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Do we really need a large number of particles to simulate bimolecular reactive transport with random walk methods? A kernel density estimation approach



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ABSTRACT

Random walk particle tracking methods are a computationally efficient family of methods to solve reactive transport problems. While the number of particles in most realistic applications is in the order of 10^6 – 10^9 , the number of reactive molecules even in diluted systems might be in the order of fractions of the Avogadro number. Thus, each particle actually represents a group of potentially reactive molecules. The use of a low number of particles may result not only in loss of accuracy, but also may lead to an improper reproduction of the mixing process, limited by diffusion. Recent works have used this effect as a proxy to model incomplete mixing in porous media. In this work, we propose using a Kernel Density Estimation (KDE) of the concentrations that allows getting the expected results for a well-mixed solution with a limited number of particles. The idea consists of treating each particle as a sample drawn from the pool of molecules that it represents; this way, the actual location of a tracked particle is seen as a sample drawn from the density function of the location of molecules represented by that given particle, rigorously represented by a kernel density function. The probability of reaction can be obtained by combining the kernels associated to two potentially reactive particles. We demonstrate that the observed deviation in the reaction vs time curves in numerical experiments reported in the literature could be attributed to the statistical method used to reconstruct concentrations (fixed particle support) from discrete particle distributions, and not to the occurrence of true incomplete mixing. We further explore the evolution of the kernel size with time, linking it to the diffusion process. Our results show that KDEs are powerful tools to improve computational efficiency and robustness in reactive transport simulations, and indicates that incomplete mixing in diluted systems should be modeled based on alternative mechanistic models and not on a limited number of particles.

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1. Introduction

The complexity associated with the simulation of the interactions between flow, transport, and chemical processes requires developing reliable, as well as predictive, reactive transport models. A major challenge in this area is the incorporation of the interaction of the reactants facilitated by pure diffusion into a dynamic system. This problem has traditionally been

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addressed in porous media using a diffusion–reaction equation. The main interest has typically relied on finding or fitting the proper parameters that describe the experimental or field observations. This generic problem, posed in terms of the spatial and temporal distribution of reactants and products, has practical applications especially in the groundwater remediation context, where the choice of remediation strategy is based on accurate modeling of the anticipated degradation rate of the contaminants. Other applications include drug delivery in biological systems [1], geological CO₂ sequestration [2], chemical weathering [3], and enhanced oil recovery [4], to name a few.

In most natural systems, the rate of reactions between the chemical species is limited by mixing because the molecules can only react when they come into physical contact to allow the corresponding bonds to occur. In well-mixed systems, like a stirred laboratory beaker, the spatial fluctuations in concentrations of the chemical species are negligible, and the rate of reaction is spatially uniform. However, if the mixing process is slow in comparison with the reaction rate, a mixing-limited regime will appear. In this regime, and when the initial spatial distribution of reactants is heterogeneous, the magnitude of concentrations as a function of time fluctuate significantly and segregated areas (islands) of one reacting species start to form in the domain [5,6]. This segregation of the species is dictated by the reduced area of contact between reactants and was described from theoretical and numerical viewpoints several decades ago [7,8]. Thus, it comes as no surprise that the prediction of reactions based on the well-mixed assumption associated with the classical transport and reaction equations within systems ranging from homogeneous systems [9,10] to heterogeneous systems [11] are bound to failure.

The study of solute transport driven by diffusion is one of the classical problems where the dichotomy between Eulerian and Lagrangian approaches has been traditionally well explained. An Eulerian approach implies setting the problem in terms of concentration of reactant species, and then postulating some macroscopic laws (either empirical or deduced from thermodynamic considerations) to describe the reaction rate based on such concentrations. The problem is then formulated from macroscopic mass balance equations such as, for example, the advection–dispersion–reaction equation (ADRE). Concentration is a macroscopic quantity (mass per unit volume) and thus it has no meaning when the volume reduces to zero. An alternative is to study the process at the molecular level, theoretically tracking the movement and fate of each individual molecule, within a Lagrangian framework [12–14]. This alternative is obviously unfeasible, as even minute concentrations result in a extremely large number of molecules (1 mol equals 6.02×10^{23} molecules); furthermore, equations of the continuum are no more applicable, and reactions should be assessed from collision theory.

Particle Tracking Methods (PTM) try to combine both approaches to provide an efficient solution to reactive transport simulations. The idea is to split the total mass into a number of particles (typical orders are 10^6 – 10^9), many orders of magnitude lower than the actual number of molecules, and devise a way to reconstruct the spatial and temporal distribution of concentrations of the different species from the location of particles at any given time. This methodology has obvious drawbacks such as: (1) the estimation of macroscopic quantities (concentrations) from discrete particle information being a non-unique process, and (2) the need to set up reactive rules applied to a finite number of particles so that, when upscaled, they properly represent reaction rules observed at the macroscale. An additional drawback would be the modeler's choice of the number of particles, and more, the meaning of the concept particle itself.

Regarding the first problem, recently an optimal method for the reconstruction of concentrations and their functionals based on Kernel Density Estimators (KDE) was developed [15]. This method has been successfully applied to estimate concentrations of conservative and reactive species [16], heavily-tailed breakthrough curves [17], reaction rates in precipitation/dissolution problems [15], and risk predictions from particle distributions [18]. Regarding the second point, the translation of macroscopic rules to PTM, a technique was proposed by Benson and Meerschaert [19] to study reactive transport for a bimolecular reaction, introducing an algorithm that accounts for the probability that two individual particles react as a function of their relative distance; this method was an extension of the original algorithm proposed by Gillespie [12] to simulate batch reactions in a stochastic framework at the molecular level. The method avoids the need to continuously reconstruct concentration maps during the course of the simulation for each individual time step, considered the main disadvantage of PT methods [20,21].

Here we combine these two ideas to develop a KDE model that can be directly used to study bimolecular reaction in diffusive problems. The main idea is to use Kernels to provide a new weighting functions for particles to interact following Benson and Meerschaert [19] approach. In this case, when particles are transformed into another species or mineral, the shape of the Kernel automatically adjust, expanding its region of influence and the region of interaction between particles [15]. This method increases the number of particles that could react at a given time. The introduction of this expanding Kernel provides some insights into a problem that has been recently raised in the literature. Benson and coworkers have studied the evolution of concentration with time in a bimolecular reactive problem susceptible to incomplete mixing [19, 5,22]. These authors represented incomplete mixing by setting up a low number of particles into the reactive system; the lower the number of particles the earlier reaction became limited. This was shown later on to represent a continuum-scale model based on the ADRE with stochastic noisy initial conditions [23,24]. While this is an intelligent approach, we would like to stress that caution should be taken when using the statistical fluctuations of a histogram, produced by sub-sampling the concentrations, to represent a true physical phenomenon. The analogy is only valid when the number of molecules is really limited or in systems with noisy initial concentrations. Other physical processes leading to incomplete mixing such as rate-limited mass transfer at the pore-scale [25] or heterogeneity in the hydraulic properties at a larger scale [26] might not be properly represented.

We thus associate incomplete mixing in some applications to the combination of low number of particles combined with an estimation of concentrations based on the particles having a zero support size, e.g., [27,20]. We contend that the limited

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