Pattern Formation in a Tunable Medium: The Belousov-Zhabotinsky Reaction in an Aerosol OT Microemulsion

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(Received 12 April 2001; published 7 November 2001)

Turing structures, standing waves, oscillatory clusters, and accelerating waves have been found in the spatially extended Belousov-Zhabotinsky system dispersed in water droplets of a reverse AOT microemulsion. The variety of patterns is determined by the tunable microstructure of the medium, i.e., by the concentration and size of water droplets. We propose a simple model to describe this system.

DOI: 10.1103/PhysRevLett.87.228301 PACS numbers: 82.40.Ck, 02.70.Uu, 68.05.Gh, 82.33.Nq

Pattern formation in reaction-diffusion systems is one of the central themes of modern nonequilibrium science. Turing [1] predicted patterns stationary in time and periodic in space (now generally referred to as Turing patterns), and patterns periodic in both time and space. One realization of the latter patterns associated with an oscillatory instability at finite wavelength is standing waves. The Belousov-Zhabotinsky (BZ) reaction, the catalytic periodic oxidation of malonic acid (MA) by bromate in acidic aqueous solution, is the prototype reaction-diffusion system for generating waves and patterns in such varied media as gels [2], membranes [3], mesoporous glasses [4], and ion-exchange resins [5]. It has become an important model system for various nonlinear processes in biological systems. Until now, neither Turing structures nor standing waves have been observed experimentally in the BZ system. In this Letter we present the first experimental observations and theoretical analysis of pattern formation in the BZ system dispersed in a water-in-oil aerosol OT (AOT) microemulsion (BZ-AOT system) [6,7]. The study of pattern formation in such microheterogeneous media may yield important insights into the development of living systems. A water-in-oil microemulsion is a thermodynamically stable mixture of water, oil, and surfactant, in which the water and surfactant molecules form spherical, nanometer-size droplets with a polar water core surrounded by a surfactant monolayer. The most widely studied water-in-oil microemulsions employ the surfactant sodium bis(2-ethylhexyl)sulfosuccinate, known as AOT [8]. The radius of water droplet cores is determined [9] by the molecular ratio \( \omega = [\text{H}_2\text{O}]/[\text{AOT}] \) and is roughly equal to \( R_w = 0.17 \omega \) (nm). As the volume fraction \( \phi_d \) of the dispersed phase (water plus surfactant) increases, clusters of droplets begin to appear [10,11]. Percolation occurs when \( \phi_d \) reaches a critical value \( \phi_p \), leading to a sharp increase of about 3 orders of magnitude in the conductivity [12]. Thus, by varying the composition, one can tune the structural properties of the medium.

Communication between droplets may occur either via exchange with and diffusion through the oil phase or via mass exchange during droplet collision/fusion/fission.

Small molecules (e.g., Br\(_2\) or BrO\(_2\)\(^{•}\)) display very different diffusion coefficients \( D \) in the oil and dispersed phases. In the former, \( D \) is about the same as the diffusion coefficient of oil molecules, roughly \( 10^{-5} \text{ cm}^2/\text{s} \) [13]. For the latter, \( D \) is determined by the diffusion of droplets in the oil phase [13] and can be as small as \( 10^{-7} \) or \( 10^{-8} \text{ cm}^2/\text{s} \). Reaction-diffusion systems with such different diffusion coefficients possess unusual properties [14–16].

Experiments were carried out under batch conditions at 23 °C. Two stock microemulsions, ME I and ME II, with the same size and concentration of water droplets, were prepared by mixing 1.5 M solutions of AOT in octane with aqueous solutions of H\(_2\)SO\(_4\) and malonic acid for ME I and ferroin and bromate for ME II [7]. The reactive microemulsion was generated by mixing equal volumes of the two stock MEs. Microemulsions with different droplet concentrations and the same droplet size were prepared by simple dilution with octane. Most of the reactive microemulsion was used to record bulk oscillations in ferriin absorption at \( \lambda = 620 \text{ nm} \) and to measure the electrical conductivity, \( \sigma \). We found \( \sigma < 1 \mu \text{S/cm} \) below the percolation threshold and \( \sigma > 100 \mu \text{S/cm} \) above it.

A small volume of the BZ-AOT mixture was sandwiched between two flat optical windows 50 mm in diameter immediately after mixing the stock MEs. The gap between the windows was determined by the thickness \( h \) (= 0.1 mm) of an annular Teflon gasket with inner and outer diameters of 20 and 47 mm, respectively. Patterns could be observed for about 1 h through a microscope equipped with a digital CCD camera connected to a personal computer. The reaction layer was illuminated by a 40 W tungsten source passing through a 450 nm interference filter.

Varying \( \omega \), \( \phi_d \), and \( r_0 = \gamma/k[\text{MA}]_0 \), where \( \gamma \) is the rate of autocatalytic growth of HBrO\(_2\) in BZ-AOT (\( \gamma = k[\text{H}_2\text{SO}_4][\text{NaBrO}_3]_0 \), \( k = 125 \text{ M}^{-3}\text{s}^{-1} \) [17], \( k' = 1 \text{ M}^{-1}\text{s}^{-1} \), and subscript 0 signifies initial concentrations in the aqueous phase), we found four major regions in the parameter space (Fig. 1). The bifurcation parameter \( r_0 \) characterizes the BZ chemistry, roughly giving the ratio of the rates of the key activation and inhibition steps. At
high $r_0$, we obtain traveling or spiral waves like those in the BZ reaction in simple aqueous solution, except that the velocity, $v$, and wavelength of the BZ-AOT waves are much smaller, about 2–10 $\mu$m/s and 0.1–0.3 mm, respectively. Calculating the effective diffusion coefficient $D_{\text{eff}}$ of the activator (HBrO$_2$) from the relation $v = 2(\gamma D_{\text{eff}})^{1/2}$ [18], we find that $D_{\text{eff}}$ ranges from $10^{-8}$ to $2 \times 10^{-7}$ cm$^2$/s, depending on $\omega$ and $\phi_d$. A diffusion coefficient of this magnitude is almost certainly associated with the diffusion of water droplets or clusters of droplets in the oil phase.

As we decrease $r_0$ and approach the boundary between steady state and dynamic behavior (Fig. 1), Turing structures, standing waves, and new types of traveling waves appear. Turing structures emerge at low $\phi_d$ ($\phi_d < 0.5$) [see Figs. 2(a) and 2(b)], for which bulk oscillations are suppressed in a stirred reactor. They persist for 1 h without changing position. Standing waves [Figs. 2(c)–2(f)] are found at intermediate $\phi_d$ ($0.5 < \phi_d < 0.7$) and, after cessation of bulk oscillations, evolve from traveling waves that form in this initially oscillatory system. The characteristic wavelengths of the Turing structures and standing waves are about 0.18 and 0.23 mm, respectively. Standing waves persist over several tens of oscillation periods, slowly filling the entire medium and finally giving way to the uniform reduced steady state. Standing waves arise most easily near the Teflon gasket, which suggests that zero-flux boundary conditions favor this phenomenon. To our knowledge, this is the first report of standing waves in a reaction-diffusion system in the absence of global coupling or external periodic perturbation [16,19–21].

At higher $\phi_d$, above the percolation threshold, oscillatory clusters and accelerating waves occur. Waves [see Figs. 3(a)–3(e)] speed up as they approach the open area left by the collision and subsequent perpendicular departure of the previous pair of waves. The velocity of the waves rises from a low $\sim(\gamma D_{\text{eff}})^{1/2}$ to a high $\sim(\gamma D_{\text{bulk}})^{1/2}$ value. As the waves approach each other, a white bridge appears between the closest points of the approaching waves. Before collision, waves with higher positive local curvature $1/r$ propagate faster, contrary to the eikonal equation [22], $v = v_0 - (1/r)D$, where $v_0$ is the velocity of a planar front. Such behavior suggests a strong dispersion dependence of the wave velocity on the wavelength [23]. At the same high $\phi_d$, but in other regions of the reactor near the boundary, oscillatory standing clusters arise [Figs. 3(f) and 3(g)]. The positions of the nodal lines remain fixed for many cycles. Clusters resemble standing waves, but do not possess an intrinsic wavelength [20].

The dependence of the patterns on $\phi_d$ can be understood in terms of the variation of the diffusion coefficients of water, $D_w$, surfactant, $D_s$, and oil molecules, $D_{\text{oil}}$, with $\phi_d$ [13]. At small $\phi_d$ ($\phi_d < \phi_p$, $\phi_p = 0.4–0.6$), $D_{\text{oil}}/D_w$ varies from 10 to 100 or more. In this region, $D_w \approx D_s$ is equal to the diffusion coefficient of water droplets, $D_d$,
The observation of Turing structures suggests that the inhibitor ($Y = Br^-$) or some species ($Z = Fe$, Br$_2$ or BrMA) that produces the inhibitor ($Z + BrMA \rightarrow Br^- , Br_2 + H_2O \rightarrow Br^- + HOBr, Br_2 + MA \rightarrow Br^-$) also diffuses rapidly [14]. Theoretically, fast diffusion of ferroin is possible, since mass exchange between water droplets is much faster for species such as ferroin that are more soluble in the surfactant layer than in the water core [25]. However, we have no direct experimental evidence for this idea. Fast diffusion of Br$_2$ in the oil phase seems more likely, but direct incorporation of Br$_2$ into a model is difficult. Instead, we assume rapid diffusion of ferroin with a diffusion coefficient intermediate between those for water droplets and Br$_2$ in the oil phase. The model equations for the bulk concentrations in BZ-AOT microemulsion are then

$$\frac{\partial x}{\partial t} = -k_{1}xy + k_{2}y - 2k_{3}x^2 + k_{4}x - k_{5}x + k_{6}fs + d_{s}\Delta x,$$

$$\frac{\partial y}{\partial t} = -k_{1}xy - k_{2}y + h_{k}x + d_{l}\Delta y,$$

$$\frac{\partial z}{\partial t} = 2k_{4}x - k_{6}z - k_{5}z + d_{z}\Delta z,$$

$$\frac{\partial s}{\partial t} = k_{f}x/\phi - k_{b}y + d_{s}\Delta s,$$

where $x = [HNBO_{3}]_{w}^{\pm}$, $y = [Br^{-}]_{w}^{\pm}$, $z = [Fe]_{w}^{\pm}$, $s = [S]_{oil}(1 - \phi_d)$, $k_{1} = k_{1}^{1}/\phi_{w}$, $k_{3} = k_{3}^{1}/\phi_{w}$, $\phi = \phi_{w}/(1 - \phi_d)$, and the subscript $w$ signifies water. The diffusion coefficients are normalized so that, with nondimensionalized spatial coordinates, $d = 1$ s$^{-1}$ corresponds to $D = 10^{-5}$ cm$^2$/s.

Equations (1)–(4) possess only one spatially uniform steady state, the stability of which we have analyzed by linear stability analysis. If the Jacobian matrix has two real, negative eigenvalues and one pair of complex eigenvalues $\lambda_{k}$ with positive real part, Re($\lambda_k$), for some $k$, then the steady state is unstable, and standing waves can arise. If all eigenvalues are real [Im($\lambda_k$) = 0, note that $\omega_k$ and $\omega$ have different meanings] and one is positive for some $k \neq 0$, Turing structures appear. Such behavior is shown in Fig. 4(a).

Figure 4(a) mimics the changes in $\phi_d$. At small $\phi_d$, when $D_{oil}/D_{w} \approx 10$, there is a positive Turing peak (max[Re($\lambda_k$)]) > 0) at $\omega_k = 0$ (curve 1). At higher $\phi_d$, when $D_{oil}/D_{w} \approx 100$, positive Re($\lambda_k$) appear at $\omega_k > 0$ (curve 2), with wave numbers $k$ smaller than that for the Turing peak, i.e., the wavelength of standing waves is larger than that of Turing structures, as seen in our experiments. A small increase in $k_b$ (due to the percolation transition or a boundary effect) leads to the disappearance of wave instability (curve 3) and the emergence of oscillatory clusters or accelerating waves at higher $\phi_d$. Far above the percolation threshold, when $d_s = d_y = d_z = d_f$, there is no positive Re($\lambda_k$). Since many of the rate constants for the BZ-AOT system are unknown, we varied our parameters over a broad range to test the model. Standing waves and Turing structures.
These observations point toward the possibility of new mechanisms of pattern selection based on interactions between “chemistry” and “structure,” phenomena that may provide better models of processes in living systems than simple reaction-diffusion systems with constant diffusion coefficients.

We thank A.M. Zhabotinsky for helpful discussions. This work was supported by the Chemistry Division of the National Science Foundation.