LAGRANGIAN SIMULATION OF BIMOLECULAR REACTIONS

YONG ZHANG

ABSTRACT. A fully Lagrangian approach is developed to model bimolecular reactions undergoing Fickian diffusion. The basis of the Lagrangian algorithm is the interaction radius \( R \), which controls the probability that nearby particles of different species react. For a closed system filled with reactants, \( R \) is derived analytically using an agent-based approach for reversible bimolecular reactions. The simulated reactive particle dynamics are checked against the kinetics for both diffusion-controlled reactions and thermodynamic well-mixed reactions. In addition, for the case of sharp contact between reactants, an empirical formula is proposed to approximate \( R \), by considering the distribution and availability of reactants. The resultant Lagrangian solver is then validated against bimolecular reactions observed in the laboratory.

1. Introduction

Efficient simulation of diffusion-controlled chemical reactions in complex media remains a challenge for multiple disciplines, including hydrology [5] and biology [9]. It is difficult to effectively couple reaction with transport, because these two processes operate on different scales. Chemical reactions occur at local scale, while the scale of transport for reactants grows with time. Transport also significantly affects the reaction rate, driving the spreading and mixing of reactants [4].

Reactive transport is often simulated using an Eulerian approach. For example, the following classical advection-dispersion-reaction (ADR) equation has been widely used to describe the elementary, bimolecular second-order reversible reaction \( A + B \rightleftharpoons C \):

\[
\begin{align*}
\frac{\partial [A]}{\partial t} &= -v \frac{\partial [A]}{\partial x} + D \frac{\partial^2 [A]}{\partial x^2} - K_f [A][B] + K_r [C], \\
\frac{\partial [B]}{\partial t} &= -v \frac{\partial [B]}{\partial x} + D \frac{\partial^2 [B]}{\partial x^2} - K_f [A][B] + K_r [C], \\
\frac{\partial [C]}{\partial t} &= K_f [A][B] - K_r [C],
\end{align*}
\]

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where $v$ is the mean flow velocity, $D$ is the macroscopic dispersion coefficient, $K_f$ and $K_r$ are the forward and backward kinetic coefficients of reaction, respectively, and $[A]$, $[B]$ and $[C]$ denote the concentration of $A$, $B$, and $C$, respectively. The continuum, averaged concentration model (1)∼(3) merges the mixing at local scale (where reactions occur) and the spreading at a larger scale [4] (i.e., Darcy-scale). This direct overlap of reaction and transport at the Darcy scale can cause serious overestimation of the rate of mixing and reaction [13, 20, 30].

To accurately simulate the coupled process, one must either upscale the reaction or downscale the transport. Various upscaling approaches have been developed in the last decade to account for the spatial mixing effects on reactive transport by hydrologists. For example, Kapoor et al. [19] applied an effective reaction coefficient corrected by the cross covariance of reactant concentrations. Cirpka [4] replaced the macrodispersion coefficient in (1)∼(3) with an effective value to improve the prediction of reaction rate. Lichtner and Kang [23] upscaled pore-scale governing equations using a multi-scale continuum formulation. Dentz et al. [6] analyzed analytically the time nonlocal reaction for transport in Darcy-scale heterogeneous media. Luo et al. [24] used the perturbation expansion approach to quantify the mixing-controlled second-order reaction. However, as reviewed by Dentz et al. [5], efficient approaches are still needed for coupled transport and reactions. In addition, assuming well-mixed reactants at the level of discretization after upscaling can decrease computational efficiency [3]. This problem can be addressed using a particle tracking scheme, which is a downscaling method, discussed below.

The most well-known downscaling method might be the stochastic simulation algorithm (SSA) developed in the chemical physics and biology communities, as reviewed briefly by Erban and Chapman [9]. One typical SSA is the compartment-based model described by the reaction-diffusion master equation, where only molecules within the same compartment can react [14, 15]. The second commonly used SSA is the grid-free simulation for the motion of individual molecules [2, 37, 12, 9]. This approach extends and modifies the pioneer work of Smoluchowski [32] (where two molecules react whenever they are close to each other) or Gillespie [10, 11] (for dilute gas particles). Recently, to solve the assumption of well-mixedness and homogeneity used by a typical SSA, Nicolau and Burrage [27] developed a Monte Carlo approach to estimate the rate constant of bimolecular reactions, and Benson and Meerschaert [3] developed a probability-based scheme to account for the overlapped effective reaction volume of two molecules. Most recently, to capture the non-Fickian transport missed by previous simulations, Edery et al. [7, 8] introduced a memory function into SSA, resulting in a reactive, continuous time random walk (CTRW) framework that captures the time-nonlocal transport process [26].

Other downscaling, particle-based numerical approaches have also been developed to simulate pore-scale reactive transport (see the excellent review by Meakin and Tartakovsky [25]), including Lattice-Boltzmann [1, 18], computational fluid dynamics
and smoothed particle hydrodynamics [34, 35]. Most of these methods, however, as reviewed by Dentz et al. [5], can be computationally very demanding.

The literature review above shows that the downscaling method using appropriate particle-based algorithms can be a promising way to accurately solve reactive transport across different scales. This motivates us to develop a fully Lagrangian framework to couple effective transport formulations with bimolecular reactions, where the “particles” represent packets of molecules. Both bimolecular reactions and reactant/product transport are described at the microscopic scale (similar to the downscaling method), where incomplete mixing can be taken into account. In the following, we focus on reactive transport in porous media.

The rest of the paper is organized as follows. In Sec. 2, a Lagrangian framework is developed to approximate reactive transport in a closed system. Both reversible and irreversible reactions are simulated, based on an “interaction radius” that controls the probability of reaction. The effectiveness of the resultant particle-tracking scheme with a pre-defined interaction radius is then checked against known reaction kinetics. In Sec. 3, sharp contact between reactants is considered, where the initial distribution and availability of reactants can be different from those in a closed system. This case represents a typical experimental setup for bimolecular reactions in the laboratory. An empirical formula for the interaction radius is developed and checked against laboratory measurements of bimolecular reactions. In Sec. 4, we discuss the possible extension of the Lagrangian framework to describe reactive transport with increased complexity. Conclusions are drawn in Sec. 5.

2. Lagrangian simulation of Fickian-diffusion controlled bimolecular reactions in a closed system

In collision theory [38], two particles can collide if their nuclei get closer than a certain distance, which is called the interaction radius. Chemical reactions will occur if the colliding particles have enough activation energy and the right orientation to break existing bonds and finish the transformation. Other properties, including temperature and pH, may also affect the reaction rate, by modifying the fraction of collisions. To capture the probabilities of encounter and combination of reactant particles that control the reaction rate of under-mixed reactions, we need to determine the interaction radius.

In the following we first consider a closed system where reactants are initially well-mixed. The closed system represents a bounded domain with a constant volume. Bimolecular reaction in a closed system has been the focus of various studies (see for example, [16, 17]), where the known chemical kinetics can be used to check the Lagrangian scheme developed by this study.

2.1. Derivation of interaction radius. The agent-based approach developed by Pogson et al. [29] is extended here to define an interaction radius $R$ for reversible
reactions. Irreversible reaction can be treated as a specific case of the reversible reaction with a zero backward rate. The interaction radius also represents the maximum distance for two molecules to collide. Any two molecules with separation exceeding $R$ cannot interact during one time step, and hence $R$ should be related to the time step.

The rate equation (i.e., the classical thermodynamic rate law) is

\[
\frac{\partial [A]}{\partial t} = -K_f [A] [B] + K_r [C].
\]

At a typically small time step $\Delta t$, the change in concentration $A$ is

\[
\Delta A = -K_f [A] [B] \Delta t + K_r [C] \Delta t.
\]

The proportion of $B$ molecules that interact with $A$ at this time step therefore is

\[
\frac{\Delta B}{[B]} = \frac{-\Delta A}{[B]} = K_f [A] \Delta t - K_r \frac{[C]}{[B]} \Delta t,
\]

where $|\Delta B| = |\Delta A|$ due to the reaction $A + B \rightleftharpoons C$ considered in this study. Assuming that: 1) the total spatial volume is $V$; and 2) $A$ and $B$ molecules distribute uniformly in the closed system with volume $V$; we obtain the correspondence between the following two dimensionless ratios (see also Pogson et al. [29] and Scheibe et al. [31])

\[
\frac{V_i}{V} = \frac{|\Delta B|}{[B]},
\]

where $V_i$ denotes the proportion of volume in $V$ where $A$ interacts with $B$.

The concentration of $A$ at time $t$ can be calculated by

\[
[A(t)] = \frac{N_A(t) m_A}{V},
\]

where $N_A(t)$ denotes the remaining number of $A$ particles at time $t$, and $m_A$ is the mass carried by each $A$ particle. Substituting (6) and (8) into (7), one obtains

\[
V_i = \left| K_f N_A(t) m_A \Delta t - V K_r \frac{[C(t)]}{[B(t)]} \Delta t \right|.
\]

We assume that an $A$ molecule may combine with a $B$ molecule if and only if this $B$ molecule is within an interaction volume $V^*$ surrounding $A$ of size

\[
V^* = \frac{V_i}{N_A(t)}.
\]

Whether the reaction will occur for colliding $A$ and $B$ molecules also depends on other conditions, such as the activation energy and orientation. A given interaction volume $V^*$ provides the interaction radius $R_c$ (where the subscript “c” denotes the case of a closed system).
For the case of a 1-d reversible bimolecular reaction, (9) and (10) give the signed interaction radius

\[ R_c(t) = \frac{K_f [A_0] L \Delta t}{N_A^0} - L K_r \frac{N_C(t) m_C}{N_A(t) N_B(t) m_B} \Delta t, \]

where \( L \) is the total domain size (i.e., length), \([A_0]\) represents the initial concentration of \( A \), \( N_A^0 \) denotes the initial number of \( A \) particles, and \( N_B(t) \) is the remaining number of \( B \) particles at time \( t \), etc. The interaction radius \( R_c(t) \) defined by (11) has units \([L] = \text{length}\). The sign of \( R_c(t) \) indicates the direction of reactions. If \( R_c(t) > 0 \), the forward reaction will dominate, since the forward rate of reaction is larger than the backward rate. Conversely, when \( R_c(t) < 0 \), the backward reaction dominates.

For a 1-d irreversible bimolecular reaction, (11) reduces to

\[ R_c^f = K_f m_A \Delta t = \frac{K_f [A_0] L \Delta t}{N_A^0}, \]

which is a positive constant, implying that only the forward reaction can occur. The superscript \( f \) denotes the forward reaction.

The interaction radius \( R_c^f \) in (12) can also be derived using an alternative approach. When reactants \( A \) and \( B \) have the same initial concentrations, the rate equation

\[ \frac{\partial [A(t)]}{\partial t} = -K_f [A(t)]^2 \]

leads to

\[ \frac{\Delta A}{[A(t)]} = K_f [A(t)] \Delta t = \frac{V^*}{V} = \frac{R_c^f N_A(t)}{L}. \]

The analytical solution for reactant \( A \) (assuming perfect mixing) is

\[ [A(t)] = \frac{[A_0]}{1 + [A_0] K_f t}. \]

Introducing (15) into (14), one obtains the interaction radius

\[ R_c^f = \frac{K_f [A_0] L \Delta t}{(1 + [A_0] K_f t) N_A(t)}, \]

which is the same as (12) since \((1 + [A_0] K_f t) N_A(t) = N_A^0\). However, the derivation of (12) is more general, since it does not rely on the assumption of equal initial concentration of reactants. In subsection 2.3 we will check the applicability of (12) for reactants with non-equal initial concentrations.

2.2. Particle-tracking scheme. Here we assume that chemical reactions do not change the flow velocity or dispersion strength. The influence of reaction on transport will be modeled in a future study (note that the particle-particle based algorithm
can be modified conveniently to account for the temporal variation of transport parameters). The flowchart in Figure 1 shows the Lagrangian framework. There are three main steps.

2.2.1. Step 1. The first step is to account for the backward reaction $C \rightarrow A + B$ only. The forward reaction will be simulated separately below. The concentration change of $C$ due to the backward reaction can be described by the following rate equation:

$$\left| \frac{\partial [C(t)]}{\partial t} \right| = K_r [C(t)] .$$

It leads to the following approximation if $\Delta t$ is small enough:

$$\frac{|\Delta C(t)|}{[C(t)]} \approx K_r \Delta t .$$

The ratio $|\Delta C(t)|/[C(t)]$ represents the percentage of $C$ particles that degenerate into reactants at time $t$ (during the interval of $\Delta t$). It can also be regarded as the
probability for each $C$ particle to experience the backward reaction. Therefore the probability for backward reaction ($P_b$) is defined by (see also [3])

$$P_b = K_r \Delta t,$$

which is a constant if $\Delta t$ remains unchanged. A uniform random number $U$ between 0 and 1 is then generated and compared with $P_b$. If $P_b > U$, then the particle of $C$ degenerates into $A$ and $B$ particles (which should be located at the same location as $C$, or separated by only the radius of two molecules); otherwise this $C$ particle remains un-transformed.

2.2.2. Step 2. The second step is to compute the displacement of all chemicals, including $C$ if this product is mobile. Particle transport is separated from reactions, following the pioneer work of Tompson and Dougherty [36]. The classical Langevin description for Fickian diffusion at the microscopic level (see for example, [21, 22]) can be used, where the random displacement of each particle is a Markov process defined by

$$dX_i = v dt_i + \xi_i \sqrt{2D dt_i},$$

where $dX_i$ denotes the particle movement at the $i$-th jump, $dt_i$ is the time step, and $\xi_i$ denotes independent normally distributed random variables with zero mean and unit variance. Here the velocity $v$ is not limited to be constant, and the Lagrangian stochastic process can be conditioned directly on local aquifer properties at any practical, measurable level and resolution [39]. It is well-known that the Brownian motion with a drift defined by (20) is governed by the classical advection-dispersion equation

$$\frac{\partial P}{\partial t} = -v \frac{\partial P}{\partial x} + D \frac{\partial^2 P}{\partial x^2}.$$

2.2.3. Step 3. The third step is to simulate the forward reaction. Note that the simulation of the forward reaction is not as straightforward as the backward reaction simulated in Step 1, since there is no “analytical” way to define the forward reaction. In the following we propose three empirical algorithms to simulate the forward reaction. The probability of reaction for two adjacent reactants, which may relate to both the interaction radius $R_c$ defined above and the distance between reactants, will be analyzed, to explore the feasibility of each empirical algorithm.

Firstly, we propose the following definition for the apparent forward reaction probability (denoted as $P^*_1$) which was also used by Edery et al. [7] (where the interaction radius is a fitting parameter)

$$P^*_1(t) = 1 \text{ for } \min\{|y_{A,i}(t) - y_{B,j}(t)| < R_c\},$$

where $y_{A,i}(t)$ and $y_{B,j}(t)$ denote the position of the $i$-th $A$ particle ($1 \leq i \leq N_A(t)$) and the $j$-th $B$ particle ($1 \leq j \leq N_B(t)$) at time $t$. The definition (21) limits the reaction for the closest pair of reactants (note that the distance should also smaller than the interaction radius $R_c$). The definition (21) follows [32] and is not uncommon. It shows that the forward reaction must occur if two reactants $A$ and $B$ meet close
enough. To find these closet reactants, two loops of iterations can be used. The outer loop iterates over $A$ particles. Then for each $A$ particle, the inner loop looks for the closest $B$ particle. The resultant actual reaction probability depends on the percentage of reactants that are located inside of the interaction radius. To avoid confusion (with the apparent probability $P^*_1(t)$), the actual reaction probability is denoted as $P_1(t)$. For equal and uniform initial concentrations $[A_0] = [B_0]$ (so that $N_A(t) = N_B(t)$), the proportion of reactants within $R_c$ can be approximated by

$$\text{Proportion} \approx \frac{R_c}{L/N_A(t)}.$$  

Hence the actual forward reaction probability is:

$$P_1(t) \approx \frac{2R_c}{L/N_A(t)}.$$  

The $B$ particle can be located either at the left or right side of the $A$ particle, doubling the reaction probability (hence the factor 2 is used in (23)).

The above scheme may however enhance artificially the reaction rate. As explained by Pogson et al. [29], the reaction actually need not necessarily occur even if two molecules are within the interaction radius, since other properties, such as the orientation and bimolecular attraction, also affect the reaction. Here we link the correct forward reaction probability (denoted as $P_{\text{correct}}$) and the interaction radius. The correct forward reaction probability can be defined as the (number or concentration) fraction of particles that react during one time step:

$$P_{\text{correct}} = \frac{\Delta N_B}{N_B(t)} = \frac{\Delta B}{[B(t)]},$$

where $\Delta N_B$ denotes the change of the number of $B$ particles. Leading (7) and (10) into (24), we obtain

$$P_{\text{correct}} = \frac{\Delta B}{[B(t)]} = \frac{V_i}{V} = \frac{V^* N_A(t)}{L} = \frac{R_c}{L/N_A(t)}.$$  

The probability $P_1(t)$ from (23) overestimates the correct reaction probability (25). Hence we propose a second apparent probability $P^*_2(t)$ to simulate forward reactions:

$$P^*_2(t) = \frac{R_c}{|y_{A,i}(t) - y_{B,j}(t)|} \frac{1}{w},$$

where $w$ is a factor that normalizes the value of $R_c/|y_{A,i}(t) - y_{B,j}(t)|$ (to meet the definition of probability). A uniform $[0, 1]$ random variable $U^*$ will then be generated to control whether the reaction will proceed for colliding particles. If $P^*_2 > U^*$, the $A$ and $B$ particles will combine to produce a $C$ particle located in the middle of the two reactants. Otherwise, no reaction occurs. The apparent probability $P^*_2$ is similar.
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Pogson et al. [29] proposed the inverse distance law to account for the non-covalent attractive forces, where the closest pair of reactant $A$ and $B$ has the highest probability (which needs not to be 1) to react. Compared to (21), here less molecules can interact.

$P_2^*$ from (26) varies with the distance $|y_{A,i}(t) - y_{B,j}(t)|$ for each pair of $A$ and $B$ particles. For equal and uniform initial concentrations $[A_0] = [B_0]$, the average of distance is proportional to the density of particles:

$$|y_{A,i}(t) - y_{B,j}(t)| w \propto \frac{L}{N_A(t)},$$

where the bar denotes the average. Leading (27) into (26), one obtains the average of the actual reaction probability

$$P_2^*(t) \propto \frac{R_c}{L/N_A(t)}.$$

Therefore, the definition of (26) links the forward reaction probability to the percentage of reacting particles.

For comparison purpose, we also propose the third apparent reaction probability $P_3^*(t)$

$$P_3^*(t) = 1 - \frac{|y_{A,i}(t) - y_{B,j}(t)|}{R_c}.$$

There are two sub-steps for this scheme. Firstly, if $|y_{A,i}(t) - y_{B,j}(t)| > R_c$, then no reaction will occur. Hence the first sub-step is to account the number of reactant pairs located inside the range of interaction radius $R_c$. Secondly, if $|y_{A,i}(t) - y_{B,j}(t)| < R_c$, then $P_3^*(t)$ from (29) (which is a positive number between 0 and 1) is compared to a newly generated uniform $[0, 1]$ random variable $U^*$. Reaction occurs only for $P_3^*(t) > U^*$, which is similar to that used for $P_2^*(t)$. Also similar to $P_2^*(t)$ defined above, here the probability $P_3^*(t)$ increases with the increase of interaction radius and the decrease of reactant distance. $P_3^*(t)$ however does not reply on the factor $w$, and hence can be computationally more convenient than $P_2^*(t)$. The two sub-steps for this scheme result in the average of the actual reaction probability:

$$P_3(t) = \text{Probability of sub-step 1} \times \text{Probability of sub-step 2} \approx \frac{2R_c}{L/N_A(t)} \times P_3^*(t) \approx \frac{2R_c}{L/N_A(t)} \times \left(1 - \frac{0.5R_c}{R_c}\right) = \frac{R_c}{L/N_A(t)}.$$

The probability of sub-step 1 should be the same as the actual reaction probability for the first empirical scheme discussed above (expressed by (23)), since they both
account for the number proportion of reactants in the range of $R_c$. Also note that the average distance $|y_{A,i}(t) - y_{B,j}(t)|$ is half of the interaction radius $R_c$, since the particles accounted by the sub-step 2 are assumed to be located uniformly in $R_c$.

We will test the applicability of the above three empirical definitions of the apparent forward reaction probability (i.e., $P^*_1(t)$ from (21), $P^*_2(t)$ from (26), and $P^*_3(t)$ from (29)) in section 2.3.

2.2.4. Discussion. Either the time-dependent interaction radius $R_c(t)$ from (11) or the constant $R_f^c$ from (12) can be used to simulate the reversible, bimolecular reaction. When (11) is used, the backward reaction (Step 1) occurs only if $R_c(t) < 0$, and the forward reaction (Step 3) only occurs if $R_c(t) > 0$. The fluctuation of $R_c(t)$ around zero induces backward or forward reactions. Note that this algorithm can be simplified further. For example, if the initial concentration of product $C$ is zero, the backward reaction can be ignored, and we only need to model the forward reaction. As $R_c(t)$ in (11) decreases gradually to zero, the reversible reaction approaches equilibrium.

On the other hand, if the constant interaction radius $R_f^c$ from (12) is used, then both Step 1 and Step 3 must be allowed. Equilibrium will be achieved when the number of $C$ particles created in the forward reaction (Step 3) approaches the number of $C$ particles destroyed in the backward reaction (Step 1). In this dynamic equilibrium, the concentration of both reactants and product fluctuates around the equilibrium. Forward and backward reactions must be separated by displacement, as shown in Figure 1. Otherwise, the particles undergoing the backward reaction are forced to experience the forward reaction in the same time step.

2.3. Numerical examples and validation.

2.3.1. Irreversible reaction. Firstly, we check the scheme proposed above for irreversible reaction, where $R_c(t)$ (11) reduces to $R_f^c$ (12). Figure 2 shows the overlap of reactants $A$ and $B$ at various times. At late times, $A$ (or $B$) particles merge and form clusters, apparently decreasing the reaction rate. As shown by Fig. 2b, the “Cluster of $A$” can not react with the “Cluster of $B$”, breaking the assumption of well-mixdeness used by the continuum model (1). These clusters were also noted by Benson and Meerschaert [3].

When $A$ and $B$ have the same concentration, and are initially well-mixed, their concentration decreases continuously (Figure 3), where the apparent forward reaction rate $P^*_3(t)$ from (29) is used. Initially, the Lagrangian solution matches the analytical solution of the rate equation (Figure 3a), since there are enough $A$ and $B$ particles remaining in the system to mix well. At late times, the Lagrangian solution of reactant concentration decreases more slowly, following a power-law function $A(t) \sim t^{-1/4}$ (Figure 3b). This is consistent with the known kinetics of mixing-controlled reactions [17, 33]. Increasing the dispersion coefficient and/or the number of particles will enhance the contact of reactants, and hence accelerate the reaction. This behavior was also observed by Benson and Meerschaert [3]. In addition, we found empirically
that the late-time asymptotic concentration for reactant $A$ is related to the interaction radius

\begin{equation}
[A(t)] \approx \sqrt{R_f^t (Dt)^{-1/4}} = \frac{K_f [A_0] L \Delta t}{N_A} (Dt)^{-1/4},
\end{equation}

where $t \gg t^*$. The symbol $t^*$ denotes the time when the concentration profile approaches the power-law defined by (31). At the early-time $t \ll t^*$, the reactant concentration follows the rate equation or thermodynamic law defined by (15). The analytical solution (15) (shown by the solid line in Fig. 3b) intercepts the asymptotic solution (31) (shown by the dashed lines in Fig. 3b). The intercept time can be regarded as the approximation of $t^*$

\begin{equation}
t^* \approx (K_f \sqrt{R_f^t D^{-1/4}})^{-4/3}, \quad \text{if } [A_0] K_f t \gg 1.
\end{equation}

We then compare the three apparent forward reaction probabilities proposed in subsection 2.2.3. Extensive numerical tests are conducted, with a few examples shown in Figure 4. When $P^*_1(t)$ from (21) is used, the simulated forward reaction (see the red dashed line in Figure 4) is even faster than the solution of the rate equation at early time. The large reaction rate is consistent to the analysis in subsection 2.2.3. When $P^*_2(t)$ from (26) is used, the simulated reaction rate varies significantly with the factor $w$. A small $w$ less than 1 will allow the reactants whose distance is larger than the interaction radius to react, and hence $w$ should always be larger than 1. On
Figure 3. Lagrangian solutions (symbols) versus the analytical solution of rate equation (solid lines) for the irreversible bimolecular reaction $A + B \rightarrow C$, where $A$ and $B$ have equal initial concentrations. (a) Parameters are: $K_f = 0.02$, $D = 0.01$, the time step $\Delta t = 1$, and the number of particles $np = 5000$. The initial concentration for $A$ is $[A_0] = 2$. The analytical solution for the rate equation is $[A(t)] = [A_0]/([A_0]K_ft + 1)$ and $[C(t)] = [A_0] - [A(t)]$ (due to the conservation law). (b) Evolution of concentration (after normalization) for reactant $A$. The dashed line denotes the asymptotic concentration. The domain size $L = 64$, and the initial concentration for $A$ is $[A_0] = 0.005$.

When $A$ and $B$ have different initial densities, the modeled concentration for reactant $A$ either decreases exponentially (if $[A_0] < [B_0]$), or reaches the limit $[A_0] - [B_0]$ (if $[A_0] > [B_0]$), as shown by Figure 5. The analytical solution for the rate equation in both Fig. 5(a) and 5(b) is 

$$[A(t)] = \frac{\omega}{(1 + \omega/[A_0])} \exp(\omega K_ft) - 1,$$

where the factor $\omega = [B_0] - [A_0]$ denotes the difference of the initial concentration for reactants (hence $\omega > 0$ for case shown in Fig. 5(a) and $\omega < 0$ for Fig. 5(b)).

2.3.2. Reversible reaction. We then check the Lagrangian solution for reversible reactions. When the constant $R_c^t$ (12) is used, the modeled concentration at late time contains more noise than that using the time-dependent $R_c(t)$ (11), as shown by Figure 6(a). This discrepancy is due to the additional reactions in the case of constant $R_c^t$ required to reach equilibrium. The analytical solution for the rate equation shown
Figure 4. Influence of the forward reaction probability $P_1^*(t)$ (21), $P_2^*(t)$ (26), and $P_3^*(t)$ (29) on the concentration of reaction $A$ for the irreversible reaction $A + B \Rightarrow C$, where $\left[A_0\right] = \left[B_0\right] = 0.005$, $K_f = 50$, $D = 0.1$, and the domain size $L = 64$. (b) is the linear-linear plot of (a). The symbols for $P_2^*(t)$ with the factor $w = 6$ (shown by the blue circle) are very close to those for $P_3^*(t)$ (shown by the green triangles). The solution for $P_2^*(t)$ with the factor $w = 0.1$ (shown by the grey circle) is similar to that for $P_1^*(t)$ (shown by the red dashed line).

Figure 5. Evolution of concentration for reactant $A$. Lagrangian solutions (symbols) versus the analytical solution of rate equation (solid line) for the irreversible bimolecular reaction $A + B \Rightarrow C$, where $A$ and $B$ have NON-EQUAL initial concentrations. (a) $\left[A_0\right] < \left[B_0\right]$, where $\left[A_0\right] = 0.005$ and $\left[B_0\right] = 0.01$. The dashed line denotes the best-fit curve with $A(t) \sim \exp(-t)$ for $D = 0.01$. The other model parameters are: $K_f = 10$, and the number of $A$ particles is 2000. (b) $\left[A_0\right] > \left[B_0\right]$, where $\left[A_0\right] = 0.005$ and $\left[B_0\right] = 0.0046$. The other model parameters are: $K_f = 60$, and the number of $A$ particles is 5000.
Figure 6. The influence of interaction radius $R$ on chemical concentration for reversible reaction $A + B \rightleftharpoons C$: the constant $R_f^l$ (12) versus the time-dependent $R_c(t)$ (11). (a) Evolution of concentration $[A(t)]$ and $[C(t)]$ solved by the analytical approach (lines) and the Lagrangian methods (symbols). Parameters are: $K_f = 0.004$, $K_r = 0.015$, $D = 0.1$, the time step $\Delta t = 1$, and the number of particles is 2000. The initial concentration is $[A_0] = [B_0] = 5$ and $[C_0] = 0$. (b) Evolution of interaction radius $R_f^l$ (12) and the time-dependent $R_c(t)$ (11).

in Fig. 6(a) is [17]

$$[A(t)] = \frac{\rho_1([A_0] - \rho_2) - \exp[-K_f (\rho_1 - \rho_2)t] \rho_2 ([A_0] - \rho_1)}{([A_0] - \rho_2) - \exp[-K_f (\rho_1 - \rho_2)t] ([A_0] - \rho_1)}$$

and $[C(t)] = [A_0] - [A(t)]$, where $\rho_1 = [-K_r + \{K_r^2 + 4K_fK_r[A_0]\}^{1/2}] / (2K_f)$ and $\rho_2 = [-K_r - \{K_r^2 + 4K_fK_r[A_0]\}^{1/2}] / (2K_f)$. Fig. 6(b) shows the evolution of the interaction radius, where the time-dependent $R_c(t)$ (11) reaches 0 gradually.

We then compare the Lagrangian solutions to the analytical solutions for rate equations with various backward rate coefficient $K_r$ (Figure 7). The deviation between the two different solutions increases with the decrease of $K_r$ (Figure 7a,b), since it takes a longer time for reactions to reach equilibrium if $K_r$ is smaller. Our numerical experiments show that, when the time reaches

$$t^* = \frac{2}{(K_r^2 + 4K_fK_r[A_0])^{1/2}},$$

the reversible reaction approaches equilibrium, with a constant concentration

$$[A^*(t)] = [A(t \to \infty)] = \left\{-K_r + (K_r^2 + 4K_fK_r[A_0])^{1/2}\right\} / (2K_f).$$

The asymptotic concentration (34) was also given by Kang and Redner [17].

When the variable interaction radius $R_c(t)$ (11) is used, the Lagrangian solution approaches equilibrium relatively faster than that using the constant $R_f^l$ (12) (see Figure 7a,b, especially for a small $K_r$).
Figure 7. Lagrangian solutions (symbols) versus analytical solutions (for well-mixed rate equation, shown by lines) for reversible reaction with initial concentration \([A_0] = [B_0] = 0.005\) and \([C_0] = 0\). (a) and (b) show solutions with various backward reaction rate \(K_r\). The other parameters in (a) and (b) are: \(K_f = 20\), \(\Delta t = 1\), \(np = 2000\), and \(D = 0.01\). (c) shows the convergence to the thermodynamic solution for Lagrangian solutions with various \(D\). The other parameters are: \(K_r = 0.001\), \(K_f = 20\), and \(\Delta t = 1\). In (a), the constant interaction radius \(R_f^l\) (12) is used, while the time-dependent \(R_c(t)\) (11) is used in (b) and (c).

The dispersion coefficient \(D\) also affects the transition to diffusion-limited reaction (Figure 7c), similar to the result observed for irreversible reactions. Note that the relative concentration \((\frac{[A(t)] - [A^*(t)]}{[A_0]}\) decays as \(\sim t^{-1/2}\) at late time (Figure 7c), following the known kinetics for diffusion-limited reactions [33].

3. Open system with sharp-interface between reactants

In the open system considered in this study, there is no overlap between different reactants at the beginning, and the volume of mixed reactants can increase with time (Figure 8). In laboratory experiments of bimolecular reactions [30, 13, 28], the two
reactants A and B typically have a sharp contact initially. One reactant was usually introduced separately into the saturated porous medium (i.e., sand column) filled with another reactant. This common case is an open system filled with initially non-overlapping reactants. The open system is practically important since it provides the experimental data to check the applicability of the Lagrangian simulator.

There is no analytical solution for the interaction radius for reactants (denoted as $R_S$, where the subscript “s” denotes the case of sharp interface) with a sharp interface. For simplicity, in this section we consider only the irreversible bimolecular reaction. We propose and test two options to estimate $R_S$. Firstly, $R_S$ can be fitted directly given the mass evolution of reactants or product observed in the laboratory, as applied by Edery et al. [7, 8]. Secondly, we can modify the constant $R_f^l$ (11) empirically

$$R_S(t) = R_f^l g,$$  

where $g$ is a (dimensionless) correcting factor accounting for the sharp interface.

The particle-tracking scheme should remain the same as the one developed in subsection 2.2, except that the constant $R_f^l$ (12) is replaced by a fitting result (in option 1) or the empirical $R_S(t)$ (35) (in option 2).

Irreversible bimolecular reactions observed in laboratory-scale sand columns by Gramling et al. [13] are used to test the applicability of the above two options. The well-known batch experiment conducted by Gramling et al. [13] is one of the pioneer works in reactive transport and has been widely cited. In their experiment, a sodium EDTA solution was displaced by a copper sulfate solute filled in a thin glass chamber.
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(17) (the chamber itself was packed with cryolite), producing copper EDTA (CuEDTA$^{2-}$) at the interface. Snapshots of CuEDTA$^{2-}$ (shown by the red symbols in Figure 9) were observed at various times and various flow rates.

We first fit the snapshots using a constant $R_S$. Best-fitting results show that different $R_S$ (not shown here) is needed to capture the spatial distribution of product observed at different flow velocities. Hence the direct fitting of interaction radius may not be efficient.

We then try to obtain an empirical formula for $R_S(t)$ (35) using trial and error. This leads eventually to the following empirical interaction radius:

$$R_S(t) = R_c^I g \approx \frac{K_f [A_0]}{N_A^0} \frac{L \Delta t}{\sqrt{2Dt} \text{Re}},$$

where Re denotes the Reynolds number. The term $L/\sqrt{2Dt}$ accounts for the variation of the mixing volume of reactants, and the Reynolds number explains the potential influence of flow velocity on the interaction radius. We first fit the CuEDTA$^{2-}$ snapshot observed at time 157 seconds and flow rate 16 ml/min (note this snapshot was selected arbitrarily), as shown by Figure 9a. There is only one fit parameter, $N_A^0$ (representing the number of particles), in the empirical formula (36). All other parameters ($D, L, K_f, \text{Re},$ and $[A_0]$) were measured in the laboratory by Gramling et al. [13]. The best-fit parameter is then used to predict the snapshots at other times or flow rates. The predictions generally match the measurements (Figure 9b~9f).

4. DISCUSSION

The flexibility of the computational method developed above allows further refinement, if sophisticated transport affecting chemical reactions needs to be accounted. Firstly, non-Fickian transport can be simulated to account for the influence of (multi-scale) medium heterogeneity on chemical reactions. Both super-diffusive and sub-diffusive anomalous diffusion can be considered. Note that the space and time Langevin analysis proposed by Zhang et al. [40] can be applied to develop an efficient Lagrangian algorithm. Secondly, the 1-d Lagrangian solver developed above can be extended to higher dimensions, to characterize real transport processes. Either Brownian motion or its generalization (i.e., Lévy motion) can be extended to multiple dimensions conveniently, and the interaction radius needs to be modified correspondingly. Thirdly, the spatial and/or temporal variation of transport parameters (velocity $v$ and dispersion coefficient $D$) needs to be modeled, to describe the influence of physical heterogeneity and/or non-stationarity. Finally, chemical heterogeneity may cause space/time variation of the interaction radius, which can be accounted conveniently by modifying $R_c$ in Step 1 and Step 3 shown in Figure 1. We will focus on these extensions in a future study.
Figure 9. The measured CuEDTA$^{2-}$ concentration (symbols, from Gramling et al. [13]) versus the model-simulated (solid lines) concentration (relative to the initial concentration 0.02 M). The dashed line denotes the Standard Pore-Scale Mixed (SPSM) Model prediction by Gramling et al. ([13], eq. (10)), by assuming perfect mixing. Note that (a) is the best-fit result, while the others are predictions. In the legends, Q denotes the flow rate, and T denotes the sampling time.

5. Conclusions

This study develops a fully Lagrangian framework to simulate mixing-limited bimolecular 2nd-order reactions, and the resultant numerical solver is checked against known chemical kinetics and laboratory experiments. Reactions between adjacent particles are combined with particle displacement defined by the Langevin equation.
at the same scale. The basis of the particle-based simulation approach is the interaction radius $R$, which depends on the distribution and availability of reactants.

The interaction radius can be derived analytically using an agent-based approach, for a closed system initially filled with reactants. For the case of irreversible reaction, $R$ is a constant; while $R$ decreases nonlinearly in time for the case of reversible reaction. An alternative simulation scheme with constant $R$ is also presented for reversible reactions, where both forward and backward reactions are simulated at each time step.

If there is a sharp contact between reactants (a typical experimental setup for bimolecular reactions in the laboratory), an empirical formula for the interaction radius is developed. The resulting Lagrangian solver successfully simulates the snapshots of product observed in the laboratory, under different flow rates.

REFERENCES


YONG ZHANG, DESERT RESEARCH INSTITUTE, LAS VEGAS, NV 89119

E-mail address: Yong.Zhang@dri.edu