

Reduced models of chemical reaction in chaotic flows

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We describe and evaluate two reduced models for nonlinear chemical reactions in a chaotic laminar flow. Each model involves two separate steps to compute the chemical composition at a given location and time. The “manifold tracking model” first tracks backwards in time a segment of the stable manifold of the requisite point. This then provides a sample of the initial conditions appropriate for the second step, which requires solving one-dimensional problems for the reaction in Lagrangian coordinates. By contrast, the first step of the “branching trajectories model” simulates both the advection and diffusion of fluid particles that terminate at the appropriate point; the chemical reaction equations are then solved along each of the branched trajectories in a second step. Results from each model are compared with full numerical simulations of the reaction processes in a chaotic laminar flow. © 2006 American Institute of Physics. [DOI: 10.1063/1.2182373]

I. INTRODUCTION

In the present work we consider the evolution of a multicomponent reaction in a laminar flow. If the chemicals are carried by an incompressible flow field $\mathbf{u}(t, \mathbf{x})$ in the region Ω , the process is described by a system of advection-diffusion-reaction equations of the form

$$\frac{\partial C_i}{\partial t} + \mathbf{u} \cdot \nabla C_i - D \nabla^2 C_i = \sum_j \nu_{ij} Y_j, \quad (1)$$

where C_i is the molar concentration of the i th component, D is the coefficient of diffusion (assumed equal for all species), ν_{ij} is a stoichiometric coefficient (with an appropriate sign) for the i th component in the j th reaction, and Y_j is the reaction rate (in moles per cubic centimeter seconds) of the j th reaction. We assume that the chemical composition and the reaction process do not affect the flow field \mathbf{u} . Using the characteristic length L , characteristic velocity U , characteristic concentration C , and characteristic reaction rate Y we introduce the following nondimensionalization of the variables: $\mathbf{u}' = \mathbf{u}/U$, $\mathbf{x}' = \mathbf{x}/L$, $t' = tU/L$, $C'_i = C_i/C$, $Y'_j = Y_j/Y$. After some algebra, Eq. (1) yields

$$\frac{\partial C'_i}{\partial t'} + \mathbf{u}' \cdot \nabla' C'_i - \frac{1}{\text{Pe}} \nabla'^2 C'_i = \frac{\text{Da}}{\text{Pe}} \sum_j \nu_{ij} Y'_j, \quad (2)$$

where the Damköhler and Péclet numbers are, respectively, $\text{Da} = YL^2/DC$ and $\text{Pe} = LU/D$. Hereinafter all variables are dimensionless and the primes are removed for the sake of simplicity.

Our focus on laminar flows is of particular relevance to microfluidic devices, which are mostly operated at low Reynolds numbers, but at high Péclet numbers.¹ Then, if the reactants are initially segregated, efficient organization of the

reaction process becomes a nontrivial problem, because the two most powerful mixing mechanisms—turbulence and molecular diffusion—are, respectively, infeasible and inefficient under these conditions. The route to effective mixing is then a chaotic laminar flow; such flows have, over the last 20 years or so, been shown to provide the paradigm for effective mixing at small scales.^{2–4}

At the initial stages of chaotic mixing, the streams to be mixed are advected and stretched by the flow and the interface between the components grows exponentially with time. A complicated structure of thin striations of the components then emerges in the mixing zone. Since the flow is incompressible, stretching in one direction means contraction in at least one other direction; the striation thickness and separation decrease, until diffusion smooths out the deviations of the concentration. These observations give rise to the so-called “lamellar” model,^{5–7} which replaces the full three-dimensional problem by a one-dimensional problem along the direction of contraction, i.e., the advection-diffusion-reaction equations in a chaotic flow are approximated by a corresponding one-dimensional problem in Lagrangian coordinates along the stable manifold of a fluid element.^{8–12}

In its simplest manifestations, the lamellar model has three significant shortcomings: first, that it is generally implemented using a single, averaged rate of contraction (rather than the distribution of contraction rates that are present in practice); second, that it is often applied using a single striation thickness, representing a balance between compression by the flow and diffusion, and, third, that it has no straightforward mechanism for the continuous regeneration of the lamellar structure through folding by the flow. To some extent, the first two difficulties may be overcome by posing nonuniform contraction-rate and striation-thickness distributions, and the third by a device such as the periodic application of a “baker map” to create new striations.¹³ An evaluation of some lamellar models, including the Lagrangian

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ian filament slice model,^{14,15} has been given by one of us recently,¹⁶ by comparing yields for a competitive-consecutive chemical reaction according to full numerical simulations with corresponding yields from the models; in summary, the models tend to perform poorly at large Péclet number.

Of course, it would be misleading to suggest that all lamellar models are necessarily crude. Indeed, considerable progress has been made recently in developing more sophisticated models based on lamellar structures: for example, Tél *et al.*¹⁷ review this progress, and show how “effective rate equations” may be derived by considering the fractal distribution of striation widths. Such an approach gives the possibility of accommodating such subtle influences on the progress of the reaction as the order in which the filaments are arranged,^{18–20} as well as the distribution of their widths. However, our purpose here is neither to review the state of the art in lamellar models (see Ref. 17) nor to evaluate existing lamellar models.

In the present investigation we use the idea of backward tracking of a fluid element²¹ to develop two sophisticated reduced models of a chaotic advection-diffusion-reaction process. The methods may be summarized as follows; in each case, we wish to determine the chemical composition of a fluid element at a given location at a given time. The first stage of the “manifold tracking model” is the calculation of a preimage of points in the neighborhood of the fluid element by integration of the equations of motion backwards in time to $t=0$. In the second stage, the calculated preimage is tracked forwards in time and the advection-diffusion-reaction equations (1) are solved approximately in Lagrangian coordinates. It is at this stage that the main simplifications are made, which significantly reduce the computation time but introduce an error into the solution. A variant, the “branching trajectories model,” again separates the problem into two distinct stages, but now the first stage accounts for both advection and diffusion, whereas the second concerns the course of the chemical reactions. In order to characterize the errors in each model, we compare the approximate solution obtained using both manifold tracking and branching trajectories with numerical simulations of the full advection-diffusion-reaction equations, and thereby evaluate the two techniques.

II. REDUCED MODELS

In this section we describe two reduced models for (2). The models will be applied here to a system that is originally two-dimensional in space, resulting in a one-dimensional approximation, although they can readily be extended to a three-dimensional problem.

The essence of the first model follows from the commonly recognized feature of a chaotic flow, that in general two neighboring fluid particles separate from one another exponentially in time. This general divergence of neighboring particles has the consequence, in an incompressible flow, that certain pairs of particles *approach* one another exponentially in time. The set of fluid particles that approach a given particle \mathbf{x}^0 as the flow evolves over time is the *stable manifold* of \mathbf{x}^0 . Likewise, the *unstable manifold* of \mathbf{x}^0 is the set of

fluid particles approaching \mathbf{x}^0 in backwards time. Since there is compression along the stable manifold and stretching along the unstable manifold, the gradients of concentration become sharp in the former direction and smooth in the latter. Thus molecular transport becomes important only along the stable manifold and the advection-diffusion-reaction equations can be approximated by a one-dimensional problem in Lagrangian coordinates.^{8–12}

The numerical realization of this approach is as follows. Our aim is to compute the chemical composition at a given point \mathbf{x}^0 at the end of the mixing process, $t=t_{\text{final}}$. To do so, we choose a small line segment L^0 tangent to the stable manifold of \mathbf{x}^0 and distribute along this line segment a small number of points: \mathbf{X}_j (for $j=0, \dots, n^0$, say). These points are then tracked backwards in time by integrating the differential equation

$$\frac{d\mathbf{X}_j(\tau)}{d\tau} = -\mathbf{u}(t_{\text{final}} - \tau, \mathbf{X}_j),$$

where $\tau=t_{\text{final}}-t$, from $\tau=0$ to $\tau=t_{\text{final}}$ (i.e., back to $t=0$). Note that this calculation involves only the advection of “perfect” fluid particles (there is no diffusion at this stage). In this (backwards) chaotic flow, the initially small segment L^0 stretches exponentially and ultimately spans the entire mixing region. A key ingredient of the proposed method is maintaining resolution of the evolving line segment, which is accomplished through the use of an adaptive tracking algorithm that is accurate and not too computationally expensive;^{22–24} note that at the end of the backwards tracking, if the line is represented by N^0 points then $N^0 \gg n^0$. Once the line segment L^0 (which serves as a proxy for the stable manifold of \mathbf{x}^0) has been mapped back to $t=0$, it provides a sample of the initial conditions for points that will lie close to \mathbf{x}^0 at t_{final} .

We next solve a one-dimensional advection-diffusion-reaction problem in forwards time along this evolving stable manifold. To do so, we retrace the forwards path of the manifold by integrating $d\mathbf{X}_j(t)/dt=\mathbf{u}(t, \mathbf{X}_j)$ (now for $j=0, \dots, N^0$), and approximating Eq. (2) with

$$\frac{\partial C_i}{\partial t} - \frac{1}{\text{Pe}} \frac{\partial^2 C_i}{\partial s^2} = \frac{\text{Da}}{\text{Pe}} \sum_j \nu_{ij} Y_j, \quad (3)$$

where s is the (time-dependent) arc length along the stable manifold. The initial condition for (3) at each point is simply the corresponding initial condition for the full problem at that point (generally we suppose that the full problem has a segregated initial state). Due to its one-dimensional nature, Eq. (3) can easily be solved by a tridiagonal solver. The approximations leading to Eq. (3) are accurate up to order $\text{Pe}^{-1/2}$ for both two- and three-dimensional flows.¹¹ Finally, the concentration $C_i(t_{\text{final}}, \mathbf{x}^0)$ is estimated as the mean concentration at each of the X_j at $t=t_{\text{final}}$.

In order to estimate the quality of the chaotic mixing one may randomly distribute the points \mathbf{x}^0 over the flow region in a batch mixer or at the outlet of a continuous-flow mixer and calculate the corresponding approximate concentration distributions at these points.

Although predictions from the above-mentioned model will be compared with the results from direct simulation in the next section, one can point out the main drawbacks of this method without doing any calculations. For example, at the beginning of the mixing process the stable manifold is not necessarily orthogonal to the interface between the reactants, and so, initially, the method *underestimates* the diffusive flux across the interface. Furthermore, as the mixing proceeds, the stable manifold contracts exponentially with time due to the chaotic nature of the flow field. Thus the thickness of the striations decreases exponentially, which implies a *superexponential* decay of the concentration variation along the stable manifold. Since the proposed method ignores the variations in the other directions (which decrease much more slowly¹¹), the method *overestimates* the mixing rate at the end of the process.

Motivated by these considerations, we propose a second model, which employs the same idea of backward tracking but treats the transport exactly (at the expense of a consequent bias in the reaction rate). Again we suppose that we wish to determine the chemical composition at a point \mathbf{x}^0 , at a time t , but now we split Eq. (2) into separate transport and reaction steps rather differently. First we use the (advection-diffusion) transport equation

$$\frac{\partial C_i}{\partial t} + \mathbf{u} \cdot \nabla C_i - \frac{1}{\text{Pe}} \nabla^2 C_i = 0 \quad (4)$$

to generate (among other things) an appropriate sample of initial conditions; then we follow the chemical reactions forwards in time according to

$$\frac{dC_i}{dt} = \frac{\text{Da}}{\text{Pe}} \sum_j \nu_{ij} Y_j. \quad (5)$$

Now let us consider the first of these steps in more detail. If one considers Eq. (4) as a system of forward Kolmogorov or Fokker-Planck equations for a stochastic process (and use the fact that $\nabla \cdot \mathbf{u} = 0$), then the backward Kolmogorov equations of the same process read

$$\frac{\partial C_i}{\partial \tau} - \mathbf{u} \cdot \nabla C_i - \frac{1}{\text{Pe}} \nabla^2 C_i = 0. \quad (6)$$

So in order to calculate the concentrations at a point \mathbf{x}^0 (the “root”) at time t we track N tracer particles backwards in time according to the stochastic differential equation that corresponds to Eq. (6), i.e.,

$$d\mathbf{x}(\tau) = -\mathbf{u}(t - \tau, \mathbf{x}) d\tau + \sqrt{2/\text{Pe}} d\mathbf{W}, \quad (7)$$

where $d\mathbf{W}$ is the increment of a vector Wiener process with independent components and unit dispersion; all of the N tracer particles “start” at \mathbf{x}^0 at $\tau=0$. The Monte Carlo estimation of the concentration then reads

$$C_i(t, \mathbf{x}^0) = \frac{1}{N} \sum_{k=1}^N C_i(t - \Delta t, \mathbf{x}_k(t - \Delta t)), \quad (8)$$

where $\mathbf{x}_k(t - \Delta t)$ is an end point of k th realization of the diffusion process (7) over a short time interval from t to $t - \Delta t$. We then take further (backwards) steps of length Δt , at each

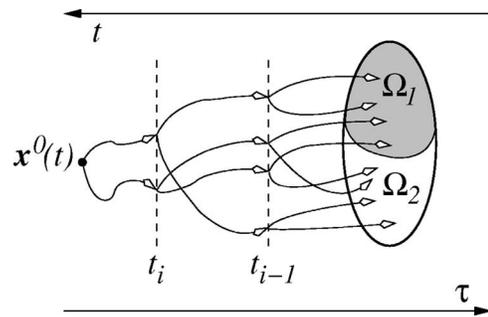


FIG. 1. Schematic view of the branching trajectories method. Transport and reaction processes are considered separately on short time intervals Δt (such as between t_i and t_{i-1}). The backwards evolution of a point $\mathbf{x}^0(t)$ (the “root”) is simulated by solving the stochastic differential equation (7); here each realization uses $N=2$ points. The flow domain Ω is partitioned into two components, Ω_1 and Ω_2 , with different initial concentrations on each. The chemical reactions are tracked from the initial state to time t using (5).

stage splitting each trajectory into N branches, as is shown schematically in Fig. 1 for the case $N=2$. In this way we generate a large number of points which sample the domain Ω at $t=0$, all corresponding to realizations of the advection-diffusion process terminating at \mathbf{x}^0 at time t .

In the second (reaction) stage we solve Eq. (5) along each branch from the top (corresponding to $t=0$) to the root (time t) of the resulting tree. Where N branches join at their “mother” branch we mix (i.e., take the mean of) the corresponding concentrations before proceeding further towards the root.

Certainly, the number of trajectories in this method scales as $N^{t/\Delta t}$ which makes a proper implementation of this method prohibitively time consuming. In order to complete calculations in reasonable time on a desktop personal computer we reduce the number of branches at each branching point to the minimum possible number, i.e., $N=2$, and use time intervals Δt which are not small in comparison to the characteristic times of the process. These simplifications do not affect the transport, i.e., no bias is introduced in the absence of the reaction. However, there is an error introduced into the reaction term, which can be illustrated using the example of a bimolecular reaction $A+B \rightarrow P$. If one represents the corresponding concentrations as the sum of mean and fluctuating parts, $C_i = \langle C_i \rangle + C_i'$, the mean reaction rate predicted by the method is $\langle AB \rangle = \langle A \rangle \langle B \rangle + \langle A'B' \rangle$, where the last term is the error. If the reactants are initially segregated, the correlation between them is negative and the proposed method underestimates the reaction rate.

III. RESULTS AND DISCUSSION

In evaluating the models described previously, we consider the evolution of the two-stage competitive-consecutive reaction^{16,25}



taking place in the (two-dimensional) “sine flow.”²⁶ The governing advection-diffusion-reaction equations corresponding to (9) are then

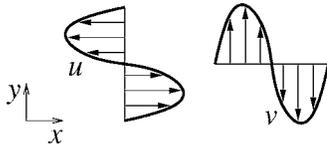


FIG. 2. Sine flow (14): flow field during first (left-hand side) and second (right-hand side) half-period.

$$\frac{\partial A}{\partial t} + \mathbf{u} \cdot \nabla A - \text{Pe}^{-1} \nabla^2 A = -k_1 AB, \quad (10)$$

$$\frac{\partial B}{\partial t} + \mathbf{u} \cdot \nabla B - \text{Pe}^{-1} \nabla^2 B = -k_1 AB - k_2 BR, \quad (11)$$

$$\frac{\partial R}{\partial t} + \mathbf{u} \cdot \nabla R - \text{Pe}^{-1} \nabla^2 R = k_1 AB - k_2 BR, \quad (12)$$

$$\frac{\partial S}{\partial t} + \mathbf{u} \cdot \nabla S - \text{Pe}^{-1} \nabla^2 S = k_2 BR. \quad (13)$$

The dimensionless fluid domain is a square box $0 \leq x, y \leq 1$ with sides $x=0$ and $x=1$ identified (so that fluid passing through one side reenters through the other), and similarly for the sides $y=0$ and $y=1$. The flow field is assumed to be time-periodic, with period T ; then²⁶

$$\mathbf{u} = \begin{cases} (\sin 2\pi y, 0), & mT \leq t < (m+1/2)T, \\ (0, \sin 2\pi x), & (m+1/2)T \leq t < (m+1)T, \end{cases} \quad (14)$$

for $m=0, 1, 2, \dots$ —see Fig. 2. We examine the “globally chaotic” case $T=1.6$, for which there are no large nonchaotic islands in the flow. The segregated initial state is given by

$$(A(x, y, 0), B(x, y, 0)) = \begin{cases} (A_0, 0), & 0 \leq x < 1/2, \\ (0, B_0), & 1/2 \leq x < 1, \end{cases} \quad (15)$$

where $A_0=B_0=2$, and $R(x, y, 0)=S(x, y, 0)=0$ for all x and y .

Governing equations (10)–(13) are solved pseudospectrally,^{27–29} with exponential time differencing,³⁰ in order to permit high accuracy, even at large Pe . The method is chosen over alternatives, such as finite-difference or finite-element methods, principally because it does not suffer from the spurious numerical diffusion associated with these alternative methods.²⁸ Details are described elsewhere,¹⁶ as are our checks on the accuracy of the scheme (see also Ref. 28). Figure 3 shows the spatial distribution of A , B , and R after 1, 2, 3, and 4 periods of the flow for $k_1=1$, $k_2=0.1$, and $\text{Pe}=10^5$. Plots of the waste product S are not shown.

Calculations using the reduced models are carried out in a manner similar to that described in Ref. 21. Since the chosen flow field is a good mixer, it is enough, for practical purposes, to estimate the extent of the reaction using only a small number of randomly generated points. For both methods the number of tracers used for the first, backward tracking step is limited to 10^6 . For the manifold tracking method, if at any stage the preimage of the stable manifold requires a greater number of points for adequate resolution, we randomly select from it a finite segment and continue tracking

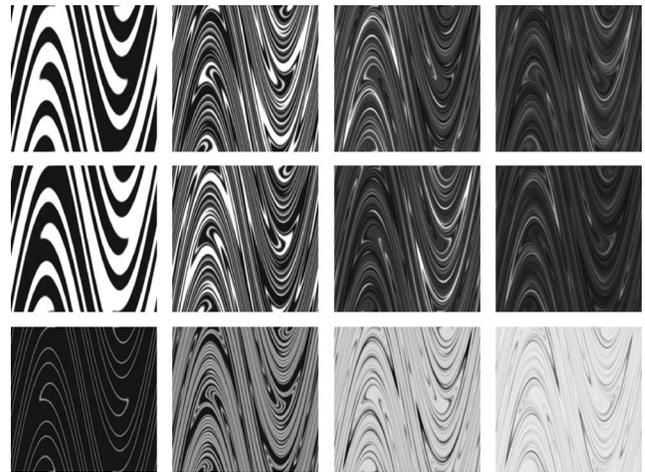


FIG. 3. Grayscale plots of $A(x, y, t)$ (top row), $B(x, y, t)$ (middle row), and $R(x, y, t)$ (bottom row) at times $t=1.6, 3.2, 4.8$, and 6.4 (i.e., after 1, 2, 3, and 4 periods of the flow). For plots of A and B , black and white correspond, respectively, to concentrations of 0 and 2; for the plot of R , these minimum and maximum concentrations are 0 and $R(x, y, \infty) \approx 0.73$.

only this part of the manifold. For the method of branching trajectories, the time between two successive branchings is set equal to one half of the period of the flow; thus the total number of tracers does not exceed 10^6 . In either case, the entire procedure takes only several minutes on a Pentium 4 processor running at 2.4 GHz (corresponding well-resolved simulations of the full two-dimensional problem, by contrast, take several days at the largest Péclet numbers).

We have carried out simulations for $\text{Pe} = 10^3, 10^4$, and 10^5 and for two sets of reaction constants: $k_1=1, k_2=0.1$ and $k_1=10, k_2=1$ (in the former set the advective and reactive time scales are comparable; in the latter the reaction is relatively fast). The results of the calculations are presented in Fig. 4. To compare the results using the reduced methods with the full two-dimensional simulations we plot spatially averaged concentrations of the products, $\langle R \rangle$ and $\langle S \rangle$; then corresponding concentrations $\langle A \rangle$ and $\langle B \rangle$ follow automatically from the material balance. Initially the method of manifold tracking underestimates the mixing rate and, as a result, the yield of the reaction. In the later stages of the process the method overpredicts diffusion along the manifold as a result of its exponential contraction. Thus the method overestimates the overall mixing rate and has very low sensitivity to variation in Pe . The method of branching trajectories is more sensitive to variations in the diffusivity but still underestimates the effect of Pe on the final yield of the product R . The main drawback of the latter method is the bias introduced in the reaction term when we replace the mean values of concentrations in Eq. (5) by their current (random) values. Since the reactants are initially segregated, the negative correlation between A and B reduces the reaction rate, as argued previously. Therefore, the species which are “under-reacted” at the beginning react at the later, better mixed stage, which in turn increases the final yield of the product R .

In conclusion, we have presented two reduced models to estimate the extent of chemical reactions in laminar chaotic

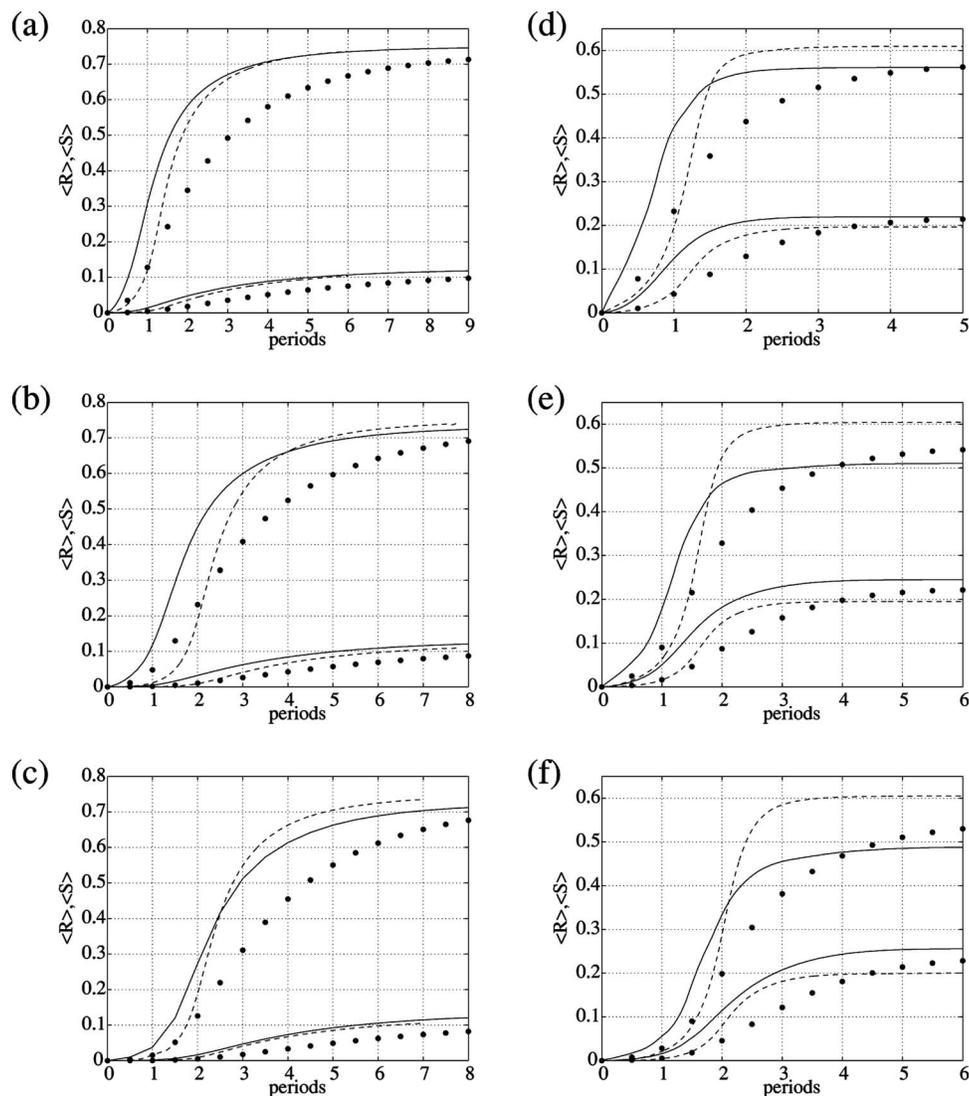


FIG. 4. Results of direct numerical simulation (solid line), manifold tracking (dashed line) and method of branching trajectories (circles) for $k_1=1, k_2=0.1$ (left-hand column) and $k_1=10, k_2=1$ (right-hand column). Concentrations of R (upper lines) and S (lower lines) for $Pe=10^3, 10^4$, and 10^5 , respectively, from top to bottom.

flows. The models are based on the idea of the backward tracking of a fluid element surrounding a randomly chosen point, and are not limited to a single reaction, nor to linear reactions. We have compared predictions using the models with results of full two-dimensional simulations. Although each reduced model is in reasonable quantitative agreement with the full simulations, the approximate nature of the models introduces a bias into either the transport or the reaction term.

We have previously presented results for a batch mixer (albeit in a rather unphysical spatially periodic geometry), but reaction in a continuous flow mixer can be estimated in a similar manner, as follows. If the reactants are fed into the mixer through two separated inlets and the product leaves the system through an outlet, test points should be distributed at the outlet with a probability proportional to the mass flow at these points. The tracers are first tracked in the counterflow direction, with those tracers reaching a specific inlet stream constituting initial conditions for the subsequent down-flow reaction step.

In the past many reduced lamellar models have been proposed and investigated (see Refs. 5, 6, 14, 15, and 18–20

for a sample). These models have two major uncertainties, namely the way in which the filaments are arranged and the compression rate across the interface. In real chaotic flows the stretching/compression rate and striation thicknesses are highly nonuniform and it is impossible to adjust an “effective” compression rate and striation thickness distribution for the reduced model. The methods proposed in the present work are free of these uncertainties. The separation rate of two neighboring points is not postulated, but is instead dictated by the flow field. Our comparison of results using the reduced methods with the direct two-dimensional simulations shows how far we can advance with a (sophisticated) one-dimensional model. The error observed in the present work cannot be associated with an incorrect compression rate or arrangement of the lamellae, rather it must be directly attributed to the one-dimensional nature of the models.

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