Modeling bimolecular reactions and transport in porous media via particle tracking

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\textbf{A B S T R A C T}

We use a particle-tracking method to simulate several one-dimensional bimolecular reactive transport experiments. In our numerical scheme, the reactants are represented by particles: advection and dispersion dominate the flow, and molecular diffusion dictates, in large part, the reactions. The particle/particle reactions are determined by a combination of two probabilities dictated by the physics of transport and energetics of reaction. The first is that reactant particles occupy the same volume over a short time interval. The second is the conditional probability that two collocated particles favorably transform into a reaction. The first probability is a direct physical representation of the degree of mixing in an advancing interface between dissimilar waters, and as such lacks empirical parameters except for the user-defined number of particles. This number can be determined analytically from concentration autocovariance, if this type of data is available. The simulations compare favorably to two physical experiments. In one, the concentration of product, 1,2-naphthoquinone-4-aminobenzene (NQAB) from reaction between 1,2-naphthoquinone-4-sulfonic acid (NQS) and aniline (AN), was measured at the outflow of a column filled with glass beads at different times. In the other, the concentration distribution of reactants (CuSO\(_{4}\) and EDTA\(^{4-}\)) and product (CuEDTA\(^{2-}\)) were quantified by snapshots of light transmitted through a column packed with cryolite sand. These snapshots allow us to estimate concentration statistics and calculate the required number of particles. The experiments differ significantly due to a ~10\(^4\) difference in thermodynamic rate coefficients, making the latter experiment effectively instantaneous. When compared to the solution of the advection-dispersion-reaction equation (ADRE) with the well-mixed reaction coefficient, the experiments and the particle-tracking simulations showed on the order of 20–40% less overall product, which is attributed to poor mixing. The poor mixing also leads to higher product concentrations on the edges of the mixing zone, which the particle model simulates more accurately than the ADRE.

\begin{equation}
\partial C_i / \partial t = - \nabla \cdot (u C_i - D \nabla C_i) - r_i
\end{equation}

where \(C_i(x, t)\) is the concentration, \(t\) is time, \(u(x, t)\) is the Darcy scale pore water velocity, \(D(x, t)\) is the hydrodynamic dispersion tensor, and \(r_i(x, t; C_1, C_2, \ldots)\) is the reaction rate of species \(i\). The reaction rate, a crucial term in ADRE, is commonly estimated from batch tests under perfect mixing conditions of the same reaction [5,6,4,7,8,3]. When this reaction rate is used in Eq. (1) to predict miscible displacement and reaction in column- and field-scale tests, the observed reaction rate is generally much smaller [6,9–11]. An effective reaction coefficient \(< 1\), is commonly applied to the last term of ADRE to account for the over-estimated reaction [12,7,6,13]. Unfortunately, the coefficient value is difficult to determine and varies from case to case (and scale to scale) [6,8].

Laboratory and numerical experiments (e.g., [8,5,12]) revealed that incomplete mixing is primarily responsible for the reduced reaction rates. The dispersion term in Eq. (1) simultaneously describes both spreading of, and mixing among, solute fronts between dissimilar water. But in real-world and synthetic tests, the spreading rate is found to be greater than the mixing rate [14,11,15–19]; therefore, an equation that correctly simulates spreading will overpredict the mixing of the water. For example, Kapoor et al. [8] theorized (and showed numerically) that the simple bimolecular reaction \((A + B \rightarrow C)\) for Poiseuille flow and Taylor
dispersion within a single tube would result in reduced reaction relative to the well-mixed rate. In a series of numerical and laboratory experiments, Raje and Kapoor [5] constructed a glass bead-filled column and showed that the product concentration in the column was approximately 40% less than what was predicted by Eq. (1) in one-dimension (1D). Gramling et al. [12] found overall product production of approximately 20% less in their column than predicted by Eq. (1) based on experiments at different flow velocities. These observations point to several deficiencies of the ADRE: (i) the deterministic concentration neglects small-scale fluctuations [5,12,7,20]; (ii) the reactants are assumed to be well-mixed, which is unusual under natural conditions [6,20,21]; and (iii) the dispersion term is forced to account for both the spreading and the dilution, or mixing, of the species [22,23].

The mixing that leads to reaction is often limited to transverse dispersion and diffusion. In porous media, these mechanisms are orders-of-magnitude lower than longitudinal dispersion [5,24,22,14]. In recent studies, both Edery et al. [20] and Tartakovsky et al. [21] noticed that the slow diffusion of reactants into and out of plume boundaries determines the reaction rate and explains why averaged concentration models over-predict the amount of reaction. A variety of studies (e.g. [25–28]) demonstrate that reactants are not perfectly mixed and diffusion is a limiting process even in free fluid flow without the structure imposed by porous media.

A series of theoretical studies [6,29,9] showed that the upscaled equations of reaction in the presence of diffusion are different from the perfectly-mixed equation and uniquely defined by the transport mechanism. These studies showed that it not necessarily proper to arbitrarily combine transport and reaction equations. Various reactive transport models have been proposed [30–32,10,33,42,34] and a variety of laboratory (e.g. [5,12,35]) and field studies (e.g. [36–40]) have been conducted to test the validity of various modeling approaches that separately account for mixing, reaction, and transport. One approach is a Lagrangian particle tracking (PT) method. The general Lagrangian framework has given rise to several algorithms that represent smaller-scale physics in different ways. For example, the smoothed particle hydrodynamics method simulates a given partial differential equation (PDE) on moving particles instead of on a fixed grid [41,42,10]. This method rests on the assumption that the chosen PDE for transport and reaction is the correct one at some smaller scale.

A different Lagrangian model from Benson and Meerschaert [29] makes no assumptions about the form of the governing equation for reaction. Their PT method simulates chemical reactions through probabilistic rules of particle collisions, interactions, and transformations. The method is based on an explicit calculation of the probability that any two particles will be co-located in any time interval, in combined with the independent probability that two particles, upon co-location, will react. The second probability is the well-mixed reaction rate scaled appropriately by the number of particles and the volume associated with that rate. Benson and Meerschaert’s [29] method is an extension of Gillespie’s [43], which uses a well-mixed assumption to calculate the probability of particle co-location (and leads to the classical mass-action reaction equations [44]). It was shown recently by Paster et al. [45] that at the limit of infinitely small time step and infinite number of particles, the PT method converges to the well-mixed ADRE (1) using the classical law of mass action for a bimolecular reaction.

Other approaches have also been proposed, such as different forms of underlying transport [9,46,47], time dependent reaction rate coefficients [48,49], stochastic perturbation models [7], and multi-rate mass transfer [50,51]. These models can be calibrated to simulate the reactive transport successfully by reproducing anomalous flux-averaged breakthrough curves [52,21]. However, as indicated by Tartakovsky et al. [21], these approaches require additional effective parameters, which can only be obtained from calibration with experimental data.

In this study, we test the hypothesis that the bulk of the experimental observations can be explained by the application of simple, physically-based rules of transport and reaction within a Lagrangian framework. The transport algorithm is based on Fickian dispersion with a mean advective drift, and the bimolecular reactions use the PT method from Benson and Meerschaert [29], in which the reaction probability only depends on the thermodynamic rate of the chemical reaction and the distribution of particles in both space and time.

2. Methods

2.1. Summary of column experiments

We consider the column experiments conducted by Raje and Kapoor [5] and Gramling et al. [12], which are widely regarded as benchmarks of reactive transport in porous media [53,20,49,46]. Raje and Kapoor [5] used a spectrophotometer to obtain the outflow concentrations of product from the transport and reaction of 1,2-naphthoquinone-4-sulfonic acid (NQS) and aniline (AN) in a column filled with glass beads. They ran two experiments, each with different flow rates and concentrations of reactants. Gramling et al. [12] took images of light transmitted through a colorimetric reaction between aqueous CuSO4 and EDTA2− within a translucent chamber packed with cryolite sand to observe the concentration distribution of compounds within the column. They ran three experiments at three different velocities with all other parameters held constant. The physical setup of all of the experiments considered here was similar. Initially, the columns were saturated with one species at concentration CO, and the other reactant was introduced at the inlet at a constant rate and the same constant concentration CO. Peclet numbers of both experiments were high, but Reynolds numbers were sufficiently low to ensure laminar flow.

Before performing the column experiments, the reaction rate constants were obtained with high confidence from well-mixed batch experiments. Dispersion coefficients at each velocity were measured via conservative tracer, and diffusion coefficients were gathered from the literature. Hydrodynamic dispersion dominated over diffusion in spreading the inert tracer at all velocities. The parameters from the two experiments under different flow conditions are summarized in Table 1.

![Image](https://via.placeholder.com/150)

Table 1. Parameters used for reactive transport modeling in the column experiments. For the well-mixed system, the law of mass action for the irreversible reaction \( A + B \rightarrow P \) can be expressed as \( r_A = r_B = r_P = \frac{dC_P}{dt} = -k_1C_AC_B \). Both groups used this law in the ADRE (1) to compare to experimental results. Raje and Kapoor [5] solved the ADRE (1) at the outflow using the finite difference (FD) scheme. Gramling et al. [12] used an analytical solution by assuming the reaction was instantaneous and the boundaries remote. Their solution is

\[
C_P = \frac{1}{2} \text{erfc} \left( \frac{x - ut}{\sqrt{2Dt}} \right),
\]

where \( C_P(x,t) \) is product concentration, and \( C_0 \) is the constant flux concentration of the injected reactant at the inlet boundary [12]. We also use an FD solution to compare to Raje and Kapoor’s [5] data and the analytic solution (2) for Gramling et al.’s [12] data.

2.2. Methodology of particle reaction and transport

Our particle tracking algorithm separately simulates transport and reactions in any given time step. For reaction, the model assumes that molecular diffusion dictates the probability that
reactants can mix and react at the pore-scale. The probability density for particle co-location is calculated as 
\[ v(s) = \int f_A(x)f_B(s + x)dx, \]
where \( f_A(x) \) and \( f_B(x) \) denote the densities of the motions of \( A \) and \( B \) particles away from their current positions, and \( s \) is the initial particle separation distance [29]. For a time step of duration \( \Delta t \), the Gaussian local diffusion has variance \( 2D_{\text{m}}\Delta t \), where \( D_{\text{m}} \) is the molecular diffusion coefficient, and the co-location density is a convolution of two of these Gaussians, which is also Gaussian but with variance \( 4D_{\text{m}}\Delta t \). For computational efficiency, Benson and Meerschaert [29] approximated the Gaussian with a piecewise linear “tent” function with the same variance:

\[ v(s) = \max \left\{ 0, \frac{-|s|}{2D_{\text{m}}\Delta t} + \left(24D_{\text{m}}\Delta t\right)^{-1/2} \right\}. \]  

(3)

The differential co-location probability \( v(s)ds \) is approximated with a finite volume \( v(s)\Delta s \) and combined with the thermodynamic probability to find the total probability of reaction using

\[ \text{Prob(react)} = k_i \Delta t \Omega C_0 v(s)/N_0 \]  

(4)

where \( k_i \) [M⁻¹L⁻¹T⁻¹] is the reaction rate constant, \( \Delta t \) is the time interval, \( \Omega \) [L⁴] is the column size in \( d \)-dimensions, \( C_0 \) is the initial concentration of the resident (say \( B \)) species [ML⁻⁴], and \( N_0 \) is the initial number of \( B \) particles [29]. The rate \( k_i \) is the rate associated with a reaction volume, taken here to be the volume associated with a particle (discussed more in Section 2.3). At every time step, each \( A \) particle is selected sequentially to see if it will react. \( B \) particles that are sufficiently close are searched, and the probability of co-location is calculated, one \( B \) particle at a time. The combined probability is compared with a random number uniformly distributed between 0 and 1. If the probability of the reaction is larger than the random number, the two particles are removed from the domain and a \( P \) particle is placed randomly between the initial \( A \) and \( B \) particle locations.

The advection–diffusion process for each particle is simulated over a time step of duration \( \Delta t \) using the approximate Langevin equation [15,54–56]

\[ X(t + \Delta t) = X(t) + \Delta tZ + Z\cdot \sqrt{2D_{\text{m}}\Delta t}, \]  

(5)

where \( X(t) \) is the location of a particle at time \( t \). \( u \) is the average pore water velocity, \( Z \) is a standard Normal random variable, and \( D \) is the reported dispersion coefficient. We substitute a shifted and scaled uniform [0,1] random variable \( \sqrt{2D_{\text{m}}\Delta t}(U(0,1) - 1/2) \) for the last term [6,29]. The selection of \( \Delta t \) is based on two criteria: (i) the maximum reaction probability (Eq. (4) with \( s = 0 \)) is less than unity to fulfill the definition of a probability; and (ii) the time interval is relatively small compared to total residence time, so that a sufficient number of random motions are completed to agree with the analytical solution of (1) for \( r_i = 0 \) (Fig. 1).

The initial conditions and boundary conditions are based on the experimental setup. They can be expressed as: \( C_A(0,0) = C_0 \) and \( C_A(x,0) = 0 \) for \( x > 0 \) (species \( B \) occupies the domain uniformly and there is no \( A \) species initially); \( C_A(0,t) = C_0 \) for \( t > 0 \) (constant concentration of \( A \) species input at the upstream end); and \( \partial C_A(L,t)/\partial x = 0 \) for \( t > 0 \) at the column end \( L \).

For every time step, the particles move in the column based on Eq. (5), and the reaction of each \( A \) particle in the domain is checked with possible \( B \) particles through Eq. (4). This process is repeated for every transport/reaction time step. Computation of the distances between every \( A \) and \( B \) particle is costly if a large number of particles are simulated. To improve efficiency, we apply the KD-tree technique of Bentley [57] as implemented by Tagliasacchi [58]. A KD-tree (short for K-dimensional) is a binary tree for efficient storage of neighbor information to be retrieved by searches [57]. The KD-tree algorithm partitions space into K-dimensional blocks with particles along edges, and maps the adjacent blocks in a tree structure so that a search can march orderly through adjacent blocks. For \( N \) particles at any time step, creating the tree takes \( \mathcal{O}(N \ln N) \) operations, and each search takes \( \mathcal{O}(N) \) operations so that each reaction time-step goes like \( \mathcal{O}(N^2) \) instead of \( \mathcal{O}(N^3) \) for a naive search.

2.3. Methodology of instantaneous reaction simulation

A cursory look at Eq. (4) would suggest that instantaneous reactions (\( k_i \to \infty \)) would require \( \Delta t \to 0 \) to keep the probability less than unity. This is clearly impossible for the numerical method, so we seek an approximation. Benson and Meerschaert [29] showed that the coefficient \( k_i \) incorporates both the thermodynamic (well-mixed) rate and the volume associated with that rate. Perfect mixing (say, by stirring a beaker) eliminates concentration fluctuations by physical homogenization [59]. At some small

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Experimental parameters.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simulation</td>
<td>Gramling et al.</td>
</tr>
<tr>
<td>Length (cm)</td>
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<tr>
<td>Rate constant (M⁻¹s⁻¹)</td>
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<td>Flow rate (mL/s)</td>
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<td>Porosity (cm/s)</td>
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<td>Dispersion coeff. (cm²/s)</td>
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<tr>
<td>Diffusion coeff. (cm²/s)</td>
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<tr>
<td>Concentration (M)</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Fig. 1. Verification of particle tracking for non-reactive transport. The red dots are experimental column-width averages of snapshots of CuEDTA²⁻ at 1023 s from [12]. The blue and black solid lines are analytical solutions of the ADE for two species flowing through a column in which one species saturates the column initially, and the other enters at constant concentration from the upstream \( (x = 0) \) end. The red and magenta lines with error bars represent the simulations using PT method. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
volume in an un-stirred system, the point-wise law of mass action is assumed to be valid, and we may interpret this as the finite volume associated with a particle, with the rate $k_i$ tied to that volume. Therefore, we require that coincident particles ($s = 0$) will react with probability one for essentially instantaneous, or high-$k_i$ reactions. In this case, plugging $\text{Prob}(\text{react}) = 1$ and $v(s = 0)$ into Eq. (4) leaves:

$$k_f(\Delta t)^{1/2} = N_0(2D)^{1/2}/(\Omega B_0).$$

(6)

All of the parameters on the right hand side are known; therefore, this equation gives a constraint on the combination of effective $k_f$ and $\Delta t$ that may be used to simulate an instantaneous reaction.

To determine whether a given reaction fits within this “instantaneous” criteria, we may check the Damkohler number, which compares the timescales of reaction relative to transport processes (e.g., dispersion, diffusion). Dentz et al. [48] stated that the effective rate can be virtually any fraction of the local rate depending on the Damkohler number, and the conclusion is consistent with the fact that laboratory measured kinetic rates can be orders of magnitudes larger than their field measured counterparts (e.g. [60,61]). The diffusive Damkohler number is a dimensionless ratio of diffusion time scale $(t_D = l^2/2D_m)$ over reaction time scale $(t_r = 1/(C_0 k_f))$ [59,23,21,56], so that $D_m = k_f/2D_m$, where $l$ is the size of concentration perturbations (e.g. [59,23,21]). The length is typically taken as the size of a pore, but may be as large as the domain size [59,6,21]. If the Damkohler number is very large, the time scale of diffusion is much longer than that of the reaction and the reaction can be deemed as instantaneous. The $D_m$ values range from 250 to 500 for Raje and Kapoor’s [5] experiments, and $9 \times 10^5$ to $5 \times 10^6$ in Gramling et al.’s [12] experiments, assuming the length of $l$ is the size of porous media particle [5]. Based on these numbers, we simulate the latter experiments with the instantaneous criteria defined by Eq. (6).

3. Results and discussion

We simulated the two experiments by Raje and Kapoor [5] and three by Gramling et al. [12] by reproducing the two breakthrough curves (BTC) from the former and six concentration profiles from the latter. To help distinguish the experiments from the two groups, we use different symbols for the experimental results in the following plots. In addition, because there is randomness in the initial positions, movements, and reaction locations for the particles, each simulation will have some randomness in the particle densities at any time. To translate the particle numbers to concentrations for comparison to experiments, the particle numbers are counted at a length interval of approximately 0.5 cm (half the length of movement due to dispersion within a time step, $\sqrt{6D}\Delta t$) in each simulation. Then each PT simulation is run from 10 to 100 independent times to calculate the concentration ensemble means and standard deviations (error bars in the graphs). This procedure is similar to simulating conservative solutes with the PT method [54].

Fig. 2 shows the PT simulations and measurements from Raje and Kapoor’s [5] experiments. We use an initial number of particles in each simulation of $N_0 = 1000$ and a time step of $\Delta t = 1$ second. All other parameters are the same as those reported for the experiment, as shown in Table 1. The number of initial particles was not rigorously optimized, but rather chosen by visual fit. Concentration spatial covariance data was not available to allow a priori estimation (see Section 3.3). The agreement between the simulations and the data is quite good considering that the only parameter with any flexibility is the initial particle number $N_0$.

In our simulation of the experiments by Gramling et al. [12], the reaction is assumed to be instantaneous. Figs. 3 and 4 illustrate...
The product zone tails of these experiments already have generated some discussion. Edery et al. [20] reviewed models using a diffusive advection–dispersion equation (ADE) along with their PT simulations using a logarithmic concentration axis (Fig. 6) reveals greater measured product mass in experiments at all three velocities look very similar. To be consistent with previous simulation work (e.g. [53,49]), we only present the results for the flow rate of 2.7 mL/min. All of our simulated rates of accumulation of reaction product are in close agreement with the experimental measurements.

The variability of the simulated concentrations, reflected in the standard deviations, is directly linked to particle numbers and incomplete mixing. As the number of particles goes to infinity, concentration variability goes to zero and the simulated reaction is perfectly mixed [29]. As the number gets very small, all of the reactant mass is in a few particles that are unlikely to come together. For a reasonable number of particles, reactions occur preferentially at interfaces, leading to increased segregation and poorer mixing. Reactions can only progress by diffusion or dispersion to the interface. In these column simulations, the fluctuations are thought to arise from non-uniformity in the pore-scale flow field [5]. Conceptually this is similar to a system where diffusion is the sole mode of transport [59], in which growing “islands” of reactants arise due to initial areas that have fluctuations in the initial reactant concentrations. The initial number of particles codes the spatial structure of the fluctuations and the decrease in particle numbers as a reaction progresses simultaneously leads to an increase in island size (chemical heterogeneity) and poorer levels of mixing.

3.1. Reaction zone tails

Besides the subdued peak product concentrations, another important finding from Gramling et al.’s [12] experiments is the larger reaction zone widths relative to the solution of the ADRE (1). In the concentration profiles (concentration vs. length), heavy leading and trailing edges are seen in the product concentration that are not evident in the analytic solution (see also [46]). A closer examination of this experiment and our PT simulations using a logarithmic concentration axis (Fig. 6) reveals greater measured product concentrations in both tails than the analytical solution (2), as well as the ability of the PT method to model this phenomenon.

The product zone tails of these experiments already have generated some discussion. Edery et al. [20] reviewed models using a Fickian advection–dispersion equation (ADE) along with their PT reaction method based on an empirical effective radius of reaction [53], as well as the empirical kinetic reaction rate method used by Sánchez-Vila et al. [49], and concluded that these methods were unable to capture the forward and backward tails of the spatial concentration profiles. To overcome this issue, Edery et al. [20]
used a continuous time random walk (CTRW) for the particle transport instead of the classical Brownian motion with the ADE governing equation. The time for each motion in CTRW is random and the heavier weights on the long-time probability cause some particles to delay their migrations relative to the mean, hence there is a broader spread of both reactants and products. Zhang and Papelis [46] extended this concept by using both random times and non-Gaussian particle migration distances to match product concentration near the tails. Both of these approaches require several additional parameters. It is unclear if these methods, invoked to account for the tails in the reactive case, were calibrated from a conservative tracer quite well, i.e., a heavy trailing edge was not evident in the original analysis (see Figs. 1, 6 and 7 in the original [5]).

Luo and Cirpka [52] posited that material heterogeneity leads to the extended tailing behavior in breakthrough curves. Taking a similar view, the tails in the reaction product may be due to the reaction itself: if poor mixing or small-scale diffusion limits the reactions, then the reactants could venture farther into “enemy territory” before reacting, and the tails of the product distribution would be enlarged relative to the tails of well-mixed reaction. This is a significant and somewhat counter-intuitive finding. If heterogeneity was thought to (uniformly) reduce reaction rates, then the measured product concentrations would be everywhere lower than the well-mixed solution. This clearly is not the case. Our PT simulations give some insight into the heavier product tails. Conceptually, some A particles may move into the displaced B particles like fingers rather than a smooth, well-mixed front. The calculation of reaction based on local diffusion allows some probability of longer particle excursions, which is consistent with the conceptualization of Cao and Kitanidis [62], who showed that the slow rate of diffusion allows concentration gradients to be sustained at the small scale and a mass of reactant can cross the interface and interact with the other reactant only through diffusion.

3.2. Instantaneous reactions

The reaction in Gramling et al.’s [12] experiments has a very high \( k_r \) and the Damköhler numbers are many orders-of-magnitude larger than unity given the range of possible correlation lengths. Here we use expression (6) to investigate the effect of different combinations of \( k_r \) and \( \Delta t \) (Fig. 7).

Various studies have provided quantitative criteria to classify a reaction as instantaneous. For instance, in a derivation of transport-controlled reaction rates, Sánchez-Vila et al. [63] showed that for a \( D_a = 100 \) or larger, the system reaches local equilibrium practically instantaneously, and results using an approximation for the reaction rate are almost indistinguishable from those using an equilibrium reaction. From their point of view, to simulate the instantaneous reaction, the reaction rate constant can be arbitrarily chosen as long as the \( D_a \) is larger than 100. Tartakovsky et al. [21] reached a similar conclusion. They found that the deterministic solutions of the diffusion–reaction equation are all the same if \( D_a > C_{m0} \), where the initial coefficient of variation, \( C_{m0} = \sigma_C/C_0 < 1 \), where \( \sigma_C \) is the concentration standard deviation. For Gramling et al.’s [12] experiments, taking a conservative characteristic length value as the size of pore space, 0.13 cm, a value of reaction rate constant larger than 0.42 M \(^{-1} \) s \(^{-1} \) satisfies the criterion of \( D_a > 100 \). We test this by using the reaction rate over an or-
3.3. Particle numbers

It may appear that the number of particles used to represent the reactants is a free parameter. However, Benson and Meerschaert [29] showed that the number of particles is directly related to the time of onset of reactant self-segregation and reduced reaction rates in simple diffusion systems. Using more particles means that the reactant concentrations are smoother functions of space, i.e., more perfectly mixed. We may test the sensitivity to this estimate by varying the numbers of particles while holding all other parameters constant in the simulation. Because of the similarity of the experiments, we present the simulation of the second experiment (flow rate of 16 mL/min) from [12] as an example. Three simulation runs are shown in Fig. 8. When using one-tenth the number of particles to represent the reactants ($N_0 = 60$), the ratio of product concentration over initial concentration is around 0.40, which over-predicts experimental observations (red dots). The simulation with the lower number of particles ($N = 60$) under-predicted the measurements, the ratio was around 0.25. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

A recent study by Bolster et al. [59] enabled a method to determine the number of particles that should be used to represent the reactants in the columns. Based on the continuum reaction equation, the authors showed that the pseudo-kinetic slowdown due to diffusion-limited mixing is directly proportional to the covariance of initial concentration perturbations. It has long been known for conservative solutes that the number of particles in a PT simulation is inversely proportional to the variance of concentration [64,65]. Therefore, the numbers of particles representing the same amount of mass should, in part, dictate the rate of reactions. As a first approximation, Paster et al. [66] considered each particle individually as a delta function of concentration, and showed that the covariance of the concentration, upon initiation of the simulation, is $C(x, 0)C(y, 0) = (C_0/N_0)^2 \delta(x - y)$. Equating the particle and continuum concentration covariance gives

$$N_0 = \frac{C_0^2 \Omega}{\sigma_t^2 l^d} \quad (7)$$

We can estimate the size and variance of concentration perturbations using the high-resolution snapshots given in Fig. 3b of [12].

Fig. 8. Effect of particle numbers, using the second experiments from [12] as a base case, shown as Fig. 4b. For all runs simulating instantaneous reaction, using the higher number of particles ($N = 6000$), the model predicted that the product concentration over initial reactant concentration was around 0.40, which over-predicts experimental observations (red dots). The simulation with the lower number of particles ($N = 60$) under-predicted the measurements, the ratio was around 0.25. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 9. (a) Example color map (after [12]) of product concentration at $t = 619$ s for flow rate $Q = 2.67$ mL/min; (b) variance of red, green, and blue color components in vertical transects and (c) example power spectrum of blue component in columns 50 through 56, showing dominant spatial frequencies of 2/50–4/50 pixels$^{-1}$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
The original raw images of light transmission are no longer available [C. Harvey, personal communication] so we use the color images for \( t = 619 \) s, which have integer values of red, green, and blue (RGB) saturations from 0 to 255. For a perfectly mixed experiment, any vertical transect of pixels would be the same color and have no variability in any color saturation. On the contrary, the measured vertical transects have systematic changes in the variance of the RGB components, from the lowest value far in front of the invading fluid (Fig. 9), to the greatest in the zone of equal reactant concentrations. Using the fact that \( \text{VAR}(AX) = \sigma^2 \text{VAR}(X) \) for a constant \( \sigma \) and assuming for this estimate that the RGB variances are additive, then the variance of concentration in the mixing zone can be estimated. This assumption is best in those areas where one color dominates the color map. The range of concentration is on the order of 0 to 0.02 M, while color saturations are between 0 and 255, or \( 10^{11} \) greater. In the area of greatest concentration contrasts, the variance of color saturation is on the order of 2800 above background noise (Fig. 9b), so that the variance of concentration is approximately on the order of \( \sigma^2 = 2000/10^{12} \text{ M}^2/\text{s}^2 \).

Furthermore, the color fluctuations have some coherent structure upon visual inspection (Fig. 9a) that can be deduced with a fast Fourier transform (FFT) (Fig. 9c). Each vertical column of pixel colors, upon FFT, has several frequencies that dominate, revealing some coherent structures. These (spatial) frequencies are typically in the range of 2–4 times the inverse of the column width of 50 pixels. Note that the mean value of each color, which is irrelevant here, is removed before each FFT so that the zero frequency value is zero. This has no effect on the other frequencies. We automated the identification of spatial structure in the column’s transverse direction by selecting the single dominant frequency (in terms of power spectrum) for each vertical trace for each color and plotting those for the entire column length after conversion to wavelength (Fig. 10). It appears that the dominant frequencies have wavelengths between 25% and 100% of the column’s 5.5 cm width (Fig. 10). This corresponds to fingers or “blobs” (half wavelength) of widths \( l \approx 0.9 \) to 2.5 cm. Using \( l = 1.4 \) cm (wavelength of 25 pixels, see Fig. 10) and plugging the other numbers into Eq. (7) gives an estimate of the number of particles of roughly 680, compared to the 600 we used to visually fit the reaction zones. This is a qualitative demonstration that the theoretical number of particles is consistent with the number we used. A more concrete estimate would require more detailed measurement of concentration variance and spatial correlation.

4. Conclusions and recommendations

In this study, we implement a novel particle tracking method that calculates the probability that any two particles under general conditions of advection, dispersion, and diffusion occupy the same position. When combined with the thermodynamic probability manifested in the well-mixed rate coefficient, the combined effects of transport and mixing-limited reaction are accurately simulated. Simulation results are tested against breakthrough curves reported by Raje and Kapoor [5] and concentration profiles from Gramling et al. [12]. Not only do the simulation results match the cumulative and peak product concentrations, but also agree with the forward and backward tails of the reaction zone. The agreement between simulations and laboratory observations shows that this particle tracking method is able to successfully simulate observations without invoking any additional parameters or coefficients.

The only flexible numerical parameter in our model, the number of particles, represents fluctuations in concentrations, i.e., the product of concentration (spatial) variance and correlation length. This information may be gained by direct measurement of the concentration field on either small [12] or large scales [67], or by stochastic means [68–70,6]. Using visual data of transmitted light in the experiments of [12], we derived particle numbers that matched the best-fit numbers very closely; however, the estimate is likely to have fairly large variability, the magnitude of which we do not endeavor to quantify at this point.

The particle transport and reaction algorithm presented here has yet to be extended to more complex reaction chains. This is not a theoretical problem as reactions with multiple reactants or uneven stoichiometry as a series of two-particle interactions (see Gillespie [71]), though it may present numerical difficulties. The particle reaction algorithm also has not been coupled to detailed 3-d velocity fields for the purpose of validating, for example, Molz and Widdowson’s [1] conjecture that poor mixing is primarily responsible for pseudo-kinetic reactions in heterogeneous flow fields at the field scale.

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