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Particle Tracking and the Diffusion-Reaction Equation

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Abstract. Particle tracking algorithms are very useful methods to model conservative transport in surface and subsurface hydrological systems. Recently, a novel *ad hoc* particle-based method was proposed to account for multicomponent reactive transport by *Benson and Meerschaert* [2008]. This one-dimensional particle method has been shown to match theoretical predictions, but to date there has been no rigorous demonstration that the particle method actually matches the governing equations for chemical transport. We generalize this particle method to two-dimensional and three-dimensional systems and rigorously demonstrate that this particle method converges to the diffusion-reaction equation at the limit of infinitely small time step. We also investigate the numerical error associated with the method.

1. Introduction

Water that flows through aquifer and surface water bodies typically changes in chemical composition along a flow path. One of the mechanisms for this is chemical reaction, either with neighboring solids and biota, or with other dissolved constituents. An accurate prediction of the chemical evolution of a system requires models (for example, governing equations) that correctly describe the chemistry and physics of the reactions across many spatial and temporal scales. Examples of these systems include radionuclide transport [*Ma et al.*, 2010; *Greskowiak et al.*, 2010; *Hammond and Lichtner*, 2010], CO_2 sequestration [*Strazisar et al.*, 2006; *Audigane et al.*, 2007; *Han et al.*, 2010], ore body generation [*Raffenspreger*, 1997; *Schardt et al.*, 2001], hydrothermal systems [*Lichtner*, 1985; *Steefel and Lasaga*, 1994], chemical and biochemical remediation of contaminated aquifers [*Molz and Widdowson*, 1988; *Knutson et al.*, 2005, 2007; *Steefel et al.*, 2005; *Mayer et al.*, 2001, 2002, 2006], and basin-scale diagenesis, reservoir rock and petroleum generation [*Lee*, 1997; *Morse et al.*, 1997; *Wilson et al.*, June, 2000; *Jones and Xiao*, 2006] to name a few, but the problem is not restricted to aqueous environments [*Searle et al.*, 1998a, b; *Monson and Kopelman*, 2000]. In many natural systems, the rate of reactions between the chemical species is limited by their mixing, because the molecules can only react when they come into physical contact. In systems that are well-mixed, like a stirred laboratory beaker, the fluctuations in concentrations of the chemical species are negligible and the rate of reaction is spatially uniform. However, if the mixing is slow in comparison to the rate of the reaction, a mixing-limited regime will emerge. In this regime, the fluctuations in concentrations possess a significant magnitude, and gradually we may begin to observe areas of the domain where one reacting species is depleted relative to the others. From a mathematical point of view, the fluctuations of concentrations become anticorrelated [*Bolster et al.*, 2012; *Tartakovsky et al.*, 2012].

This segregation of the system into such “islands”, in which the overall reaction rate is dictated by the reduced area of contact between reactants, was described from theoretical and numerical viewpoints several decades ago [*Ovchinnikov and Zeldovich*, 1978; *Toussaint and Wilczek*, 1983; *Kang and Redner*, 1984]. These authors showed that, in a simple chemical system that was dominated by diffusive transport, the segregation into islands was self-generated. The depletion of one of the reacting species inside the islands largely limits the reactions to island interfaces. As a result, the overall reaction rate is slower than the one anticipated for a well-mixed system. A small-scale experiment confirmed these results [*Monson and Kopelman*, 2004]. The slow-down of reaction rate has practical importance, especially in the groundwater remediation context, where the choice of remediation strategy is based on accurate modeling of the anticipated decay rate of the contaminants. To this end, a Lagrangian technique was proposed that could be implemented at any scale [*Benson and Meerschaert*, 2008]. The algorithm accounts for the increased probability that nearby particles will have for co-location (mixing) and reaction. It is the exact calculation of reaction probability that allows explicit simulation of poor mixing and reactant segregation. These numerical results were shown to correspond to perturbed continuum reaction-diffusion equations [*Bolster et al.*, 2012; *Tartakovsky et al.*, 2012]. *However, to date the Lagrangian method has never been shown to converge to a specific governing equation.* It is therefore a phenomenological procedure: the particle methods can be used to solve for diffusion-limited reaction, but exactly what is being solved? And what do changes in the numerical parameters represent in terms of physical properties and numerical error? Our goal here is to show that the Lagrangian method proposed by *Benson and Meerschaert* [2008] does correspond to a continuum equation of transport and reaction, and that the numerical errors can be quantified and controlled by the user.

The classical (continuum) approach to describe the fate and transport of a chemical species is the advection-diffusion-reaction equation. In the special case of constant advection, the system can be transformed by a Galilean transformation and described by the simpler diffusion-reaction equation (DRE)

$$\partial C_i/\partial t = \nabla \cdot (D \nabla C_i) - r_i \tag{1}$$

where C_i is the concentration of the chemical species i [mol/L^d], D is the diffusion coefficient [L^2/T], and r_i is the net rate of decay of the species [mol/L^{d}T]. Here, d is **the** dimension of the system ($d = 1, 2, 3$).

For the case of radioactive decay, $A \to C$, the rate is typically described by the linear rate $r_i = k_d C_A$, and the equation can be solved by means of Lagrangian particle tracking in a straightforward manner [*Sherman and Peskin*, 1986; *Kinzelbach*, 1987]. In the context of this paper we are interested in more complicated case of a bi-molecular reaction described by

$$A + B \to C \tag{2}$$

For this type of reaction, the rate is usually modeled by the (nonlinear) law of mass action, i.e.

$$r_i = k C_A C_B \tag{3}$$

where $i = A, B$, and k is the constant rate coefficient [L^d/ mol T].

The modeling of coupled advection-diffusion-reaction equations with bi-molecular reaction rate (3) is the subject of extensive research [*Dentz et al.*, 2011]. *Benson and Meerschaert* [2008] described a novel particle tracking (PT) approach for bi-molecular reactive flow in a one-dimensional case with zero advection and a constant diffusion coefficient, and demonstrated that the PT approach is capable of capturing the continuum of well-mixed to incomplete mixing regimes. In short, within each time step, the PT approach moves particles by random walk and then annihilates part of them at a probability related to their distance apart. A novel feature of the PT approach is that it is purely Lagrangian and grid-less. As such, it can accurately model incomplete mixing at all scales. This is in contrast with approaches that assume complete mixing within the domain [*Gillespie*, 2000] or within volume elements [*Isaacson*, 2008]. In addition, the PT approach has an advantage over the particle-grid approach of *Tompson and Dougherty* [1992], because the latter involves calculation of the concentrations at grid points at every time step in order to compute the reaction term. This is no longer needed within the purely PT scheme, and the interpolation error involved with such a calculation is avoided. The analogy between a random walk and the diffusion equation is well known [e.g., *Einstein*, 1906; *Chandrasekhar*, 1943; *Kinzelbach*, 1987]. It remains to be shown that the addition of the particle annihilation within the PT approach reflects the reaction term correctly. In other words, we need to show that there is a mathematical analogy between the PT approach and the DRE (1) in the limit of an infinitely small time step. Furthermore, we generalize the PT approach to arbitrary dimension d and try to clarify some of the aspects of the PT approach, with special care regarding numerical errors and the meaning of the initial condition, namely the initial particle numbers.

2. Description of the PT simulation

The PT approach purports to solve (1) for a specified domain with appropriate initial and boundary conditions. In the PT approach, the particles of species A represent the concentration of that species, C_A, in a statistical manner. In other words, the specific locations of the particles in a specific simulation are usually meaningless; it is the ensemble average and other spatial and temporal statistical properties that are investigated.

2.1. Initialization of the PT

The primary advantage of the PT approach over deterministic approaches is in cases where the initial condition is non-deterministic and is given in terms of statistical parameters. A good example for this case is a system with an initial condition of a uniform mean concentration with some noise around it. Suppose that the mean concentration is equal for both species and given by

$$\langle C_i(x, t = 0)\rangle = C_0 \tag{4}$$

where $\langle \cdots \rangle$ denotes the ensemble average, $i = A, B$, and C_0 is a uniform prescribed initial concentration over the entire domain Ω^d. Initially, the concentration fluctuations over the ensemble average, i.e. $C_i' = C_i - \langle C_i \rangle$, are assumed to have a short-range correlation that can be mathematically described by a Dirac-delta function,

$$\left\langle C_i'(\mathbf{x}, t = 0) C_i'(\mathbf{y}, t = 0)\right\rangle = \sigma^2 l^d \delta(\mathbf{x} - \mathbf{y}). \tag{5}$$

We note that the cross-correlation of the fluctuations is determined by the constant σ, denoting the magnitude of the concentration fluctuations [mol/L^d], and the constant l, denoting the length scale of these fluctuations [L]. The use of Dirac-delta function is known to be a good approximation of short-range correlations, such as Gaussian correlation and exponential correlation [*Neuweiler et al.*, 2003; *Bolster et al.*, 2009; *Tartakovsky et al.*, 2012].

For a domain of volume Ω^d, this initial condition is modeled in the PT system by spreading N_0 particles in the domain in a random manner. It has been shown by statistical analysis [*Paster et al.*] that the initial condition ((4)–(5)) dictates the initial density of the particles,

$$\frac{N_0}{\Omega^d} = \frac{C_0^2}{\sigma^2 l^d}. \tag{6}$$

In other words, the total number of particles is correlated to the initial condition: the more noise in the initial condition, the less particles need to be spread. Note that if the system is always completely smooth (i.e., perfectly mixed), then $\sigma \to 0$, and the problem may not be satisfactorily solved using the PT approach, because the large number of particles can be impractical. We define the mass of a single particle (the amount of moles described by a single numerical particle) by m_p [mol/particle]. As all particles carry the same mass, it is given by the total mass in the system divided by the number of particles,

$$m_p = C_0 \Omega^d / N_0. \tag{7}$$

Because we spread N_0 particles for each species, we end up with a total number of $2N_0$ particles in the domain. Due to the random nature of the spread of the particles, there is no correlation initially between the locations of the A particles and the B particles, reflecting the initial condition

$$\langle C'_A(x, t=0) C'_B(y, t=0) \rangle = 0. \tag{8}$$

2.2. Description of PT steps

A single simulation time step in the PT approach describes the change of state of the system between t to $t + \Delta t$. It is composed of two sub-steps: random walk and reaction.

The random walk is an implementation of a Langevin equation,

$$x_j(t + \Delta t) = x_j(t) + \xi_j \sqrt{2D\Delta t} \tag{9}$$

where x_j is the j-th component of the particle location ($j = 1, \ldots, d$), and ξ_j is a random number of standard normal distribution, with zero mean and unit variance, i.e. $\xi_j \sim \mathcal{N}(0, 1)$. Thus, for each particle, its location is updated in all d dimensions by random values that account for the diffusion in this time step.

The reaction is then implemented by sequentially looping through all possible AB couples of particles in the system. Here, an AB couple is any combination of one A particle and one B particle (order being immaterial). For each such couple, a probability of forward reaction during the time step between those particles is then given by

$$p_f = k m_p \Delta t \, v(s) \tag{10}$$

where s is the distance between the particles, and $v(s)$ is the co-location probability density function (pdf). This is the pdf for two particles to co-locate over the time step, which for Brownian motion diffusion with coefficient D is given by [*Benson and Meerschaert*, 2008]:

$$v(s) = \frac{1}{(8\pi D\Delta t)^{d/2}} e^{-\frac{s^2}{8D\Delta t}}. \tag{11}$$

The probability of reaction, calculated by (10), is the probability of the AB couple to annihilate in this time step. Technically, this is done by producing a random number of uniform distribution $\xi \sim U(0, 1)$, and comparing these probabilities. Then, if $p_f > \xi$, the particles are annihilated, i.e. removed from the system. The choice of time step must be such that $p_f < 1$ is assured.

If one is interested in the fate of the product of the reaction (or in the case of backward reaction), a single C particle is placed into the domain. The location of this particle is randomly distributed, with the mean location at the mid point between the annihilated A, B particles, and with a variance of $D\Delta t$. It may be advected and diffused by a Langevin equation just as the A, B particles, and, depending on the reversibility of reaction, have a certain probability to decay back into A, B particles in some future time step.

The PT steps are repeated until the time for simulation end is approached, or, in the case of irreversible reaction, until all particles are consumed by the reaction. The PT simulation is repeated in a Monte Carlo fashion, so that results can be statistically analyzed with any specified degree of confidence. Typically, one would be interested in determining the average concentration in the system as a function of time, but other parameters, such as the concentration variance, or higher moments, can be computed as well.

3. The analogy of the PT approach with the DRE

We now show the analogy between the numerical PT scheme and the DRE equation. Start by defining $W_A(\mathbf{x}, t)d\mathbf{x}$ as the expected number of A particles in the infinitesimal volume $d\mathbf{x}$ centered at $\mathbf{x}$. The expected density of particles is then given by $W_A(\mathbf{x}, t)$, such that $\int_{\Omega^d} W_A(\mathbf{x}, t)d\mathbf{x} = N(t)$, where N is the total number of the A particles. For $t = 0$, $N(t) = N_0$.

An initial distribution $W_A(x, t = 0)$ in a specific simulation is the sum of N_0 delta functions, positioned randomly in the domain Ω^d. At later times, the distribution is smeared by the diffusion and reduced by the reactions. It is worth noting that the density distribution is similar in essence to a probability density function, in the sense that it is non-negative, but different in the sense that the integration over the distribution does not sum to unity, but rather to $N(t)$.

After the particles have moved by the random walk, the expected particle density is the sum of the densities of all particles multiplied by the probability that they jump to location $\mathbf{x}$. This sum, neglecting boundary effects, is given by

$$W_A^*(\mathbf{x}, t + \Delta t) = \int W_A(\mathbf{y}, t) \frac{1}{(4\pi D \Delta t)^{d/2}} e^{-\frac{(\mathbf{x}-\mathbf{y})^2}{4D\Delta t}} d\mathbf{y} \tag{12}$$

where the star denotes the resulting intermediate distribution, before the reaction sub-step takes place. A similar expression is found for W_B^*, by replacing A by B in (12).

Next, the reaction takes place and is expected to annihilate a fraction of this particle density, such that the new distribution is given by

$$W_A(\mathbf{x}, t + \Delta t) = W_A^*(\mathbf{x}, t + \Delta t) - \Delta W_A^*(\mathbf{x}, t + \Delta t) \tag{13}$$

where $\Delta W_A^*(\mathbf{x}, t + \Delta t)$ is the annihilated density. To express this density, we consider $\Delta W_A^*(\mathbf{x}, t + \Delta t)\Delta \mathbf{x}$, the number of particles in the volume $[\mathbf{x}, \mathbf{x} + \Delta \mathbf{x})$ that will be annihilated. Clearly, if one A particle existed in this segment, and only one B particle would have been in its proximity, this probability would have been simply p_f, the forward reaction probability between two particles (10). However, neither the number of A particles in this segment, nor the number of nearby B particles, is necessarily unity. Therefore we need to multiply p_f by the actual number of A and B particles, and sum over the whole domain by means of integration. We can now write

$$\Delta W_A^*(\mathbf{x}, t + \Delta t) = W_A^*(\mathbf{x}, t + \Delta t) \int p_f(\mathbf{x} - \mathbf{x}') W_B^*(\mathbf{x}', t + \Delta t) d\mathbf{x}' \tag{14}$$

with $p_f(\mathbf{x}-\mathbf{x}') = km_p v(\mathbf{x}-\mathbf{x}')\Delta t$. Substituting (12) and (14) into (13), we get

$$\begin{aligned}
&W_A(\mathbf{x}, t+\Delta t) = \\
&\qquad W_A^*(\mathbf{x}, t+dt)\left[1 - km_p\Delta t \int W_B^*(\mathbf{x}', t+\Delta t) v(\mathbf{x}-\mathbf{x}') d\mathbf{x}'\right] = \\
&\qquad \int W_A(\mathbf{y}, t)\frac{1}{\sqrt{4\pi D\Delta t}} e^{-\frac{(\mathbf{x}-\mathbf{y})^2}{4D\Delta t}} d\mathbf{y} \\
&\qquad \times \left[1 - km_p\Delta t \int v(\mathbf{x}-\mathbf{x}') d\mathbf{x}' \int W_B(\mathbf{y}', t)\frac{1}{\sqrt{4\pi D\Delta t}} e^{-\frac{(\mathbf{x}'-\mathbf{y}')^2}{4D\Delta t}} d\mathbf{y}'\right] \qquad (15)
\end{aligned}$$

Expanding in a Taylor series for $W_A(\mathbf{x}, t)$ we get, for the one dimensional case

$$W_A(y, t) = W_A(x, t) + \Delta x \frac{\partial W_A}{\partial x} + \frac{(\Delta x)^2}{2!}\frac{\partial^2 W_A}{\partial x^2} + \ldots \qquad (16)$$

For the two-dimensional case, we get

$$\begin{aligned}
W_A(\mathbf{y}, t) = W_A(\mathbf{x}, t) + \Delta x_1 \frac{\partial W_A}{\partial x_1} + \Delta x_2 \frac{\partial W_A}{\partial x_2} + \\
\frac{1}{2!}\left[(\Delta x_1)^2 \frac{\partial^2 W_A}{\partial x_1^2} + 2\Delta x_1 \Delta x_2 \frac{\partial^2 W_A}{\partial x_1 \partial x_2} + (\Delta x_2)^2 \frac{\partial^2 W_A}{\partial x_2^2}\right] + \ldots \qquad (17)
\end{aligned}$$

where $\Delta\mathbf{x} = \mathbf{y} - \mathbf{x} = (\Delta x_1, \Delta x_2)$. For the three-dimensional case,

$$\begin{aligned}
W_A(\mathbf{y}, t) = W_A(\mathbf{x}, t) + \Delta x_j \frac{\partial W_A}{\partial x_j} + \frac{1}{2!}\left[(\Delta x_j)^2 \frac{\partial^2 W_A}{\partial x_j^2} + \right. \\
\left. 2\Delta x_1 \Delta x_2 \frac{\partial^2 W_A}{\partial x_1 \partial x_2} + 2\Delta x_1 \Delta x_3 \frac{\partial^2 W_A}{\partial x_1 \partial x_3} + 2\Delta x_2 \Delta x_3 \frac{\partial^2 W_A}{\partial x_2 \partial x_3}\right] + \ldots \qquad (18)
\end{aligned}$$

where Einstein notation is applied and $\Delta\mathbf{x} = (\Delta x_1, \Delta x_2, \Delta x_3) = \mathbf{y} - \mathbf{x}$. Substitution of the appropriate Taylor expansion (16-18) into the integral in (15) yields

$$\int W_A(\mathbf{y}, t)\frac{1}{(4\pi D\Delta t)^{d/2}} e^{-\frac{(\mathbf{x}-\mathbf{y})^2}{4D\Delta t}} d\mathbf{y} \;=\; W_A(\mathbf{x}, t) \;+\; D\Delta t \frac{\partial^2 W_A}{\partial x_j \partial x_j} \;+\; \mathcal{O}((D\Delta t)^2) \qquad (19)$$

and similarly

$$\int W_B(\mathbf{y}', t)\frac{1}{(4\pi D\Delta t)^{d/2}} e^{-\frac{(\mathbf{x}'-\mathbf{y}')^2}{4D\Delta t}} d\mathbf{y}' \;=\; W_B(\mathbf{x}', t) \;+\; D\Delta t \frac{\partial^2 W_B}{\partial x_j \partial x_j} \;+\; \mathcal{O}((D\Delta t)^2). \qquad (20)$$

By substituting (19) and (20) into (15) we get

$$\begin{aligned} W_A(\mathbf{x}, t+\Delta t) &= \left[W_A(\mathbf{x}, t) + D\Delta t \frac{\partial^2 W_A}{\partial x_j \partial x_j} + \ldots \right] \times \\ &\left\{ 1 - k m_p \Delta t \int v(\mathbf{x} - \mathbf{x}) d\mathbf{x}' \left[W_B(\mathbf{x}', t) + D\Delta t \frac{\partial^2 W_B}{\partial x_j \partial x_j} + \ldots \right] \right] \right\} = \\ &W_A(\mathbf{x}, t) + D\Delta t \frac{\partial^2 W_A}{\partial x_j \partial x_j} - k m_p \Delta t W_A(\mathbf{x}, t) \int v(\mathbf{x} - \mathbf{x}') W_B(\mathbf{x}', t) d\mathbf{x}' + \mathcal{O}((\Delta t)^2) \end{aligned} \quad (21)$$

Taking the integral on the RHS of (21), expanding W_B once more in a Taylor series as in (16-18), and using (11), we find

$$\begin{aligned} &\int v(\mathbf{x} - \mathbf{x}') W_B(\mathbf{x}', t) d\mathbf{x}' = \\ &\qquad \int \frac{1}{(8\pi D\Delta t)^{d/2}} e^{-\frac{(\mathbf{x}-\mathbf{x}')^2}{8D\Delta t}} W_B(\mathbf{x}', t) d\mathbf{x}' = \\ &\qquad\qquad W_B(x, t) + 2D\Delta t \frac{\partial^2 W_B}{\partial x_j \partial x_j} + \ldots \end{aligned} \quad (22)$$

Substituting (22) into (21), subtracting $W_A(\mathbf{x}, t)$ from both sides, and dividing by Δt, we find

$$\frac{W_A(\mathbf{x}, t+\Delta t) - W_A(\mathbf{x}, t)}{\Delta t} = D \frac{\partial^2 W_A}{\partial x_j \partial x_j} - k m_p W_A(\mathbf{x}, t) W_B(\mathbf{x}, t) + \mathcal{O}(\Delta t) \quad (23)$$

As $\Delta t \to 0$, this equation becomes

$$\frac{\partial W_A}{\partial t} = D \frac{\partial^2 W_A}{\partial x_j \partial x_j} - k m_p W_A W_B. \quad (24)$$

Finally, we recognize that the density of the particles W_A (of units $[L^{-d}]$) can be expressed in terms of concentration of the species (of units $[mol/L^d]$) by simply multiplying it by the mass of a single particle m_p, i.e.

$$C_A = W_A m_p. \quad (25)$$

Hence, multiplying both sides of (24) by m_p we get the one-dimensional DRE for constant D,

$$\frac{\partial C_A}{\partial t} = D\nabla^2 C_A - kC_A C_B. \tag{26}$$

Thus, we have shown that the PT approach, at the limit of $\Delta t \to 0$, converges to the DRE.

4. Discussion and Conclusions

The utility of the PT approach for non-reactive particles is clear: the approach does not suffer from numerical dispersion and is potentially highly parallelizable. The problem of using the approach for reactive particles was first addressed by *Tompson and Dougherty* [1992], who discretize space into bins, count particles, convert to concentrations, calculate classical reactions, and re-convert concentrations to particles. The PT method of *Benson and Meerschaert* [2008] obviates the particle/concentration conversion at each time step, and eliminates the assumption of perfect mixing at the bin (or Eulerian block) scale. On the other hand, the PT approach had not been linked definitively to a differential equation of transport and reaction. In this work we were able to show the analogy between the diffusion-reaction equation (DRE) and the PT approach. This was done at the limit of $\Delta t \to 0$, i.e. an infinitely small time step. To this aim, we defined a density function of the particles, and described its evolution over time due to random walks and reaction between particles. Using Taylor series expansions and basic mathematical concepts we were able to show that the density is described by the DRE at the $\Delta t \to 0$ limit. This was done for an arbitrary physical dimension ($d = 1, 2, 3$). We also showed that the error induced by the scheme is $\mathcal{O}(\Delta t)$.

This analysis strictly speaking is limited to zero (or spatially constant) advection, whereas transport in natural porous media is typically characterized by a velocity field that can vary in space. Derivation of a particle tracking approach for solving the advection-diffusion-reaction in porous media is therefore a very important next step that is beyond the scope of this paper. It appears that the appropriate approach for this problem is to perform operator splitting, i.e., take the advective, diffusive, and reactive steps sequentially. As shown theoretically and experimentally by *Taylor* [1953], advection, even when heterogeneous, does not cause mixing of solutes, only diffusion does. Therefore, as long as the time step is sufficiently small that any errors induced by operator splitting are small, it should be sufficient to show that the reaction-diffusion part of the particle approach is correctly modeling the equation. This remains to be proven.

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