# Evolution of a Lamellar System with Diffusion and Reaction: A Scaling Approach

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We study, by means of computer simulation and scaling analysis, the time evolution of one-dimensional arrays of reactive lamellae described by various initial striation thickness distributions. An infinitely fast reaction $A+B \rightarrow 2P$ occurs at the junctures of the lamellae. As the reaction proceeds thin striations are eaten by thick neighboring striations altering the distribution. The system converges toward a universal striation thickness distribution.

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Complex lamellar structures, consisting of stretched and folded striations, are generated during the mixing of fluids with similar properties. A particularly striking example involves the stretching and folding of passive tracers in two-dimensional chaotic flows, such as in the experiment reproduced in Fig. 1.[1] In many cases of interest, such as combustion[2] or polymerizations,[3] the striations interdiffuse and undergo complex chemical reactions, and the central question is to predict the value of the overall rate of reaction. The simplest types of analyses assume that the concentration of reacting species is uniform; however, in the case of very fast reactions, diffusion dominates the picture, and it becomes necessary to account for fluid mechanical mixing and the distribution of striations in an explicit way. One possibility is to use a *lamellar model*:[4] At time $t=0$ the reactants are arranged in a one-dimensional lamellar structure (bottom of Fig. 2) which is generated by the fluid mechanics. Fluid motions stretch the striations, reducing the diffusional distances and increasing the contact area for interdiffusion; in the case of infinitely fast reactions, the reaction occurs at the interfaces between striations.

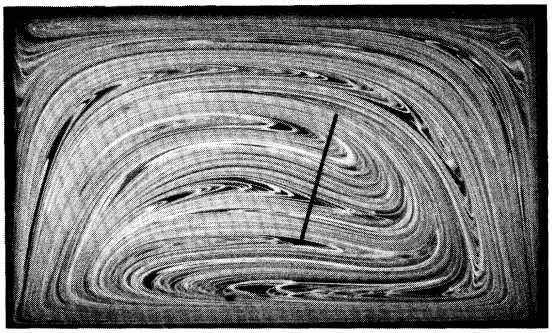

FIG. 1. Photograph showing typical structures produced by chaotic mixing in a cavity flow apparatus under creeping flow conditions (Ref. 1). Two fluids of about the same viscosity and negligible interfacial tension are mixed by moving the top and bottom walls of the cavity in a time-periodic fashion. A lamellar structure is generated, composed of thousands of striations of distributed thicknesses. The line represents a cut across the striations such as the one represented at the bottom of Fig. 2.

Until now analyses considered situations with the same thickness; in fact, the problem consisting of distributed striation thicknesses was considered nearly intractable.[5] In this Letter we present the results of a simple scaling analysis and the confirmation of the predictions by means of a novel numerical procedure capable of handling a large number of striations (details on the numerical method as well as additional results will be presented at a later date[6]). We believe that this is the first time that scaling behavior has been observed in the context of this class of diffusion-reaction systems. Other diffusion-reaction problems leading to scaling solutions have been studied by Kang and Redner;[7] in these cases, however, the systems were "well mixed" to start with and became unmixed as a result of magnification of concentration fluctuations.

The system consists of two reactants, $A$ and $B$, dissolved in a common solvent, and placed in initially alternate striations in a lamellar system (Fig. 2). Both reactants diffuse to the interfaces between the lamellae, where they undergo an infinitely fast reactions. The diffusion coefficient of both species, $D$, is the same ($D=1$). The thickness of the striations is distributed; the *striation thickness distribution* (STD) is given by

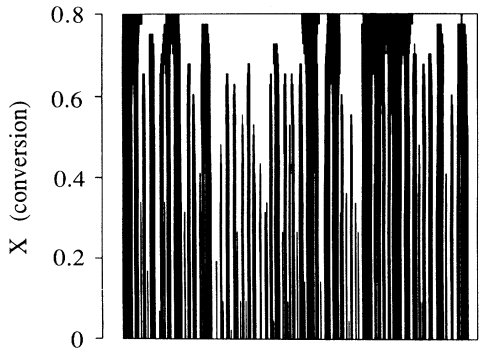


FIG. 2. Evolution of a lamellar system; the initial condition corresponds to the bottom of the figure. The conversion $X$ increases linearly along the vertical axes, $X=0$ at the bottom and $X=0.80$ at the top. As $X$ increases, thin lamellae are eaten by larger neighbors, the total number of lamellae decreases, and the mean thickness $S$ increases.

$f(s,t)$, that is, the frequency of occurrence of lamellae of thickness $s$ at time $t$.

The initial STD, $f(s,0)=dn/ds$, where $dn$ is the number of lamellae of thickness between $s$ and $s+ds$, is the main parameter in the system. From the prescribed $f(s,0)$, the thickness of the lamella are generated as follows. If each lamella is identified in increasing thickness, the thickness increment between two adjacent size lamella is given by

$$ds=dn/f(s,0)=1/f(s,0), \tag{1}$$

where we take $dn\equiv 1$. We obtain a set $\{s\}$ of values of $s$ by recursive application of Eq. (1), where $s\in\mathbb{R}$. However, because the measure of the thickness of a lamella is the number of equally spaced nodes used to represent it in a finite-difference discretization, only integer values of $s$ can be allowed. We substitute each value of $s$ in $\{s\}$ by its nearest integer $s'$, obtaining a new set $\{s'\}$ with $s'\in\mathbb{Z}^+$. The continuous distribution $f(s,0)$ is approximated by a discrete distribution $n(s',0)$, obtained by counting the number of lamellae of thickness $s'$ that are present in $\{s'\}$. We place additional requirements on the initial distribution: $\sum_0^\infty n(s',0)=600$ lamellae, and $\sum_0^\infty s'n(s',0)=150000$ nodes. The initial value of the mean striation thickness, $S(0)$, is therefore $S(0)=[\sum_0^\infty s'n(s',0)]/[\sum_0^\infty n(s',0)]=250$ nodes. We generate two identical lists, one for lamellae of $A$, $\{s'_A\}$, and the other for lamellae of $B$, $\{s'_B\}$, thus making the total number of lamellae equal to 1200 and the total size of the system equal to 300000 nodes. *Each list is randomly reordered.* Subsequently, we build a master list by taking the first lamella from the $A$ list, then the first lamella from the $B$ list, then the second lamella from the $A$ list, and so on. In this way, the thicknesses of the lamellae obey $f(s,0)$, but the thicknesses of neighbors are uncorrelated. At time $t=0$, nodes in $A$ lamellae are assigned the values of concentration $c_A=1$, $c_B=0$, and nodes in $B$ lamellae are assigned $c_A=0$, $c_B=1$. The amounts of $A$ and $B$ are identical in the initial distribution; moreover, due to the stoichiometry of the reaction, they remain equal to each other for all times.

The core of the simulation consists of solving the diffusion equation

$$\partial c/\partial t=D\,\partial^2 c/\partial z^2, \tag{2}$$

where $c(z,t)$ is the concentration of either $A$ or $B$ at a given position and time, and $z$ is the spatial coordinate in the direction transverse to the boundaries of the lamellae. An infinitely fast reaction occurs at the interfaces between striations [i.e., $s^2/D\gg$ (characteristic time of reaction)]. Under these conditions, the reaction is actually a boundary condition for each lamella and at every boundary,

$$c_A=c_B=0, \tag{3a}$$

$$\partial c_A/\partial z\,|_{A\text{ side}}=-\partial c_B/\partial z\,|_{B\text{ side}}. \tag{3b}$$

The main difficulty is that, due to the reaction, the boundaries between lamellae move, the thicknesses of the lamellae change, and the implementation of an effective discretization scheme becomes rather complicated. In order to overcome this problem we use the following approach, based on the fractional-step method:[8] Given the concentration field at time $t$, we solve the diffusion equation for the entire domain for $t'=t+\Delta t$ without considering the reaction [we use an explicit, constant-increment, finite-difference scheme with a coefficient $\alpha=D\Delta t/(\Delta z)^2=1/6$; for this value of $\alpha$ the error terms are fourth order in $dz$ [9]]. After that, we compute the effects of the reaction by simple bookkeeping: If $\Delta t$ is small enough, the violation of the simultaneity of the diffusion and the reaction processes is relatively unimportant. Boundaries are the locations where $c_A=c_B=0$, and their positions are automatically generated by the algorithm.

We check the performance of the code in three ways: First, we compare the values of the concentration gradient of $A$ and $B$ at opposite sides of each boundary. The boundary condition (3b) is closely verified; the relative differences in the values of the concentration gradients of $A$ and $B$ are smaller than 0.01 for all lamellae larger than 20 nodes. Second, we simulate a constant-thickness system (all the lamellae are of the same thickness), for which a series solution for the conversion as a function of time is available.[5] We found an excellent agreement between both methods; the relative errors in the conversion $X$ $[=1-\int c(z,t)dz/\int c(z,0)dz]$ are smaller than 0.001 for all values in the interval $0<X<0.95$. The third test consists of computing the evolution of the thickness of a striation surrounded by much larger neighbors. A comparison between the analytical solution and the simulation show that the relative errors in thicknesses are smaller than 0.01 for all lamellae with initial thickness larger than 20 nodes.

The dispersion in striation thickness has a deep impact on the dynamics of the system. Figure 2 shows the time evolution of a typical system. The figure is created as follows: We take snapshots of the system at different values of $X$, "cut" thin horizontal strips from each snapshot, and pile the strips up in increasing conversion order. Horizontal cuts of Fig. 2 correspond to states of the system at different conversions (times). The conversion $X$ increases linearly along the vertical axis. As $X$ increases, the total number of lamellae decreases, and the mean striation thickness $S$ increases. At the top of the figure, corresponding to $X=0.80$, only 16 of the original 200 lamellae survive.

The results presented in this paper correspond to a selection of three extreme cases of initial conditions: A random initial STD in which all thicknesses have the same frequency, a normal initial STD with standard deviation of 125 nodes, and a linearly decreasing initial STD. We run ten simulations for the random and normal cases, and forty for the linear case. Different simu-

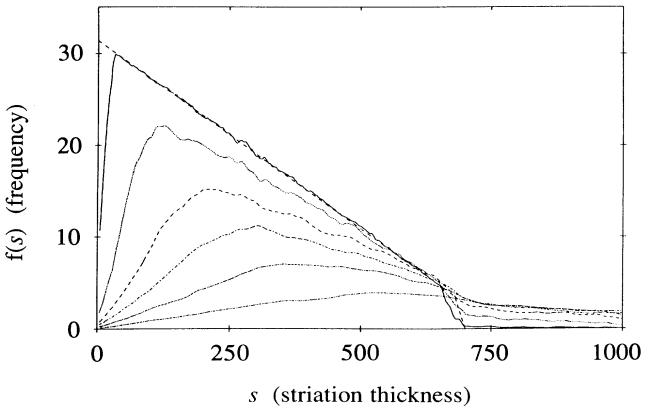


FIG. 3. Evolution of a system with a linearly decreasing initial striation thickness distribution (STD). The system is initially composed of 1200 lamellae with thicknesses distributed with a frequency $f(s,0)=a-bs$, where $a=3.2386$ and $b=0.004266$. The STD, which is shown for $X(t)=0$, 0.05, 0.20, 0.35, 0.45, 0.55, and 0.65, evolves into a mildly peaked shape that also appears at moderate to large $X$ for many other initial STD's.

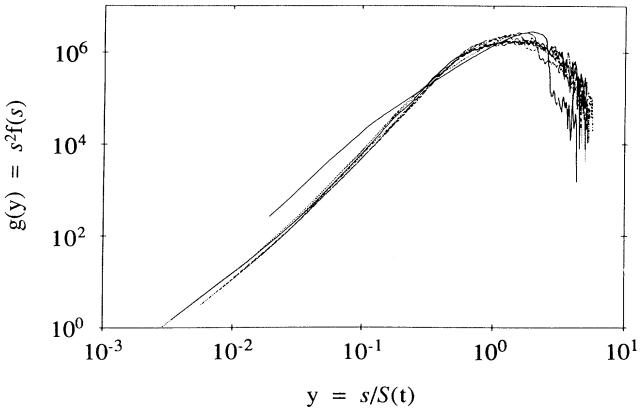


FIG. 4. The scaling behavior that is present in the evolution of the STD. The distributions in Fig. 3 are plotted as $g(y)=s^2f(s,t)$ as a function of $y=s/S(t)$, where $S(t)$ is the mean thickness at time $t$. All curves collapse into a single, master curve, except those corresponding to very low conversions ($X<0.35$). The master curve is the scaling solution for the STD. The large amount of scattering that occurs at large conversions and at large values of $s/S(t)$ are due to the small values of $f(s,t)$ under those conditions. The results are the average of forty simulations.

lations corresponding to the same initial STD have the same list of thicknesses $\{s'\}$ ordered in a different random sequence. The results we present in this Letter are the average of all the simulations for each initial STD.

Figure 3 shows that the STD suffers profound changes as $X$ increases (and $t$ increases). Thin lamellae are eaten by thick lamellae, their frequency diminishes, and a linear frequency region develops for small values of $s$. Large lamellae are generated in the process and the distributions develop a tail in the large-$s$ region. In spite of the differences in initial conditions, the STD in all systems evolves into a characteristic shape that is shown in Fig. 3. More extensive calculations with other initial STD's show the same, mildly peaked shape at moderate to large conversions.[6]

The implication of these results is that the system evolves into a particular STD regardless of the initial conditions. If this is indeed true, as systems with different initial conditions achieve this distribution at different values of conversion, time, and mean striation thickness, it then follows that this universal STD should exhibit time invariance in scaled form. We make the hypothesis of the existence of a universal, time-invariant scaling solution for the STD at moderate to large conversions. This hypothesis can be tested by using the same scaling techniques that have been extensively used to describe critical phenomena[10] and aggregation processes.[11,12] We postulate that

$$s^{\theta}f(s,t)=g(s/S(t)), \tag{4}$$

where $g(y)$ is the scaling solution and $y=s/S(t)$ is the scaling argument. Because lamellae grow at the expense of their neighbors, the total size of the system, $M$ $[=\int_0^{\infty}sf(s,t)ds]$, is constant, and it follows that $\theta=2$.[6]

Figure 4 shows the scaled distribution corresponding to a system with a linear initial STD, for different values of $X$ in the interval $X=0$ to $X=0.85$, and $\theta=2$. As the conversion $X$ increases, the scaled STD indeed converges toward a master curve, becoming time invariant. The collapse of the data is good; a similar type of collapse is obtained for the other two initial conditions: For $X>0.35$, any individual curve overlaps the master curve, except in a narrow region at $y\approx 1$. For $X>0.5$, all curves lie nearly on top of each other. The scattering is due to the finite number of lamellae considered; it is larger at high conversions and also at large values of $y$, due to the progressive thinning of the data that occurs at larger values of $X$ and $s$. As conversion increases, the number of surviving lamellae decays very rapidly. Similarly, we can only have a few very thick lamellae at any given time; the frequency $f(s,t)$ is very small for large values of $s$. The scaling solution is the same for the different initial STD's. Figure 5 shows a scaled STD corresponding to each of the initial distributions. The agreement between the curves is very good, demonstrating the universality of the scaling solution.

An exception to this scaling is when all the striations have the same thickness; in such a case the boundaries do not move. The uniform-thickness case is a fixed point of the STD; it remains invariant for all times. However, it is an unstable fixed point: A small amount of dispersion in the striation thickness will produce imbalances and the thicker lamellae in the population will eventually eat the thinner ones, producing more dispersion in the

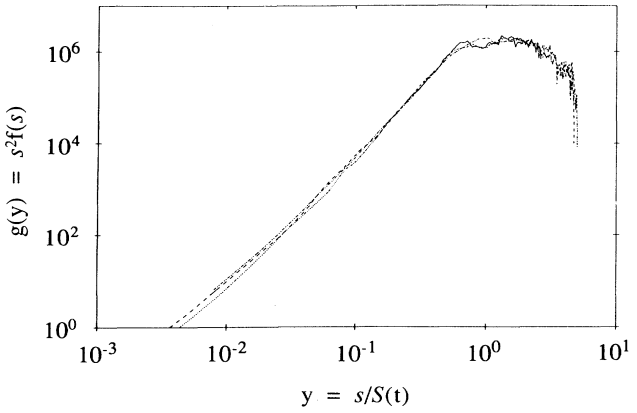


FIG. 5. The scaled STD's for a system with a random initial STD, $X=0.7$, a system with a normal initial STD, $X=0.8$, and a system with a linear initial STD, $X=0.55$. The curves are almost indistinguishable, demonstrating that the scaling solution $g(y)=s^2f(s,t)$ is independent of the initial conditions.

STD.

The scaling behavior has important consequences on the overall dynamics of the process. Detailed calculations show that two different, well characterized kinetic schemes describe the behavior of the system at short and long times. The short-time regime is dominated by diffusion in length scales much smaller than the mean thickness, and therefore it is relatively insensitive to the initial distribution in the striation thickness. The long-time regime, which is fully determined by the scaling behavior, is universal. A matching of the two regimes allows the prediction of the system for all times.[6]

All these effects are magnified if the reaction leads to the formation of a product which is nearly impervious to the diffusion of the reactants, as in the case of polymerizations. However, before such questions can be addressed, we should probably consider simpler issues. One such possibility is incorporating fluid mechanical effects via stretching of the striations and warped times; another is whether or not the scaling behavior persists when the intrinsic speed of the reaction is finite. Work in these directions is in progress.

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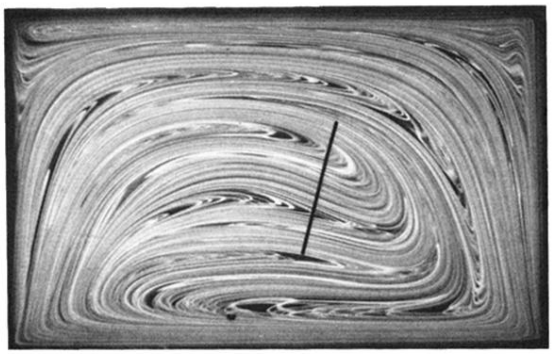

FIG. 1. Photograph showing typical structures produced by chaotic mixing in a cavity flow apparatus under creeping flow conditions (Ref. 1). Two fluids of about the same viscosity and negligible interfacial tension are mixed by moving the top and bottom walls of the cavity in a time-periodic fashion. A lamellar structure is generated, composed of thousands of striations of distributed thicknesses. The line represents a cut across the striations such as the one represented at the bottom of Fig. 2.