Communication: A full solution of the annihilation reaction $A + B \rightarrow \emptyset$ based on time-subordination

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The connection between the governing equations of chemical reaction and the underlying stochastic processes of particle collision and transformation have been developed previously along two end-member conditions: perfectly mixed and maximally diffusion-limited. The complete governing equation recognizes that in the perfectly mixed case, the particle (i.e., molecular or macro-particle) number state evolution is Markovian, but that spatial self-organization of reactants decreases the probability of reactant pairs finding themselves co-located. This decreased probability manifests itself as a subordination of the clock time: as reactant concentrations become spatially variable (unmixed), the time required for reactants to find each other increases and the random operational time that particles spend in the active reaction process is less than the clock time. For example, in the system $A + B \rightarrow \emptyset$, a simple approximate calculation for the return time of a Brownian motion to a moving boundary allows a calculation of the operational time density, and the total solution is a subordination integral of the perfectly-mixed solution with a modified inverse Gaussian subordinator. The system transitions from the well-mixed solution to the asymptotic diffusion-limited solution that decays as $t^{-d/4}$ in d-dimensions. © *2013 American Institute of Physics*.
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I. INTRODUCTION

Accurate predictions of combined transport and reaction are required in settings as variable as particle physics,[1,2] biology,[3] economics,[4–6] social sciences,[7] technology transfer,[8] warfare studies,[9] and ecology.[10] The predictions are often confounded by the coupled effects of transport and reaction, which may lead to incomplete mixing of the reactants. The primary consequence of incomplete mixing is that the rate of reaction can be slowed many orders-of-magnitude relative to the rate that is measured in a well-mixed (laboratory) setting. Incomplete mixing can occur for a variety of reasons including the natural emergence of stochastic fluctuations in concentration,[1,11,12] irregular boundary conditions,[13] and heterogeneity in flow systems[14–17] such as those imposed by porous media. When segregation of reactants occurs, the reaction is limited by how quickly they can be brought together, which is dictated by the underlying transport process.[11,18–24] The experimental observations of incomplete mixing from micron- to kilometer-scales highlight the need to develop improved models capable of describing its effects.

II. CHEMICAL REACTIONS AND STOCHASTIC PROCESSES

For nearly a century,[1,2,25–30] the exact link between stochastic particle collision/transformation models and upscaled partial differential equations (PDEs) of chemical reaction has been sought. In every case, an assumption is made about the degree of mixing in the system at hand. When

considering chemical reactions from a stochastic perspective, there are two probabilities that, in combination, describe the propensity for reactions to occur. The first is the probability that two reactant particles (molecules or larger particles of mass) become co-located. The second is the conditional probability that two co-located particles favorably transform in a reaction. The co-location is dictated by random motion, which can be diffusive or anomalous. The end-members of "well-mixed" versus "diffusion-limited" reaction are found when, on average, one of these probabilities is much smaller than the other. We briefly describe these two end members and then show the process that contains both end members and all conditions in between.

Perfect Mixing: The Markov Reaction Process.—If the probability of particles of different species coming into contact is high compared to the probability of reaction, the system will behave as well-mixed. Define the random state of the system by $N(t)$, where the components N_i are the integer number of molecules or macro-particles of component i. Under the condition of perfect mixing, $N(t)$ is a Markov process, because the reactions depend only on the current numbers of molecules. Thus the probability of the state follows:[28]

$$\frac{dP(N, t | N_0)}{dt} = \sum_{j=1}^{M} a_j(N - n_j)P(N - n_j, t | N_0) - a_j(N)P(N, t | N_0),$$

(1)

where a_j are the propensity functions for each reaction channel j, and n_j are vectors of actual molecule number changes for the same reactions. The functions a_j depend on the

current state and account for the probability of creating (or destroying) molecules of each species through all possible reaction pathways. One may write (1) as a coupled set of i equations, one for each N_i. Take the ith equation, multiply each term by N_i, sum over the possible number of molecules and divide by the volume enclosing the molecules to get the expected number

$$\frac{d[N_i]}{dt} = \sum_{j=1}^{M} n_{i,j} a_j([\boldsymbol{N}]) \quad i = 1, \ldots, N, \qquad (2)$$

where now $[N_i]$ denotes the real-valued expected concentration of the ith species. For simplicity let us focus on a simple system,[1,11,20,31] the bimolecular precipitation (or annihilation) reaction $A + B \rightarrow \emptyset$. The expected concentrations in (2) follow

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -a_1([A], [B]), \qquad (3)$$

because each reaction reduces the number of molecules by one: $n_{A,1} = n_{B,1} = -1$. The propensity function a_1 depends on the number of molecules of A and B, which have been converted to concentrations by division by the volume. In the well-mixed case, the probability of particle encounter is given exactly by the number of possible combinations of particles in a volume, regardless of their locations. For $A + B \rightarrow \emptyset$ within a fixed volume, there are $N_A \times N_B$ potential reaction pairs, and $a_1 = K_f[N_A][N_B]$, where K_f is the rate associated with the thermodynamic probability of reaction given a collision. This is the link between the Markov evolution equation (3) and the law of mass action PDE,[28]

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -K_f[A][B]. \qquad (4)$$

This assumes that any A particle is equally available to all B particles: there is no discrimination based on distance. It would also appear that the deterministic rate equation (4) is derived from the underlying stochastic process and is exact as written. However, even under the conditions of perfect mixing, (3) and (4) are equivalent only when the expected number and concentration are equivalent, which implies ergodicity.

III. A PHYSICS-BASED CALCULATION

Rather than assume that all molecules are equally accessible to all others, one may explicitly consider the random motion of particles. In general, this is an intractable analytic problem considering the joint density of interaction for all molecules,[27] but it is relatively straightforward to simulate.[12,32] For symmetric motions such as unbiased diffusion, the probability density of collision is the convolution of the individual motion densities over some time period: $v(s) = \int f_A(x) f_B(s - x) dx$, where $f_A(x)$ and $f_B(x)$ denote the densities of random motion of an A and B particle pair. Nearby particles are more likely to collide and react, which causes a self-organized segregation of reactants and a reduced overall reaction rate. Any randomness in the positions of particles can be expected to engender "islands" in which the interiors are devoid of one of the reactants.[1,11,20,21] It is difficult, in a

mixing-limited environment, to get one of the reactants into close contact with another.

Due to independence, the probability of forward reaction is the product of the probability of co-location and the thermodynamic probability of reaction given by the well-mixed reaction rate K times the infinitesimal time interval dt, and the total mass represented by a single particle. Consider a 1-d domain of size Ω that initially contains N_0 particles representing concentrations $[A]_0 = [B]_0$. Then the probability[32] that an A and B particle pair with initial separation s react to form a C particle is $P(\text{forward}) = K dt \frac{\Omega[A]_0}{N_0} v(s) ds$. The rate coefficient K is specified along with the volume associated with that rate ds. The product $K ds \equiv K_f$ has units of inverse concentration in d-dimensions $\times$ time $[L^d T^{-1} M^{-1}]$ and is equivalent to the classical bimolecular rate coefficient (compare to K_f in (4)). The differential volume represents the volume in which the rate coefficient K is applicable, i.e., the volume under which perfect mixing may be assumed. In any well-mixed system, K_f will be equivalent to the classical thermodynamic rate coefficient measured in a stirred beaker. The final probability, when cast using the same rate coefficient as the continuum equation (4) and discretized in a way that may be simulated reads

$$P(\text{forward}) = K_f \Delta t \Omega[A]_0 v(s)/N_0. \qquad (5)$$

In a transport/reaction algorithm, this probability is compared to a uniform [0,1] random number to assess if a reaction occurs. The Δt is chosen so that the maximum probability possible (when $s = 0$) is less than 0.1. Each A particle is evaluated against B particles until either reaction occurs or pairs are exhausted. Alternating with the reaction calculations, each particle is moved by random walks to simulate molecular diffusion using standard methods. We may compare these simulations to the solution for a well-mixed system following (4). For equal and uniform initial concentrations $[A]_0 = [B]_0$ the solution $[A](t) = [A]_0([A]_0 K_f t + 1)^{-1}$ decays proportional to t^{-1} at late time. In all Lagrangian simulations using (5) and purely diffusive particle transport, the concentration $[A](t)$ is always greater than, or equal to, the well-mixed concentration (Fig. 1(a)) and follows $t^{-d/4}$ in d-dimensions at late time. This decay rate was derived asymptotically[1,11] using scaling arguments of the growth rate of "islands" of the reactants that follows $\sim t^{1/2}$. The self-organized islands form due to small perturbations in the system—areas with slightly more of one reactant will deplete the lesser. The islands grow diffusively[33] and swallow nearby smaller islands. The probabilities of collision become smaller than that of the thermodynamic reaction (and continue to become smaller as islands grow and coalesce), and a different functional regime—with a governing equation necessarily different from (4)—applies.

IV. TIME-SUBORDINATION

We may exploit the fact that chemical reactions are Markovian. The advance of the state depends only on the current state. However, when the particles are not well-mixed, the time *devoted to the reaction process* is not deterministic for each particle. Every particle within an island of similar reactant executes a random walk and reaches a reaction spot at the interface with the other reactant in a random amount of time T.
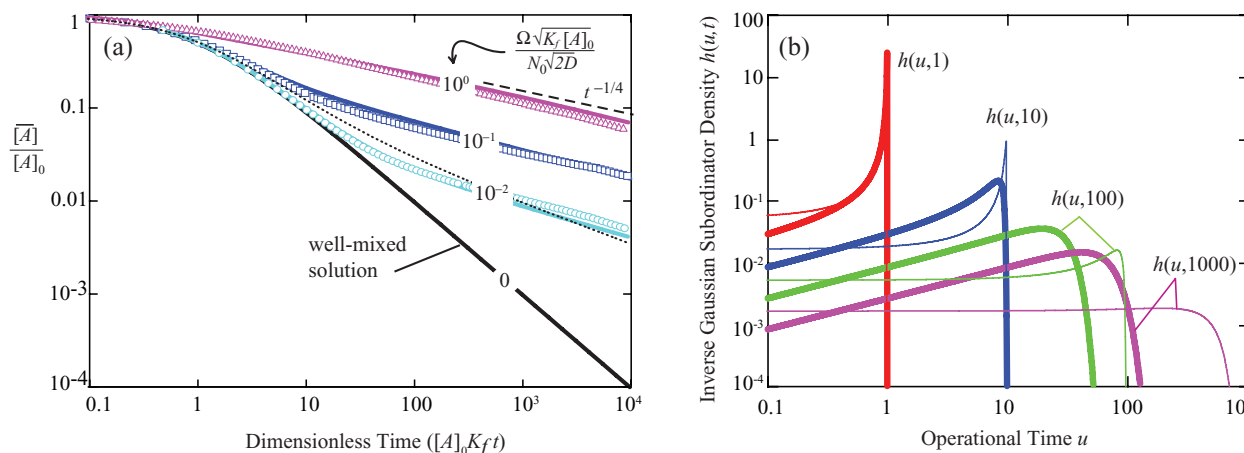
FIG. 1. (a) Comparison of simulated (symbols) versus analytic solutions via subordination (curves). The solid curves, largely obscured by the symbols, use the subordinator (7) for diffusion toward moving boundaries with $2H = 1.5$. The dotted line assumes fixed island size of $5\Omega/N_0$ and $2H = 1$. The particle simulations are invariant with dimensionless constant $\frac{\Omega\sqrt{K_f[A]_0}}{N_0\sqrt{2D}}$. (b) Example subordinator densities $h(u, t)$ for stationary boundaries (thin lines) versus moving boundaries (thick lines) for $\beta = 0.1$. Each density is shown at 4 different clock times t. While similar at early time (red curves), the moving boundaries severely reduce operational time at later time (purple curves) due to increasing distance to island boundaries.

The times at the boundary, while not engaged in the sojourn, are the operational times $U(t)$. At any clock time t, every particle has some random time $0 \leq U \leq t$ that it might be in a favorable location for reaction. Under certain restrictions, *Feller*[34] showed that the deterministic time in a Markov process should be replaced by a random time, i.e., $N(t) \rightarrow N[U(t)]$. This subordination process, which randomizes the clock time, has been extensively used in trapping systems where motion processes are interrupted by transfer into immobile states.[35] If the expectation of the molecular number state in a well-mixed system is given by $E[N(t)] = z(t)$, then the subordinated process $z[U(t)]$ can be solved by conditioning, if the density $h(u, t)$ of $U(t)$ is known. The entire solution, which we now denote $q(t)$, is given by the subordination integral

$$q(t) = \int_0^t z(u)h(u, t)du. \quad (6)$$

The key to solving this problem is calculating the density $h(u, t)$, upon which subordinating the known well-mixed solution $z(t)$ is trivial.

Here we compare the analytic solutions of (6) to a one-dimensional Lagrangian simulation of diffusion and reaction (described above) of the system $A + B \rightarrow \emptyset$ with $\overline{[A]}_0 = \overline{[B]}_0$.[1, 11] An equal number N_0 of A and B particles were positioned uniformly randomly in a 1D periodic domain. Every case was run a sufficient number of times to get an ensemble average of the spatially-averaged concentration. In all cases, the system follows a well-mixed solution until the probability of co-location is globally smaller than the thermodynamic probability (Fig. 1(a)), at which time the solution transitions to the well-known $t^{-1/4}$ scaling.

To calculate the density of $U(t)$ for (6), it is often easier to calculate the random hitting time T required to reach an active site. The fact that $T(u)$ and $U(t)$ are inverse processes[35] gives $h(u, t)$ via $P[U(t) \leq u] = P[T(u) \geq t]$. For a series of examples that illustrate the role of the subordinator density

$h(u, t)$ in the 1D diffusion-reaction system, first assume the unlikely and very simple scenario that every particle spends exactly 9/10 of its clock time inside an island, away from an active reaction site. Then the operational time actively in reaction has density $h(u, t) = \delta(u - t/10)$, and the subordination integral (6) gives a reaction solution $[A](t) = q(t) = z(t/10) = [A]_0([A]_0K_ft/10 + 1)^{-1}$. This is identical to using an effective rate coefficient one-tenth of the well-mixed rate, which would shift the entire well-mixed solution an order of magnitude to the right (Fig. 1(a)). This use of an effective reaction rate is a common approach that misses the essential character of the different decay rate induced by poor mixing.

Now assume a more realistic picture in which the particles diffuse by $\sqrt{2D}W_t$, where W_t is a standard Brownian motion in an infinite half-space, to a fixed boundary distance l roughly representing the nearest side of an island. The particle executes a series of walks to the boundary. The standard inverse Gaussian density $L(t) = \frac{1}{\sqrt{4\pi t^3}}\exp(-1/4t)$ and the diffusion/distance constant $\beta = l/\sqrt{2D}$ allows a calculation[36] of the hitting time density for one walk $\beta^{-2}L(t/\beta^2)$. Because the random time that a particle survives at the boundary is exponential with rate $K_f[A]_0$ (for the Markov reaction process[37]), the total accumulated time for a series of walks inside the islands separated by times at the interfaces is compound Poisson, so that $T(u)$ has a Laplace transform density (see Ref. 35) $g(t) \mapsto g(s) = \exp(-us - \beta(K_f[A]_0u)^{2H}s^{1/2})$. For fixed island sizes, the coefficient $2H = 1$, which we soon generalize. Grouping the constants into $\beta = l(K_f[A]_0)^{2H}/\sqrt{2D}$, the operational time can be exactly calculated (using the method in Ref. 35) as

$$h(u, t) = \left(1 - 4H + \frac{4Ht}{u}\right)\frac{1}{(\beta u^{2H})^2}L\left(\frac{(t-u)}{(\beta u^{2H})^2}\right). \quad (7)$$

This density converges to the delta function $h(u, t) = \delta(u - t)$ for $\beta \rightarrow 0$, i.e., perfect mixing (Fig. 1(b)). The assumption of fixed island size with $2H = 1$ gives solutions that are

better than the Dirac delta function in the previous example, but diverge from the simulations at later times. One example, using a fixed island size of five times the initial particle spacing, underpredicts reaction rates at early time and over-predicts at late time (dotted curve in Fig. 1(a)).

To incorporate the fact that the islands grow in time, consider that a particle that has not met the boundary by time t is unaware of the boundary moving outward ahead of it. At the time a particle has reached the boundary, we may consider the time-dependent boundary position explicitly via $\beta = \beta_0 u^{1/2}$, where β_0 is given by the reaction and diffusion constants and an initial island size l_0. Now the scale of the hitting time of the random walk inside the island grows super-linearly, which is identical to keeping β_0 constant—representing initial chemical variability—and adding 1/2 to the exponent on u for the island growth, i.e., replacing $2H = 1$ with $2H = 1.5$ in (7). Now $\beta = l_0(K_f[A]_0)^{2H}/\sqrt{2D}$ codes an initial distance of a particle to an island edge along with the moving boundaries. We may compare analytic solutions with particle simulations that start with uniformly random particle positions, so that the initial island size can be approximated by the inter-particle spacing (Ω/N_0). By the reflection principle we need only consider a half island, and the average starting position is half of this distance, so $l_0 \approx \Omega/(4N_0)$ and $\beta = \frac{\Omega(K_f[A]_0)^{2H}}{4N_0\sqrt{2D}}$ is given by known quantities: initial chemical variability, reaction, and diffusion parameters. By including island growth, the subordinator has significantly reduced operational time, all other things held equal (Fig. 1(b)). This derivation of the subordinator gives very accurate solutions of chemical reaction—from initially well-mixed to late-time diffusion-limited (thick lines, Fig. 1(a))—considering the other neglected factors including the influence of the other island boundary, the distribution of island sizes, and the mixture of particle starting distances from the boundaries.[13]

The subordination is derived from the self-organization of the reactants and the decreased mixing rate as they disappear. The simplicity of this example system allows a reasonable *a priori* calculation of the subordinator. The return of A and B from a dissolution process in $A + B \rightleftharpoons C$ would re-homogenize the reactants to a degree dictated by the ratio of forward and backward rate coefficients, and the operational time may tend toward some constant fraction of the clock time. Conceivably, the form of the subordinator for more complicated reaction chains and/or geometries could be discerned through an inversion of (6) using prior knowledge of $z(t)$ by the classical differential equation of well-mixed reaction, and an experiment that measures $q(t)$. The subordination equation would then allow a quick calculation of the subordinator for upscaled systems that suffer from imperfect mixing.

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