



# Simulation of chemical reaction via particle tracking: Diffusion-limited versus thermodynamic rate-limited regimes

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[1] Chemical reactions may be simulated without regard to local concentrations by applying simple probabilistic rules of particle interaction and combination. The forward reaction  $A + B \rightarrow C$  is coded by calculating the probability that any  $A$  and  $B$  particles will occupy the same volume over some time interval. This becomes a convolution of the location densities of the two particles. The backward reaction is a simple exponential decay of  $C$  particles into  $A$  and  $B$  particles. When the mixing of reactants is not a limiting process, the classical thermodynamic reaction rates are reproduced. When low mixing (as by diffusion) limits the reaction probabilities, the reaction rates drop significantly, including the rate of approach to global equilibrium. At long enough times, the law of mass action is reproduced exactly in the mean, with some irreducible deviation in the local equilibrium saturations (the equilibrium constant divided by the mass action expression) away from unity. The saturation variability is not sensitive to numerical parameters but depends strongly on how far from equilibrium the system is initiated. This is simply due to a relative paucity of particles of some species as the reaction moves far to one side or the other.

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## 1. Introduction

[2] Chemical reactions are commonly idealized as an interaction between fluids with certain concentrations of reactants and products. However, on a molecular level, the reactions are the result of collisions, combinations, and/or decay into different species. Each of these actions occur with some probability that is independent of the numbers of molecules some distance away. Only upon space and time averaging do the concepts of concentration, reaction rate, and equilibrium appear. Similarly, solute advection and dispersion were initially envisioned as operations that acted upon concentration. Only later were the operations specified as acting on “particles” that represent packets of molecules. The formal connection is made by relating the probability density of particle location and concentration [e.g., *Tompson and Dougherty*, 1992]. In this paper, a similar distinction is made between abstract solute particles that interact according to simple probabilistic rules, and the changes in apparent reactive solute concentrations.

[3] The motivation to simulate solute reaction via Lagrangian particles and probabilities is twofold: First, the Lagrangian approach is a simple and efficient method to simulate complex nonlocal advection, dispersion, and

mobile/immobile phase partitioning [*Zhang et al.*, 2006; *Valocchi and Quinodoz*, 1989; D. A. Benson and M. M. Meerschaert, A simple and efficient random walk solution of multi-rate mobile/immobile mass transport equations, submitted to *Advances in Water Resources*, 2008]. Because each particle is independent of all others, the transport simulations can be solved with nearly linear speedup with the number of parallel processors. We seek to add chemical reaction without the burden of converting particle numbers to concentrations at every time step. Second, within any single Eulerian “block” of material, the concentrations of reactants are everywhere equal, and a well-mixed formula applies at the level of discretization. In reality, very small pockets of unmixed reactants may occur in close proximity [*Kapoor and Kitanidis*, 1998; *Kitanidis*, 1994], and an Eulerian approach must use small enough blocks to capture the chemical heterogeneity. In a Lagrangian approach, the particles can occur in “clumps” anywhere in the domain. We take advantage of this to more faithfully simulate unmixed reactants at all scales while employing a coarse velocity grid.

[4] Recent work has focused on the rate of the forward bimolecular reaction in the deceptively simple system  $A + B = C$ . The forward rate discerned from batch tests is found to be too high for column and field tests, which is attributed to the incomplete mixing of the reactants in porous media [*Raje and Kapoor*, 2002; *Gramling et al.*, 2002]. *Jose and Cirpka* [2004] show that mixing is responsible by allowing a 1-D test in homogeneous sand to progress long enough that mixing and hydrodynamic dispersion parameters approach each other. In natural heterogeneous media, however, *Molz and Widdowson* [1988] and *Cirpka and Kitanidis* [2000]

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demonstrate that mixing lags far behind hydrodynamic dispersion. Approaches to account for this include classical perturbative and numerical approaches [Kapoor *et al.*, 1997; Kapoor and Kitaniadis, 1998; Dentz *et al.*, 2000; Luo *et al.*, 2008].

## 2. Background

[5] There is a long history of reductionism associated with connecting an observed “continuum” behavior, modeled by some PDE, to an underlying particle- or molecular-based rule of action. Shortly after Einstein [1906] explained the diffusion equation via particle collisions and the central limit theorem, von Smoluchowski [1917] explained macroscopic chemical reaction rates by a model of microscopic particle collision and transformation. The mathematical connection between chemical reaction PDEs and the underlying process of molecular motion (either ballistic or diffusive), collision, and transformation becomes exceedingly complex because of the interactions of multiple potential reaction “partners” that can appear and disappear. von Smoluchowski [1917] treated this in a continuum manner with concentration gradients around a target particle, effectively ruling out a purely Lagrangian implementation. Further studies treated the joint probabilities of collocation with multiple particle pairs. To be tractable, many assumptions must be made, such as uniform distributions of reactants or independence of individual interaction distributions [Waite, 1957; Collins and Kimball, 1949; van Kampen, 1992; Gardiner, 2004]. The assumptions make it unclear exactly how to implement a tractable stochastic numerical model. The most popular methods include (1) placing the reactants on a lattice and allowing particles to hop only to adjacent sites and react if the site is already occupied by the appropriate reactant and (2) allowing particles to react when they are found within some arbitrary distance apart [Toussaint and Wilczek, 1983; Kang and Redner, 1985; Dawkins and ben-Avraham, 2001]. These have been proven equivalent to von Smoluchowski’s method when the lattice spacing goes to zero, which essentially rules out an implementation in a field-scale hydrologic model. But the studies by Toussaint and Wilczek [1983] and Kang and Redner [1985] point out the importance of diffusion-limited interaction that might arise from poor reactant mixing. In this regime, the rate of forward reaction (for a bimolecular reaction) slows significantly relative to the well-mixed regime, and the approach to equilibrium slows from an exponential to a power law rate.

[6] Gillespie’s relatively recent [1977] method is easily implemented and mimics the rate-limited (not diffusion or mixing limited) kinetics dictated by the PDEs of reaction. However, the method assumes that (1) reactants are randomly and uniformly dispersed around any given particle and (2) the “volume” of space probed by a moving particle is linear in time. The assumptions are inherited from the underlying model of dilute gas particles that move at constant velocity between collisions and are quickly and completely mixed. However, it cannot handle a heterogeneous environment. In a hydrologic setting, the Gillespie method was modified [Srinivasan *et al.*, 2007] by adding an empirical random factor that changes the reaction rate at any place and time. This number has no basis in the local physics or local mixing, and the physical shortcomings of

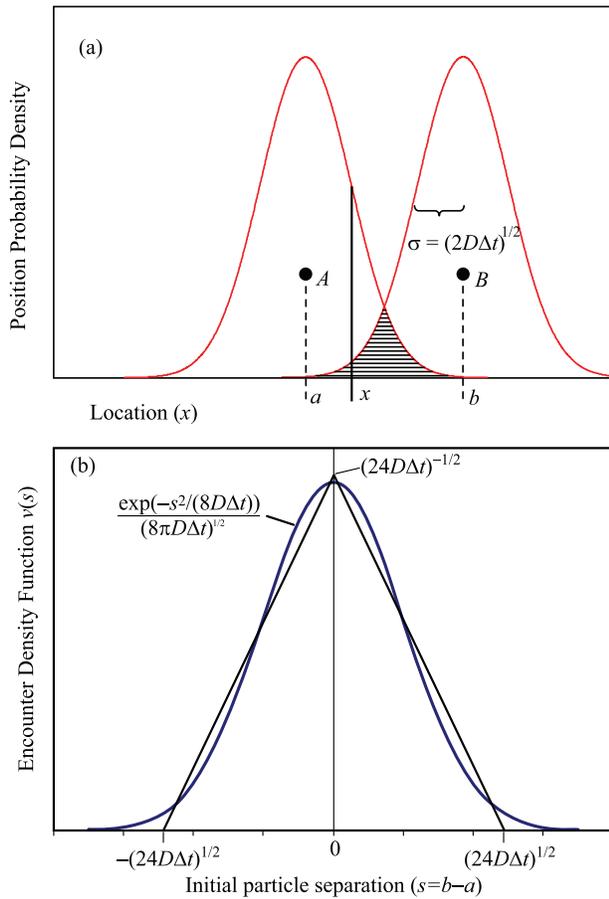
such a factor in a similar form are discussed by Collins and Kimball [1949]. More recently, the smoothed particle hydrodynamics (SPH) method was implemented for advection, diffusion, and reaction with incomplete mixing by Tartakovsky *et al.* [2008]. The qualitative effects of poor mixing are striking; however, at its core, SPH uses a kernel to average over particles to simulate the continuum variables, so the reaction rates should directly depend on an empirical choice of kernel shape and size. We suspect that a correct choice of kernel might replicate the physics of diffusion-limited reaction.

[7] In the present work, we take a new look at the problem by formulating the probability that two particles, under any general conditions of diffusive or dispersive motion, will occupy the same differential volume. This probability may, but does not have to, be linked to macro-dispersive spreading in heterogeneous material. The probability is multiplied by the classical thermodynamic rate that dictates the probability that, upon “collision,” the particles will react. Particles are allowed to react (or not) sequentially, in a physically realistic, and computationally simple manner. The algorithm is implemented and shown to correspond, in a well-mixed setting, to the upscaled PDEs of reaction (i.e., the law of mass action). The algorithm makes no assumptions about the distribution or availability of reactants, or that Fick’s law is the correct model of diffusion. Therefore, the algorithm may treat anomalous diffusions and will (by construction) automatically account for the relative abundance or paucity of reactants at all locations and times. To our knowledge, this is the first discussion of this model of particle interaction. Under conditions that mimic undermixed reactants, the random walk algorithm has significantly reduced rates of reaction, a condition often observed at the lab and field scale [Molz and Widdowson, 1988].

## 3. Reaction $A + B = C$

[8] The backward reaction is simplest to simulate. A particle of  $C$  spontaneously degenerates into  $A$  and  $B$  particles. Each particle of  $C$  does so independently of any other particles. The probability statement that makes this equivalent to a rate of reaction  $K_b$  is  $P(\text{backward react}) = K_b \Delta t$  for some simulation time step  $\Delta t$ . For  $N$  independent particles of  $C$ , this results in an approximation of the differential equation  $dN_C/dt = -K_b N_C$  and an exponential conversion of the concentration of  $C$ , denoted  $[C]$ , into  $[A]$  and  $[B]$ . This approximation is  $O(\Delta t)$ , so in practice  $K_b \Delta t < 0.1$ . The implementation of this reaction is easy to code and test; verification is not shown for brevity.

[9] For the forward (second-order) reaction to occur, a molecule of  $A$  must be close enough to  $B$  that they may interact. The whereabouts of any particle in some time interval in a natural (unstirred) system is dictated by the distance that each molecule might diffuse or hydrodynamically disperse, particularly in the transverse direction to flow [Dentz *et al.*, 2000; Jose and Cirpka, 2004]. Given two independent particles  $A$  and  $B$  with initial locations  $a, b$  respectively, let  $X_A, X_B$  denote the particle locations after some time step  $\Delta t$ . These are given by the  $d$ -dimensional densities of motion on a small timescale (Figure 1a). Write  $X_A = a + \Delta X_A$  and  $X_B = b + \Delta X_B$ . The probability that the two particles will occupy the same position is  $P(X_A = X_B) =$



**Figure 1.** Illustration of the probability that two independent particles may be coincident during some time interval  $\Delta t$ . (a) Brownian diffusion gives two overlapping Gaussian densities. The integral of the product of the density functions in the shaded region gives the probability density for the event that the  $A$  and  $B$  particles come into contact. (b) Density  $v(s)$  associated with two particles occupying the same space when initially separated by a distance  $s = a - b$ . Gaussian diffusion and the equivalent uniform densities give similar results.

$P(a + \Delta X_A = b + \Delta X_B) = P(\Delta X_A - \Delta X_B = b - a) = P(D = s)$  where  $D = \Delta X_A - \Delta X_B$  is the relative displacement of the two particles, and  $s = b - a$  is the initial separation distance (Figure 1a). The two particles will be in contact if the relative displacement equals the initial separation, bringing the final displacement to zero. If  $v(s)$  is the density of  $D$ , then we can write  $P(X_A = X_B) = v(s)ds$ . If either of the particle movements is symmetric (call it  $B$ ) then  $\Delta X_B$  is identically distributed with  $-\Delta X_B$  and since  $\Delta X_A$  and  $\Delta X_B$  are independent,  $D$  is identically distributed with  $\Delta X_A + \Delta X_B$ . Then  $v(s)$  is the density of the sum of two independent random variables, which is known to be the convolution of the two densities:  $v(s) = \int f_A(x)f_B(s-x)dx$ , where  $f_A(x)$  and  $f_B(x)$  denote the densities of the motions away from the current positions. If neither particle motion density is symmetric, then  $v(s) = \int f_A(x)f_B(x-s)dx$ . Note that  $v(s)$  has dimensions of inverse volume in  $d$  dimensions since  $v(s)ds$  is dimensionless.

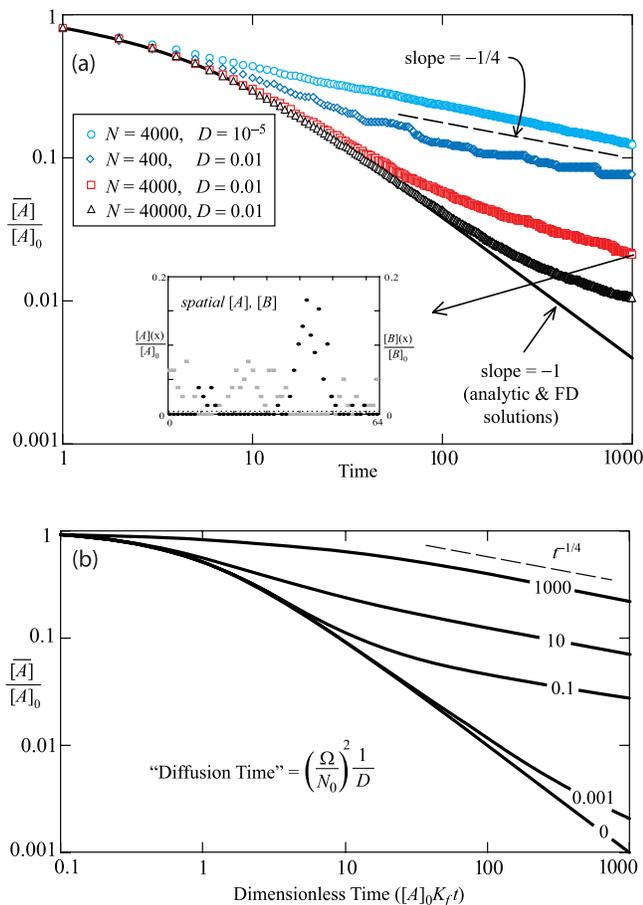
[10] A few simple 1-D examples illustrate the construction. If  $A$  is immobile at position  $x = a$ , and the location of  $B$  has a density function  $f_B(x - b)$  starting at location  $b$  after some fixed time interval, the probability that  $A$  and  $B$  occupy the same position is  $\delta(x - a) * f_B(x - b)dx = f_B(a - b)ds = f_B(s)ds$ , merely the probability of  $B$  finding itself at  $A$ 's location when initially separated by  $s$ . If  $A$  and  $B$  diffuse under Brownian motion, but with different diffusion coefficients  $D_A$  and  $D_B$ , the density function  $v(s)$  associated with collocation after an interval  $\Delta t$  is the convolution of the two Gaussian densities, i.e., another Gaussian with variance  $2(D_A + D_B)\Delta t$ . An example of practical importance is a location density for each of  $A$  and  $B$  described by a uniform density in  $(-\sqrt{6D\Delta t}, \sqrt{6D\Delta t})$ , which has the same variance  $(2D\Delta t)$  as a Brownian diffusing particle over the time interval  $\Delta t$ . The convolution of the two location densities is a tent function with peak value  $1/\sqrt{24D\Delta t}$  when the initial separation is zero (Figure 1b). This convolution approximates the “actual” convolution of two mean zero, variance  $2D\Delta t$ , Gaussian densities, which is itself a mean zero Gaussian with variance  $4D\Delta t$  (Figure 1b). The tent function is slightly more computationally efficient and is adopted for this study. The location densities of each particle can be given any shape in several dimensions to simulate anisotropic dispersion and mixing. In this way, two particles in the same dip direction may react more favorably than two separated by layers of different material. A convolution of any number of 3-D multi-Gaussians is also multi-Gaussian and straightforward to calculate. The dispersion “halos” may also be velocity-dependent. If one assumes that particles move under the influence of Brownian motion, then the volume “probed” by a particle grows at the rate of  $\sqrt{\Delta t}$ . This is in contrast to Gillespie’s [1977] derivation based on ballistic motion that results in encounter probability growing linearly with time and eventually an exponential reaction probability.

[11] The probability of forward reaction combines the probability of close proximity just described, multiplied by the reaction rate times the time interval, and the total mass (or moles) represented by a single particle. For simplicity, imagine a 1-D domain of size  $\Omega$  that initially contains  $N_0$  particles representing concentrations  $[A]_0 = [B]_0$ . Then the probability that an  $A$  and  $B$  particle pair with initial separation  $s$  react to form a  $C$  particle is

$$P(\text{forward}) = K\Delta t \frac{\Omega[A]_0}{N_0} v(s)\Delta V \quad (1)$$

This probability is compared to a uniform  $[0,1]$  random number ( $U(0,1)$ ) for particle pairs. An  $A$  particle is evaluated against  $B$  particles until either reaction occurs (if  $P(\text{forward}) > U(0,1)$ ) or pairs are exhausted. Using the tent function instead of the Gaussian for  $v(s)$  limits the number of possible pairs, greatly speeding calculations.

[12] The probability (1) contains an intrinsic space/time relationship that can be used to define the scale at which sufficient mixing occurs: A rate coefficient  $K$  is specified along with the volume associated with that rate  $\Delta V$ . The product  $K\Delta V \equiv K_f$  has units of  $L^d T^{-1} M^{-1}$  and is therefore equivalent to the classical bimolecular rate coefficient (compare to  $K_f$  in the next section). The volume is theoretically defined as a differential separation distance, and



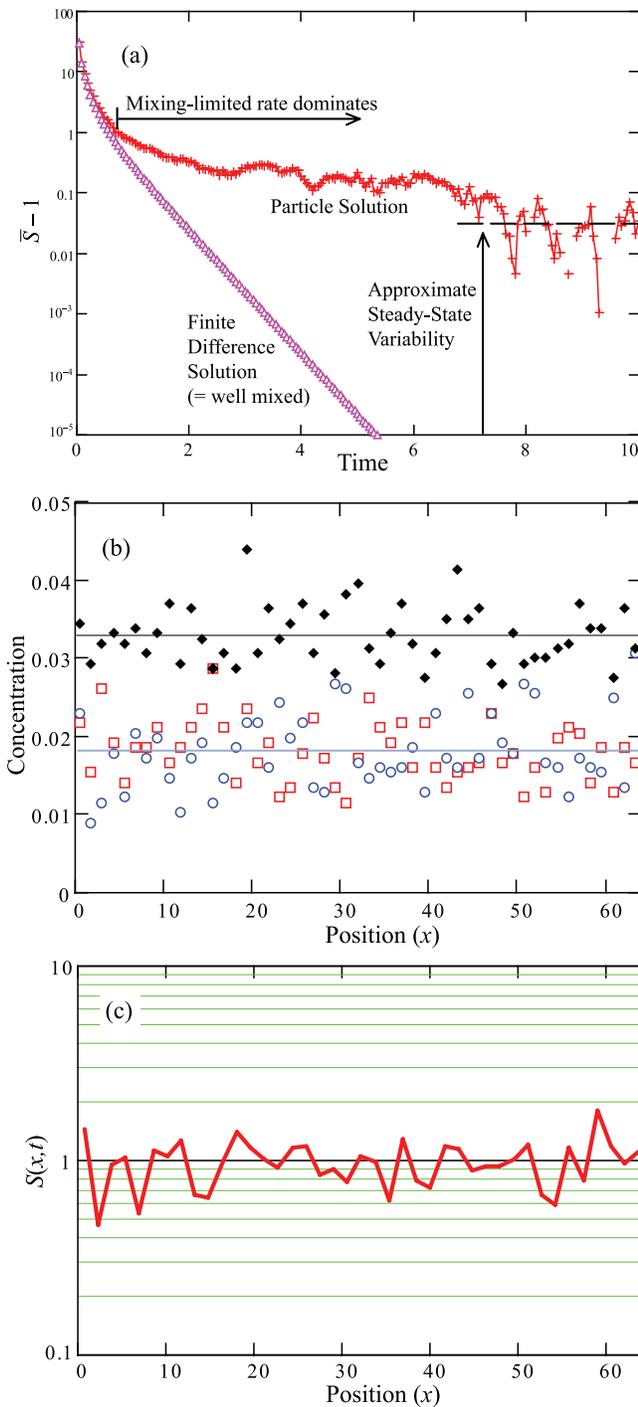
**Figure 2.** (a) Concentration change simulated by particle models (symbols) and analytic solution to continuum, rate-limited equations (solid curve). Changes of a single numerical parameter are denoted on the plot. Deviations from the rate-limited solution are due to diffusion-limited reaction. (inset) Spatial concentration segregation of  $[A]$  and  $[B]$  in 4000 particle,  $D = 0.01$  simulation at  $t = 1000$ . The asymptotic  $-1/4$  slope and reactant segregation are predicted by *Toussaint and Wilczek* [1983] and *Kang and Redner* [1985]. (b) Dimensionless concentration versus dimensionless time curves, labeled by various values of a characteristic “diffusion time”  $\Omega^2/(N_0^2 D)$ .

represents the volume of a particle. In practice, this represents the volume of water in which the rate coefficient  $K$  is applicable. At the pore scale, for example, *Jose and Cirkpa* [2004] show that mixing occurs very rapidly. At this scale the well-mixed thermodynamic rate coefficient is used for  $K_f$ . One may also choose to measure reaction rates directly in a 1-D column experiment. This rate would associate  $\Delta V$  with the cross-sectional area of the column times the porosity. In any well-mixed system,  $K_f$  will be equivalent to the classical thermodynamic rate coefficient measured in a beaker. Any segregation of the reactants on a large enough scale so that the diffusion (mixing) times are greater than the inverse of the reaction rates will lead to potentially lower observed reaction rates [*Toussaint and Wilczek*, 1983; *Kang and Redner*, 1985]. A recent accessible discussion of rate- versus diffusion-limited reaction regimes was given by *Dawkins and ben-Avraham* [2001].

[13] On the face of expression (1), it appears that choosing to double the number of particles (e.g., for better spatial resolution) will not change the reaction rate; furthermore, a change in the time discretization is accounted for in the same manner as the backward reaction. Either doubling  $N_0$  or halving  $\Delta t$  doubles the potential number of encounters in any given  $t \gg \Delta t$ , so the probability of each encounter must be halved. This preserves the same rate of reaction. We will see that this does indeed hold when the reactions are rate limited. Care should be taken not to choose modeling parameters (such as  $\Delta t$ ) that allow a calculated probability greater than unity, since this violates the underlying approximation of the probability.

[14] For equal and uniform initial concentrations  $[A]_0 = [B]_0$  in the continuum model, the classical thermodynamic rate law  $d[A]/dt = -K_f[A][B]$  has a concentration solution  $[A](t)/[A]_0 = ([A]_0 K_f t + 1)^{-1}$  [e.g., *Kang and Redner*, 1985]. This decay is characteristic of rate-limited reaction: there are sufficient numbers of collisions between  $A$  and  $B$  that the probability of reaction is controlled by the thermodynamic probability held in  $K_f$ . A particle tracking and reaction simulation was run with uniform initial concentrations  $[A]_0 = [B]_0 = 1/200$  in a periodic domain of size  $\Omega = 64$ , with transport and reaction dictated by pure diffusion with a diffusion coefficient  $D = 0.01$  and rate coefficient  $K_f = 50$ . The domain-averaged simulated  $\overline{[A]}(t)$  evolution matches the analytic solution of the classical thermodynamic rate law (and the finite difference solution described in the next section) at early time (Figure 2a), then slows because of segregation of the remaining particles. The time at which the reactions change from rate- to diffusion-limited depends on the number of initial particles and the diffusion coefficient. A simulation with  $N_0 = 4000$  initial particles and a small diffusion coefficient (all else held the same) reveals the characteristic  $t^{-1/4}$  decay in 1-D (Figure 2a). All simulations tend toward this solution at late time, and all behave identically with any acceptable choice of  $\Delta t$ . *Toussaint and Wilczek* [1983] and *Kang and Redner* [1985] show analytically that this initial value problem for  $A + B \rightarrow 0$  (inert) will decay asymptotically by  $t^{-d/4}$ , and that the domain will self-organize into “islands” of segregated  $A$  and  $B$  species (Figure 2a inset). Fewer initial particles, or a lower diffusion coefficient, spawn unmixed regions more quickly.

[15] The data in Figure 2a suggest that the curves may overlap when plotted using dimensionless axes. A series of runs were performed that confirm similar behavior when the average initial distance between particles is compared to the diffusion coefficient (Figure 2b), resulting in a characteristic “diffusion time”  $\frac{\Omega^2}{N_0^2} \frac{1}{D}$ . A finite difference solution of the problem overlaps the analytic solution of the classic thermodynamic rate exactly, even as the discretization is made finer and finer. This identifies the classical rate law as identical to either  $D \rightarrow \infty$  or average distance between reacting particles  $\rightarrow 0$  in our formulation. It also predicts an even distribution of reactants (no islands). We think that a realistic model of reaction must be able to recreate both the rate-limited and diffusion-limited regimes shown by the particle model (Figure 2). This implies that the number of particles used to represent a reactive plume may directly affect the results. Indeed, the global particle density dictates



**Figure 3.** (a) Approach to equilibrium ( $\bar{S} = 1$ ) for the continuum model (2) versus the RWARS solution (parameters listed in text). After about  $t = 6$ , the RWARS solution always varies around  $\bar{S} = 1 \pm 0.05$ . The missing connecting line shows where  $\bar{S} < 1$ . (b) Local concentrations and (c) saturation within the globally equilibrated RWARS simulation shown in Figure 3a at  $t = 100$ . Solid diamonds represent  $[C]$ , and open squares and circles are  $[A]$  and  $[B]$ , respectively. Horizontal lines in Figure 3b are the finite difference solutions to the same initial value problem. To output concentration at the end of a simulation, 50 bins in the  $\Omega = [0, 64]$  periodic domain were used.

the magnitude of local fluctuations in particle density, hence concentration fluctuations. The global particle density should be chosen to reflect the actual variance of concentration observed in a field plume. This places a restriction on the number of particles that may be used to represent an actual plume: arbitrarily increasing the number of particles may impart more smoothness to a plume than is actually present.

[16] Note that our particle simulations progress without regard to local “concentration;” the concentration data are output at the end based on particle numbers for comparison to other methods. This reaction was combined with standard advection-dispersion routines and the backward reaction for the following analyses.

#### 4. Approach to Global Equilibrium and Local Disequilibrium

[17] The random walks and reactions (RWARS) simulations are compared to an Eulerian finite difference (FD) solution of the advection-dispersion-reaction equations:

$$\begin{aligned} \frac{\partial[A]}{\partial t} &= -v \frac{\partial[A]}{\partial x} + D \frac{\partial^2[A]}{\partial x^2} - K_f[A][B] + K_b[C] \\ \frac{\partial[B]}{\partial t} &= -v \frac{\partial[B]}{\partial x} + D \frac{\partial^2[B]}{\partial x^2} - K_f[A][B] + K_b[C] \\ \frac{\partial[C]}{\partial t} &= K_f[A][B] - K_b[C] \end{aligned} \quad (2)$$

For simplicity in all simulations, the domain is 1-D and periodic and initial concentrations are uniform in the domain.  $A$  and  $B$  are mobile with the same transport parameters;  $C$  is immobile. The FD solution was used to check that the idealized continuum reactions would evolve to within a few thousandths of a percent of equilibrium concentrations. Checking the RWARS simulations for rate-limited reactions, the solutions matched (2) closest when the backward reaction was split into two parts per time step, one before and one after the forward reaction, making an effective predictor-corrector.

[18] In a rate-limited scenario where the probability of reaction is dominated by the thermodynamics of reaction, rather than the ability to commingle, the approach to equilibrium is exponentially fast. This is shown by the FD solution (Figure 3a). When diffusive motion restricts the forward reaction rate, the approach to equilibrium is vastly slower, following a power law. In this case, however, the reactants are not organized into islands, since the backward reaction was chosen at a high enough rate to replenishes the reactants. In these simulations,  $\Omega = [0, 64]$ , the initial number of  $A$  and  $B$  particles is 4000,  $D = 0.001$ ,  $K_f = 50$ ,  $K_b = 5$ ,  $[A]_0 = [B]_0 = 0.05$ ,  $[C]_0 = 0.001$ .

[19] The spatial data (Figures 2 (inset) and 3b) suggest that significant variability may be found within any single transport-and-reaction realization because of the random motion and mixing-limited reaction rates. Furthermore, variability may exist in the global reaction from realization to realization. A number of simulations were run to examine the effects of numerical parameters on the equilibrium concentrations  $[A]$ ,  $[B]$ , and  $[C]$ . The law of mass action states that when the forward rate of reaction  $= K_f[A][B]$  and

backward rate of reaction  $= K_b[C]$  are equal, then  $\frac{[C]}{[A][B]} = \frac{K_f}{K_b}$ , where the constant  $K_f/K_b$  is the equilibrium constant. We can define a generalized degree of saturation ( $S$ ), which is a measure of disequilibrium and is the ratio of the two sides:

$$S = \frac{[A][B]K_f}{[C]K_b} \quad (3)$$

Here  $S = S(x, t)$  refers to a local measurement in a single system or realization, and  $\bar{S}$  refers to the global domain-average value. For  $S > 1$  an overabundance of reactants exists relative to equilibrium.

[20] Given enough time in a periodic 1-D domain,  $\bar{S}$  should reach an expected value of unity regardless of the local diffusion coefficient, magnitudes of the rate coefficients, or the various numerical constants such as time step size and number of particles. On the other hand, the choices of all of the parameters have potential effects on the variability of local saturations at late time. This will be reflected in the variance of  $S(x)$  in a single run and  $\bar{S}$  from run to run. A series of simulations were run with different  $D$ ,  $\Delta t$ ,  $N_0$ , and initial concentrations. The simulations were run long enough to ensure that  $\bar{S} \approx 1$  except for these random fluctuations. Because the saturation is bounded below by zero, we analyzed  $\ln(S)$  and found empirically that changes in  $D$ ,  $\Delta t$ , and initial  $N$  had no significant effect on the normalized value of saturation variance  $\frac{N_0 \Delta x}{\bar{S}} \text{VAR}(\ln S)$ . It is significant that increasing  $N_0$  while decreasing  $\Delta x$  maintains the same variance of  $\ln(S)$ : a point measurement in a plume of initial fixed mass (with ratio  $N_0/\Delta x$  constant) will have some irreducible deviation from equilibrium, and changing the support scale  $\Delta x$  alone changes the interpretation of equilibrium in addition to the speed of reaction [see also *Binning and Celia*, 2008]. The only “parameters” that were observed to significantly change the variance of  $\ln(S)$  were the initial concentrations. When the domain is started in global equilibrium, then particles behave similarly to independent wandering particles. However, the farther the initial conditions are from equilibrium, the more variance is found in the local saturations because of the sometimes drastic change in the number of particles at equilibrium. We expect that the same thing happens in real systems as reactants are exhausted in some locations.

## 5. Remarks and Conclusions

[21] The equilibrium coefficient  $K_f/K_b$  is directly related to the free energies of the products and reactants. Therefore, in principle, any particle interaction can be coded on the basis of the thermodynamics of the reactions. Any number of reactants is possible, although the numerical advantages or disadvantages are not known. The potential dimensionless numbers that represent the bounds of stable numerical solutions have not been investigated here.

[22] These results reinforce the conclusions of *Molz and Widdowson* [1988], *Kapoor et al.* [1997], and *Luo et al.* [2008], among many others, who show that the variability of macroscale concentrations and velocities should lead to variability of local saturation and/or reaction rates. This effect is built in to the random walk solution and may obviate the need to account for the variability by other

means. It does imply, however, that the number of particles used to simulate a plume is not a free modeling choice at the discretion of the user. The number of particles should reflect the measured variability of the plume concentrations. Using more particles will make the simulated plume smoother than the real plume, and potentially change the reaction rates.

[23] The most computationally difficult portion of the RWARS algorithm is searching for nearby  $B$  particles for every  $A$  particle. At worst, a naive search would take  $N^2$  operations, but effective ordering of the particle location arrays means that only nearby “candidates” are searched, at best closer to  $N$  operations. Also, when probabilities of reaction are high, the inner “ $B$ ” loop is terminated more quickly. For equilibrium reactions, it pays to set  $K_f$  and  $K_b$  high while maintaining a constant ratio. This logic implies that forward reactions like  $A + B + D \rightarrow E$  should be handled as a sequence of  $A + B \rightarrow C$  and  $C + D \rightarrow E$ . A future paper will investigate higher-order reactions.

[24] On the basis of the relatively simple numerical experiments described herein, the following conclusions may be reached: (1) It is possible to simulate chemical reactions via discrete particles not on a lattice using the probabilities of encounter and combination. (2) The reaction rates reflect the true physics of particle encounters. (3) The reactions can be added easily to particle-tracking codes. (4) Only in the well-mixed scenario do these probabilistic interactions result in chemical reactions that duplicate, in the average sense, continuum descriptions of chemical reaction. (5) Specifically, for the forward reaction  $A + B \rightarrow 0$  (inert), the reaction rate strongly depends on the density of particles. A rate-limited (well-mixed) regime decays asymptotically with  $t^{-1}$ ; the diffusion-limited regime follows  $t^{-d/4}$ . Because of self-organized islands of reactants, the reaction rate may be expected to transition from the former to the latter. (6) The rate of approach to equilibrium is also much slower (power law versus exponential) for the diffusion-limited regime. (7) The apparent chemical saturations remain inherently variable when normalized by particle number and discretization, indicating that chemical reactions in real aquifer systems are not a homogeneous process at any scale. Reactants and products can remain in disequilibrium in arbitrarily small volumes. In other words, in a globally equilibrated system, any sample may be far from equilibrium. (8) Bimolecular reaction rates governed by values of local diffusion will be less than or equal to those measured in well-mixed reactors. The reduced rates can be simulated directly with the random particle model.

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