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Spiral instability to line sources in forced chemical pattern turbulence

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Abstract. – A stably rotating spiral wave in the Belousov-Zhabotinsky reaction studied in an open spatial reactor becomes unstable when forced by a periodic chemical oscillation. The instability starts from the spiral center and occurs when the ratio of the spiral-rotation period to that of the forcing is close to 3/2. The resulting disordered state involves drifting line sources that emit waves in both directions. These unusual objects are reminiscent of the travelling hole solutions to the one-dimensional complex Ginzburg-Landau equation.

The study of the dynamics of two-dimensional patterns often includes the observation of spatiotemporal disorder, sometimes called turbulence in analogy to fluid dynamics. Such *pattern turbulence* has been observed in a wide variety of spatially extended experimental systems with different governing mechanisms [1]. The general study of model equations for these systems has led to the delineation of the categories: phase turbulence [2], spatiotemporal intermittency [3], and defect-mediated turbulence [4], [5]. The transition from a simple regular pattern (for example stripes, hexagons, or a spiral) to time-dependent disorder often involves the spontaneous nucleation of defects in the pattern, which can move through the system as individual entities, or coherent structures. One promising path to a dynamical theory of pattern turbulence is the search for the equations of motion, interactions, and stability of these structures [1], [6], but so far these approaches have explicitly considered only point-like defects.

Spirals have been observed in reaction-diffusion systems as diverse as the aggregation of *Dictyostelium amoebae* [7], the catalytic oxidation of CO on platinum [8], and the well-known Belousov-Zhabotinsky (BZ) chemical reaction [9], [10]. Much effort has been devoted to understanding the different properties of the spirals obtained in the BZ reaction [10], but the study of the mechanism by which they lose their stability has been relatively neglected. In fact, transitions from spirals to pattern turbulence have been observed chiefly in numerical simulations [2], [4], [11]. To our knowledge only two experimental scenarios have been documented for the BZ reaction [12], [13], the most recent example being understood as a transition

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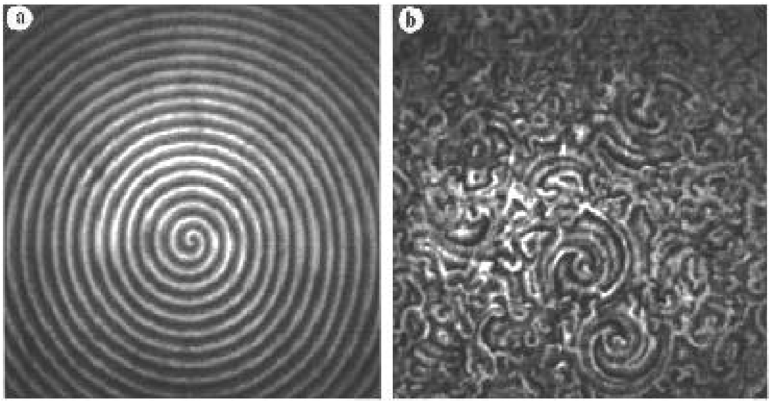


Fig. 1. – From single spiral to turbulence: *a*) a stable spiral at $[H_2SO_4]_{AB} = 0.38$ M, with pitch 0.46 mm and rotation period $T_{sp} = 7.9$ s; *b*) full turbulent state at $[H_2SO_4]_{AB} = 0.60$ M. The region shown is 12.0 mm × 12.0 mm.

to defect-mediated turbulence through a convective instability. A similar defect-mediated instability was seen in liquid crystals [14]. In both of these experiments, the defects which mediate the pattern turbulence are small rotating wave tips that do not develop into spirals, called *spiral defects*.

Imposing a global periodic forcing on a system and studying its response provides fundamental information about its dynamical behavior. In a reaction-diffusion system, the forcing adds an effective global coupling to the local elements, which can lead to new stable patterns, or coherent structures within a disordered state. Indeed a variety of patterns have been observed in experiments with global forcing, such as CO oxidation [8], [15], [16] and nematic-liquid-crystal convection [17], and also in numerical simulations of the two-dimensional complex Ginzburg-Landau equation [18]. In the BZ reaction, a number of studies have involved the periodic global forcing of spirals [19], but none have led to instabilities.

In this letter we present the experimental study of a simply rotating spiral wave in the BZ reaction, subjected to a global periodic chemical forcing in a well-controlled system (fig. 1 *a*)). As the control parameter is increased, a transition occurs to pattern turbulence (fig. 1 *b*), for the same experiment) via the spontaneous nucleation of curved *line sources* of travelling waves. These non–point-like coherent structures have a finite length, and drift perpendicular to their length as they emit waves in the forward and backward directions. Their coexistence with spiral defects characterizes the asymptotic turbulent state.

The BZ reaction consists in the oxidation of malonic acid by bromate in an acidic aqueous solution, catalyzed by a metal ion such as cerium, manganese, or iron; our experiments were conducted in the ferroin-catalyzed reaction [20]. We use an open spatial reactor in our experiments, which allows for the study of true asymptotic states; it has been described previously [13], [21]. Its essential aspect is a thin porous glass disk, of thickness 0.4 mm and diameter 25.4 mm (Vycor glass, Corning Inc.), sandwiched between two continuously fed and well-mixed reservoirs (A and B), in which the chemical concentrations are homogeneous. In the absence of forcing, the concentrations in these reservoirs are constant, and each contains different reaction components so that the pattern-forming reaction occurs only in the glass disk. It is a pure reaction-diffusion system since any hydrodynamic motion is suppressed by the porous medium.

Using the fact that the waves in this system are sensitive to red laser light, we initially

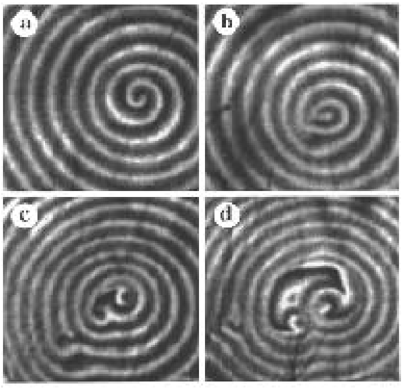


Fig. 2.

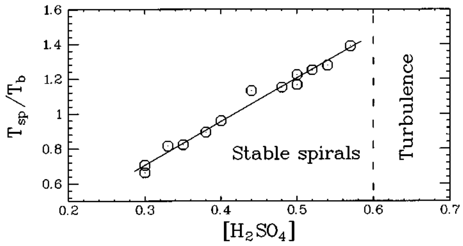


Fig. 3.

Fig. 2. – The spiral instability at the transition to turbulence, $[H_2SO_4]_{AB} = 0.60$ M. *a*) $t = 0$ s, distortions beginning near the spiral center; *b*) $t = 98$ s, before breaking up; *c*) $t = 150$ s, the central part of the spiral has given way to a line source, which emits waves both outwards and in towards the center; *d*) $t = 209$ s, the line source has elongated and drifted outward. The region shown is 4.5 mm $\times$ 4.5 mm.

Fig. 3. – The ratio of the measured spiral-rotation period T_{sp} to the measured bulk oscillation period T_{b} as a function of sulfuric-acid concentration. The solid line is a linear fit to the data. The dashed line at $[H_2SO_4]_{AB} = 0.60$ M indicates the transition to turbulence, at which point $T_{\mathrm{sp}}/T_{\mathrm{b}} = 1.5$ (extrapolated).

prepare the experiment with a single spiral [13]. The input concentration of sulfuric acid $[H_2SO_4]_{AB}$ is our control parameter ([1]), which we vary from 0.2 to 1.2 M. The other input concentrations are fixed at: $[NaBrO_3]_{AB} = 0.4$ M, malonic acid $[CH_2(COOH)_2]_A = 0.4$ M, $[\mathrm{ferroin}]_B = 0.5$ mM, $[NaBr]_A = 30$ mM, and $[SDS]_A = 0.03$ mM ([2]). The residence time of chemicals in the reservoirs is 15 min, and the temperature is regulated at 23 ± 0.1°C. To apply a global forcing to the spiral, a small amount of malonic acid (0.05 M) is fed into reservoir B, inducing a bulk oscillation with a well-defined period T_{b}. Thus, the oscillatory BZ reaction is actually occurring in this reservoir. Under this chemical forcing, the spiral executes simple rotation around its center for concentrations up to $[H_2SO_4]_{AB} = 0.60$ M, where the instability reproducibly occurs.

Figure 2 illustrates the onset of the instability. The spiral becomes distorted near the center (fig. 2 *a*)), and the "break" always occurs within the first few turns (fig. 2 *b*)). The first line source seems to nucleate *between* the turns of the spiral, in a gap that occurs during its distortion (fig. 2 *c*)); usually a few spiral defects are also created. The line source elongates as it slowly moves away from the center, and eventually the central region is almost surrounded by a single curved line which sends waves both inward and outward. As the line source continues to drift outward, more lines and spiral defects nucleate spontaneously in the central turbulent region, which grows to fill the system. If the periodic forcing is stopped, the line sources disappear, and the spiral defects remain, eventually developing into stable spirals. Without the bulk oscillation, the spiral is stable up to $[H_2SO_4]_{AB} = 1.2$ M, at which point it breaks far from its center [13].

As the concentration of H_2SO_4 is increased from 0.30 M to 0.57 M, the rotation period of

([1]) The subscript denotes the reservoir containing the chemical (*i.e.* H_2SO_4 is in both A and B).

([2]) A small amount of sodium dodecyl sulfate (SDS) is fed into reservoir A to reduce bubble formation; SDS does not affect the reaction [22].

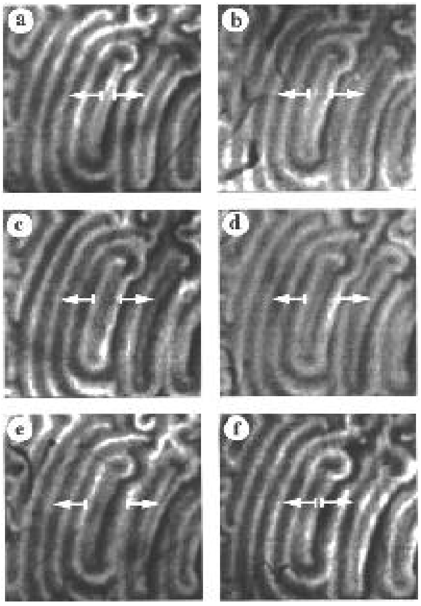
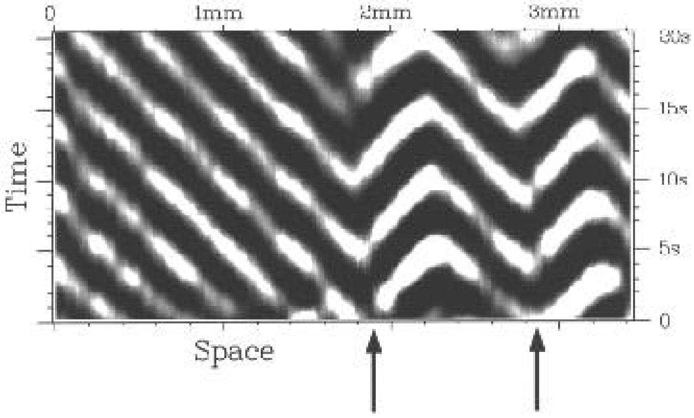


Fig. 4. – A slightly curved line source for $[H_2SO_4]_{AB} = 0.60$ M. The white arrows indicate the direction of the waves emitted to either side. The time elapsed between each frame is 1 s, and the sequence shows about one emission period T_e. The area of each frame is 4.0 mm × 4.0 mm.

the spiral T_{sp} decreases from 10.8 s to 5.7 s, and the pitch decreases from 510 μm to 430 μm. In the same range, the period of bulk oscillations T_b decreases from 16.3 s to 4.1 s, and at $[H_2SO_4]_{AB} = 0.60$ M, $T_b = 3.9$ s. As shown in fig. 3, the ratio of these two periods, T_{sp}/T_b, increases linearly with concentration of H_2SO_4, and $T_{sp}/T_b \simeq 1.5$ at the spiral instability. This suggests that a strong 3/2 resonance mechanism is involved.

We now focus on the characteristics of the line source itself, an example of which is shown in fig. 4. Although the source is not visible, it is defined by the waves it emits to the left and right. In fig. 4 *a*), two wavefronts have just been emitted, and are seen to separate into the following frames (fig. 4 *b*)-*f*)). This source has an approximate length of 2 mm, about 5 times the emitted wavelength; we observe lengths up to 6 mm. In many cases there is a spiral defect at one or both ends; in fig. 4 one is visible on the upper end. Note another line source to the right of the central one: they tend to be aligned. We have not yet investigated the interactions of these coherent structures.

To analyze the dynamics of the source shown in fig. 4, we plot in fig. 5 the intensity of a single line across the video image (x-axis) as a function of time (y-axis). The global forcing would appear as periodic horizontal stripes in this figure, but these have been filtered out. The waves are emitted with a well-defined period $T_e = 4.8$ s, slower than the bulk oscillation ($T_b = 3.9$ s), with which we observe no phase locking. The line sources drift in the direction of their convex side (to the left in fig. 4 and 5) with a velocity $v_d = 0.7$ mm/min. The waves emitted in the direction of forward motion have a velocity $v_f = 4.9$ mm/min, whereas in the opposite direction $v_b = 4.2$ mm/min. Thus the drift velocity of emitting line sources is: $v_d = v_f - v_b$. It is clear from fig. 4 and 5 that there is a different wavelength for the forward and backward waves (λ_f and λ_b, respectively), and from the previous relation we obtain: $v_d = (\lambda_f - \lambda_b)/T_e$. This suggests a qualitative similarity between these line sources and the



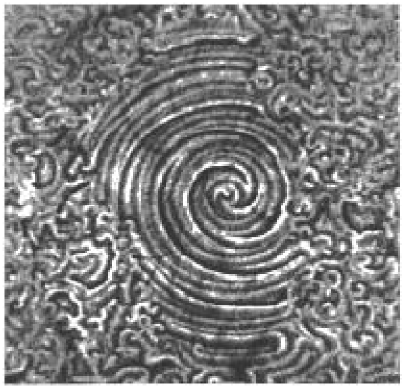


Fig. 5. Fig. 6.

Fig. 5. – A space-time plot of the intensity of a horizontal line from fig. 4 taken over 20 s, after filtering out the global forcing. The initial locations of the line sources are indicated by arrows; they drift to the left while emitting waves forwards and backwards.

Fig. 6. – A spiral of line sources, surrounded by a turbulent state of coexistent line sources and spiral defects, at $[H_2SO_4]_{AB} = 0.60$ M. The region shown is 13.4 mm × 13.4 mm.

travelling hole solutions of the one-dimensional complex Ginzburg-Landau equation [23]; no two-dimensional analogue has been previously reported.

In fig. 6 we present a pattern occasionally observed in our experiments, which illustrates that the aligning tendency of the line sources can lead to long-range ordering. In this case, just after the onset of the instability the line sources form a spiral shape, as new lines develop at the center and move outwards (as discussed above for fig. 2). The spontaneous formation of spiral defects is suppressed in the central region, though they are clearly evident in the surrounding area. Eventually this organized structure of line sources loses its coherence, and the pattern becomes fully disordered.

Although the mechanism responsible for these line sources is not yet clear, the fact that a spatially extended wave emitter occurs in a diffusion-dominated system indicates long-range correlations, certainly due to the global forcing. Several qualitatively similar phenomena have been observed elsewhere. For example, by forcing two spirals to annihilate in the BZ reaction, a crescent-shaped wave source has been produced [24]. Also, a "backfire" or "wave-splitting" instability is observed in one-dimensional simulations, in which a propagating pulse emits other pulses in the opposite direction [15], [25]. Recently, a striking observation was made of a drifting domain wall loop in liquid-crystal convection under external periodic forcing [17]. What is clearly needed is a general theoretical framework for extended defects and structures in reaction-diffusion systems.

Our experiment has shown a new mechanism of spiral instability in which the center becomes unstable, provided a global periodic forcing is applied. This instability is probably triggered by a strong resonance between the spiral and the forcing. Previously observed mechanisms involved either a front instability [12] or a wave instability at a distance from the center [13]. We have also observed a new type of pattern turbulence, mediated by finite-length line sources. Intriguingly, although the forcing is necessary to sustain the line sources, their periods seem to be unrelated. In the BZ reaction these lines are a new coherent structure, not a spiral defect, but a kind of target pattern with an elongated center. It may be that what we have seen is just defect-mediated turbulence, with a new kind of mediating structure. An investigation of all such coherent structures and their properties is perhaps the first necessary step before any theory of pattern turbulence can be written.

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