Spiral Waves of Chemical Activity

Abstract. The Zhabotinsky-Zaikin reagent propagates waves of chemical activity. Reaction kinetics remain to be fully resolved, but certain features of wave behavior are determined by purely geometrical considerations. If a wave is broken, then spiral waves, resembling involutes of the circle, appear, persist, and eventually exclude all concentric ring waves.

Zaikin and Zhabotinsky reported (1) the spontaneous appearance of periodic structure in an initially homogeneous fluid in a gradient-free environment—a "dissipative structure" (2), of chemical rather than hydrodynamic origin. In this aqueous solution, phenanthroline catalysts the oxidative decarboxylation of malonic acid. The reaction oscillates with a period of several minutes, turning from red to vivid blue where phenanthroline is reversibly oxidized. Pseudo waves (phase gradients in bulk oscillation) sweep across the reagent at variable speed. In addition, blue waves propagate in concentric rings at fixed velocity from isolated points (pacemaker centers) with a period shorter than the period of the bulk oscillation. Unlike pseudo waves, these waves are blocked by impermeable barriers. They are not reflected. They are annihilated in head-on collisions with one another. The outermost wave surrounding a pacemaker is eliminated each time the outside fluid undergoes its spontaneous red-blue-red transition during the bulk oscillation. Because of uniform propagation velocity and mutual annihilation of colliding waves, faster pacemakers control domains which expand at the expense of slower ones: each slow pacemaker is eventually dominated by the regular arrival of waves at intervals shorter than its spontaneous period.

I have slightly altered the Zhabotinsky-Zaikin reagent to retain propagating excitability while suppressing spontaneous bulk oscillation (3). If this altered reagent is splattered into isolated droplets clinging to a glass surface, a very few contain pacemaker centers at first. The rest remain red for 1/4 to 1/2 hour before they turn transiently blue.

Spontaneously generated pacemaker centers seem to arise at nuclei on the air-liquid or solid-liquid interfaces. Their periods are seldom very regular and range from several minutes to 1/4 minute.

At 25°C in liquid 1 mm deep blue waves propagate about 6 mm/min. They run faster in the meniscus, where the liquid is deeper, and slower when crossing a shallow 0.1 mm deep or less, and when close behind a preceding wave. A blue wave never overtakes another from behind. The mutual annihilation and sharp cusps resulting from oblique collision show that the reagent is inexhaustible immediately behind a wave.

This nonoscillating reagent was prepared in order to test an argument that, because concentration isobars in a two-dimensional continuum are closed (like the potential contours of electrostatics or the level contours of cartography) and a wavefront is a concentration isobar, no stable wave could arise which has a free end—for example, a spiral wave. Though the argument is specious because, as Fig. 1C shows, a spiral wave need not contain a terminating isobar, its conclusion seems correct in the sense that spiral waves never arise spontaneously from homogeneous initial conditions (it is difficult to imagine how an isolated nucleus could induce a spiral). But more importantly, it led to the rediscovery (4) of spiral waves of chemical activity induced by hydrodynamic flow in the medium.

To induce such waves (as well as a diversity of less stable forms) it is only necessary to briefly tilt the dish in which waves are propagating in a thin layer. Where flow parallels the wavefronts, it has no effect; but a flow component along the direction of propagation mixes phases. An elaborate morphogenesis ensues in which segments of blue waves vanish. Near each free end is a center around which the remaining blue half-line propagates, winding into a spiral, as in the development of crystal growth spirals from a screw dislocation's line of emergence (5).

The eventual geometry of the spiral seems independent of its (still unresolved) chemical kinetic basis, for it can be calculated from the observed symmetry as follows. We ask, "Is there a wave shape, described in polar coordinates as θ (r), for which rotation and time-translation are interchangeable?" Taking the wavelength and rotation period as units of space and time, we require that propagation normal to itself at unit velocity during any interval must be equivalent to rotation through an angle 2πt radians. In differential terms, each segment of such a curve moves through a distance dr = dr at angle θ to the radius normal (Fig. 1A). Hence

\[ \frac{dr}{dθ} = \tan θ \]  
and 
\[ \frac{dz}{dθ} = -\sin θ \]  

Eliminating θ between Eqs. 1 and 2, and interchanging dr with dθ/2π, we obtain the differential equation

\[ (2π)^2 = 1 + \left( \frac{dθ}{dφ} \right)^2 \]  

The solution of Eq. 3, for 2π ≲ 1, is

\[ θ(φ) = \left( (2π)^2 - 1 \right)^{1/2} \cos^{-1} \left( 1/2π \right) + c \]  

This is an involute of a circle, constructed by revolving a pen around a cylindrical core of unit circumference, to which it is tethered by an unwinding string (Fig. 1B). At φ ≳ 1/2π, it approximates an Archimedes'("phonograph groove") spiral, ρ = ± 0/2π.
Symmetry considerations suggest that the other isobars of phenanthroline oxidation-reduction should run parallel to this wavefront—that is, they should be rotated involutes of the same circle, 2πρ = 1. Along the relatively flat extreme of oxidation-reduction, local deviations from this idealized concentration profile should result in local hills and hollows: the extreme contours should fragment into chains of concentric ring contours (Fig. 1C). Normal propagation cannot be maintained inside 2πρ = 1: the involute wave solution terminates perpendicularly on a circle (thin curve, Fig. 1C) of unit circumference, around which it propagates at unit velocity in unit time. Time-lapse photography shows that the blue wave does have approximately this geometry. It rotates every ¼ minute, the minimum period of pacemaker centers. Wavelength is accordingly about 1 mm. The free end seems to circulate around a core of 1 ± 0.5 mm circumference. However, this core is often quite indistinct and changeable in color, form, and position (6).

The principal reactants, having molecular weights near 100, have diffusion constants near 10⁻⁵ cm²/sec in water and would therefore diffuse about

\[(2DT)^{1/3} = (2 \times 10^{-5} \text{ cm}^2/\text{sec} \times 15 \text{ sec})^{1/3} = 1/6 \text{ mm}\]
during one rotation. Thus diffusion must smooth the concentration isobars inside the core, making the involute solution inexact near its termination. In state 1C the involutes are connected speculatively through the core, and the region of sufficiently visible blue is shaded. The homogenizing effect of diffusion theoretically attenuates the reaction to a stationary state at the center. If the excitability of the medium reflects interactions between two distinct chemical factors, there must be a second reactant with isobars of the same shape outside the core. Their continuation inside the core is speculatively sketched in the dotted contours of Fig. 1C. On the curvilinear chemical coordinate grid so formed, each volume element of fluid traverses a circular orbit at constant velocity every ¼ minute.

The involute describes a wave of stably self-renewing geometry. Its stability apparently depends on achieving the minimum wavelength possible in this medium. Thus all spirals have the same (minimum) period. Consequently waves from a spontaneous pacemaker and a spiral collide successively closer to the pacemaker until it is entrained. In contrast, spirals do not encroach upon each other. They partition the fluid into polygonal domains separated by lines of sharp cusps where waves collide. In this state the entire wave configuration repeats at ¼ minute intervals, as time lapse movies show. Like crystal grain boundaries, the domain boundaries are only historically determined and presumably could be metastably displaced, for example, by a transient temperature gradient.

As in crystal growth (5), m adjacent spiral cores rotating in the same direction cooperate, if not too close together, to produce a spiral of m parallel arms. The cusps formed by collision and fusion of contributing waves at a low angle are smoothed out within a few minutes. Pairs of counterrotating cores form dipole or quadrupole pacemakers, radiating a ring every ¼ minute.

In its spontaneously oscillating form and its merely excitable form, the Zhabotinsky-Zaikin reagent provides a convenient model for investigation of chemical waves in living organisms. Periodic wave propagation has been postulated by Goodwin and Cohen to play an important role in pattern formation in embryos (7). Implicit in their analysis of discrete-state cellular networks is the propagation of self-sustaining involute spirals. Similar self-regenerating waves have been observed in related models of neural networks (8) and of fibrillating heart muscle (9) and in populations of social amoebas (Dictyostelium discoideum) propagating waves of cyclic adenosine monophosphate (10, 11).

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References and Notes
3. The modified reagent is prepared as follows (all reagents anhydrous; all solutions aqueous): to 67 ml water add 2 ml of sulfuric acid and 5 g of sodium bromide (total 70 ml). To 6 ml of this (in a glass vessel) add ½ ml of sodium bromide solution (1 g/10 ml). Add 1 ml of malarionic acid solution (1 g/10 ml) and wait for bromine color to vanish. Add 1 ml of 25 mM (standard phenanthroline ferrous sulfate and a drop of 1 g/1000 ml Triton X-100 surfactant to facilitate spreading. Mix well, pour in a covered 90-mm petri dish illuminated from below. Bubbles of CO₂ can be removed every 15 minutes by stirring the liquid; it turns blue, then reverts to red, and ring propagation begins anew. The reagent turns permanently blue after about 45 minutes at 25°C. The reagent oscillates if the bromide is omitted. It is sometimes convenient to gel the reagents with an equal volume of fine chromatographic SiO₂.
6. I am indebted to J. Maynard Smith for observing that replacement of 2π by 2π/N in this argument still results in self-consistent
Giant Amphipod from the Abyssal Pacific Ocean

Abstract. A baited camera has recorded a lysianassid amphipod that is twice as large as the largest amphipod previously recorded. The locality for this mobile omnivore is the sterile bottom of the eastern North Pacific Ocean, at a depth of 5304 meters.

In the deep sea, many of the megafaunal taxa are either so rare or so wary that it is unlikely they will be recorded by conventional photographic surveys or captured by ordinary trawls or grabs. As a result, our understanding of the deep-sea fauna may harbor significant biases. New techniques are likely to reveal unsuspected aspects of the deep-sea benthos. This was demonstrated by the discovery of a giant amphipod in some photographs taken by a free-vehicle bottom camera known to its users as the monster camera.

The monster camera, as used in the lowering discussed here, consists of a weighted can of bait with a camera suspended above it. A strobe light is fastened to a long arm extending out to the side of the camera, and floats and beacon extend above the camera. The camera has a capacity of 100 feet of 35-mm film and can take pictures at intervals of 5, 10, and 15 minutes. When a clock release operates, or a magnesium link dissolves away, the camera returns to the surface and leaves the weighted bait can on the bottom (1).

On free-vehicle mission 515 of the Marine Life Research Group of the Scripps Institution of Oceanography, 29–30 November 1968, the monster camera was employed 780 miles east-northeast of Oahu in the northeastern Pacific Ocean (23°54.5’S, 144°04.9’W). The depth to the red clay bottom was 5304 m. Because of depth, remoteness from land, and the low productivity of the surface waters, this portion of the abyss is one of the least productive regions in the world’s oceans (2). The camera ran 20 hours, with exposures every 10 minutes. The bait (assorted dead fish) was held in a 19-liter (5-gallon) bait can whose top was 235 mm square.

The first animals to be attracted to the bait were nantantian decapod crustaceans, which appeared 1 hour after bottom contact. Fish appeared after approximately 4 hours. The first large amphipod arrived after 5 hours, and one or more amphipods were recorded intermittently for the next 11 hours. By then the bait can had been emptied and presumably had lost much of its attractiveness.

As many as three amphipods appeared in a single exposure. Judged by the different sizes, at least five individuals visited the bait. These swam and walked about the can, nested into (and fed on?) bait that had been dislodged from it, or even went completely into the can when it was nearly empty. With the bait can used for scale, some of the amphipods were measured. The largest was 282 mm long, twice as long as any amphipod previously recorded. The prior record belongs to Alciclla gigantea Chevreux (3), from the eastern North Atlantic Ocean at a depth of 5285 m, which attained only 140 mm.

A few other large gammarid Amphipoda have been recorded from bathypelagic or abyssal locations; for example, Eurythenes gryllos (Lichtenstein) (family Lysianassidae), taken in the North and South Atlantic and Pacific oceans from the surface to 6500 m, reaches 90 mm (3, 4). Most other large amphipods are considerably smaller; for example, Parargissa galathea J. L. Barnard (family Hyperiopsidae), 42 and 50 mm long, from the eastern tropical Pacific and Indian oceans at 3750 and 4360 m (4), and the bathypelagic or abyssopelagic Hirondellea gigas (Birstein and Vinogradov) (family Lysianassidae), 32 mm, in the Kurile-Kamchatka Trench at 6000 to 6400 m (5) and, 20 to 25 mm, from a trawl in the Philippine Trench down to 10,190 m (6).

There is little doubt that the amphipods photographed by the monster camera belong in the family Lysianassidae. Although most detailed diagnostic features are not visible, the stout