Reactive random walk particle tracking and its equivalence with the advection-diffusion-reaction equation

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Key Points:

• Equivalence between reactive random walk particle tracking and the advection-diffusion-reaction equation is shown
• Key parameters of the reactive random walk algorithm are discussed
• Algorithm is validated for constant and variable flow scenarios under slow and fast reaction kinetics

Abstract
We present a reactive random walk particle tracking approach to describe bimolecular chemical reactions and show its equivalence with the advection-diffusion-reaction equation. The method is able to efficiently simulate reactions in d-dimensional systems with homogeneous and spatially variable advection. Reactions among particles are determined by the reaction probability that is given in terms of the reaction rate coefficient, the total number of particles and an interaction radius which describes the well-mixed support volume at which all particles have the same probability to interact. The method is meshless and free of numerical dispersion. The method is validated for the bimolecular irreversible chemical reaction $A + B \rightarrow C$ in scenarios characterized by slow and fast chemical kinetics under diffusion and heterogeneous advection and diffusion.

1 Introduction

In recent years a variety of particle-tracking methods coupled with reactions have been proposed to model reactive transport in porous media [Berkowitz et al., 2016]. Random walk particle tracking (RWPT) models coupled with reactions assume that particle pairs react according to some probabilistic rules when particles are within some reaction radius $r$. There has been some ambiguity regarding the definition of this reaction radius in the literature. In the following, we will briefly discuss implementations of the reaction radius in reactive random walk particle tracking algorithms for irreversible bimolecular reactions.

Several alternative definitions of $r$ have been used to quantify reactive transport in porous media. For instance, fast kinetic reactions have been properly simulated applying simplistic reaction rules based on proximity between reactant particles (two particles react whenever they are at a distance smaller than $r$) [Edery et al., 2009, 2010]. However, in these models $r$ must be calibrated using empirical data or based on physical properties of the medium as grain or pore size to represent the degree of mixing between reactants. Therefore $r$ cannot represent the same reaction if the medium properties or size changes. The parameter $r$ has been linked to the reaction rate coefficient $k$, the mass carried by each particle, and the time step $\Delta t$ [Zhang et al., 2013]. This coupling suggest a dependency between the reactants mass and kinetics that overestimates reaction. Other approaches employ a time variable reaction radius $r(t)$ based on kernel density estimators (KDE) [Rahbaralam et al., 2015; Schmidt et al., 2017]. However, these
reaction algorithms coupled with KDE methods are not without their limitations. If the reactions are simulated as a birth/death process of particles the reaction radius may increase over time. At late times, a finite number of particles combined with an increased \( r \) may overestimate the reaction efficiency and oversmooth the spatial distributions of the reacting species. Other approaches employ a collocation probability that depends on the separation distance between reactant particles that may underestimate the reaction kinetics when \( k \) is defined through the number of particles [Benson and Meerschaert, 2008; Ding et al., 2013; Hansen et al., 2014; Paster et al., 2014].

Here, we present a reactive RWPT methodology which is fully equivalent to the advection-diffusion reaction equation. The derivation of the equivalence between the two frameworks sheds some light on the meaning of the reaction radius and its choice.

2 Reactive random walks

We consider the irreversible bimolecular reaction \( A + B \rightarrow C \). In the particle, or agent-based modeling approach employed here, the concentrations of \( A, B \) and \( C \) particles are represented by the number densities

\[
c_i(x,t) = \frac{N_i(x,t)}{N_0 \Delta V} \quad \text{for} \quad i = A, B, C,
\]

where \( N_i(x,t) \) is the number of particles belonging to species \( i \) in a support volume \( \Delta V \) located at the position \( x \) at time \( t \) and \( N_0 \gg 1 \) is the total number of particles that are contained in the initial volume \( V_0 \). The support volume \( \Delta V \) is well-mixed, which means that there are no mass transfer limitations on the support scale. This notion and its implications are discussed further below. The definition of concentration considers the limit of large particle numbers \( N_0 \rightarrow \infty \) such that \( N_i(x,t)/N_0 \) remains finite. The molar concentration \( \mu_i(x,t) \), this means number of moles \( m_i(x,t) \) of a species per \( \Delta V \) is defined by

\[
\mu_i(x,t) = \frac{m_i(x,t)}{\Delta V}.
\]

Thus, the relation between the number density \( c_i(x,t) \) and the molar concentration \( \mu_i(x,t) \) is given by

\[
\mu_i(x,t) = m_0 c_i(x,t),
\]

where \( m_0 \) is the total initial molarity, which means the sum of moles of the species contained in the initial volume \( V_0 \). In the following, we first consider reactions in a well mixed
reactor. Then, we show the equivalence between reactive random walks and the advection-diffusion reaction equation.

2.1 Well-mixed reactor

In the following, we develop the reaction probability for a single particle in a well-mixed reactor of volume $V_0$ without mass transfer limitations. Thus, the species concentrations $c_i(x, t) = c_i(t)$ are independent of the spatial position and given by

$$c_i(t) = \frac{N_i(t)}{N_0 V_0},$$

where here $N_0$ here is the total initial number of particles. We focus on the survival and reaction probabilities from the point of view of a $B$ particle. The lack of any mass transfer limitations implies that a $B$ particle has an equal chance to interact with any of the surrounding $N_A(t)$ $A$ particles and there is no memory between successive reaction events.

We denote by $p_r(\Delta t)$ the probability for an individual particle-particle interaction to occur in the time $\Delta t$. Thus, the probability that a $B$ particle survives an individual reaction event in $\Delta t$ is $1 - p_r(\Delta t)$. The well-mixed condition implies that the survival probability for a $B$ particle after $\Delta t$ is

$$P_s(t; \Delta t) = [1 - p_r(\Delta t)]^{N_A(t)}.$$

The reaction probability $P_r(t; \Delta t)$ is accordingly given by

$$P_r(t; \Delta t) = 1 - [1 - p_r(\Delta t)]^{N_A(t)}.$$

The survival probability (5) can also be written as the ratio of the number of surviving particles at time $t + \Delta t$ to the number of particles at time $t$ as

$$P_s(t; \Delta t) = \frac{N_B(t + \Delta t)}{N_B(t)}.$$

By combining (5) and (7), we obtain

$$N_B(t + \Delta t) = N_B(t) [1 - p_r(\Delta t)]^{N_A(t)}$$

Reactions between particles occur at a constant rate. Thus, the reaction probability is set to

$$p_r(\Delta t) = \alpha \Delta t \leq 1,$$
where $\alpha$ is a rate defined below. Using this definition, we can write

$$N_B(t + \Delta t) = N_B(t) \left[1 - \alpha \Delta t\right]^{N_A(t)}$$  \hspace{1cm} (10)

In the limit $\Delta t \to 0$, we obtain the rate equation

$$\frac{dN_B(t)}{dt} = -\alpha N_A(t) N_B(t).$$  \hspace{1cm} (11)

Using definition (4) of the species concentrations, we obtain the well known kinetic rate law for the number densities

$$\frac{dc_B(t)}{dt} = -kc_B(t)c_A(t).$$  \hspace{1cm} (12a)

where $k$ is the reaction rate coefficient. The rate $\alpha$ is thus given in term of $k$, $V_0$ and $N_0$ as

$$\alpha = \frac{k}{N_0 \Delta V}.$$  \hspace{1cm} (12b)

The equations for the concentration of the $A$ and $C$ species are analogously given by

$$\frac{dc_A(t)}{dt} = -kc_A(t)c_B(t), \quad \frac{dc_C(t)}{dt} = kc_A(t)c_B(t).$$  \hspace{1cm} (12c)

Note that the reaction rate coefficient $k$ here is referred to the number densities $c_i(t)$.

The reaction rate coefficient with respect to the molar concentrations $\mu_i(t)$ is $k' = k/m_0$.

The characteristic reaction time is $\tau_r = 1/kc_0$, where $c_0$ is a characteristic concentration. For example, for the initial concentrations $c_A(0) = c_B(0) = 1/2V_0 = c_0$, the solution for $c_A(t)$ is

$$c_A(t) = \frac{c_0}{1 + kc_0t}.$$  \hspace{1cm} (13)

### 2.2 Reaction under advection and diffusion

The position $\mathbf{x}(t)$ of a $B$ particle under advection and diffusion is described by the Langevin equation [Risken, 1996]

$$\frac{d\mathbf{x}(t)}{dt} = v[\mathbf{x}(t)] + \sqrt{2D}\xi(t),$$  \hspace{1cm} (14)

where $\xi(t)$ is a vectorial Gaussian white noise characterized by $\langle \xi(t) \rangle = 0$ and $\langle \xi_i(t)\xi_j(t') \rangle = \delta_{ij}\delta(t-t')$. Note that we use here the notation of the textbook by Risken [1996] and denote the particle position by $\mathbf{x}(t)$ and the position vector in space by $\mathbf{x}$. The former
is distinguished from the latter by its argument. The angular brackets denote the white noise average. The density, or concentration of $B$ particles can be written as

$$c_B(x, t) = \langle \delta [x - x(t)] P_s(t) \rangle,$$

(15)

where $\delta(x)$ is the Dirac delta and $P_s(x, t)$ is the probability of survival of a $B$ particle until time $t$.

### 2.2.1 Survival probability

The probability of survival until $t + \Delta t$ is given by the probability of survival until time $t$ multiplied by the probability $P_s(t; \Delta t)$ to survive in the time interval $[t, t + \Delta t]$. This means

$$P_s(t + \Delta t) = P_s(t)P_s(t; \Delta t).$$

(16)

As in the previous section, the probability $P_s(t; \Delta t)$ of survival during $\Delta t$ in the well-mixed support volume $\Delta V$ centered in $x = x(t)$ is given by

$$P_s(t; \Delta t) = [1 - p_r(\Delta t)]^{N_A[x(t), t]},$$

(17)

where $N_A[x(t), t] = c_A[x(t), t]N_0\Delta V$ is the number of $A$ particles in the support volume centered in $x(t)$. Note that the concentration $c_A[x(t), t]$ is constant over the well mixed support volume, and that the $B$ particle located at $x(t)$ can react with any of the $N_A[x(t), t]$ $A$ particles in its vicinity with equal probability within the time interval $\Delta t$. The reaction probability during $\Delta t$ is given accordingly by

$$P_r(t; \Delta t) = 1 - [1 - p_r(\Delta t)]^{N_A[x(t), t]},$$

(18)

In analogy to (9) we set

$$p_r(\Delta t) = \frac{k\Delta t}{N_0\Delta V},$$

(19)

where we used expression (12b) for the rate $\alpha$. Inserting the latter into (17) and performing the limit $N_0 \to \infty$ gives for the survival probability

$$P_s(t; \Delta t) = \exp(-kc_A[x(t), t]\Delta t).$$

(20)

It is assumed that $c_A[x(t), t]$ is approximately constant during $\Delta t$, which is a good approximation if $\Delta t \ll \tau_r$. Note that (18) and (20) imply that the survival probability
\( P_s(t; t' - t) \) over a time interval \( t - t' \gg \Delta t \) is given by

\[
P_s(t; t' - t) = \exp \left( -k \int_0^{t-t'} dt'' c_A[x(t-t''), t-t''] \right).
\] (21)

This expression may be useful in random walk schemes characterized by variable transition times.

### 2.2.2 Kramers-Moyal expansion

In order to derive the governing equation for \( c_B(x, t) \), we expand (15) as

\[
c_B(x, t + \Delta t) = \langle \delta[x - x(t + \Delta t)]P_s(t + \Delta t) \rangle.
\] (22)

By noting that

\[
x(t + \Delta t) = x(t) + v[x(t)]\Delta t + \sqrt{2D \Delta t} \int_t^{t+\Delta t} dt' \xi(t')
\] (23)

and using relation (20) we can write tautologically

\[
c_B(x, t + \Delta t) = \int dx' \langle \delta[x' - x(t)]P_s(t) \exp(-kc_A[x(t), t] \Delta t) \delta[x - x' - \Delta x(t)] \rangle,
\] (24)

where we defined

\[
\Delta x(t) = v[x(t)]\Delta t + \sqrt{2D \Delta t} \int_t^{t+\Delta t} dt' \xi(t').
\] (25)

The first Dirac delta on the right side of (24) implies that \( x(t) = x' \) so that we can write

\[
c_B(x, t + \Delta t) = \int dx' c_B(x', t) \exp[-kc_A(x', t) \Delta t] p(x - x'; x', \Delta t),
\] (26)

where \( p(x - x'; x', \Delta t) = \langle \delta[x - x' - \Delta x(t)]|_{x(t)=x'} \rangle \) denotes the probability for a particle to make a transition from \( x' \) to \( x \) within the time \( \Delta t \). Performing a Kramers-Moyal expansion [Risken, 1996] of (26) gives

\[
c_B(x, t + \Delta t) = [1 - \nabla \cdot v(x) \Delta t + D \Delta t \nabla^2 + \ldots] c_B(x, t) \exp[-kc_A(x, t) \Delta t]
\] (27)

where the dots denote contributions of order \( \Delta t^2 \). We expand both sides of the equation consistently up to order \( \Delta t^2 \) to obtain

\[
c_B(x, t) + \frac{\partial c_B(x, t)}{\partial t} \Delta t + \ldots =
[1 - \nabla \cdot v(x) \Delta t + D \Delta t \nabla^2] c_B(x, t) - c_B(x, t)kc_A(x, t) \Delta t + \ldots.
\] (28)
The limit $\Delta t \to 0$, gives the advection-diffusion reaction equation (ADRE)

$$\frac{\partial c_B(x,t)}{\partial t} + \nabla \cdot v(x)c_B(x,t) - D\nabla^2 c_B = -kc_B(x,t)c_A(x,t). \quad (29a)$$

The derivations for $c_A(x,t)$ and $c_C(x,t)$ are analogous and yield

$$\frac{\partial c_A(x,t)}{\partial t} + \nabla \cdot v(x)c_A(x,t) - D\nabla^2 c_A = -kc_B(x,t)c_A(x,t) \quad (29b)$$

$$\frac{\partial c_C(x,t)}{\partial t} + \nabla \cdot v(x)c_C(x,t) - D\nabla^2 c_C = kc_A(x,t)c_B(x,t). \quad (29c)$$

Thus, the reactive random walk particle tracking scheme based on the Langevin equation (14) combined with the survival and reaction probabilities (17) and (18) for a well-mixed local support volume are exactly equivalent to the system (29) of advection-diffusion reaction equations. Note that the equivalence between the Lagrangian and Eulerian frameworks does not require the definition of a collocation probability of $A$ and $B$ particles as given for example in Benson and Meerschaert [2008], but merely relies on the concept of a well-mixed support volume $\Delta V$.

### 2.3 Numerical implementation

The Langevin equation (14) governing the motion of particles belonging to the $A$, $B$ and $C$ species is discretized using an Euler scheme as

$$x(t + \Delta t) = x(t) + v[x(t)]\Delta t + \sqrt{2D\Delta t}\eta(t) \quad (30)$$

where the $\eta(t)$ are independent identically distributed Gaussian random variables characterized by 0 mean and unit variance. The time increment $\Delta t$ is conditioned on the scale of variability $\tau_v$ of the Lagrangian velocity $v[x(t)]$ in that the discretization (30) requires that

$$\int_t^{t + \Delta t} dt' v[x(t')] \approx v[x(t)]\Delta t. \quad (31)$$

This means, $v[x(t)]$ is only weakly variable during the time $\Delta t$.

At each time step, the position of each particle is recorded and the distances between a given $B$ and $A$ particles are calculated. Note that the algorithm consider either the point of view of a $B$ of an $A$ particle. We describe the point of view of a $B$ particle, the one of an $A$ particle is analogous. The number $N_A[x(t)]$ of $A$ particles within a volume $\Delta V$ centered at the position $x(t)$ of the $B$ particle determines the reaction probability (18). The occurrence of a reaction event is obtained from a Bernoulli trial. If the
reaction occurs, the $B$ particles and the closest $A$ particle are removed and a particle $C$ is placed at the middle point of the $A$ and $B$ particle locations. Note that these details on removal of $A$ and $B$ and placing the $C$ particles have no impact on the simulated reaction behavior or the equivalence of the particle scheme with the ADRE derived in the previous section. The motion of the produced $C$ particles follows (30). Recall that the notion of a well-mixed support volume $\Delta V$ is a central item for the equivalence between the Lagrangian and Eulerian reaction models. For 1 dimension, the well-mixed support volume here is given by $\Delta V = 2r$, in 2 dimensions, it is given by a disk, such that $\Delta V = \pi r^2$ and in three dimensions by a sphere such that $\Delta V = 4\pi r^3/3$. The selection of the reaction radius is discussed in the following section.

### 2.4 Well-mixed support volume and reaction radius

As pointed out in the introduction, a question that has given rise to some debate concerns the determination of the volume $\Delta V$ or equivalently the determination of the reaction radius $r$. Edery et al. [2009] discuss the use of a normal distribution for the reaction radius, or relating the radius to the reaction rate coefficients. Benson and Meerschaert [2008] use a collocation probability with a characteristic reaction radius $r \sim \sqrt{2D\Delta t}$ based on the reasoning that the typical area probed by a particle due to random motion during a time $\Delta t$ is $2D\Delta t$. For the definition and use of a collocation probability see also Hansen et al. [2014] and Paster et al. [2014].

The derivation presented in Section 2.2 invokes the well-mixed condition, which here means that all particles within a fixed radius, or support volume have the same probability to react in a time interval $\Delta t$. Thus, instead of a collocation probability, we use a fixed reaction radius $r$. Within the time $\Delta t$ each particle must be able to reach any other particle in the support volume. The characteristic diffusive particle displacement during time $\Delta t$ is $\sigma(\Delta t) = \sqrt{2dD\Delta t}$, where $d$ is the spatial dimension. For $r \lesssim \sigma(\Delta t)$ the support volume may be considered well-mixed. We use here $r = \sigma(\Delta t)$. Note that this condition on the reaction radius may be relaxed at longer simulation times because the mixing scale $s(t)$ [Villermaux, 2012; Le Borgne et al., 2013; Dentz and de Barros, 2015] grows diffusively as $s(t) \propto \sqrt{2Dt}$ in heterogeneous non-chaotic flow scenarios. The concentration content on the mixing scale may be assumed uniform. Thus, if one is interested in observation times $t \gg \Delta t$, the reaction radius may be chosen $0 < r < \sqrt{2Dt}$. 
In order to resolve kinetic reactions, the time increment $\Delta t$ needs to be smaller than the characteristic reaction time scale $\tau_r = 1/c_0k$ with $c_0$ a characteristic concentration. Thus, as $\Delta t$ is by definition of the reaction radius $r$ the characteristic mass transfer time on the support scale, the microscopic Damköhler number is $Da_m = \Delta t c_0 k < 1$, which means that reactions at the support scale are not limited by mass transfer.

Fast or instantaneous chemical reactions can be modeled in two ways. First, particles may react with certainty upon encounter. This means the probability $p_r(\Delta t)$ for an individual reaction is set to 1. In this case there is no condition on $\Delta t$ regarding the reaction. Second, finite kinetics can be considered. If the time increment $\Delta t$ is chosen larger than the reaction time $\tau_r$, the microscopic Damköhler number is $Da_m \geq 1$ and the reaction is mass transfer limited already on the support scale. The kinetic part of the reaction is not resolved by the time discretization and the reaction is instantaneous on the relevant observation times. Note however, that $\Delta t$ may be also conditioned by the temporal variability of the Lagrangian velocity, see (31).

The work by Porta et al. [2012] defines a fixed support volume by discretizing space into a cubic lattice. The reaction probability in each cell is given by the species concentrations in a cube, the particle residence times, and the reaction rate coefficient. The characteristic mass transfer time across a cell of size $a$ is $a^2/D$. Thus, the microscopic Damköhler number in this approach is $Da_m = c_0ka^2/D$. In order to resolve kinetic reactions, $Da_m \leq 1$ sets a criterion for the grid size.

3 Validation

We validate the reactive random walk particle tracking algorithm presented in the previous section in 4 scenarios. First, we consider slow chemical reactions in a closed domain for well-mixed and segregated initial species distributions. Second, we consider fast chemical reactions for a plug flow reactor and a laminar flow reactor setup with initially segregated reactant species. For the well-mixed scenario, the numerical data are compared to the exact analytical solution for the concentration of the $A$ species. In the remaining scenarios, we focus on the total product mass

$$m_C(t) = \int dxc_c(x,t),$$

and validate against analytical solutions.
3.1 Slow reactions

We consider a 1-dimensional domain with reflecting boundary conditions. The diffusion coefficient is set to $D = 10^{-3}$ cm$^2$/s, the reaction rate coefficient is $k = 8$ cm/s. The time step is $\Delta t = 10^{-2}$. According to the previous section, this setup is equivalent to the diffusion reaction problem

$$\frac{\partial c_i(x,t)}{\partial t} - D \frac{\partial^2 c_i(x,t)}{\partial x^2} = -kc_A(x,t)c_B(x,t), \quad i = A, B \quad (33a)$$

$$\frac{\partial c_C(x,t)}{\partial t} - D \frac{\partial^2 c_C(x,t)}{\partial x^2} = kc_A(x,t)c_B(x,t). \quad (33b)$$

3.1.1 Well-mixed scenario

We consider an initially well-mixed reactor. This means particles are uniformly distributed across the 1-dimensional domain of length $L = 1$ cm, which implies that the initial concentrations are $c_A(x, t = 0) = c_B(x, t = 0) = c_0 = 1/2$ cm$^{-1}$ and $c_C(x, t = 0) = 0$. The total particle number is $N_0 = 10^4$. Due to the uniform initial distributions there are no macroscopic mass transfer limitations and thus $c_i(x, t) = c_i(t)$ and the system (33) reduces to (12) with the analytical solution (13). Figure 1 compares the data from the random walk particle tracking simulations and the analytical solution (13). They are in agreement.

![Figure 1](image_url)

**Figure 1.** Evolution of the $A$ species from (symbols) reactive random walk simulations and (solid lines) the analytical solution (13).
3.1.2 Segregated scenario

Here we consider initial segregation of the reactant species such that all the $A$ particles are uniformly distributed in the left, the $B$ particles in the right half of the domain. Thus, the initial concentrations are $c_A(x, t = 0) = c_B(x, t = 0) = c_0 = 1 \, \text{cm}^{-1}$ and $c_C(x, t = 0) = 0$. The total particle number is $N_0 = 10^5$. The numerical results are validated against the early time solution for the total product mass. At early times, this means $t \ll \tau_r = 1/kc_0$, the concentrations of the $A$ and $B$ species can be approximated by [Bandopadhyay et al., 2017],

$$
c_A = \frac{c_0}{2} \left[ 1 - \text{erf} \left( \frac{x - 1/2}{\sqrt{4Dt}} \right) \right], \quad c_A = \frac{c_0}{2} \left[ 1 + \text{erf} \left( \frac{x - 1/2}{\sqrt{4Dt}} \right) \right],
$$

which are the solutions for an infinite medium in the absence of reactions. These approximations are valid at early times, which are smaller than $\tau_r$ and at which the diffusion front is far away from the boundaries. Thus, the evolution of the total product mass can be approximated by

$$
\frac{dm_C(t)}{dt} = \frac{k c_0^2}{4} \int_{-\infty}^{\infty} dx \left[ 1 - \text{erf} \left( \frac{x - 1/2}{\sqrt{4Dt}} \right) \right]^2.
$$

The integrals can be solved analytically, which gives

$$
\frac{dm_C(t)}{dt} = k c_0^2 \sqrt{Dti}.
$$

Thus, we obtain for the initial evolution of the product species

$$
m_C(t) = \frac{kc_0^2 \sqrt{2Di}}{3\sqrt{\pi}}.
$$

The numerical data is in agreement with this analytical solution as shown in Figure 2.

3.2 Fast reactions

We consider two scenarios of fast chemical reactions. In both scenarios, the reactants are initially segregated. The first scenario is 1-dimensional and characterized by a constant flow velocity, the second scenario is 2-dimensional and characterized by a parabolic Poiseuille flow profile.

3.2.1 Plug flow reactor

The plug flow scenario is inspired by the Darcy scale setup of the laboratory experiment reported in [Gramling et al., 2002]. The injection region is $L = 60$ cm in an
Figure 2. Evolution of the product mass $m_C(t)$ from (symbols) reactive random walk simulations and (solid lines) the analytical early time solution (37).

Figure 3. (Top) Comparison of $c_C(x, t) \ t = 20 \ s$ obtained from (symbols) numerical simulations and (solid line) the analytical solution (38). (Bottom) Total product mass $m_C(t)$ obtained from (symbols) numerical simulations and (solid line) the analytical solution (39).

infinite flow domain. The total particle number is $N_0 = 2 \cdot 10^5$. Initially $10^5 \ A$ particles are uniformly distributed in the left and $10^5 \ B$ particles in the right half of the injection region, which yields the initial concentrations $c_A(x, t = 0) = c_B(x, t = 0) = 1/60 \ cm^{-1}$ and $c_C(x, t = 0) = 0$. The diffusion coefficient is set to $D = 1.75 \cdot 10^{-1} \ cm^2/s$ the velocity $v = 0.67 \ cm/s$. The time step is $\Delta t = 10^{-2} \ s$. The reaction probability is set to $p_r = 1$. The numerical results are validated against the exact analytical solutions for the concentration of the product $C$, which is given by [Gramling et al.,]
Figure 4. Total mass of product $C$ obtained from (symbols) numerical simulations and the analytical (solid line) short and (dashed line) long time approximations.

$$c_C(x, t) = \frac{c_0}{2} \text{erfc} \left( \frac{|x - vt|}{2\sqrt{Dt}} \right).$$  \hspace{1cm} (38)

The total product mass $m_C(t)$ is obtained from (32) as

$$m_C(t) = 2c_0\sqrt{\frac{Dt}{\pi}}.$$ \hspace{1cm} (39)

Figure 3 compares the product concentration and total product mass obtained from the reactive random walk simulations to the analytical solutions (38) and (39). The validity of the numerical approach is confirmed.

3.2.2 Laminar flow reactor

We consider a 2-dimensional infinitely long channel of width $2a = 1$ cm. Flow through the channel is laminar and characterized by the parabolic velocity profile

$$\mathbf{v}(y) = v_0 \left( 1 - \frac{y^2}{a^2} \right) \mathbf{e}_x,$$ \hspace{1cm} (40)

where $\mathbf{e}_x$ is the unit vector in $x$-direction and $v_0$ is the maximum velocity. The mean flow velocity is $\bar{v} = 2v_0/3$. We set here $v_0 = 0.65$ cm/s. The diffusion coefficient is set to $D = 3.5 \cdot 10^{-3}$ cm$^2$/s. This scenario can be characterized by the Péclet number $Pe = \sqrt{\tau_D/\tau_v} = \bar{v}a/D$, which compares the relative importance of advective and diffusive transport mechanisms. The diffusive time scale is $\tau_D = 2a^2/D$, the advective time
\( \tau_v = 2D/\bar{v}^2 \). The Péclet number here is \( Pe = 61 \), this means, the scenario is advection dominated. The total particle number is \( N_0 = 2 \cdot 10^5 \). Initially \( 10^5 \) \( A \) particles are distributed in the left and \( 10^5 \) \( B \) particles in the right half of the injection region of length \( L_x = 20 \text{ cm} \). The vertical domain boundaries are open, the horizontal boundaries are reflecting. The time step is set to \( \Delta t = 10^{-2} \text{ s} \), the reaction radius is \( r = \sqrt{4D\Delta t} \) and the reaction probability is \( p_r = 1 \). The numerical results are validated against analytical solutions for \( m_C(t) \) at early times \( t < \tau_v \) and late times \( t > \tau_D \). For \( t < \tau_v \) transport is diffusion-dominated, this means the flow variability is subleading. The product mass is given by (39). For \( t > \tau_D \), the species are fully mixed over the channel cross-section and transport can be characterized by the mean velocity \( \bar{v} \) and the Taylor dispersion coefficient \( D = D + 2\nu^2 a^2 / 105D \). Thus, the evolution of \( m_C(t) \) is given again by (39) with \( D \) substitute by the Taylor dispersion coefficient \( D \). Figure 4 shows the agreement between the simulation data for \( m_C(t) \) and the analytical solutions for the early and late time behaviors. The intermediate behavior, which is dominated by the flow heterogeneity, is not captured by these analytical solutions. An upscaled model for the full behavior can be found in Perez et al. [2018].

4 Conclusions

We demonstrate the equivalence between reactive random walk particle tracking and the advection-diffusion-reaction equation. This equivalence is established based on the concept of a well-mixed support volume, which acts as a well-mixed reactor during the time increment \( \Delta t \). The reactive random walk method is simple and free of numerical dispersion and artificial oscillations compared to grid-based Eulerian approaches. All particles within the reaction radius, which represents the support volume, are statistically equal and have an equal probability to react. As a result of the locally well-mixed assumption, reactions occur at constant rate and the reaction probability \( p_r \) is determined by the reaction rate coefficient \( k \) and the time increment \( \Delta t \). Thus, within a constant reaction radius, particle reactions are determined combinatorially based on the reaction probability for individual reaction events. The reaction radius is chosen of the order of the typical diffusive particle displacement \( \sigma(\Delta t) = \sqrt{2D\Delta t} \) during a time step \( \Delta t \). As the mixing scale in heterogeneous mixtures under non-chaotic flow conditions increases as \( \sim \sqrt{D\Delta t} \), the reaction radius may be chosen larger than \( \sigma(\Delta t) \) for times \( t \gg \Delta t \).
We have validated the reactive random walk method for two slow and two fast reaction scenarios dominated by diffusion and (heterogeneous) advection-diffusion. In all cases the simulation data agree with available analytical solutions. The presented method may be extended to include more complex physical and non-linear chemical processes because complex reactions, such as biodegradation or enzymatic reactions, are composed of a cascade of elementary unimolecular and bimolecular reactions similar to the one studied in this Technical Note.

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