Effect of spatial concentration fluctuations on effective kinetics in diffusion-reaction systems

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[1] The effect of spatial concentration fluctuations on the reaction of two solutes, $A + B \rightharpoonup C$, is considered. In the absence of fluctuations, the concentration of solutes decays as $A_{det} = B_{det} \sim t^{-1}$. Contrary to this, experimental and numerical studies suggest that concentrations decay significantly slower. Existing theory suggests a $t^{-d/4}$ scaling in the asymptotic regime (d is the dimensionality of the problem). Here we study the effect of fluctuations using the classical diffusion-reaction equation with random initial conditions. Initial concentrations of the reactants are treated as correlated random fields. We use the method of moment equations to solve the resulting stochastic diffusion-reaction equation and obtain a solution for the average concentrations that deviates from $\sim t^{-1}$ to $\sim t^{-d/4}$ behavior at characteristic transition time t^*. We also derive analytical expressions for t^* as a function of Damköhler number and the coefficient of variation of the initial concentration.

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1. Introduction

[2] Incomplete mixing of solutes and spatial fluctuations in concentration fields have been identified as a major cause of failure of deterministic effective models, such as deterministic diffusion-reaction equations, to accurately simulating mixing-controlled reactions. Spatial fluctuations in the concentration of the reactive species can be caused by the thermal fluctuations of molecules [*Ovchinnikov and Zeldovich*, 1978; *Toussaint and Wilczek*, 1983], turbulent flows [*Hill*, 1976] or highly nonuniform laminar flows (e.g., flow in porous media) [*Tartakovsky et al.*, 2008, 2009; *Raje and Kapoor*, 2000; *Luo et al.*, 2008; *Bolster et al.*, 2011; *Le Borgne et al.*, 2011].

[3] In the case of porous media, the fluctuations cause the classical advection-dispersion-reaction (ADR) equations with constant transport coefficients to overestimate the extent of the mixing controlled reactions [*Battiato and Tartakovsky*, 2011; *Battiato et al.*, 2009; *Tartakovsky et al.*, 2009; *Le Borgne et al.*, 2010]. Similar problems occur in a purely diffusive systems where thermal fluctuations of molecules lead to incomplete mixing [*Ovchinnikov and Zeldovich*, 1978; *Toussaint and Wilczek*, 1983]. In order to tackle the discrepancies with traditional homogenous (ADE) equations, a variety of novel models have emerged. These include stochastic Langevin approaches [*Tartakovsky et al.*, 2008; *Tartakovsky*, 2010], perturbation

models [*Luo et al.*, 2008], and adaptations of a variety of popular nonlocal models such as continuous time random walks [*Edery et al.*, 2009, 2010], fractional ADEs [*Bolster et al.*, 2010], multirate mass transfer [*Donado et al.*, 2009; *Willmann et al.*, 2010], memory effect models [*Dentz et al.*, 2011] and models with time-dependent rate coefficients [*Sanchez-Vila et al.*, 2010]. However, many of these approaches involve effective parameters, which cannot be computed a priori from the physical properties of the system and have to be found through model calibration with experimental data.

[4] In this work, we use the moment equation approach [e.g., *D. M. Tartakovsky et al.*, 2002, 2003; *A. M. Tartakovsky et al.*, 2003, 2004a, 2004b] to quantify the effect of incomplete mixing in diffusion-reaction systems. We focus on a nonlinear reaction involving diffusion of two species, A and B, that react with each other kinetically as $A + B \rightarrow C$. We assume that A and B have the same initial concentration and are macroscopically well mixed before the onset of the reaction. In the absence of spatial fluctuations (i.e., a fully mixed system at all times), a well known analytical solution exists and the average concentrations decay as $A_{det} = B_{det} \sim t^{-1}$.

[5] Recent numerical studies by *Benson and Meerschaert* [2008] and *de Anna et al.* [2011] suggest that while this analytical solution may be valid at early times, at late times a different slower scaling emerges. These observations are in line with previous observations from the physics community [*Hill*, 1976; *Toussaint and Wilczek*, 1983; *Kang and Redner*, 1985] and a variety of theoretical models [*Ovchinnikov and Zeldovich*, 1978; *Toussaint and Wilczek*, 1983; *Kang and Redner*, 1985]. The latter are based on late time asymptotic arguments, and suggest a late asymptotic decay of the concentrations that is proportional to $t^{-d/4}$, where d is the spatial dimensionality of the problem. These models established that, for sufficiently fast

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reactions, initial fluctuations in the concentrations cause segregation of the reactants into separate islands of A and B, (i.e., parts of the domain occupied dominantly by species A or B). In this situation, reactions are limited by how quickly diffusion of particles can cause mixing of A and B across the boundaries of the islands. Thus, the mixing of species is limited and the temporal decay of the concentrations slows down. This anomalous scaling of diffusion-limited reactions, related to segregation of reactants into islands, was experimentally observed by *Monson and Kopelman* [2004].

[6] These past theoretical works have focused primarily on the establishment of the late asymptotic behavior of the concentrations. Also, in the previous studies the initial fluctuations of each species were assumed to be uncorrelated (fluctuations with zero correlation length). The standard deviation of the fluctuations was implicitly assumed to be equal to the square root of the initial number of the reactive particles. In a number of important applications (e.g., turbulent mixing and transport in porous media), the initial fluctuations in concentrations may have nonzero correlation lengths. For example, if the reactive solutions are rapidly brought in contact by nonuniform advection (and allowed to diffuse and react), then the initial correlation length of the concentration fluctuations will depend on the statistics of the velocity field, and can in principle be as large as the size of the domain. The standard deviation of the concentrations in these applications represents the degree of mixing, and can also be arbitrarily large.

[7] To study the effect of fluctuations, we employ a diffusion-reaction equation with random initial conditions. In the past, diffusion-reaction type equations have been used to study the effect of random concentration fluctuations on scales ranging from the molecular scale [*Ovchinnikov and Zeldovich*, 1978] to the field scale [*Sanchez-Vila et al.*, 2008], though advection is usually also considered in the latter case. Here the initial concentrations of the reactants are treated as correlated random fields with spatially constant and equal statistical means and variances. The random initial conditions render the diffusion-reaction equation stochastic. We use the moment equation approach to derive deterministic equations for the mean and variance of the concentrations. The solution for the mean concentrations shows that the average concentration deviates from $\sim t^{-1}$ to $\sim t^{-d/4}$ behavior at a characteristic transition time t^*, which depends on the Damköhler number, Da. We obtain analytical expressions for t^* as a function of Da. The solutions are used to study the effect of initial average concentration, variance, correlation length, cross correlation, and the size of the domain on the $A + B \longrightarrow C$ reaction.

2. Problem Formulation

[8] Our goal is to study the effect of random fluctuations in concentration fields on chemical reactions. Specifically, we study an irreversible reaction between two species, A and B, that is described by a diffusion-reaction equation:

$$\frac{\partial I(\mathbf{x},t)}{\partial t} = D\Delta I(\mathbf{x},t) - kA(\mathbf{x},t)B(\mathbf{x},t), \qquad \mathbf{x} \in \Omega \qquad I = A, B,$$

$$(1)$$

where A and B are the concentrations of species A and B, D is the diffusion coefficient, k is the rate coefficient of the

irreversible reaction, and $\Delta = \nabla^2$ is the Laplace operator. We consider two special cases: (1) diffusion in an infinite d-dimensional domain Ω ($d = 1, 2, 3$) and (2) diffusion in a finite one-dimensional domain $\Omega = (0, L)$ subject to periodic boundary conditions.

[9] We treat the concentrations as random variables:

$$A(\mathbf{x},t) = \overline{A}(\mathbf{x},t) + A'(\mathbf{x},t) \qquad B(\mathbf{x},t) = \overline{B}(x,t) + B'(\mathbf{x},t), \quad (2)$$

where the overbar designates an ensemble average and the prime denotes zero-mean fluctuations about the average. We assume equal initial ensemble averaged concentrations of A and B:

$$\overline{A}(\mathbf{x},0) = \overline{B}(\mathbf{x},0) = C_0. \qquad (3)$$

Unlike previous work [*Ovchinnikov and Zeldovich*, 1978; *Toussaint and Wilczek*, 1983], we assume the initial fluctuations, $A'(\mathbf{x},0)$ and $B'(\mathbf{x},0)$, to be spatially correlated fields. This allows us to study the effect of spatial correlation of the concentrations on the chemical reaction. In the following we study this system for several initial autocovariance functions. Specifically, we consider initial exponential and delta autocovariance functions. The exponential autocovariance function has a form:

$$\overline{A'(\mathbf{x},0)A'(\mathbf{y},0)} = \overline{B'(\mathbf{x},0)B'(\mathbf{y},0)} = \sigma^2 e^{-\frac{|\mathbf{x}-\mathbf{y}|}{l}}, \qquad (4)$$

where σ^2 is the initial variance of the concentrations (σ is the initial standard deviation of fluctuations) and l is the initial correlation length. Assuming that the initial fluctuations of A and B are caused by the same physical processes, we prescribe the same variances and correlation for both reactants.

[10] When the correlation length is small relative to the size of the domain, one can replace the exponential autocovariance function with the delta autocovariance function:

$$\overline{A'(\mathbf{x},0)A'(\mathbf{y},0)} = \overline{B'(\mathbf{x},0)B'(\mathbf{y},0)} = \sigma^2 l^d \delta(\mathbf{x} - \mathbf{y}). \qquad (5)$$

[11] In a well-mixed purely diffusive system (in the absence of reactions), the fluctuations in the concentrations are caused by thermal fluctuations of particles. In this case, the fluctuations have a correlation length, l, of the order of the particle diameter, and under most circumstances the delta autocovariance function will provide an accurate representation of the spatial correlation of the fluctuations. In other nonreactive, but hydrologically related stochastic model studies the delta correlation has been shown to give asymptotically similar results as short-range correlation functions such as exponential and Gaussian [e.g., *Neuweiler et al.*, 2003]. We show in section 4.2.2 that the delta function approximation can be used only to predict the mean and variance of the concentrations for times larger than $t_D/8\pi$, where t_D is the diffusion time:

$$t_D = \frac{l^2}{D}. \qquad (6)$$

In the absence of reaction, t_D is the time it takes for a region of size l to become well mixed by diffusion. For

smaller times, the delta function approximation leads to unphysical behavior of the ensemble average and/or variance of the concentrations.

[12] Initial large-scale concentration fluctuations can be caused by poor mechanical mixing of two solutes due to fluctuations in advective velocities that brought two solutes in contact. In this case, the correlation length depends on the degree of mixing and can be of the same order (or smaller) as the domain size. Under such conditions, we chose the exponential autocovariance function (4) to describe initial correlation of the fluctuations of A and B, but one could also consider other correlation functions.

[13] To complete the problem formulation, we specify a cross-covariance function $\overline{A'(\mathbf{x},0)B'(\mathbf{y},0)}$ at time $t = 0$. We consider two types of cross correlations: anticorrelation and no cross correlation. The initial anticorrelation assumes that in a volume with a large concentration of one reactant (relative to the average value of the concentration) the concentration of another reactant is small. The anticorrelation is described by a cross-covariance function:

$$\overline{A'(\mathbf{x},0)B'(\mathbf{y},0)} = -\sigma^2 e^{-\frac{|\mathbf{x}-\mathbf{y}|}{l}} \qquad (7)$$

if both concentrations, A and B, have the initial exponential correlation and

$$\overline{A'(\mathbf{x},0)B'(\mathbf{y},0)} = -\sigma^2 l^d \delta(\mathbf{x}-\mathbf{y}) \qquad (8)$$

if A and B are initially δ correlated.

[14] For completeness, we also consider a case where the initial cross covariance is zero,

$$\overline{A'(\mathbf{x},0)B'(\mathbf{y},0)} = 0. \qquad (9)$$

[15] *Kang and Redner* [1985] previously justified the emerging scaling law $t^{-\frac{d}{4}}$ with the formation of islands of segregated solutes. The initial anticorrelation is a necessary but not a sufficient condition for the existence of the islands and the initial condition (7) or (8) does not imply presence of islands at $t = 0$. Furthermore, the following analysis shows that after the onset of the reaction, the scaling changes from t^{-1} to $t^{-\frac{d}{4}}$ regardless of the initial cross correlation, but the transition time from one scaling law to another depends on variance, correlation length and the form of cross-covariance function.

[16] The random initial concentrations render the diffusion-reaction equation (1) stochastic. The full solution of this equation is the probability density functions for distribution of A and B. In this work, we are mainly interested in the average behavior of the concentrations and we focus on the leading moments of the distributions namely the mean (ensemble averaged) concentrations and the concentration variances (a measure of uncertainty). The differential equations for the leading moments are obtained using the method of moment equations [*D. M. Tartakovsky et al.*, 2003]. The details of the derivation of the moment equations are given in Appendix A.

[17] The average concentrations $\overline{A}$ and $\overline{B}$ satisfy an ordinary differential equation:

$$\frac{\partial \overline{I}}{\partial t} = -k\overline{A}\,\overline{B} - k\overline{A'B'}, \qquad I = A, B, \qquad (10)$$

where $\overline{A'(\mathbf{x},t)B'(\mathbf{x},t)} = \overline{B'(\mathbf{x},t)A'(\mathbf{x},t)}$. In equation (10), $\overline{A}$ and $\overline{B}$ satisfy the same initial condition (equation (3)), and hence,

$$\overline{A}(t) = \overline{B}(t). \qquad (11)$$

[18] Now let us define $f(\mathbf{x},\mathbf{y},t) = \overline{A'(\mathbf{x},t)B'(\mathbf{y},t)} - \overline{A'(\mathbf{x},t)A'(\mathbf{y},t)}$ and $g(\mathbf{x},\mathbf{y},t) = \overline{A'(\mathbf{x},t)B'(\mathbf{y},t)} + \overline{A'(\mathbf{x},t)A'(\mathbf{y},t)}$. The governing equations for these functions are (Appendix A)

$$\frac{\partial f(\mathbf{x},\mathbf{y},t)}{\partial t} = 2D\Delta f(\mathbf{x},\mathbf{y},t) \qquad (12)$$

$$\frac{\partial g(\mathbf{x},\mathbf{y},t)}{\partial t} = 2D\Delta g(\mathbf{x},\mathbf{y},t) - 4k\overline{A}(\mathbf{x},t)g(\mathbf{x},\mathbf{y},t), \qquad (13)$$

where $\mathbf{y} \in \Omega$.

[19] It is important to note that in the derivations of (13) we disregard the third moment. Once we have solved for f and g, the autocovariance and cross covariance can be calculated as $2\overline{A'(\mathbf{x},t)A'(\mathbf{y},t)} = g(\mathbf{x},\mathbf{y},t) - f(\mathbf{x},\mathbf{y},t)$ and $2\overline{A'(\mathbf{x},t)B'(\mathbf{y},t)} = g(\mathbf{x},\mathbf{y},t) + f(\mathbf{x},\mathbf{y},t)$.

[20] The autocovariances $\overline{A'(\mathbf{x},t)A'(\mathbf{y},t)}$ and $\overline{B'(\mathbf{x},t)B'(\mathbf{y},t)}$ $(\overline{A'(\mathbf{x},t)A'(\mathbf{y},t)} = \overline{B'(\mathbf{x},t)B'(\mathbf{y},t)})$ satisfy either initial conditions (4) or (5) and the cross covariance $\overline{A'(\mathbf{x},t)B'(\mathbf{y},t)}$ satisfies initial conditions (7), (8) or (9) depending on the type of initial autocorrelation and cross correlation of the fluctuations. These initial conditions define initial conditions for f and g.

[21] The boundary conditions for the autocovariance and cross covariance defined on the infinite d-dimensional domain Ω are

$$g(\mathbf{x},\mathbf{y},t) = 0, \qquad x_i = \pm\infty, \qquad i = 1, \dots, d, \qquad (14)$$

$$f(\mathbf{x},\mathbf{y},t) = 0, \qquad x_i = \pm\infty, \qquad i = 1, \dots, d, \qquad (15)$$

respectively, where $\mathbf{x} = (x_1, x_2, x_3)^T$ and $\mathbf{y} = (y_1, y_2, y_3)^T$. These boundary conditions specify that the autocovariance and cross covariance are zero far away from the point $\mathbf{y}$. Furthermore, without loss of generality, we set $y_i = 0$ ($i = 1, \dots, d$).

[22] In the case of the one-dimensional periodic finite size domain $(0, L)$, the domain can always be centered around the point y (i.e., y in the one-dimensional version of (12) and (13) can be set to $y = y^* = L/2$). For the considered initial conditions, only homogeneous Neumann boundary conditions for equations (12) and (13) can satisfy the periodic conditions. Then the appropriate boundary conditions for equations (12) and (13) are

$$\frac{\partial f(x,y,t)}{\partial x} = 0, \qquad x = 0, L, \qquad (16)$$

$$\frac{\partial g(x,y,t)}{\partial x} = 0, \qquad x = 0, L, \qquad (17)$$

respectively.

3. Solution of the Deterministic Diffusion-Reaction Equation

[23] If the initial fluctuations are absent or very small and can be disregarded, then the diffusion-reaction equation reduces to a deterministic equation:

$$\frac{\partial I_{det}}{\partial t} = -kI_{det}^2, \qquad I_{det} = A_{det}, B_{det}, \tag{18}$$

where the subscript *det* stands for the deterministic concentrations (with zero initial fluctuations). The solution of this equation, subject to the initial conditions $A_{det}(0) = B_{det}(0) = A_0$, is

$$A_{det}(t) = B_{det}(t) = \frac{A_0}{A_0 kt + 1}. \tag{19}$$

4. Moment Equations for Initially Anti-Cross-Correlated A and B

[24] For initially anticorrelated A and B, the autocovariance and cross-covariance functions satisfy the initial condition

$$\overline{A'(\mathbf{x},0)A'(\mathbf{y},0)} = -\overline{A'(\mathbf{x},0)B'(\mathbf{y},0)} = \sigma^2\rho(\mathbf{x}-\mathbf{y}), \tag{20}$$

where $\rho(\mathbf{x}-\mathbf{y})$ is the exponential or delta correlation function. For this initial condition, we can solve the moment equations (12) and (13) by recognizing that $\overline{A'(\mathbf{x},t)A'(\mathbf{y},t)} = -\overline{A'(\mathbf{x},t)B'(\mathbf{y},t)}, f = 2\overline{A'(\mathbf{x},t)B'(\mathbf{y},t)}$ and $g \equiv 0$. Then equation (12) can be reduced to

$$\frac{\partial\overline{A'(\mathbf{x},t)B'(\mathbf{y},t)}}{\partial t} = 2D\Delta\overline{A'(\mathbf{x},t)B'(\mathbf{y},t)}, \tag{21}$$

subject to initial condition (20). The boundary conditions for the infinite *d*-dimensional domain are given by equation (15). For the one-dimensional domain, equation (21) is subject to the homogeneous boundary conditions that can be obtained from equations (16) and (17). Note that equation (12) for *f* is exact, and therefore, the system of the moment equations (10) and (21) is also exact.

4.1. Solution of the Moment Equations for Finite One-Dimensional Domain

[25] In a one-dimensional domain, the one-dimensional version of the diffusion equation for the cross covariances satisfies the homogeneous Neumann boundary conditions (17) and the initial condition (7). The solution can be found using the method of separation of variables and is given by

$$\overline{A'(x,t)B'(y^*,t)} = c_0 + \sum_{n=1}^{\infty} c_n(y^*)e^{-2D\frac{n^2\pi^2}{L^2}t}\cos\left(\frac{n\pi x}{L}\right), \tag{22}$$

where $y^* = L/2$,

$$c_0 = -\frac{2l\sigma^2}{L}\left[1 - e^{-\frac{L}{2l}}\right], \tag{23}$$

$$c_n = -\frac{2l\sigma^2}{L}\left[2\cos\left(\frac{n\pi}{2}\right) - e^{-\frac{L}{2l}} - e^{-\frac{L}{2l}}\cos(n\pi) + \frac{n\pi l}{L}e^{-\frac{L}{2l}}\sin(n\pi)\right] \\ \times \left(1 + \frac{n^2\pi^2l^2}{L^2}\right)^{-1}. \tag{24}$$

[26] The variance of the concentrations A and B is

$$\overline{A'A'}(t) = \overline{B'B'}(t) = -\overline{A'(y^*,t)B'(y^*,t)}, \tag{25}$$

and the mean concentrations $\overline{A}(t)$ and $\overline{B}(t)$ $(\overline{A}(t) = \overline{B}(t))$ satisfy the nonlinear ordinary differential equation:

$$\frac{\partial\overline{I}}{\partial t} = -k\overline{I}^2 - k\overline{A'(y^*,t)B'(y^*,t)}, \qquad I = A, B. \tag{26}$$

[27] In general, this equation should be solved numerically. For very large domains and/or early times $(Dt/L^2 \ll 1)$, the series in equation (22) converges slowly, but the solution for this case can be simplified by solving the diffusion-reaction equation in the infinite domain $(L \rightarrow \infty$ limit).

4.2. Solution in the $L \rightarrow \infty$ Limit

[28] In a system with observation time much smaller than $\frac{L^2}{D}$, we can assume that the domain Ω is infinite. Then equation (21), subject to boundary condition (15) and initial cross covariance $\overline{A'(\mathbf{x},0)B'(\mathbf{y}^*,0)}$, has a solution [*Carslaw and Jaeger*, 1972]:

$$\overline{A'(\mathbf{x},t)B'(\mathbf{y}^*,t)} = \frac{1}{\sqrt{8\pi Dt}}\int_\Omega \exp\left[-\frac{(\mathbf{x}-\mathbf{z})^2}{8Dt}\right]\overline{A'(\mathbf{x},0)B'(\mathbf{y}^*,0)}d\mathbf{z}. \tag{27}$$

4.2.1. Initial Exponential Correlation of Fluctuations

[29] In a one-dimensional domain, the cross covariance (27), subject to the initial condition (7), is given by

$$\overline{A'(x,t)B'(y^*,t)} = -\frac{\sigma^2}{\sqrt{8\pi Dt}}\int_{-\infty}^{\infty}\exp\left[-\frac{(x-z)^2}{8Dt}\right]\cdot\exp\left[-\frac{|z-y^*|}{l}\right]dz. \tag{28}$$

[30] The variance and covariance of the concentrations can be found by setting $x = y^*$ in equation (28) such that

$$\overline{A'(y^*,t)A'(y^*,t)} = \overline{B'(y^*,t)B'(y^*,t)} = -\overline{A'(y^*,t)B'(y^*,t)} \\ = \sigma^2\exp\left[\frac{2Dt}{l^2}\right]\left[\text{erf}\left(\frac{\sqrt{2Dt}}{l}\right) - 1\right]. \tag{29}$$

This is a function of time only, and not of space. Expanding this solution in a Taylor series and gathering low-order terms yields a simplified form for the cross variance (and the variances of the concentrations):

$$\overline{A'(y^*,t)B'(y^*,t)} = \overline{A'B'}(t) = \begin{cases} -\sigma^2\left(1 - \left(\frac{8D}{\pi l^2}\right)^{\frac{1}{2}}t^{\frac{1}{2}}\right), & t \ll \frac{t_D}{2} \\ \\ -\sigma^2\left(\frac{l^2}{2\pi D}\right)^{\frac{1}{2}}t^{-\frac{1}{2}}, & t \gg \frac{t_D}{2}. \end{cases} \tag{30}$$

4.2.2. Initially Delta-Correlated Fluctuations

[31] For initially delta function correlated A and B, the cross covariance in the d-dimensional domain takes the form

$$\overline{A'(\mathbf{x},t)B'(\mathbf{y}^*,t)} = -\frac{\sigma^2 l^d}{(8\pi Dt)^{d/2}} \int_\Omega \exp\left[-\frac{(\mathbf{x}-\mathbf{z})\cdot(\mathbf{x}-\mathbf{z})}{8Dt}\right]\delta(\mathbf{z}-\mathbf{y}^*)dz$$

$$= -\frac{\sigma^2 l^d}{(8\pi Dt)^{d/2}} \exp\left[-\frac{(\mathbf{x}-\mathbf{y}^*)\cdot(\mathbf{x}-\mathbf{y}^*)}{8Dt}\right].$$

(31)

Setting $\mathbf{x}=\mathbf{y}^*$, we obtain an expression for the variance and covariance of the concentrations:

$$\overline{A'(t)A'(t)} = -\overline{A'(t)B'(t)} = \frac{\sigma^2 l^d}{(8\pi Dt)^{d/2}}. \qquad (32)$$

[32] The solution for the variance of A, equation (32), is obtained by approximating the exponential autocorrelation function with a delta autocorrelation function. This approximation is not valid for small times. For example, at time $t=0$ the variance of the concentration should be equal to σ^2, but equation (32) results in an infinite variance. Also, the averaged concentration, obtained from equations (10) and (32), increases for times smaller than

$$t < \frac{t_D}{8\pi}, \qquad (33)$$

which is unphysical for the reaction system considered here. To rectify the situation with equation (32), we neglect time smaller than $t=t_D/8\pi$, essentially assuming that no, or negligible, reaction occurs until then. At time $t=t_D/8\pi$ the variance of A, given by equation (32), is equal to the initial variance, $\overline{A'A'}(t_D)=\sigma^2$, and for time $t>t_D$ the average concentration decreases with time, as should be the case for the irreversible reaction studied here. We shift time by introducing a new variable, $\tau=t-t_D/8\pi$, and rewrite equation (10) as

$$\frac{\partial \overline{\tilde{A}}}{\partial \tau} = -k\overline{\tilde{A}}^2 + k\frac{\sigma^2 l^d}{(8\pi D)^{d/2}}\left(\tau+\frac{t_D}{8\pi}\right)^{-d/2}, \quad \tau>0, \qquad (34)$$

subject to the initial condition

$$\overline{\tilde{A}}(\tau=0) = A_0, \qquad (35)$$

where $\tilde{A}(\tau)=A(t+t_D/8\pi)$. The solution of equation (34) can be found analytically as

$$\overline{\tilde{A}}(\tau) =$$
$$-\frac{\sqrt{-ak}(\tau+\frac{t_D}{8\pi})^{1-\frac{d}{4}}(c_1 J_{b_1}(w) - c_1 J_{b_2}(w) - 2J_{-b_1}(w)) - c_1 J_{b_3}(w)}{2k(\tau+\frac{t_D}{8\pi})(c_1 J_{b_3}(w) + J_{-b_3}(w))},$$

(36)

where c_1 is given by the initial condition (35), $J_a(z)$ is a Bessel function of the first kind, and

$$a = \frac{\sigma^2 l^d}{(8\pi D)^{\frac{d}{2}}}, \qquad w = \frac{4\sqrt{-ak}}{4-d}\left(\tau+\frac{t_D}{8\pi}\right)^{1-\frac{d}{4}}, \qquad b_1 = \frac{2-d}{4-d},$$

$$b_2 = \frac{6-d}{4-d},$$

(37)

$$b_3 = -\frac{2}{4-d}. \qquad (38)$$

Setting $d=1$ in equation (32) recovers the scaling behavior of the one-dimensional covariance with initial exponential correlation, equation (30), for $t > t_D/2$. This means that for times greater than $t > t_D/2$, the average concentration forgets the initial correlation of the fluctuations and the initial δ correlated can be taken as a good approximation. For time smaller than t_0, the solution can be obtained using the covariance function (30).

[33] Defining a new variable, $r=|\mathbf{x}-\mathbf{y}|$, we rewrite equation (31) as $\overline{A'A'}(r,t) = -\frac{\sigma^2 l^d}{(8\pi Dt)^{d/2}}\exp\left[-\frac{r^2}{8Dt}\right]$. The correlation length of the fluctuations can be defined as

$$\lambda(\tau) = \int_0^\infty \frac{\overline{A'A'}(r,\tau)}{\overline{A'A'}(0,\tau)}dr = \int_0^\infty \exp\left(-\frac{r^2}{8D\left(\tau+\frac{t_D}{8\pi}\right)}\right)dr$$

$$= \sqrt{2\pi D\left(\tau+\frac{t_D}{8\pi}\right)}. \qquad (39)$$

[34] The correlation length is a measure of the average size of a subdomain where one of the two reactants is absent. For time $\tau \gg \frac{t_D}{8\pi}$, λ grows as $(D\tau)^{\frac{1}{2}}$. In this regime, the concentration field is composed of segregated "islands" of A and B [*Kang and Redner*, 1985]. Then $\lambda(t)$ becomes a statistical measure of the size of these islands, and according to equation (39) the size grows with time as $t^{\frac{1}{2}}$. A similar scaling law for the size of the islands was phenomenologically postulated, but not explicitly derived, by *Kang and Redner* [1985].

5. Moment Equations for A and B With Initially Zero Cross Correlation

[35] Here we consider a case when A and B are initially uncorrelated, $\overline{A'(x,0)B'(y,0)} = 0$. We obtain a solution for the mean and variance of the concentrations in a one-dimensional infinite domain. For conciseness, here we consider a solution for the delta function correlation. The solution for the exponential correlation function can be obtained in a similar way. Using the delta function approximation of the exponential autocovariance function for A and B, equations for the mean and variance of the concentration have the form (Appendix B)

$$\overline{A'B'}(t) = \frac{\sigma^2 l}{2\sqrt{8\pi Dt}}\left[e^{-4k\int_0^t \overline{A}(t')dt'} - 1\right], \qquad t>0, \qquad (40)$$

$$\frac{\partial \overline{A}}{\partial t} = -k\overline{A}^2 - k\frac{\sigma^2 l}{2\sqrt{8\pi Dt}}\left[e^{-4k\int_0^t \overline{A}(t')dt'} - 1\right], \qquad t>0, \quad (41)$$

$$\overline{A'A'}(t) = \frac{\sigma^2 l}{2\sqrt{8\pi Dt}}\left[e^{-4k\int_0^t \overline{A}_{(t')}dt'} + 1\right], \qquad t > 0, \qquad (42)$$

subject to the initial condition $\overline{A}(t=0) = A_0$.

[36] As in the case of initially anticorrelated A and B, using the δ correlation approximation of the exponential correlation function leads to an unphysical behavior such as infinite variance of the concentrations, $\overline{A'A'}(t)$, at time zero. To make use of the δ correlation approximation, we assume that the reaction does not occur until $t = t_D/8\pi$ and equations (40)–(42) can be rewritten using a new variable, $\tau = t - t_D$, as

$$\overline{A'B'}(\tau) = \frac{\sigma^2 l}{2\sqrt{8\pi D(\tau + t_D/8\pi)}}\left[e^{-4k\int_0^\tau \overline{A}_{(\tau')}d\tau'} - 1\right], \quad \tau > 0,$$

$$(43)$$

$$\frac{\partial \overline{A}}{\partial \tau} = -k\overline{A}^2 - k\frac{\sigma^2 l}{2\sqrt{8\pi D(\tau + t_D/8\pi)}}\left[e^{-4k\int_0^\tau \overline{A}_{(\tau')}d\tau'} - 1\right], \quad \tau > 0,$$

$$(44)$$

$$\overline{A'A'}(\tau) = \frac{\sigma^2 l}{2\sqrt{8\pi D(\tau + t_D/8\pi)}}\left[e^{-4k\int_0^t \overline{A}_{(\tau')}d\tau'} + 1\right], \quad \tau > 0,$$

$$(45)$$

subject to the initial condition $\overline{A}(\tau = 0) = A_0$.

[37] The covariance of A is given by equation (B16). The correlation length is given by

$$\lambda(\tau) = \int_0^\infty \frac{\overline{A'A'}(r, \tau)}{\overline{A'A'}(0, \tau)}\, dr = \int_0^\infty \exp\left(-\frac{r^2}{8D(\tau + t_D/8\pi)}\right)dr$$

$$= \sqrt{2\pi D(\tau + t_D/8\pi)},$$

$$(46)$$

which at late times scales as $\tau^{\frac{1}{2}}$. This is the same scaling behavior as we saw earlier for the correlation length for fluctuations with initial anticorrelation (equation (39)). The comparison of equations (39) and (46) shows that the correlation length of A (and B) for initially anticorrelated A and B grows with the same rate as the correlation length for initially uncorrelated A and B.

6. Results: Impact of Concentration Fluctuations on Effective Kinetics

6.1. Infinite Domain

[38] For the anticorrelated case, Figures 1 and 2 show the averaged concentration and the standard deviation of the concentration for two different Damköhler numbers, $Da = \frac{t_D}{t_k} = \frac{A_0 k l^2}{2D}$, defined as the ratio between the characteristic diffusion and reaction times, $t_D = \frac{l^2}{2D}$ and $t_k = \frac{1}{A_0 k}$. In Figure 3 we compare the anticorrelated case with the zero cross-correlated case. In Figures 1–3, at early times when variance and covariance of the concentrations are relatively small, $\overline{A}$ and $\overline{B}$ follow the deterministic solution (19). At later times, when $\overline{A}$ and $\overline{B}$ become comparable to $\sqrt{-\overline{A'B'}}$,
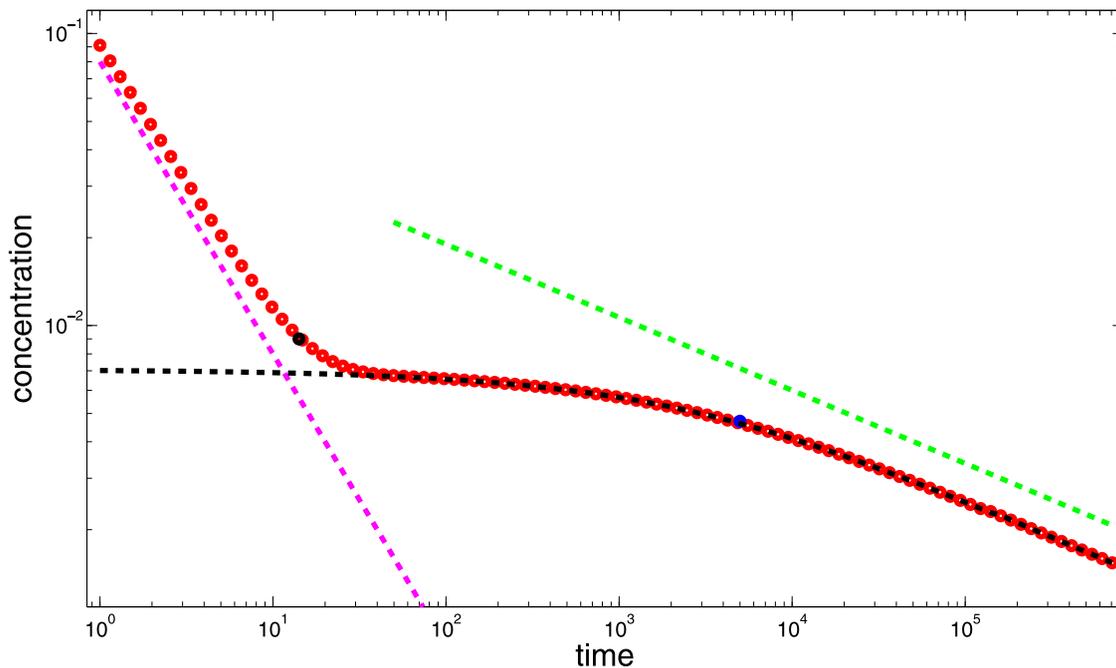
Figure 1. Average concentration (red dotted line) versus time in a one-dimensional infinite domain. The blue dot is the concentration at the diffusion time $t_D = \frac{l^2}{2D}$, and the black dot is the concentration at the transition time given by equation (50). The black dashed line is $\sqrt{-\overline{A'B'}}$, the magenta dashed line shows t^{-1} scaling, and the green line shows $t^{-1/4}$ scaling. The parameters are $l = 0.1$, $D = 10^{-6}$, $\sigma^2 = 10^{-5}$, and $k = 10$, which correspond to $Da > C_{\nu 0}$.

the average concentration deviates from the deterministic solution. Note that the term $\overline{A'B'}$ is negative for all the initial conditions considered (equations (29), (32) and (43)). Therefore, $-\overline{A'B'}$ is a source term while $-\overline{A}^2$ is a sink term for equation (10), and the system dynamically balances at $\overline{I} \approx \sqrt{-\overline{A'B'}}$ ($I = A, B$). Since $\overline{A'B'} \approx t^{-d/2}$ (equations (30), (32) and (43)), the average concentration switches its behavior from t^{-1} to $t^{-d/4}$. The coefficient of variation,

$$C_v(t) = \frac{\sqrt{\overline{A'A'}(t)}}{\overline{A}(t)}, \tag{47}$$

increases with time and asymptotically approaches unity. For the early times, $\overline{A}^2 \gg \overline{A'A'} = -\overline{A'B'}$ and the term $k\overline{A'B'}$ in equation (26) can be ignored. Thus, $\overline{A}$ behaves like the deterministic concentration, $A_{det} = \frac{\overline{A}_0}{\overline{A}_0 kt+1}$. As time increases, so does the covariance term $-k\overline{A'B'}$ relative to the reaction term $k\overline{A}^2$, and this slows the decay of $\overline{A}$.

[39] Figure 3 compares the mean and the standard deviation of the concentrations for different initial cross correlations of fluctuations of A and B. The solutions are obtained for one-dimensional infinite domains for initially anticorrelated (equation (8)) and uncorrelated (equation (9)) fluctuations. In both cases, the initial autocovariance function (5) is assumed. Figure 3 shows that the variance of the concentration A (and B) is larger for initially anti-cross-correlated fluctuations than for initially uncorrelated fluctuations for

all times greater than zero. The same is true for the average concentrations. Also, average concentrations for initially anti-cross-correlated fluctuations transition earlier to the $t^{-1/4}$ behavior than the average concentrations with initially uncorrelated fluctuations.

6.2. Finite Domain

[40] Figures 4–6 show the average one-dimensional concentration $\overline{A}(t)$ versus time for various parameters obtained from the numerical integration of equation (26). Figure 4 depicts $\overline{A}$ versus t for various domain sizes L. The azure line shows the deterministic solution (19) without the fluctuations. This solution decreases to zero as t^{-1} after $t > (A_0 k)^{-1}$. As for the infinite domain, the average concentration first follows the deterministic solution (scales as t^{-1}), but later the scaling of the average concentration changes to $t^{-1/4}$ and finally asymptotically approaches c_0. Thus, the fluctuations slow the rate of decrease in the concentration. As the domain size L increases, the solution rapidly approaches the solution for the infinite domain.

[41] As a result of the reaction, the average concentration decreases from its initial value to an asymptotic value c_0 (equation (23)) that depends on the initial variance of the concentration, the correlation length, and the size of the domain. This means that, on average, not all of A and B react. This is because owing to initial random fluctuations in concentrations A and B, in a domain of finite size in each particular realization, the initial total mass of A is not exactly equal to the initial total mass of B. This shows that the random concentration field in a finite domain has not attained
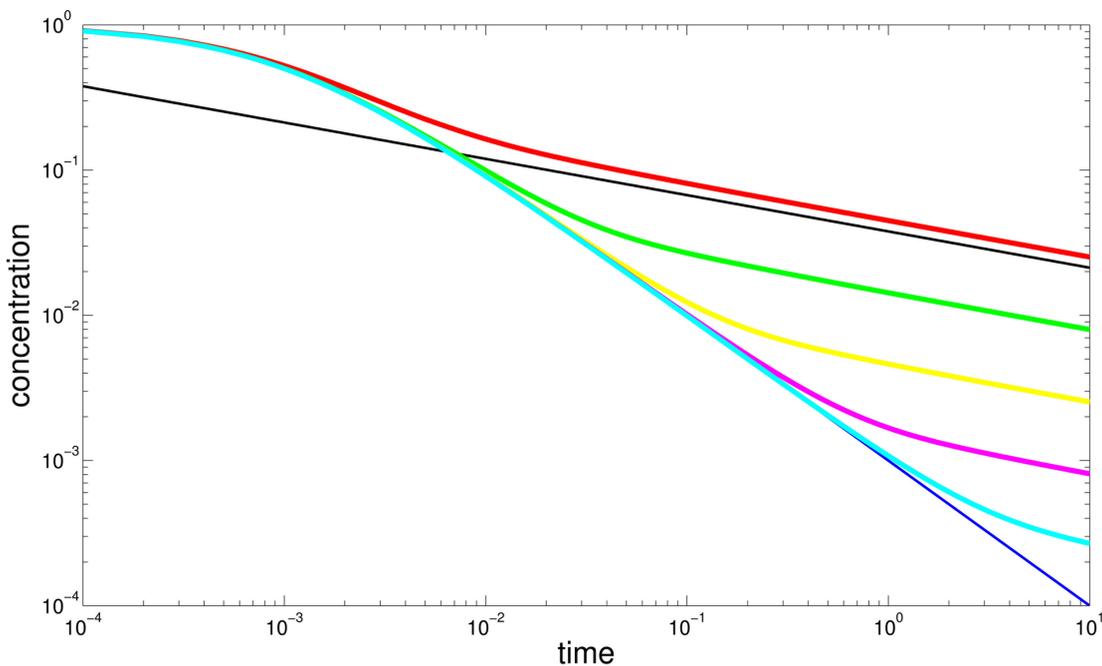
Figure 2. Average concentration (red dotted line) versus time in a one-dimensional infinite domain. The blue dot is the concentration at the diffusion time $t_D = \frac{l^2}{2D}$, and the black dot is the concentration at the transition time given by equation (50). The black dashed line is $\sqrt{-\overline{A'B'}}$, the magenta dashed line shows t^{-1} scaling, and the green line shows $t^{-1/4}$ scaling. The parameters are $l = 0.1$, $D = 10^{-2}$, $\sigma^2 = 10^{-5}$, and $k = 10$, which correspond to $1 < Da < C_{v0}$.
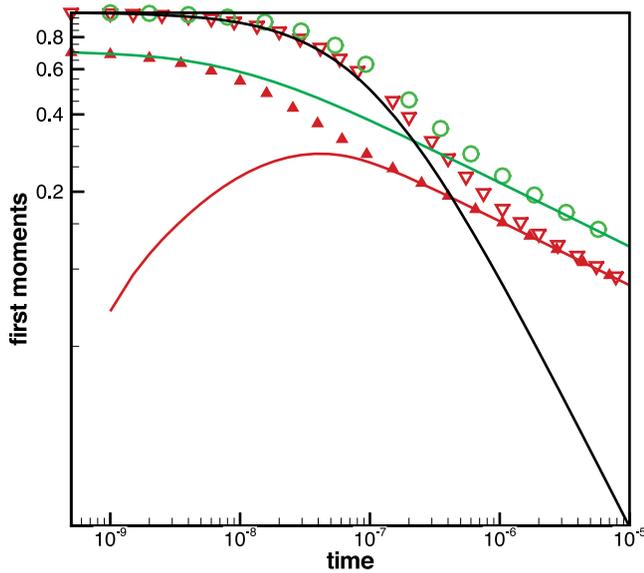
Figure 3. Average concentration and the standard deviation of the concentration for initial fluctuations with zero cross correlation and anti–cross correlation in an infinite one-dimensional domain. Red open triangles depict the average concentration for initially uncorrelated fluctuations. Open green circles denote the average concentration for initially anticorrelated fluctuations. The red line is $\sqrt{-\overline{A'B'}(t)}$ for initially uncorrelated fluctuations. Red solid triangles depict $\sqrt{\overline{A'A'}(t)}$ for initially uncorrelated fluctuations. The green line is $\sqrt{-\overline{A'B'}(t)} = \sqrt{\overline{A'A'}(t)}$ for initially anticorrelated fluctuations. The black line is A_{det}. The values of the parameters are $l = 0.00015$, $D = 0.1$, $\sigma^2 = 0.5$, $k = 10^7$, and $Da = 2.25$.

ergodic conditions and the spatial average of the concentration in each particular realization is not equal to its ensemble average. Problems associated with ergodicity are common in the application of stochastic models to water resources. The system becomes ergodic as the domain size approaches infinity. The standard deviation of the concentrations decreases from its initial value to the constant c_0. The asymptotic value c_0 goes to zero with decreasing l/L and decreasing initial variance of the fluctuations.

[42] Figure 5 displays $\overline{A}$ versus t for various correlation lengths l. The solution for the average concentration with initial correlation length $l = 0$ is equivalent to the solution for deterministic concentration (blue line). For $l > 0$, the average concentration follows the deterministic solution (decreases as t^{-1}) at early times, but later the average concentration decays as $t^{-1/4}$ and eventually approaches the asymptotic value c_0.

[43] Figure 6 shows $\overline{A}$ versus t for different σ^2. In the limit $\sigma^2 = 0$, the system is a deterministic homogeneous mixture and the solution for $\overline{A}$ is given by A_{det} (blue line). For $\sigma^2 > 0$, $\overline{A}$ follows A_{det} (decreases as t^{-1}) at the early time, and later $\overline{A}$ decays as $t^{-1/4}$ and eventually approaches the asymptotic value c_0.

[44] It is evident from Figures 4–6 that disregarding fluctuations leads to an overestimation of the extent of the reaction and an underestimation of the averaged concentration. The error increases with increasing σ^2 and l and decreasing L. Such quantitative results play an important role in determining reaction rates in real systems such as porous media or turbulent streams where mixing is often incomplete and segregation of reactants into islands is commonplace. The analysis in this work is presented to provide an analytical foundation for extensions to such cases.

7. Characteristic Transition Time t^*

[45] In a purely diffusive system, the variance of the fluctuations, σ^2, is usually small, regardless of the origin of the fluctuations. Therefore, the initial coefficient of variation, C_{v0}, should be a small number:

$$0 < C_{v0} = \frac{\sigma}{A_0} < 1. \tag{48}$$

[46] We demonstrated above that in the diffusion-reaction system, equation (1), for any nonzero $C_{v0} = C_v(0)$ at late times $C_v(t)$ approaches unity. The asymptotic increase of the coefficient of variation from an arbitrarily small value to unity is the primary cause of different early and late time scalings of the average concentrations.

[47] Here we derive estimates for the characteristic transition time t^* after which the scaling behavior of the average concentrations change to $t^{-d/4}$. We obtain the estimates of t^* for diffusion and reaction in infinite d-dimensional domains for fluctuations with different initial autocorrelation and cross correlation.

7.1. Infinite One-Dimensional Domain: Initially Anticorrelated Fluctuations With Exponential Autocovariance Function

[48] For early times, $C_v \ll 1$; therefore, the average concentrations are well described by the solution for the deterministic concentration A_{det}. The solution will deviate from A_{det} at time t^*, when the term $\overline{A'B'}$ is comparable to $-A^2$.

[49] The characteristic time t^* can be found as the solution of an algebraic equation:

$$A_{det}(t^*) = \sqrt{-\overline{A'B'}(t^*)}. \tag{49}$$

The solution of this equation depends on the Damköhler number, $Da = \frac{A_0 k l^2}{D}$. For times greater than the characteristic chemical time $t_k = \frac{1}{A_0 k}$, the deterministic solution decreases as $A_{det} \sim (kt)^{-1}$.

[50] We consider t^* for different Damköhler numbers: (1) $Da > C_{v0}^{-1}$, fast reaction and $t_k < t_D$ (Figure 1); (2) $1 < Da < C_{v0}^{-1}$, medium reaction and $t_k < t_D$ (Figure 2); and (3) $Da < 1$, slow reaction and $t_k > t_D$.

7.1.1. Case 1: $Da > C_{v0}^{-1}$

[51] The curves for $A_{det}(t)$ and $\sqrt{-\overline{A'B'}(t)}$ intersect at time t^* such that: $t_k \ll t^* \ll t_D$. Within this interval, $A_{det}(t) \approx \frac{1}{kt}$ and $\sqrt{-\overline{A'B'}} \approx \sigma$, and the solution of equation (49) is

$$t^* = \frac{1}{k\sigma} = t_k C_{v0}^{-1}. \tag{50}$$
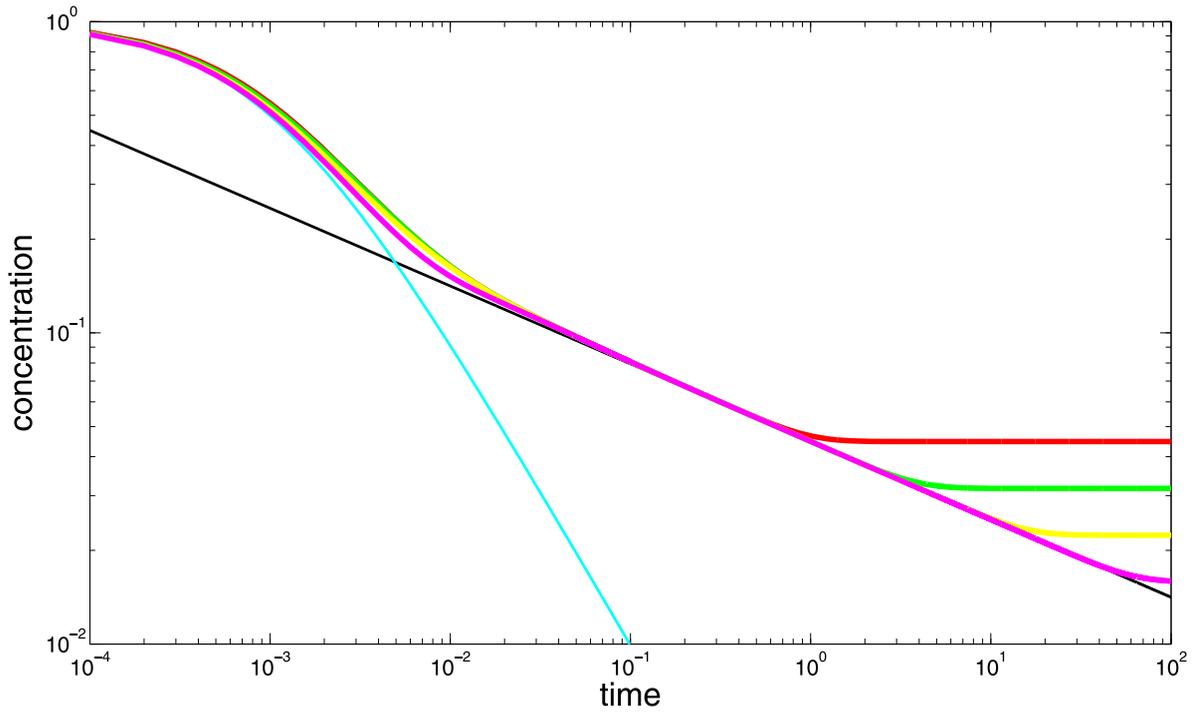
Figure 4. Average concentration in the finite one-dimensional domain versus time as a function of the domain of size L: red line, $L = 0.5$; green line, $L = 1$; yellow line, $L = 2$; magenta line, $L = 4$. For all curves, $l = 0.001$, $D = 0.01$, $\sigma^2 = 0.5$, and $k = 1000$. The azure line is the A_{det} solution. The black line represents the law $t^{-\frac{1}{4}}$.
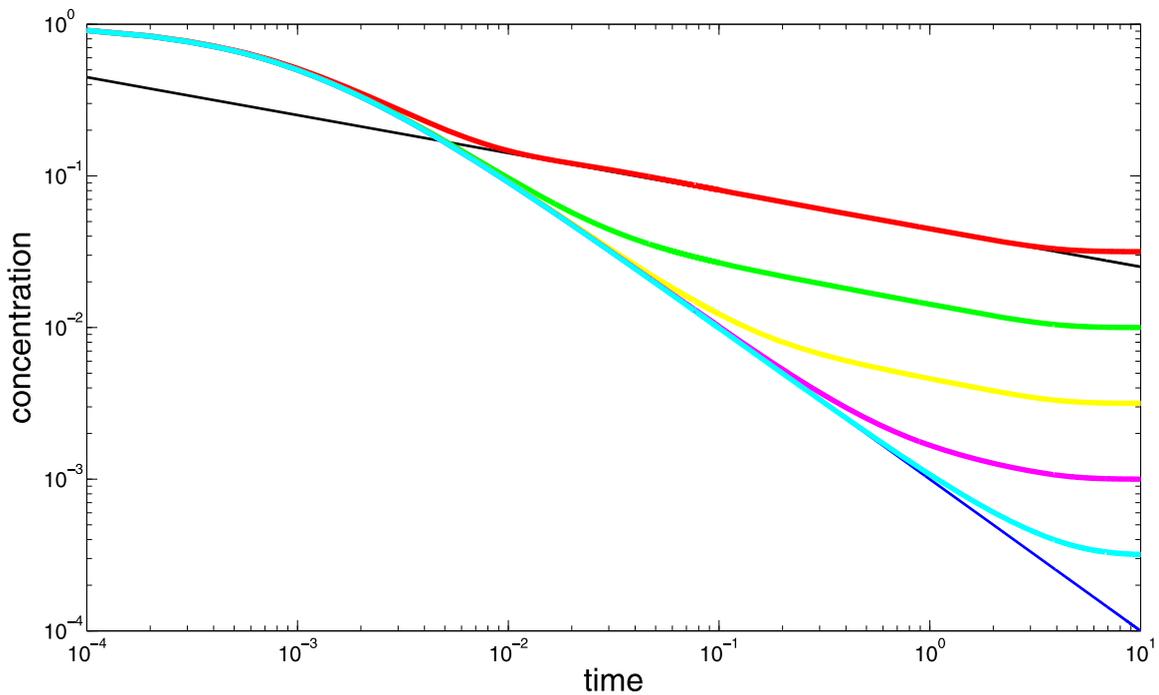
Figure 5. Average concentration in the finite one-dimensional domain versus time as a function of the correlation length l: red line, $l = 10^{-3}$; green line, $l = 10^{-4}$; yellow line, $l = 10^{-5}$; magenta line, $l = 10^{-6}$; azure line, $l = 10^{-7}$; blue line, $l = 0$. For all curves, $L = 1$, $D = 0.01$, $\sigma^2 = 0.5$, and $k = 1000$. The black line represents the law $t^{-\frac{1}{4}}$.
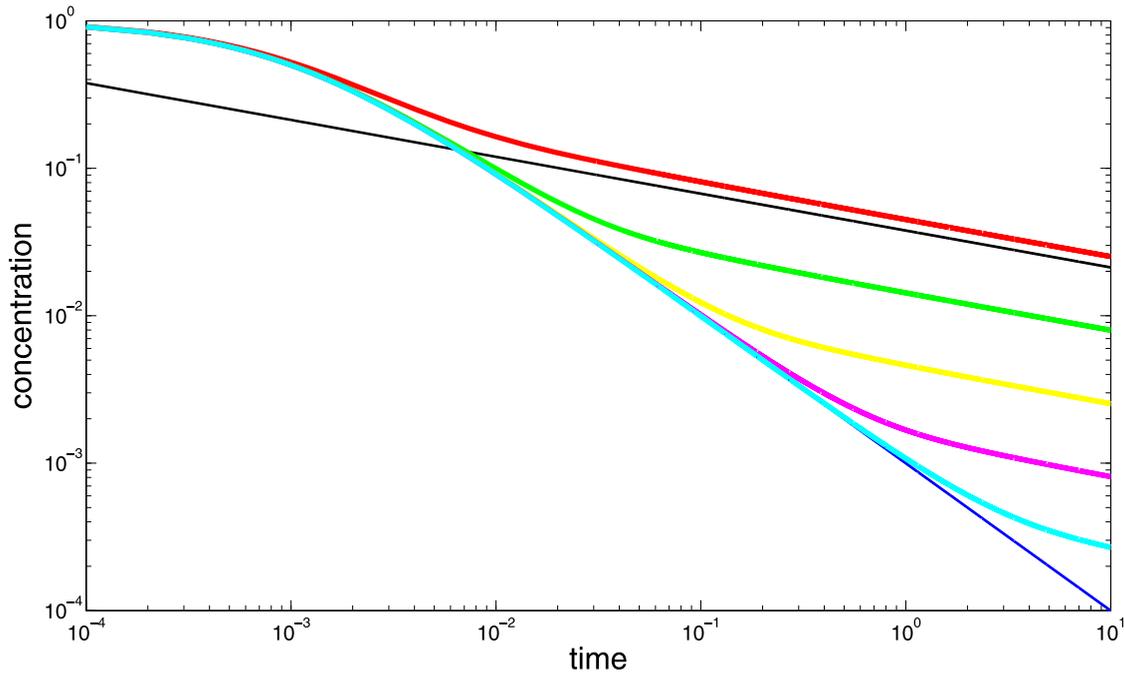
Figure 6. Average concentration versus time in the finite domain of size L: red line, $\sigma^2 = 5 \times 10^{-2}$; green line, $\sigma^2 = 5 \times 10^{-3}$; yellow line, $\sigma^2 = 5 \times 10^{-4}$; magenta line, $\sigma^2 = 5 \times 10^{-5}$; azure line, $\sigma^2 = 5 \times 10^{-6}$. For all curves, $L = 1$, $D = 5 \times 10^{-6}$, $l = 0.001$, and $k = 1000$. The blue curve is the A_{det} solution, and the black line represents the scaling $t^{-\frac{1}{4}}$.

7.1.2. Case 2: $C_{v0}^{-1} > Da > 1$

[52] The two curves, A_{det} and $\sqrt{-\overline{A'B'}}$, cross at time $t^* > t_D$. For $t > t_D$, $A_{det}(t) \approx \frac{1}{kt}$ and $\sqrt{-\overline{A'B'}} \approx \sigma(\frac{l^2}{2\pi D})^{\frac{1}{4}} t^{-\frac{1}{4}}$, and the solution of equation (49) is

$$t^* = t_k \left(\frac{\pi}{DaC_{v0}^4} \right)^{\frac{1}{3}}. \tag{51}$$

[53] Figures 1 and 2 show the exact solutions for $Da > C_{v0}^{-1}$ and $C_{v0}^{-1} > Da > 1$, respectively. Figures 1 and 2 demonstrate that t^*, calculated from equations (50) or (51) (depending on the magnitude of Da), accurately predicts deviation of the average concentration from $A_{det}(t) \sim t^{-1}$ to $\sim t^{-1/4}$ behavior.

7.1.3. Case 3: $\mathcal{D} < 1$

[54] In this case, $t_k > t_D$. To estimate t^*, we can use the same approximations for A_{det} and $\sqrt{-\overline{A'B'}}$ as in case 2. Then t^* is given by equation (51). The characteristic transition time increases with decreasing Damköhler number (and the reaction rate k). Consequently, for very small Da the average concentrations will not be affected by the spatial fluctuations and will be well described by the solution $A_{det}(t)$.

7.2. Infinite d-Dimensional Domain: Initially Anticorrelated Fluctuations With δ Autocovariance Function

[55] Next we consider an approximate solution for an infinite n-dimensional domain with initial delta-autocorrelated and anti-cross-correlated fluctuations. The two curves,

A_{det} and $\sqrt{-\overline{A'B'}}$, cross at time $t^* > t_k$. For $t > t_k$, $A_{det}(t) \approx \frac{1}{kt}$ and $\sqrt{-\overline{A'B'}} = \sigma\left[\frac{l^2}{8\pi D}\right]^{\frac{d}{4}} t^{-\frac{d}{4}}$, and the solution of equation (49) is

$$t^* = t_k^{\frac{4}{4-d}} t_D^{\frac{d}{d-4}} C_{v0}^{\frac{4}{d-4}} (4\pi)^{\frac{d}{4-d}}. \tag{52}$$

[56] For time $t > t^*$, the average concentrations are given by

$$\overline{A(t)} = \overline{B(t)} = \sqrt{-\overline{A'(t)B'(t)}} = \frac{A_0 C_{v0}}{(8\pi)^{d/4}} t_D^{\frac{d}{4}} t^{-\frac{d}{4}}. \tag{53}$$

[57] This asymptotic scaling of the average concentrations with time, $t^{-d/4}$ agrees with the asymptotic scaling results of *Toussaint and Wilczek* [1983], *Kang and Redner* [1985], and *Benson and Meerschaert* [2008].

7.3. Infinite One-Dimensional Domain With Zero Cross Correlation

[58] Finally, to study the effect of the initial cross-correlation between fluctuations of A and B we consider an approximate solution for an infinite one-dimensional domain with delta-autocorrelated and zero-cross-correlation fluctuations. The two curves, A_{det} and $\sqrt{-\overline{A'B'}}$, cross at time $t^* > t_k$. For $t > t_k$, $A_{det}(t) \approx \frac{1}{kt}$ and $\sqrt{-\overline{A'B'}} \approx \sqrt{0.5}\sigma\left[\frac{l^2}{8\pi D}\right]^{\frac{1}{4}} t^{-\frac{1}{4}}$, and the solution of equation (49) is

$$t^* = t_k^{\frac{4}{3}} t_D^{-\frac{1}{3}} C_{v0}^{-\frac{4}{3}} (8\pi)^{\frac{1}{3}}. \tag{54}$$

[59] Comparing equation (54) and the one-dimensional version of equation (52) shows that the characteristic

transition time t^* for initially uncorrelated fluctuations is $2^{1/3}$ times greater than the transition time for the initially anti-cross-correlated concentrations.

8. Conclusions

[60] In the absence of fluctuations, the concentration of solutes during chemical reaction $A + B -> C$ decays as $A_{det} = B_{det} \sim t^{-1}$. Contrary to this, experimental and numerical studies suggest that concentrations decay significantly slower. Existing theory suggests a $t^{-d/4}$ scaling in the asymptotic regime (d is the dimensionality of the problem). We have studied the effect of spatial concentration fluctuations in this nonlinear irreversible reaction using the classical diffusion-reaction equation with random initial conditions, where the initial concentrations of the reactants were treated as correlated random fields. We used the moment equation approach to derive equations for the mean and variance of the concentrations and for the characteristic transition time t^*, a time when scaling of the concentration with time changes to $t^{-d/4}$. The moment equations were used to study the effect of the initial autocorrelation and cross correlation of the concentrations on the leading moments of the concentrations. When fluctuations are driven by thermal noise, the initial statistics of the concentration fluctuations can be found from statistical mechanics [*Ovchinnikov and Zeldovich*, 1978]. If fluctuations are caused by the fluctuations in the advective velocities that mixed two solutes (our analysis is for the case when the flow ceased after fluids were mixed), then the initial statistics of the fluctuations can be found from the moment equation method or polynomial chaos solution of the stochastic advection-dispersion equations [*Morales-Casique et al.*, 2006; *Jarman and Tartakovsky*, 2011; *Lin and Tartakovsky*, 2009, 2010; *Lin et al.*, 2010].

[61] We first considered a case of initially anticorrelated A and B. For d-dimensional ($d = 1, 2, 3$) infinite domain and delta-autocorrelated initial concentrations, we obtained analytical solutions for the mean and variance of the concentrations. At late times, the average concentrations scale as $t^{-d/4}$, which agrees with the classical results of *Toussaint and Wilczek* [1983] and numerical observations [*Benson and Meerschaert*, 2008; *de Anna et al.*, 2011]. For infinite domains, we obtained analytical expressions for t^* as function of Da. The characteristic transition time t^* increases with increasing reaction time, $t_k = \frac{1}{kA_0}$ and decreasing diffusion time and the initial coefficient of variation, C_{v0}.

[62] For equations defined on a one-dimensional finite domain, we obtain an analytical solution for the variance of concentrations. The variance decreases asymptotically from the prescribed value to c_0^2, where the constant c_0 is proportional to initial variance of the concentrations σ^2 and the ratio of the initial correlation length of the concentration l to the size of the domain L. We also obtain a one-dimensional solution for the average concentrations via numerical integration of the corresponding ordinary differential equation. This solution shows that the scaling behavior of the average concentrations changes from $\sim t^{-1}$ to $\sim t^{-1/4}$ at t^* that increases with increasing L and decreasing l and σ^2.

[63] Our analytical results support earlier explanations of the change in the scaling behavior of the average concentrations from $A_{det} = B_{det} \sim t^{-1}$, that attributed it to the presence of islands of segregated A and B. Our solutions for various parameters indicate that the transition in the scaling behavior occurs at t^* when (1) A and B are anticorrelated and (2) the cross covariance $\overline{A'B'}$ is equal to the square mean concentration $\overline{A}^2$ (or $\overline{B}^2$). Hence, we conclude that these are the conditions describing the formation of the islands of A and B (i.e., parts of the domain occupied dominantly by species A or B).

[64] The comparison of different initial cross correlations of A and B shows that, for initially uncorrelated fluctuations, t^* is $2^{1/3}$ times greater than the transition time for the initially anti-cross-correlated concentrations. On the other hand, the correlation length of the concentrations growth as $(Dt)^{\frac{1}{2}}$ regardless of the initial cross correlation. The increasing autocorrelation of the concentrations A and B and negative (anti) cross correlation between A and B indicate that A and B segregate into separate islands. The size of the islands is statistically related to the correlation length of the concentrations and our solution suggests that the islands grow as $(Dt)^{\frac{1}{2}}$. A similar scaling law for the size of the islands was phenomenologically postulated in [*Kang and Redner*, 1985].

[65] For very small Da, our results show that the chemical reaction is slow and that diffusion has enough time to mix the system, destroying all the islands of segregated A and B.

[66] We illustrate that fluctuations in concentration have an important role on reactive transport and disregarding the fluctuations can lead to erroneous results. Even though our solutions are derived for the diffusion-reaction equation, they can also be applied to the advection-dispersion-reaction (ADR) equations ($\partial I / \partial t + \mathbf{u} \cdot \nabla I = \mathbf{D} \nabla^2 I - kAB$, $I = AB$) with a uniform advection velocity field ($\mathbf{u} = $ const) and a constant dispersion coefficient $\mathbf{D}$. This is because the ADR equation can be reduced to a diffusion-reaction equation with an anisotropic diffusion coefficient via the Galilean transformation [e.g., *Farlow*, 1982]. We should note that while there are convincing experimental and numerical findings that our analysis accurately describes the behavior of purely diffusive-reactive systems, we are not aware of any experimental results or direct pore-scale simulations that confirm transition to $t^{-d/4}$ scaling for advection-dispersion-reaction systems. Furthermore, the ADR equation accounts only for the first and second moments of a pore-scale velocity distribution (the first moment gives the Darcy scale advective velocity, and the second moment contributes to the dispersion coefficient). Hence, the ADR equation may not be a good model for a multicomponent reactive transport in porous media, because pore-scale velocity affects mixing-controlled reactions in many different ways. For example, variations in pore-scale velocity may prevent or delay segregation of reactants. On the other hand, there is much evidence showing that the deterministic advection-diffusion-reaction equation, which disregards the effect of the concentration fluctuations, overestimates the effective rate of mixing controlled reactions. Further investigations are needed to understand the effect of concentration and pore-scale velocity fluctuations on multicomponent reactive transport in porous media.

Appendix A:　Moment Equations

[67] Substituting equation (2) into the diffusion equation yields

$$\frac{\partial(\overline{I}+I')}{\partial t}=D\Delta(\overline{I}+I')-k(\overline{A}+A')(\overline{B}+B'),\qquad I=A,B.$$

(A1)

[68] Taking ensemble average yields

$$\frac{\partial\overline{I}}{\partial t}=D\Delta\overline{I}-k\overline{A}\,\overline{B}-k\overline{A'B'},\qquad I=A,B,$$

(A2)

where all the variables are functions of $\mathbf{x}$ and t

[69] Subtracting equation (A2) from equation (A1) gives a diffusion-reaction equation for fluctuations:

$$\frac{\partial I'}{\partial t}=D\Delta I'-k\overline{A}B'-k\overline{B}A'-kA'B'+k\overline{A'B'},\qquad I=A,B.$$

(A3)

[70] To obtain the equations for the variance $\overline{A'(\mathbf{x},t)A'(\mathbf{x},t)}$ and covariance $\overline{A'(\mathbf{x},t)B'(\mathbf{x},t)}$, we write equations for $A'-B'$ and $A'+B'$:

$$\frac{\partial(A'-B')}{\partial t}=D\Delta(A'-B'),$$

(A4)

and

$$\frac{\partial(A'+B')}{\partial t}=D\Delta(A'+B')-2k\overline{A}B'-2k\overline{B}A'-2kA'B'+2k\overline{A'B'}.$$

(A5)

[71] We first obtain an equation for $f(\mathbf{x},\mathbf{y},t)=\overline{A'(\mathbf{x},t)B'(\mathbf{y},t)}-\overline{A'(\mathbf{x},t)A'(\mathbf{y},t)}$. To do so, we multiply equation (A4) with $A'(\mathbf{y},t)$:

$$A'(\mathbf{y},t)\frac{\partial(A'(\mathbf{x},t)-B'(\mathbf{x},t))}{\partial t}=D\Delta(A'(\mathbf{x},t)A'(\mathbf{y},t)-B'(\mathbf{x},t)A'(\mathbf{y},t)).$$

(A6)

[72] Next, we multiply equation (A4) with $B'(\mathbf{y},t)$:

$$B'(\mathbf{y},t)\frac{\partial(A'(\mathbf{x},t)-B'(\mathbf{x},t))}{\partial t}=D\Delta(A'(\mathbf{x},t)B'(\mathbf{y},t)-B'(\mathbf{x},t)B'(\mathbf{y},t)).$$

(A7)

[73] Summing the last two equations, taking ensemble average, and recognizing that for considered boundary conditions,

$$\overline{A}(t)=\overline{B}(t)$$

(A8)

$$\overline{A'(\mathbf{x},t)A'(\mathbf{y},t)}=\overline{B'(\mathbf{x},t)B'(\mathbf{y},t)},$$

(A9)

we obtain the equation for f:

$$\frac{\partial f(\mathbf{x},\mathbf{y},t)}{\partial t}=2D\Delta f(\mathbf{x},\mathbf{y},t).$$

(A10)

[74] In a similar manner, we obtain an equation for $g(\mathbf{x},\mathbf{y},t)=\overline{A'(\mathbf{x},t)B'(\mathbf{y},t)}+\overline{A'(\mathbf{x},t)A'(\mathbf{y},t)}$:

$$\frac{\partial g(\mathbf{x},\mathbf{y},t)}{\partial t}=2D\Delta g(\mathbf{x},\mathbf{y},t)-4k\overline{A}(\mathbf{x},t)g(\mathbf{x},\mathbf{y},t).$$

(A11)

[75] It is important to notice that in the derivations of equation (A11) we disregarded the third moment $\overline{A'B'B'}$. This approximation is only valid for $\sigma/\overline{A}_0<1$.

Appendix B:　Moment Equations for Uncorrelated A and B

[76] Here we solve the moment equations in one-dimensional infinite domain for A and B with zero cross correlation. Fluctuations of A and B satisfy the initial conditions (5) and (9). We first solve for

$$f(x,y,t)=\overline{A'(x,t)B'(y,t)}-\overline{A'(x,t)A'(y,t)},$$

(B1)

which satisfies

$$\frac{\partial f(x,y,t)}{\partial t}=2D\Delta_x f(x,y,t),\qquad x,y\in(0,L).$$

(B2)

[77] This equation is subject to the initial condition

$$f(x,y,0)=-\sigma^2 l\delta(x-y)$$

(B3)

and the homogeneous Dirichlet boundary condition at $x=\pm\infty$. The solution of this equation is [*Carslaw and Jaeger*, 1972]

$$f(x,y^*,t)=-\frac{\sigma^2 l}{(8\pi Dt)^{1/2}}\exp\left[-\frac{(x-y^*)^2}{8Dt}\right]$$

(B4)

$$f(t)=\frac{\sigma^2 l}{(8\pi Dt)^{1/2}}.$$

(B5)

[78] Next, we solve for $g=\overline{A'(x,t)A'(y,t)}+\overline{A'(x,t)B'(y,t)}$ that satisfies

$$\frac{\partial g(x,y^*,t)}{\partial t}=2D\Delta_x(x,y^*,t)-4k\overline{A}(t)g(x,y^*,t).$$

(B6)

[79] The Fourier transform of g is

$$\hat{g}(\psi)=\int_{-\infty}^{+\infty}g(x)e^{-2\pi ix\psi}dx.$$

(B7)

[80] Multiplying both parts of the equation with $e^{-2\pi ix\psi}$ and integrating over x yields

$$\frac{\partial\hat{g}(\psi,y^*,t)}{\partial t}=-2D\psi^2\hat{g}(\psi,y^*,t)-4k\overline{A}(t)\hat{g}(\psi,y^*,t),$$

(B8)

subject to the initial condition

$$\hat{g}(\psi,y^*,0)=\sigma^2 le^{-2\pi iy^*\psi}.$$

(B9)

[81] The solution of this equation is

$$\hat{g}(\psi, y^*, t) = \sigma^2 l e^{-2\pi i y^* \psi} e^{-2D\psi^2 t - 4k \int_0^t \overline{A}(t')dt'} \qquad (B10)$$

[82] The inverse Fourier transform is

$$g(x, y^*, t) = \sigma^2 l \int_{-\infty}^{+\infty} e^{-2\pi i y^* \psi} e^{-2D\psi^2 t - 4k \int_0^t \overline{A}(t')dt'} e^{2\pi i x \psi} d\psi, \qquad (B11)$$

or

$$g(x, y^*, t) = \frac{\sigma^2 l}{\sqrt{8\pi Dt}} \exp\left[-\frac{(x - y^*)^2}{8Dt} - 4k \int_0^t A(t')dt' \right], \qquad (B12)$$

$$g(y^*, y^*, t) = \frac{\sigma^2 l}{\sqrt{8\pi Dt}} e^{-4k \int_0^t \overline{A}(t')dt'}. \qquad (B13)$$

[83] The covariance is found as

$$\overline{A'B'}(t) = \frac{1}{2}(f(y^*, y^*, t) + g(y^*, y^*, t)) = \frac{\sigma^2 l}{2\sqrt{8\pi Dt}} \left[e^{-4k \int_0^t \overline{A}(t')dt'} - 1 \right]. \qquad (B14)$$

[84] Substituting this into the equation for the average concentration yields

$$\frac{\partial \overline{A}}{\partial t} = -k\overline{A}^2 - k\frac{\sigma^2 l}{2\sqrt{8\pi Dt}} \left[e^{-4k \int_0^t \overline{A}(t')dt'} - 1 \right]. \qquad (B15)$$

[85] The autocovariance of A is

$$\overline{A'(x,t)A'(y^*,t)} = \frac{1}{2}\frac{\sigma^2 l}{\sqrt{8\pi Dt}} \left[\exp\left(-4k \int_0^t A(t')dt' \right) + 1 \right]$$
$$\times \exp\left(-\frac{(x-y^*)^2}{8Dt} \right), \qquad (B16)$$

and the variance of the concentration is equal to

$$\overline{A'A'}(t) = \overline{A'(y^*,t)A'(y^*,t)} = \frac{\sigma^2 l}{2\sqrt{8\pi Dt}} \left[e^{-4k \int_0^t \overline{A}(t')dt'} + 1 \right]. \qquad (B17)$$

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