

Breathing Spots in a Reaction-Diffusion System

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A quasi-2-dimensional stationary spot in a disk-shaped chemical reactor is observed to bifurcate to an oscillating spot when a control parameter is increased beyond a critical value. Further increase of the control parameter leads to the collapse and disappearance of the spot. Analysis of a bistable activator-inhibitor model indicates that the observed behavior is a consequence of interaction of the front with the boundary near a parity breaking front bifurcation. [S0031-9007(96)00591-1]

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Oscillations in spatially extended chemical systems are often the result of underlying oscillating dynamics of the local chemical kinetics [1]. In systems with nonuniform spatial structures, oscillations may also be driven by *diffusion*. Spiral waves and breathing spots in excitable and bistable media are examples of oscillatory behaviors where the local kinetics without diffusion converge to stationary uniform states, while spatial structures undergo oscillations. Chemical spirals have been observed and studied for more than two decades [2], but breathing spots have not been previously observed although they have been found in numerical and analytical studies of activator-inhibitor models [3,4].

Figure 1 shows an example of the breathing spots observed in our study of a ferrocyanide-iodate-sulfite (FIS) reaction [5] in a quasi-2-dimensional reactor. The breathing motion arises as a control parameter is increased and an initially stable circular front (the spot boundary) becomes unstable. Further increase in control parameter eventually leads to the front rebounding from the cell boundary and propagating inward until the spot collapses and disappears. The breathing motion is interpreted as transitions between left and right propagating fronts near a parity breaking front bifurcation [6]. The rebound phenomenon leading to spot collapse is attributed to crossing the front bifurcation as the control parameter is increased. We will first describe the experimental system and then present the observations and the interpretation of the results in terms of a model reaction-diffusion system.

The chemical patterns form in a thin gel layer that allows reaction and diffusion processes but prevents convection. The apparatus is similar to that used by Lee and Swinney [7]. A polyacrylamide gel layer (25 mm diameter, 0.3 mm thick) is in contact with a well-stirred reservoir (2.8 ml volume) that is continuously fed with reagents of the FIS reaction. Reagents are fed first to a premixer (1.0 ml volume) in two streams, one with H_2SO_4 and NaIO_3 and the other with Na_2SO_3 and $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$. The output of the premixer is fed to a stirred reservoir that is in contact with the gel layer. The reservoir diameter is 22 mm; thus

the outer 1.5 mm width edge of the gel is not in contact with the reservoir. The entire system is immersed in a water bath maintained at $T = 30^\circ\text{C}$. The side of the gel opposite the chemical reservoir is a window through which the gel is illuminated with blue light (400–440 nm), and the patterns are viewed using a video camera. The system is studied in a range in which the homogeneous FIS reaction has two stable states, one with low pH (about 4) and the other with high pH (about 7) [5,7]. In the observed patterns the black and white regions correspond to the low and high pH states, respectively [7].

We will now describe experiments that yield oscillating spots. At low flow rates the gel reactor is uniformly black; at high flow rates, uniformly white [7]. When the system is switched on at intermediate flow rates, a black spot emerges in the center of the reactor. The spot is initially irregular but evolves to a circular spot centered in the reactor. Above a critical flow rate (about 150 ml/h for the reagent concentrations used; see Fig. 1), the circular spot oscillates in size as it approaches its asymptotic

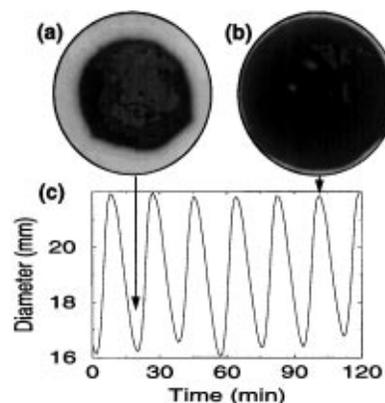


FIG. 1. An oscillating circular spot at (a) minimal size and (b) maximal size. (c) Time evolution of the spot diameter. The input concentrations to the reservoir in contact with the gel reactor are $[\text{H}_2\text{SO}_4] = 3.35 \text{ mM}$, $[\text{IO}_3^-] = 75.0 \text{ mM}$, $[\text{SO}_3^{2-}] = 89 \text{ mM}$, and $[\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}] = 20 \text{ mM}$. The flow rate is 179 ml/h.

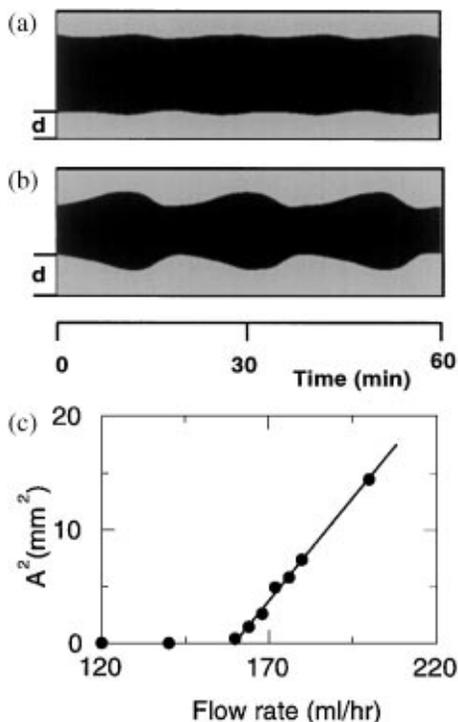


FIG. 2. Time evolution of the cross section of a spot. (a) Sinusoidal oscillations just beyond the onset of instability ($F = 160$ ml/h). (b) Relaxation oscillations far beyond the instability onset ($F = 200$ ml/h). (c) The square of the spot oscillation amplitude as a function of flow rate.

stationary state. Beyond a higher critical value of the flow rate (158 ml/h), the circular spot becomes unstable and begins to oscillate in size, as Fig. 2 illustrates. The oscillations are nearly sinusoidal just beyond the onset of instability [Fig. 2(a)], while well beyond onset they become relaxational [Fig. 2(b)]. Measurements of the amplitude A of the oscillation as a function of flow rate indicate that the transition is a Hopf bifurcation: A^2 increases linearly with distance above transition, as shown in Fig. 2(c).

Beyond a yet larger flow rate (260 ml/h), a shrinking spot does not stop shrinking at a minimum size but instead continues to shrink until the spot disappears. As the spot collapses, a new black ring emerges near the outer edge of the reactor, creating two new fronts, as Fig. 3(d) illustrates. The inner front travels inward while the outer front initially travels towards the boundary but then rebounds and travels inward. The ring then collapses to a black spot that shrinks and disappears. The space-time diagram in Fig. 3(d) shows that this whole process is periodic.

We interpret these observations as interactions of the chemical front with the reactor boundary in the vicinity of a parity breaking front bifurcation. The parity broken front states correspond to a black state invading a white state (black-white front) and a white state invading a black state (a white-black front). Although the two fronts connect the same states, they differ in their inner structures and consequently in their direction of propaga-

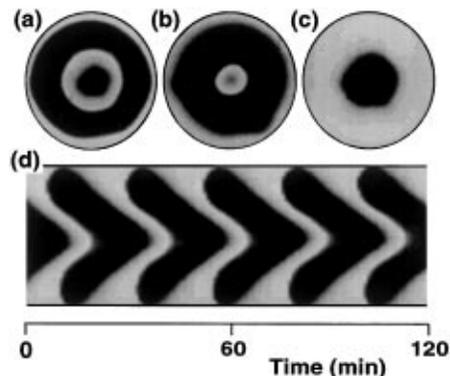


FIG. 3. Periodic emergence of black rings near the boundary leading to spot collapse near the center of the reactor. (a)–(c) The dynamics of a single period, viewed at 80, 85, and 93 min, respectively; the time origin is arbitrary. (d) The space-time evolution of a cross section of the reactor image. The flow rate is 280 ml/h.

tion. To develop this interpretation we consider a model of a bistable reaction-diffusion system that exhibits pattern phenomenology similar to that observed in the FIS reaction [8], and is simpler for analysis than the Gáspár-Showalter model for this reaction [5]. The model equations in one space dimension are

$$u_t = u - u^3 - v + u_{xx}, \quad (1a)$$

$$v_t = \epsilon(u - a_1 v - a_0) + \delta v_{xx}, \quad (1b)$$

where the subscripts x and t denote partial derivatives. For a fixed $a_1 > 1$ there is a parameter range where the system is bistable; it has two coexisting stable stationary uniform states (u_+, v_+) and (u_-, v_-) . The parameter a_0 will be associated with the flow rate F , and the two states (u_+, v_+) and (u_-, v_-) with the white (high pH) and black (low pH) states, respectively.

For $a_0 = 0$ and fixed δ the system (1) exhibits a pitchfork front bifurcation [also known as the nonequilibrium Ising-Bloch (NIB) bifurcation] as the parameter ϵ is decreased past a critical value, ϵ_c . For $\epsilon > \epsilon_c$ there is a single, stationary front solution connecting (u_+, v_+) at $x = -\infty$ to (u_-, v_-) at $x = \infty$. At $\epsilon = \epsilon_c$ the stationary front solution becomes unstable and a pair of counter-propagating front solutions with velocities $c \propto \pm \sqrt{\epsilon_c - \epsilon}$ appear. These are the parity broken front states corresponding to the black-white ($c < 0$) and the white-black ($c > 0$) fronts. When $a_0 \neq 0$ the pitchfork bifurcation becomes imperfect, i.e., unfolds into a saddle node bifurcation where, at $\epsilon = \epsilon_c(a_0)$, a stable-unstable pair of front solutions appears in addition to the stable front solution that already exists.

The front bifurcation can also be traversed by varying other parameters, in particular by increasing $a_0 < 0$. We will investigate the effect of a no-flux boundary on the dynamics of a front as a_0 is increased. Using a singular perturbation approach with ϵ/δ as a small parameter, we

derive a relation between the front velocity, c , and the distance from the front to the boundary, d . The Hopf bifurcation observed in the experiment will be associated with the c - d relation becoming multivalued.

In a moving coordinate system (1) becomes

$$u_{zz} + cu_z + u - u^3 - v = 0, \quad (2a)$$

$$\delta v_{zz} + cv_z + \epsilon(u - a_1v - a_0) = 0, \quad (2b)$$

where $x_f(t)$ is the position of the narrow front structure, $z = x - x_f(t)$, and $c = \dot{x}_f$ is the front velocity. The boundary conditions are $(u, v) \rightarrow (u_-, v_-)$ as $z \rightarrow \infty$ and $(u_z, v_z) = (0, 0)$ at $z = -d$, where d is the distance from the front to the boundary. In obtaining (2) we assume that the front velocity $\dot{x}_f = c$ is small so that the explicit time dependence in the moving frame can be neglected. The front velocity can be controlled by varying a_1 ; increasing a_1 leads to lower velocities.

We first solve Eqs. (2) in the front, or "inner," region. Letting $\mu = \epsilon/\delta \rightarrow 0$ at finite $\eta = \sqrt{\epsilon\delta}$, we obtain the equation $u_{zz} + cu_z + u - u^3 - v_f = 0$, subject to the boundary conditions $u \rightarrow u_+(v_f)$ as $z \rightarrow -\infty$ and $u \rightarrow u_-(v_f)$ as $z \rightarrow \infty$. Here, v_f is the value of v at the front, and $u_{\pm}(v_f)$ are the largest and smallest roots of $u - u^3 - v_f = 0$. Solving the inner problem yields

$$v_f = -\frac{\sqrt{2}}{3}c. \quad (3)$$

Another relation between c and v_f is obtained by solving the equations in the regions to the left and to the right of the front, the "outer" regions. Rescaling the coordinate system according to $\zeta = \sqrt{\mu}z$ and letting $\mu \rightarrow 0$ gives [4]

$$v_{\zeta\zeta} + \frac{c}{\eta}v_{\zeta} - q^2(v - v_+) = 0, \quad \zeta < 0,$$

$$v_{\zeta\zeta} + \frac{c}{\eta}v_{\zeta} - q^2(v - v_-) = 0, \quad \zeta > 0,$$

with the boundary conditions $v(0) = v_f$, $v(\infty) = v_-$, and $v_{\zeta}(-\sqrt{\mu}d) = 0$. Here, $q^2 = a_1 + 1/2$ and $v_{\pm} = (\pm 1 - a_0)/q^2$. Solving this boundary value problem and matching the derivatives of v at $\zeta = 0$ we find

$$v_f = -\frac{1}{q^2} \left[\frac{c}{\alpha} + a_0 + \left(1 - \frac{c}{\alpha} \right) e^{-\alpha d/\delta} \right], \quad (4)$$

where $\alpha = \sqrt{c^2 + 4\epsilon\delta q^2}$.

Equating (3) and (4) gives an implicit relation between c and d . In the limit $d \rightarrow \infty$ this relation reproduces the front bifurcation line [4], which we may write as $a_0 = a_{0b}(\epsilon)$. Figure 4(a) shows a graph of the c - d relation far into the single front regime; Fig. 4(b), near the front bifurcation; and Fig. 4(c), beyond the bifurcation. The figures also show trajectories representing the front dynamics as obtained by direct numerical solution of Eqs. (1).

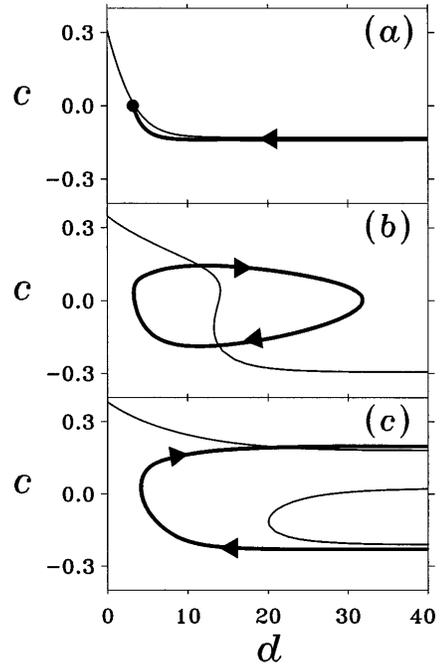


FIG. 4. The dynamics of fronts near a boundary. The thick lines represent the front distance from the boundary, d , and front speed, c , computed from the numerical solution of Eqs. (1). The thin lines are the solutions to Eqs. (3) and (4). (a) Far into the single front regime, a front approaching from large x values stops at a fixed distance from the boundary; $a_0 = -0.2$, $\epsilon = 0.025$. (b) Near the front bifurcation the c - d relation is multivalued and the front begins oscillating; $a_0 = -0.1$, $\epsilon = 0.0025$. (c) After crossing the front bifurcation the upper branch of the c - d relation exists for all d and the approaching front rebounds and propagates away from the boundary to infinity; $a_0 = -0.01$, $\epsilon = 0.0025$. In all three cases, $a_1 = 5$ and $\delta = 2.0$.

The monotonic velocity relation and the corresponding trajectory in Fig. 4(a) describe the approach of a black-white front from the far right (large x) to the boundary at $x = x_f - d$. The solution converges to a stationary front at some $d = d_0$. The negative slope at $(c, d) = (0, d_0)$ implies stability of the stationary solution. We associate with this scenario the formation of a black spot observed at low flow rates in the experiment.

As a_0 is increased, the slope of the c - d relation at $(c, d) = (0, d_0)$ increases in absolute value and at a critical point, $a_{0c} = -1 + 2q^3\sqrt{2\epsilon\delta}/3$, diverges to infinity. Beyond a_{0c} the slope is positive and the c - d relation is multivalued in some range of distances from the boundary [Fig. 4(b)]. The critical point a_{0c} corresponds to the onset of oscillatory front motion, and explains the Hopf bifurcation to a breathing spot observed in the experiment.

The oscillations can be regarded as periodic transitions between left and right propagating fronts represented by the upper and lower branches of the c - d relation in Fig. 4(b) [9]. The dynamics actually do not follow these branches because we have neglected the explicit time dependence of the u and v fields in the moving frame.

Near the bifurcation, v_f becomes an active degree of freedom responsible for transitions between the fronts [10]. The present analysis, however, accurately predicts (within 3% for $a_1 = 5$) the onset of breathing motion and describes the dynamics far from the front bifurcation [see Figs. 4(a) and 4(c)].

Beyond the front bifurcation, $a_0 > a_{0b}(\epsilon)$, the upper branch in the c - d relation extends to infinity, i.e., exists for all distances d . As Fig. 4(c) demonstrates, this type of c - d relation results in the rebound of a front approaching the boundary along the lower branch (black-white front) and the escape to infinity along the upper branch (white-black front). This behavior together with the circular geometry of the experimental apparatus explains the rebound and collapse of black spots observed at high flow rates. Possible instabilities to transverse perturbations [7,8] are damped in the present experiment by high curvature (small spots) and by the interaction with the circular reactor boundary (large spots). The observation of traveling rings in the same parameter range as the collapsing spots (Fig. 3) provides further evidence for this interpretation since crossing the front bifurcation is associated with the appearance of traveling waves [4]. The periodic production of waves near the boundary might be due to heterogeneities, which become significant near the oscillatory regime at high flow rates, or global coupling effects. The latter possibility is not highly probable as discussed below.

We have been able to explain breathing spots in terms of dynamic front transitions near a parity breaking front bifurcation. The generic nature of this bifurcation suggests that similar behavior can be expected in other systems with fronts. Breathing spots can also arise from global coupling, as found by Middy and Luss in model equations [11]. Indeed, we find that decreasing the strength of a global coupling term added to (1a) leads to a scenario similar to that observed: stationary, oscillating, and collapsing spots. In our experiment global coupling can arise from diffusion of chemicals from the gel back into the stirred reservoir. To test whether such coupling is significant, we monitor the pH in the reservoir. We

find that, despite the oscillations in the gel, the pH in the reservoir is time independent. This suggests that the primary mechanism leading to the oscillating spots is not global coupling but the one presented in this Letter: interactions of the front with the boundary near a parity breaking bifurcation.

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