Autocatalysis in a shear flow

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We present numerical results indicating that the application of a laminar shear flow to an autocatalytic reaction front can lead to an enhanced rate of reaction. This is a result of the formation of a nonplanar wave front propagating at a speed approaching that of the shear amplitude. [S1063-651X(96)02008-9]

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The isothermal autocatalytic reactions

$$A+nB\rightarrow(n+1)B, \quad (\text{rate})=kab^n,$$

where k is the rate constant for the reaction and a and b are the chemical concentrations, describe processes within a variety of chemical systems. The most studied of these correspond to quadratic ($n=1$) or cubic ($n=2$) autocatalysis or to a mixture of these. Quadratic autocatalysis occurs, for example, in the combustion of hydrogen in oxygen [1], while applications of the cubic autocatalytic process include the iodate-arsenite reaction [2].

One of the most striking phenomena associated with autocatalytic reaction-diffusion systems is their capacity to generate traveling wave fronts of uniform speed and constant concentration profile [3]. The wave front is the transition layer between a region containing only reactant A and a region where only the catalyst B is present and advances as a result of B consuming A. If the diffusion coefficient of the reactant is comparable with that of the autocatalyst, the plane-wave-front solution is stable to perturbations [4]. Such fronts can be readily observed experimentally [5]. If the reactant has a significantly larger diffusivity than the autocatalyst, then the planar fronts are no longer stable. Instead, nonplanar fronts occur, which, depending upon the parameter values, can exhibit constant, oscillatory, or chaotic behavior [4]. Nonplanar fronts can also occur as the result of convective effects associated with temperature and concentration gradients, which arise when, for example, the front is traveling up a vertical tube. It has been shown both theoretically and experimentally that such a front is stable to perturbations if the tube diameter is small enough [6].

The effect of imposed shear flows on these autocatalytic reactions appears to have received little attention. The theoretical studies have concentrated mostly upon the stability of reaction-diffusion-advection systems [7]. In this paper we examine the result of applying a shear flow to these wave fronts. We show that, with the introduction of a shear flow, stable nonaccelerating fronts of permanent form still occur. As with the convective system, the wave fronts are nonplanar. The most important feature is that their speed is of the order of the maximum imposed flow velocity. This means that in regions where the imposed velocity is zero or even negative, the wave front still propagates at approximately the shear velocity amplitude. For large shear amplitudes this behavior of the wave front results in an enormously enhanced rate at which the reactant is consumed.

We focus upon the cubic autocatalytic reaction, although our numerical work suggests that similar nonplanar wave fronts are produced in the quadratic case. We consider a two-dimensional region with boundaries at $y=\pm L$. If a laminar shear flow $U=U(y)$ is applied and the effect of the reaction on the flow is ignored, the system is governed by the equations

$$\frac{\partial a}{\partial t}+U\frac{\partial a}{\partial x}=D_A\nabla^2 a-kab^2,$$
$$\frac{\partial b}{\partial t}+U\frac{\partial b}{\partial x}=D_B\nabla^2 b+kab^2. \tag{1}$$

Here we consider only the case of equal diffusion coefficients and an isotropic reactor. This is a good approximation for isothermal chemical systems, although it is now technically possible, by suitable pretreatment of the reactor, to produce differences in diffusion coefficients of an order of magnitude or greater, even for these simple systems. We employ the dimensionless variables $a'=a/a_0$, $b'=b/a_0$, $x'=x/L$, $y'=y/L$, $t'=D_At/L^2$, and $U'=U'(y')=LU(Ly')/D_A$ and introduce the dimensionless parameter $\mu=a_0^2L^2k/D_A$, where a_0 is the initial uniform concentration of A in the completely unreacted region. On adding equations (1) (with $D_A=D_B$) it can be seen that if $a+b=1$ everywhere at $t=0$, it will remain so for all time. For such initial conditions, we therefore need consider only the concentration of b, now given by the equation

$$b_t+Ub_x=b_{xx}+b_{yy}+\mu b^2(1-b), \tag{2}$$

in which the primes have been dropped for convenience. We will be examining the effects of a linear shear $U=uy$ and a parabolic shear flow of the form $U=u(1-y^2)$ for constant u. We impose no-flux boundary conditions on $y=\pm 1$ and hence our model is for the laminar flow between two parallel, extended plates.

Equations (1) were solved numerically using the alternating direction implicit method with the nonlinear terms

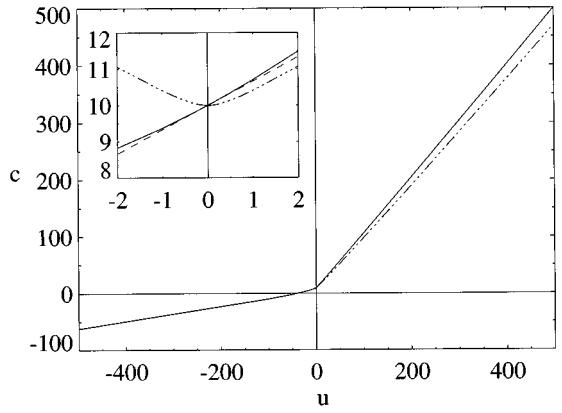

FIG. 1. Shear amplitude–wave-front velocity plot. The full curve is for parabolic shear; the dash-dotted curve is for linear shear. The inset shows the behavior for small-amplitude shears. The broken line is the first-order result from the perturbation analysis for a parabolic shear. The wave-front velocity for a linear shear is an even function of u. For clarity, the positive u results reflected about $u=0$ are shown only in the inset.

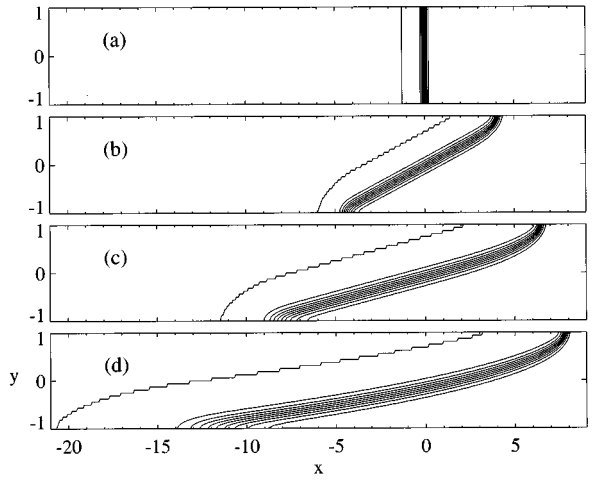

FIG. 2. Contour plots of b showing the evolution of a plane-wave front in the presence of the linear shear flow $U=100y$ at times $t_a=0$, $t_b=0.05$, $t_c=0.1$, and $t_d=1$. The region containing B only is on the left-hand side, and for this and subsequent figures, the contour levels are at intervals of 0.1.

treated explicitly. The accuracy of the method was verified by using it to solve systems whose solutions are known. The solutions were also found to converge on decreasing the temporal and spatial step sizes. Typically we used a time step of 10^{-4} and a spatial step size of 1/32. The domain size in the x direction was made sufficiently large so that the boundaries did not influence the solution in the central region of interest. No-flux boundary conditions were applied at the ends of this domain.

For our initial condition we used the cubic-Fisher planar wave-front solution [3] to Eq. (2) when $U=0$ and there is no y dependence, namely,

$$b=b_0\equiv\frac{1}{2}\left(1-\tanh\frac{c_0x}{2}\right), \tag{3}$$

where $c_0\equiv\sqrt{\mu/2}$. It was found that the form of the wave front evolved until the rate of increase of the total quantity of B in the region became constant. This corresponded to the front attaining its final permanent form and advancing at a constant speed. This rate was therefore used to determine the average velocity of the advancing front. The stationary character of the wave front was checked by feeding this velocity back into the advection term in the calculations so that the reference frame was moving at the same velocity. If this was done continually during the calculation, it ensured that the wave front stayed within the central region of the computational domain and so it was not necessary to use a mesh much larger than the longitudinal extent of the front.

We found that, for whatever value of the shear amplitude we chose, a stationary traveling wave front was eventually formed both for a linear and parabolic shear and also for both cubic and quadratic autocatalysis. The asymptotic velocity of the wave front c for both positive and negative values of u for the cubic autocatalytic system is shown in Fig. 1. The calculations for quadratic autocatalysis required a much finer grid in order to obtain accurate results and resources did not permit the determination the front speed for many values of the shear velocity. In the case of parabolic flow, for large and positive shear amplitude, the wave-front velocity is approximately equal to u, although there is some indication that it may be falling below this value for extremely large shears. For large negative u there also appears to be an approximately linear relation between c and u.

In Fig. 2 we show the evolution of a planar wave front subjected to a linear shear. By $t=1$, the wave front has acquired its final form. In Fig. 3 we see the asymptotic form of the wave fronts in the presence of parabolic shears of equal magnitude, but applied in an opposite sense. For both linear and parabolic shears we have found that the wave fronts have approximately the same shape for a range of u, but increase in length with increasing amplitude of the shear. In Fig. 4 we show the effect of introducing a localized amount of autocatalyst into a background of reactant in a parabolic shear flow. The autocatalyst initially generates a radially expand-

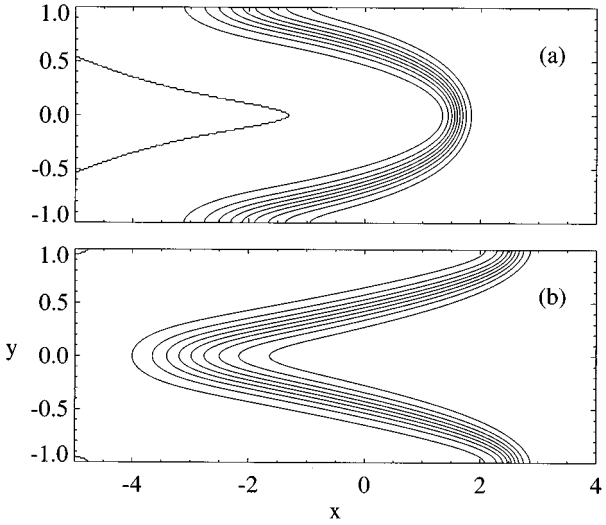

FIG. 3. Final forms of the wave fronts in the presence of the parabolic shear flows: (a) $U=100\ (1-y^2)$ and (b) $U=-100\ (1-y^2)$.

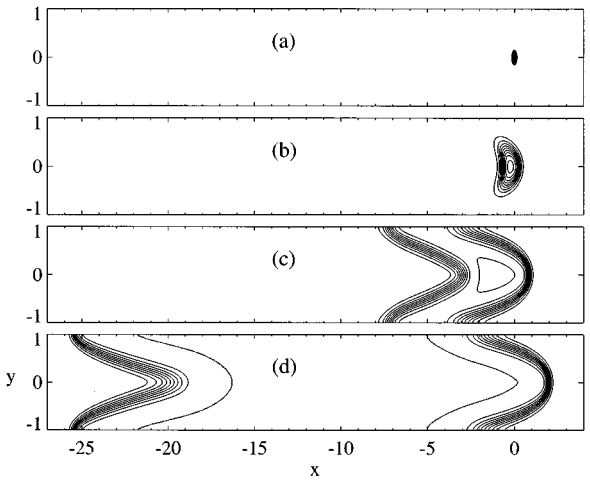

FIG. 4. Evolution of the initial condition $b=\exp[-100(x^2+y^2)]$ subjected to the parabolic shear flow $U=-100y^2$. $t_a=0$, $t_b=0.1$, $t_c=0.2$, and $t_d=0.4$.

ing front, which on reaching the boundaries forms an expanding region of B bordered by the two types of front shown in Fig. 3. All the results presented are for $\mu=200$.

The shape of the wave front can, to some extent, be accounted for by considering the eikonal equation for reaction-diffusion fronts modified for the case of an underlying fluid flow [8], namely,

$$c=U+(c_0+D\kappa)\sec\theta, \tag{4}$$

where here c is the x component of the front velocity, c_0 is the speed of a plane front, κ is the curvature of the front, and θ is the angle between the normal to the front and the x axis. A positive κ implies that the center of curvature lies within the unreacted region. In order to arrive at a front speed that is independent of y, variations in the underlying fluid velocity must be compensated for by the inclination of the front to the flow and by the front curvature. At the center of the flow, the curvature provides a negative contribution, as the center of curvature is within the fully reacted region, while at the boundaries where the underlying fluid velocity approaches zero, the curvature is very large. In the region in between, a significant contribution to the velocity is provided by the very oblique motion of the front.

To investigate analytically the wave-front solutions to (2) traveling at speed c, we transform to the coordinate system $x'=x-ct$. Since in this frame we are considering only time-independent solutions, after dropping the primes we are left with

$$b_{xx}+b_{yy}+(c-U)b_x+\mu b^2(1-b)=0. \tag{5}$$

With no y dependence and $U\equiv 0$, this becomes the cubic-Fisher equation with solution (3). We attempt to find a perturbation solution to (5) for $u\ll c_0$ by expanding the solution about b_0 and c_0:

$$b=b_0+u\sum_{n=-\infty}^{\infty}\beta_n^{(1)}e^{inpy}+u^2\sum_{n=-\infty}^{\infty}\beta_n^{(2)}e^{inpy}+\cdots, \tag{6}$$

$$c=c_0+c_1u+c_2u^2+\cdots. \tag{7}$$

After writing U as a Fourier series in y, we substitute the expansions into Eq. (5). To first order in u and for $n=0$ we obtain

$$\beta_{0,xx}^{(1)}+c_0\beta_{0,x}^{(1)}+c_0^2(2b_0-3b_0^2)\beta_0^{(1)}=(\Upsilon_0-c_1)b_{0,x}, \tag{8}$$

where Υ_0 is the zeroth Fourier coefficient of U/u. It can be seen that $b_{0,x}$ is the complementary function for Eq. (8) that satisfies homogeneous boundary conditions. To obtain a solution to the full equation that satisfies all the required boundary conditions a compatibility condition must be satisfied. This leads to choosing $c_1=\Upsilon_0$, which is the mean value of the shear. Hence, for linear shear flow $c_1=0$ and for parabolic flow we have $c_1=2/3$. Referring back to the numerical results shown in the insert of Fig. 1, we see that for $u\ll 10$ the linear dependences predicted by our analysis are obtained.

To conclude, in this article we have presented results that show that a superimposed laminar shear flow can greatly enhance the rate at which the reactant in an autocatalytic scheme is consumed. This is a result of the occurrence of a stable wave front of permanent form propagating with a velocity comparable to that of the maximum of the shear velocity.

[1] P. Gray, J.F. Griffiths, and S.K. Scott, Proc. R. Soc. London Ser. A **394**, 243 (1984).

[2] A. Saul and K. Showalter, in *Oscillations and Travelling Waves in Chemical Systems*, edited by R.J. Field and M. Burger (Wiley, New York, 1984).

[3] K. Showalter, Nonlin. Sci. Today **4**, 3 (1995); P. Gray and S.K. Scott, *Chemical Oscillations and Instabilities* (Clarendon, Oxford, 1990); S.K. Scott and K. Showalter, J. Phys. Chem. **96**, 8702 (1992).

[4] D. Horvath, V. Petrov, S.K. Scott, and K. Showalter, J. Chem. Phys. **98**, 6332 (1993).

[5] A. Hanna, A. Saul, and K. Showalter, J. Am. Chem. Soc. **104**, 3838 (1982).

[6] J. Masere, D.A. Vasquez, B.F. Edwards, J.W. Wilder, and K. Showalter, J. Phys. Chem. **98**, 6505 (1994).

[7] C. Doering and W. Horsthemke, Phys. Lett. A **182**, 227 (1993); E.A. Spiegel and S. Zaleski, Phys. Lett. **106A**, 335 (1984).

[8] B.F. Edwards, J.W. Wilder, and K. Showalter, Phys. Rev. A **43**, 749 (1991).