Convective Fingering of an Autocatalytic Reaction Front

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Abstract

We report experimental observations of the convection-driven fingering instability of an iodate-arsenous acid chemical reaction front. The front propagated upward in a vertical slab; the thickness of the slab was varied to control the degree of instability. We observed the onset and subsequent nonlinear evolution of the fingers, which were made visible by a pH indicator. We measured the spacing of the fingers during their initial stages and compared this to the wavelength of the fastest growing linear mode predicted by the stability analysis of Huang *et. al.* [*Phys. Rev. E*, **48**, 4378 (1993), and unpublished]. We find agreement with the thickness dependence predicted by the theory.

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Most studies of pattern-forming chemical reactions are carried out in thin horizontal layers, or in gels, under conditions where the coupling between chemical concentrations and hydrodynamic effects is suppressed. This coupling arises because reactions usually modify the density of the solution, giving rise to buoyancy forces and hydrodynamic flow. This flow then advects the reacting solution, adding new transport terms to the already complex reaction-diffusion problem. In this paper, we study chemical reaction driven convection in a very simple context, in the autocatalytic reaction of iodate and arsenous acid in a narrow vertical slot [1]. This system may be regarded as a simplified prototype for the study of hydrodynamic instabilities in more complex pattern-forming chemical systems, such as the Belousov-Zhabotinsky reaction [2].

In the absence of hydrodynamic effects, the iodate-arsenous acid reaction [3] produces a single, sharply defined reaction front which propagates at a speed governed by the diffusion of the iodide autocatalyst. When such a front propagates upward in a circular tube, it has been shown that the solution near the front is unstable to convection when the tube diameter exceeds a critical value [4]. In this direction of propagation, the unreacted solution, which is denser, lies above the lighter reacted solution in a potentially unstable arrangement. For the vertical slot geometry, which is analytically simpler, there exists a well developed theory [1,5,6] of the linear instability of a flat front. The theory predicts that the initial instability takes the form of convective rolls which corrugate the front into a series of fingers. In the limit of sharp fronts, the reaction-diffusion part of the problem can be reduced to an eikonal relation in which the local front speed depends on the front curvature [8]. The relative strength of buoyancy is measured by a dimensionless parameter S, described below, which is proportional to the cube of the slot thickness. The spacing of the finger pattern results from the competition between convection, which tends to extend the fingers vertically, and diffusion, acting via the eikonal relation, which tends to smooth the front. More realistic models, which include the full reaction-diffusion equations needed to describe a finite front thickness, have recently been proposed [11].

A flat front in a laterally extended slot is expected to be unstable to a periodic chain of

convection cells which are analogous to those found in other simple fluid systems, such as Rayleigh-Bénard convection [9]. This instability also bears some analogy to that of a flame front [10]. The objective of the present study is to examine this instability as it grows out of a flat front, and to compare the spacing of the pattern of fingers to what is predicted from the linear theory in the thin-front limit. We also qualitatively observed the instability after it had become fully developed, in which the front dynamics is dominated by interactions between fingers. This highly nonlinear regime is the subject of some recent simulations [11].

Fig. 1 shows the experimental arrangement. The slot was formed of two glass plates held apart by a rubber gasket. The spacing $a \sim 1mm$ of the cell was determined by steel shims outside the gasket, which were not in contact with the solution. The width of the slot w was $32 \pm 0.5mm$. The back face of the cell, which was painted white to make the reaction more visible, was in good thermal contact with a copper block at room temperature, $23°C$. The reaction front was initiated by an electrical trigger which consisted of two thin steel electrodes on opposite sides of the slot which were in contact with the solution. A DC voltage $\approx 10V$ was applied to the electrodes for a few seconds to initiate the reaction. The reaction front, made visible by an indicator dye, was photographed through the front face of the cell. The camera and cell apparatus were mounted on a common stand which could be oriented with respect to vertical.

The working solution was prepared as follows. Solid As_2O_3 powder was dissolved in distilled water which had been made strongly basic by the addition of KOH. When the powder had dissolved, the resulting solution was filtered and neutralized with concentrated HCl. This was mixed with a solution of KIO_3 and a solution of Congo Red indicator, so that the final concentrations were $[H_3AsO_3] = 0.005$M, $[KIO_3] = 0.0025$M, with 0.0001M of indicator. In some thinner cells, a higher concentration of indicator was used. The unreacted solution was adjusted to have a pH ≈ 6. Congo Red changes from red to blue near pH ≈ 5.2. With this high initial pH value, the reaction does not start spontaneously, but can be initiated quickly on an electrode as described above. As the reaction front passes a point, a sharp transition in color is seen; additional color gradations in the blue region

behind the front served to delineate some flow structures within the fingers. The front speed in the absence of convection, measured for downward propagation in narrow capillary tubes, was $c_0 = (3.47 \pm 0.03) \times 10^{-3} mm/s$ for this solution. This is an order of magnitude smaller than that observed in previous studies [4], which used somewhat different concentrations and pH.

We performed runs in cells with various thicknesses a and did not vary the width w, the temperature, or the chemical concentrations. In runs in which the front was initiated at the top of the slot and propagated downward, the initial front irregularities grew only slightly during propagation. Fronts which were initiated at the bottom and propagated upward showed strong fingering in all but the thinnest cells. The fingers that formed soon became nonsinusoidal, taking on a scalloped shape, with broad upper ends and narrow cusps between fingers on the lower side. One could clearly see a plume-like structure within each finger in color gradations of the blue state of the indicator. The precise relation of these to the flow is not clear, but they presumably map varying pH regions which persisted behind the front. The fingers were reasonably regular initially, but soon after initiation, some fingers are overtaken and suppressed by their neighbors. There also developed a tendency for fingers to avoid the lateral edges of the cell. We did not generally observe tip splitting or mechanisms which nucleated new fingers. In the late stages, the front advanced farthest, still carrying interacting fingers, near the lateral midpoint of the cell. Eventually, a large central plume of width $\approx w/2$ developed which was accompanied by a strong suppression, or even a reversal, of the front advancement near the ends of the cell. In the thinnest cells, as discussed below, no fingering was observed in the early stages, and the only distortion of the front was the development of this large plume.

We measured the spacing of the fingers directly from photos, at the earliest stages of their development for cells of various thickness. Fig. 2 shows a plot of the wavelength λ of the fingers, defined as the mean trough-to-trough spacing, exclusive of end effects, as a function of the thickness of the cell. For cells thinner than 0.4 mm, no clear fingers were observed before the broad plume reached the top of the cell. The main uncertainties in the

finger spacing came from the small number of fingers across the cell (3 - 7), imperfections of the starting conditions, which tended to be amplified by the instability, and, for thicker cells, the tendency of the fingers to interact and overtake one another at an early stage. However, a clear trend to narrower fingers for thicker cells was evident. The solid line in Fig. 2 is a fit discussed below.

According to the linear analysis [1,5,6], the dimensionless parameter that controls the instability is given by

$$S = \frac{\delta g a^3}{\nu D_C},$$
(1)

where g is the acceleration of gravity, a is the cell thickness, ν is the kinematic viscosity and D_C the diffusion constant of the autocatalyst. The density change across the front is parameterized by the dimensionless density jump $\delta = (\rho_u/\rho_r) - 1$, with ρ_r and ρ_u the densities of the reacted and unreacted solutions. The density change is almost completely due to concentration change, so that the thermal expansion of the fluid due to the heat released by the reaction can be neglected [7]. For a laterally unbounded slot [1], linear stability analysis predicts that fronts are unstable to convection rolls within a band of wavenumbers q, with $0 \leq q \leq q_c(S)$ for *any* $S > 0$. The critical wavevector $q_c \to 0$ as $S \to 0$. The predicted neutral stability curve $S_c = S(q_c)$, given by Eqn. 40 of Ref. [1], is shown in Fig. 3. Physically, this limit means that fronts in wide slots will be unstable to long wavelength convection, even when the slot is made very thin (*i.e.*, even for small S). For slots of finite width w, one naturally expects a cutoff when the unstable band implies pattern wavelengths $\lambda \approx w$. The data shown in Fig. 2, for which $w = 32 \pm 0.5mm$, are consistent with this expectation; no fingers are seen in cells with $a < 0.40mm$, a thickness for which only two or three fingers would fit across the width of the cell.

The theory also predicts the fastest growing linear mode q_{max}, which lies near the mid-point of the unstable band. Fig.3 shows the finger spacing data on a dimensionless plot of S vs. q, with lengths scaled by the cell thickness a. We fit the data to the locus of maximum growth rate [11] using a one parameter fit of the form $S = ka^3$ vs. $q = 2\pi a/\lambda$, with k

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adjustable. The fit minimized the sum of the absolute deviations, a criterion which is more robust to outliers than the usual least squares. We found $k = (2.05 \pm 0.30) \times 10^{11} m^{-3}$. The fit parameter is simply related to the various parameters in Eqn. 1. Using the measured value [4,5] for $D_C = 2.0 \times 10^{-9} m^2/s$, and taking ν as the viscosity of water, we find that the density jump required by Eqn. 1, is $\delta \approx 4 \times 10^{-5}$. This is about 50% smaller than the value [4,5] previously measured for the isothermal density change. The smaller value of this parameter, and our smaller front speed c_0, are probably the result of the different chemical concentrations and pH of our solution.

The wavelength $\lambda_{max} = 2\pi a/q_{max}$ corresponding to the fastest growing linear mode is shown as the solid line in Fig. 2. It is interesting to note that the linear theory for a laterally unbounded slot predicts that λ_{max} tends to infinity as $a \to 0$ and to a constant $\lambda_\infty \approx 15(\nu^2/g\delta)^{1/3}$ as $a \to \infty$, and passes through a minimum at intermediate values of a [11]. For our solution, this minimum is expected near $a \approx 1.1\ mm$, for which $\lambda_{max} \approx 4.6\ mm$, which is unfortunately just beyond the range of our data. Observation of this curious minimum would be a very interesting confirmation of the theory. In a slot of finite width, the λ_{max} approaches $\lambda_w \sim w$, as $a \to 0$, due the constraint that at least one convection roll must fit across the slot width. In the late stages of the nonlinear evolution of our fronts, it is evident that flow eventually develops on the scale of λ_w, in the form of a large upflow at the midpoint of the cell, with downflows near each end.

We have compared our data to the existing theory which is valid in the limit of zero front thickness [1]. In fact, the front has a finite thickness $d_r \sim D_c/c_0$, which is approximately 0.6 mm for our solution. Thus $d_r \sim a$ for most if not all of our data. While our data do behave as predicted by the simple theory, we expect that a more accurate model which includes the effects of finite front thickness will be required for more detailed comparison to future experiments.

In conclusion, we have observed the fingering instability of a vertically propagating chemical reaction front in a cell with a slot geometry. We find that the spacing of the fingers in the early stages of their development is consistent with the fastest growing mode according

to the linear theory of convection driven by concentration-induced buoyancy. We find a long wavelength cutoff consistent with the effect of the finite lateral extent of the cell. As the instability develops, we observed interactions of fingers which tended to reduce their number, eventually leading to broad flows on the scale of the cell width. In future experiments, we plan to extend this study to wider cells, with better control over the cell geometry, and to cells which are continuously fed with reactants. With these arrangements, it should be possible to precisely study the onset of the instability and the dynamical evolution of the fingers in the nonlinear regime.

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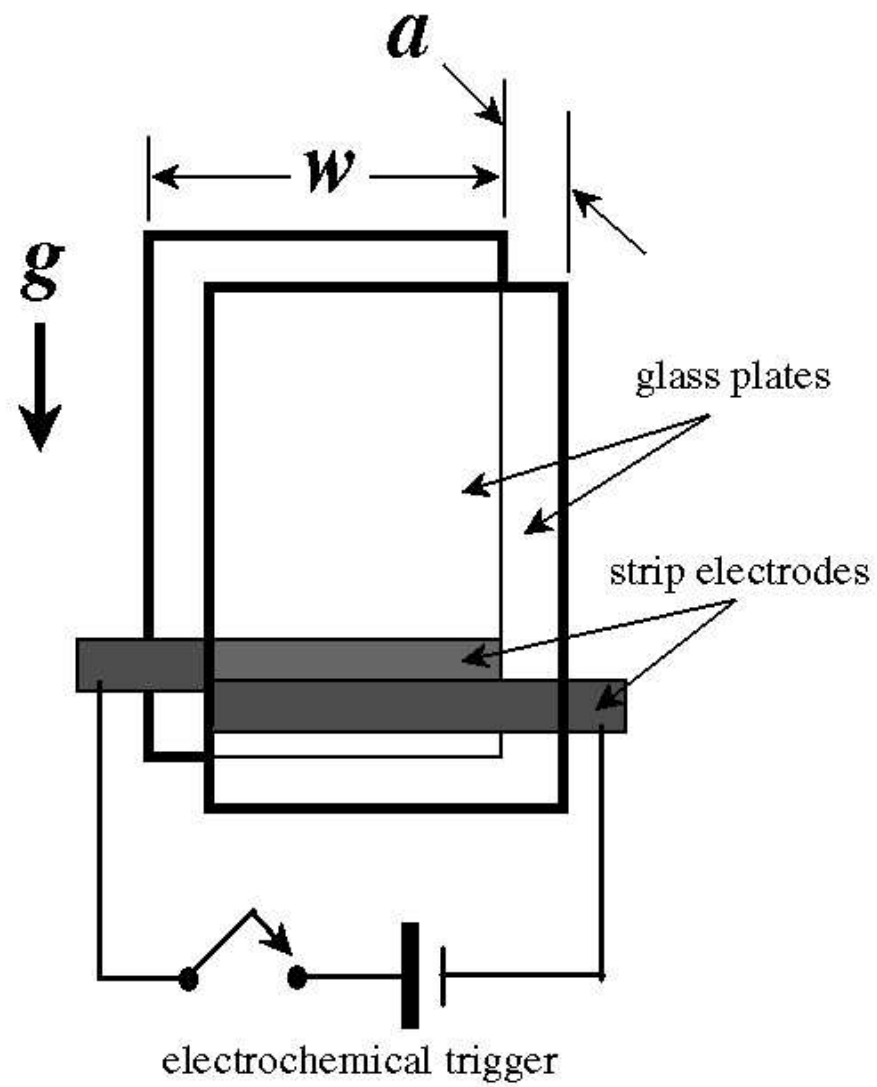
FIG. 1. A schematic of the apparatus. The width w of the cell was $32mm$. The thickness $a \sim 1mm$ was varied in the experiment.
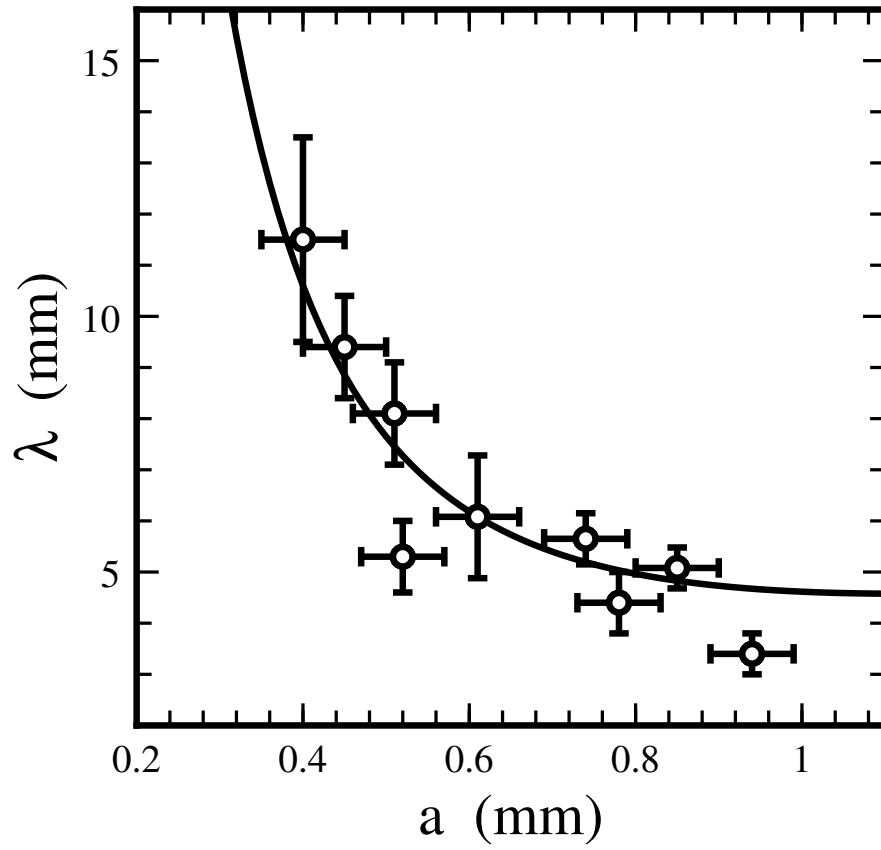
FIG. 2. The pattern wavelength (spacing of the fingers) *vs.* the cell thickness *a*. The solid line is a fit to the linear theory.
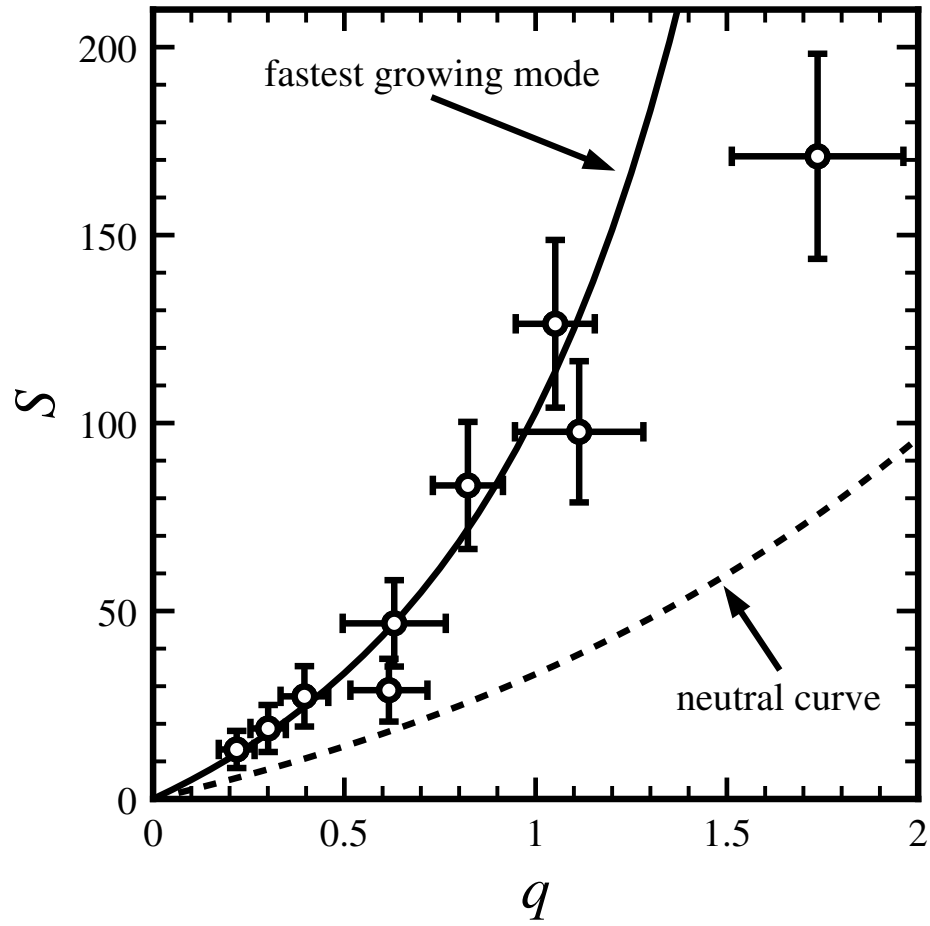
FIG. 3. The dimensionless control parameter S *vs.* the wavevector q of the instability, according to the linear theory of Ref. [1]. The data are fit to the fastest growing linear mode [11].