volume $d\mathbf{x}^*$ and define $W^*_A(\mathbf{x}^*,t^*)d\mathbf{x}^*$ as the expected mass of particles in this infinitesimal volume, centered at $\mathbf{x}^*$. Hence, the expected mass density of particles is given by $W^*_A(\mathbf{x}^*,t^*)$ and it evolves due to the random walk to

$$W^{*\prime}_A(\mathbf{x}^*,t^*+\Delta t^*)=\int W^*_A(\mathbf{y}^*,t^*)g(\mathbf{x}^*-\mathbf{y}^*\,;\Delta t^*)d\mathbf{y}^*, \tag{B4}$$

where the prime denotes the updated distribution after the random walk, and *g* is the Gaussian

$$g(\mathbf{x}^*-\mathbf{y}^*\,;\Delta t^*)=\frac{1}{(4\pi\Delta t^*/Da)^{d/2}}e^{-\frac{(\mathbf{x}^*-\mathbf{y}^*)^2}{4\Delta t^*/Da}}. \tag{B5}$$

A similar expression can be written for $W^{*\prime}_B$. Expanding a Taylor series of $W^*_A(\mathbf{y}^*,t^*)$ about point $\mathbf{x}^*$ and substituting it in (B4) gives

$$\int W^*_A(\mathbf{y}^*,t^*)g(\mathbf{x}^*-\mathbf{y}^*,\Delta t^*)d\mathbf{y}^*=W_A(\mathbf{x}^*,t^*)+\frac{\Delta t^*}{Da}\frac{\partial^2 W^*_A}{\partial x^{*2}}+\mathcal{O}((\Delta t^*/Da)^2). \tag{B6}$$

A similar expression arises for the *B* species. The expected mass density loss in the reaction step (B2) and (B3) is given by

$$\Delta W^{*\prime}_A(\mathbf{x}^*,t^*+\Delta t^*)=W^{*\prime}_A(\mathbf{x}^*,t^*+\Delta t^*)\int v^*(\mathbf{x}^*-\mathbf{x}^{*\prime})W^{*\prime}_B(\mathbf{x}^{*\prime},t^*+\Delta t^*)d\mathbf{x}^{*\prime}\Delta t^*. \tag{B7}$$

Therefore, the remaining mass density is

$$\begin{aligned}W^*_A(\mathbf{x}^*,t^*+\Delta t^*)=W^{*\prime}_A(\mathbf{x}^*,t^*+\Delta t^*)-\Delta W^{*\prime}_A(\mathbf{x}^*,t^*+\Delta t^*)=\\ W^{*\prime}_A(\mathbf{x}^*,t^*+\Delta t^*)\left[1-\Delta t^*\int v^*(\mathbf{x}^*-\mathbf{x}^{*\prime})W^{*\prime}_B(\mathbf{x}^{*\prime},t^*+\Delta t^*)d\mathbf{x}^{*\prime}\right],\end{aligned} \tag{B8}$$

which becomes after substitution of (B4),

$$\begin{aligned}\int W^*_A(\mathbf{y}^*,t^*)g(\mathbf{x}^*-\mathbf{y}^*\,;\Delta t^*)d\mathbf{y}^*\left[1-\Delta t^*\int v^*(\mathbf{x}^*-\mathbf{x}^{*\prime})\int W^*_B(\mathbf{y}^{*\prime},t^*)g(\mathbf{x}^{*\prime}-\mathbf{y}^{*\prime}\,;\Delta t^*)d\mathbf{y}^{*\prime}d\mathbf{x}^{*\prime}\right]=\\ \left[W^*_A(\mathbf{x}^*,t^*)+\frac{\Delta t^*}{Da}\frac{\partial^2 W^*_A}{\partial x^{*2}}+\mathcal{O}(\Delta t^{*2})\right]\left[1-\Delta t^* W^*_B(\mathbf{x}^*,t^*)+\mathcal{O}(\Delta t^*)\right].\end{aligned} \tag{B9}$$

Taking first-order terms this implies

$$\frac{W^*_A(\mathbf{x}^*,t^*+\Delta t^*)-W^*_A(\mathbf{x}^*,t^*)}{\Delta t^*}=\frac{1}{Da}\frac{\partial^2 W^*_A}{\partial x^{*2}}-W^*_A(\mathbf{x}^*,t^*)W^*_B(\mathbf{x}^*,t^*), \tag{B10}$$

which converges as $\Delta t^* \to 0$ to

$$\frac{\partial W_A^*}{\partial t^*} = \frac{1}{Da} \frac{\partial^2 W_A^*}{\partial x^{*2}} - W_A^* W_B^*. \tag{B11}$$

A similar expression for W_B^* can be obtained as well. Thus, the leading order of the evolution of mass density in our particle system converges in the limit $\Delta t^* \to 0$ to the governing equation of concentration of the system we model (equation (2)).

This result can be extended to the case where advection is present, i.e., when a term $\mathbf{u} \cdot \nabla C$ appears in the LHS of equation (2). In this case the PT algorithm includes an advection step, where to first-order the particles are translated by $\mathbf{u}\Delta t$. The formal derivation of this extension is straightforward (via operator splitting) and is not presented here in detail. The interested reader may refer to the work of *Uffink* [1988] or *LaBolle et al.* [2000].

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