Oscillatory Clusters in the Periodically Illuminated, Spatially Extended Belousov-Zhabotinsky Reaction

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Cluster-cluster transitions in the periodically illuminated photosensitive Belousov-Zhabotinsky (BZ) reaction-diffusion system exhibit the same scenario as in the autonomous BZ system with negative global feedback: two-phase clusters ↔ three-phase clusters ↔ irregular clusters ↔ localized clusters. Transitions induced by changing the dark (T_D) or light (T_L) phases of the periodic external square wave illumination are dependent not only on the frequency of illumination at constant T_D/T_L, but also on the ratio T_D/T_L at constant frequency (when $T_D + T_L =$ const).

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Pattern formation in spatially extended reactive systems is of interest to scientists in a variety of fields, including physics, biology, chemistry, and geology. Traveling wave patterns and Turing structures, which arise due to local interactions and have an intrinsic wavelength, are well characterized [1,2]. Recently, a new type of pattern, the cluster pattern, which originates from global interactions and does not have an intrinsic wavelength, has been found in heterogeneous systems. Oscillatory antiphase clusters [3–10] consist of several spatial domains in which all of the elements in a domain oscillate with the same amplitude and phase. Clusters also arise in the homogeneous, spatially extended $Ru(bpy)_3{}^{2+}$-catalyzed Belousov-Zhabotinsky (BZ) reaction subjected to uniform periodic illumination.

Two groups of experiments have produced clusters in the photosensitive BZ reaction. In the first case (Texas experiments) [11,12], clusters were obtained under periodic external forcing. In the other (Brandeis experiments) [13,14], clusters were generated in an autonomous system with photochemical negative global feedback. In both instances, the spatially extended photosensitive BZ reaction was illuminated periodically, and synchronization with the frequency of the BZ system oscillations was established. With global feedback, the intensity of actinic light was proportional to the difference between the spatial average of the catalyst concentration, $[Ru(bpy)_3{}^{3+}]_{av}$, in the medium, a thin layer of silica gel, and a target value. A rise in $[Ru(bpy)_3{}^{3+}]_{av}$ indicates that autocatalysis is occurring in some part of the gel. Actinic light of sufficiently high intensity suppresses the autocatalysis, returning the system to its reduced state, which in turn causes the light to shut off. In the case of periodic forcing, synchronization of the chemical oscillations with the square pulses of external periodic illumination occurs as a result of frequency locking near rational ratios of the applied frequency, f_e, and the natural frequency of the system, f_0. In the Brandeis experiments, different types of clusters emerged as the feedback coefficient and, consequently, the light intensity were increased. In the Texas experiments, so-called front (or Ising front) clusters and labyrinthine standing waves appeared when f_e was increased at constant maximum intensity of the external light [12]. Recently, the Texas experiment was extended [11]. An increase in the intensity of square-wave light pulses at constant f_e resulted in a transition from labyrinthine standing waves to front clusters, when $f_e > 2f_0$. If $f_e < 2f_0$, the only oscillatory standing patterns found were front clusters.

In both sets of experiments, the same types of clusters were found. Standing, or front, clusters contain two different domains with fixed spatial boundaries and oscillate periodically in time. Such clusters have also been found in heterogeneous systems with global feedback [3–10]. The three-phase clusters found in both sets of experiments [12,14] also resemble one another. Other types of patterns differ somewhat. In the case of periodic forcing, labyrinthine standing-wave and bubble patterns were found. In the global feedback experiments, irregular clusters, localized irregular clusters, and localized standing clusters were obtained.

We seek to understand what the key parameters are that give rise to cluster-cluster bifurcations and how the bifurcation scenario depends on these parameters and on the details of synchronization between the natural frequency and the external signal. Direct comparison of the two experiments is difficult, however, since they were conducted under different conditions. We employed [13,14] a one-sided continuously fed unstirred reactor (CFUR), in which concentration gradients of the major reactants are minimal. The two-sided CFUR used in the Texas experiments gives rise to large gradients of such key reactants as $BrO_3{}^-$, Br^-, malonic acid, and $Ru(bpy)_3{}^{2+}$.

We have therefore undertaken experiments with periodic forcing of the BZ reaction in a one-sided CFUR under the conditions of our earlier global feedback experiments. We have modified our experimental arrangement [13,14] by replacing the feedback with a periodic external impulse that controls the light attenuator (a pair of crossed polarizers)

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independently of the system behavior. We employ square light pulses [see Fig. 1(a)], as in the Texas experiments, but we vary the duration of the light and dark phases (T_L and T_D, respectively) independently.

In the T_L-T_D plane [see Fig. 1(b)], clusters are found in a central triangular region (the "cluster triangle"), which is bounded by the nearly vertical line $T_L \approx T_{cr}$, the almost horizontal line $T_D \approx T_{ind}$, and a third line, $T_D + T_L = T_b$. T_{cr}, which depends on the intensity of actinic light I_{act}, is the time required to suppress all wave patterns in the system by constant illumination. T_{ind} is the induction period for the initiation of autocatalysis after the actinic light is switched off [see Fig. 1(c)]. T_b slightly exceeds the period of bulk oscillations T_0 without illumination. In our experiment, $T_b \cong 19$ s and $T_0 = 17$ s.

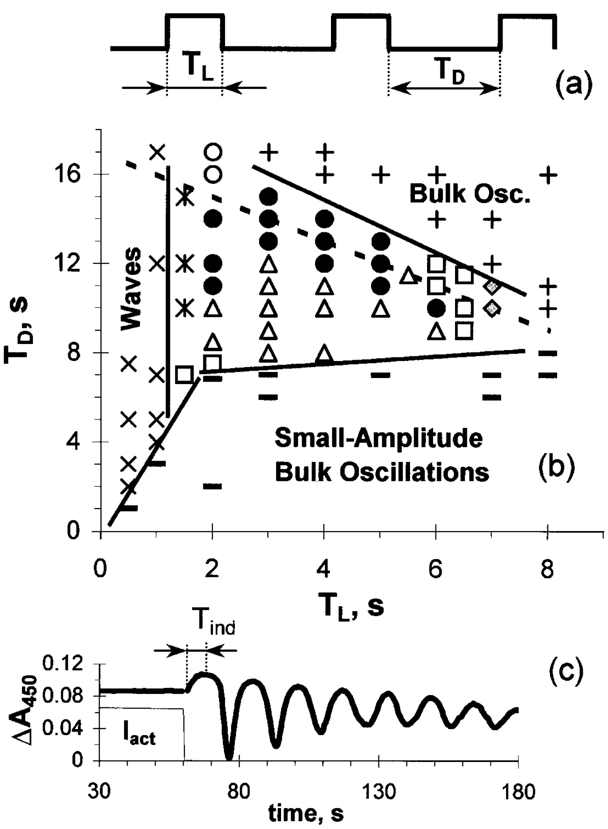

FIG. 1. (a) Shape of external actinic light signal. During period T_L, $I_{act} = 15$ mW/cm^2, during T_D, $I_{act} = 0$. (b) Dependence of system behavior on T_L and T_D; symbols: (×) wave patterns, (−) small amplitude bulk oscillations, (+) high amplitude bulk oscillations, (●) standing clusters, (△) three-phase clusters, (□) irregular clusters, (◆) localized clusters, (*) mixed behavior—clusters and waves in different parts of gel, (○) mixed behavior—bulk oscillations and clusters alternate. Along the dotted line, $T_L + T_D = T_0$. Initial reagent concentrations, 1.5 mM of immobilized $Ru(bpy)_3{}^{2+}$ in gel, $[H_2SO_4]_0 = 0.75$ M, $[NaBrO_3]_0 = 0.312$ M, [malonic acid]$_0 = 0.375$ M, and $[NaBr]_0 = 0.125$ M in the feeding chamber. (c) Behavior of absorption A_{450} averaged over gel surface for photosensitive oscillatory BZ reaction in a thin layer ($h = 0.0412$ cm) of silica gel after actinic light, I_{act} (arbitrary units), is turned off at $t = 60$ s.

If $T_D < T_{ind}$ and $T_L > T_{cr}$, all patterns are suppressed, and the entire system displays small amplitude bulk oscillations in the absorption at $\lambda = 450$ nm averaged over the gel surface [450 nm is the wavelength of maximum absorbance of $Ru(bpy)_3{}^{2+}$]. The frequencies of the chemical oscillations and the external light are the same; we are in a 1:1 locked regime. When $T_D + T_L > T_b$, $T_L > T_{cr}$, and $T_D > T_{ind}$, we find high amplitude bulk oscillations locked with the frequency of illumination.

If $T_L < T_{cr}$ and $T_D > T_{ind}$, wave patterns arise. The waves split periodically at the frequency of the external light and may produce wave patterns with a characteristic wavelength (for example, splitting spirals) or wave-induced chaos.

When $T_L < T_{cr}$ and $T_D < T_{ind}$ the periodic external illumination is essentially equivalent to constant light of intensity $I_{av} = I_{act}T_L/(T_L + T_D)$. If $I_{av} > I_2$, the minimum intensity of constant illumination that suppresses all waves in the gel, then wave patterns are suppressed, and the system displays only small-amplitude bulk oscillations. If $I_{av} < I_2$, then wave patterns develop in the system. Thus, the border between the wave region and the small amplitude bulk oscillation region corresponds to the line $T_D = T_L(I_{act}/I_2 - 1)$, starting from the point $T_L = T_D = 0$ and ending near the point ($T_L = T_{cr}$, $T_D = T_{ind}$).

We have found four types of clusters in the cluster triangle: standing clusters (SC), three-phase clusters (3pC), irregular clusters (IC), and localized clusters (LC). All of these types of clusters were seen in our earlier feedback experiments [14]. Examples are shown in Figs. 2 and 3. All of the patterns presented in the figures emerge slightly before or immediately after the light is switched on and persist for a time T_{cr}. During the remaining portion of each cycle, a duration of roughly $T_D + T_L - T_{cr}$, no patterns are visible.

Standing clusters [see Fig. 2(a)] occur near the line $T_D + T_L = T_0$. Despite the fact that $f_0 \cong f_e$, the local frequency of oscillation is $f_e/2$, so we are in a 2:1 locking regime. In effect, the photosensitive BZ reaction is "frozen" in the reduced steady state during the illuminated period T_L, leading to a significant increase in the period of oscillations at each spatial point. The shape of SC is determined by the spatial initial conditions.

Two types of 3pC are found: three-phase moving clusters (3pMC) and three-four-phase clusters (3-4pC) [see Figs. 2(b) and 2(c)]. Both of these clusters are unstable. The movement of black (or white) domains of 3pMC may be followed in four small snapshots taken each even period [Fig. 2(b)]. As in the case of SC, white domains emerge in place of formerly black domains (compare snapshots $20T_e$ and $21T_e$). Instability originates from gray domains, which appear 1–2 s after the white domains [Fig. 2(b), $21T_e$], splitting the latter. At the next period of the external signal, white domains appear only in regions that were previously black (compare snapshots $21T_e$ and $22T_e$).

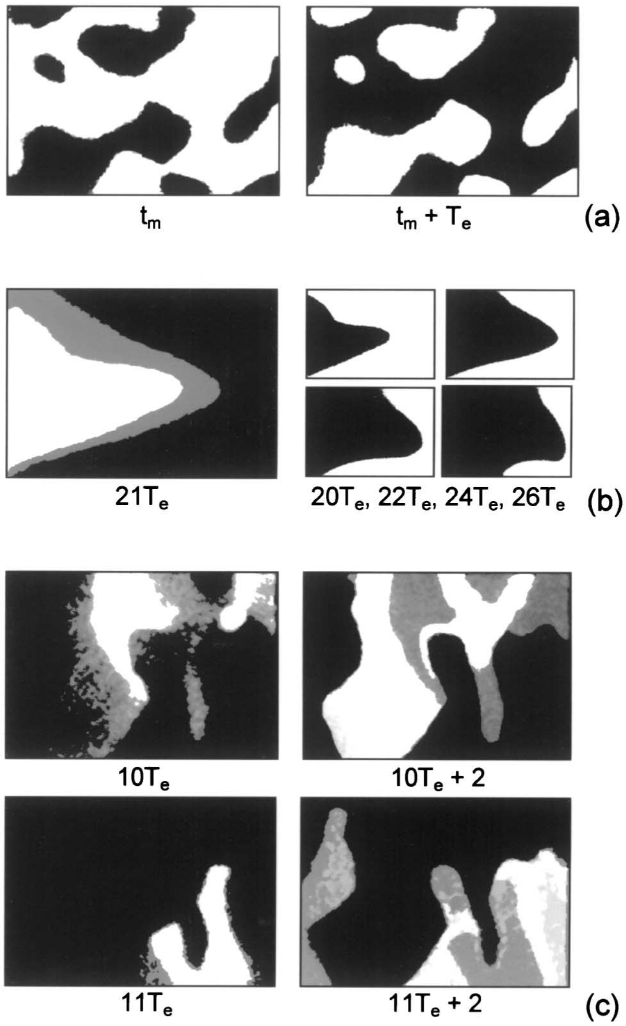

FIG. 2. (a) Standing clusters, $T_L = 3$ s, $T_D = 15$ s. Time t_m corresponds to a maximum of A_{450} after several tens of periods of system oscillations, when the pattern does not change. (b) Three-phase moving clusters, $T_L = 3$ s, $T_D = 10$ s. Left snapshot taken at the 21st period of illumination after periodic forcing is switched on. The four small snapshots on the right are taken at even periods of illumination. The top right snapshot corresponds to the 22nd period of illumination. Gray levels quantify $[Ru(bpy)_3{}^{3+}]$, with white corresponding to maximum and black to minimum. (c) Three-four-phase clusters, $T_L = 5.5$ s, $T_D = 11.5$ s. Expressions under frames show time in s. Frame size $= 7 \times 9.5$ mm^2.

The 3-4pC, which are found primarily near $f_e = f_0$, are more stable than 3pMC, and the three phases of oscillations (white, gray, and black domains in each snapshot) are more pronounced. Two pairs of snapshots in Fig. 2(c), ($10T_e$, $10T_e + 2$) and ($11T_e$, $11T_e + 2$), show that the white domains in the left snapshots start to fade and become gray in the right snapshots, while neighboring regions become white and parts of the black area become gray. The phase shift between white and gray domains in each pair of snapshots is small (2 s) with respect to the full period ($2T_e = 34$ s). Adjacent domains at two consecutive periods of external light (compare black areas in snapshots $10T_e + 2$ and $11T_e + 2$) are in antiphase, as in SC. Thus, during one full period ($2T_e$), we can see four phases of oscillation. The white and gray domains slowly change their shape.

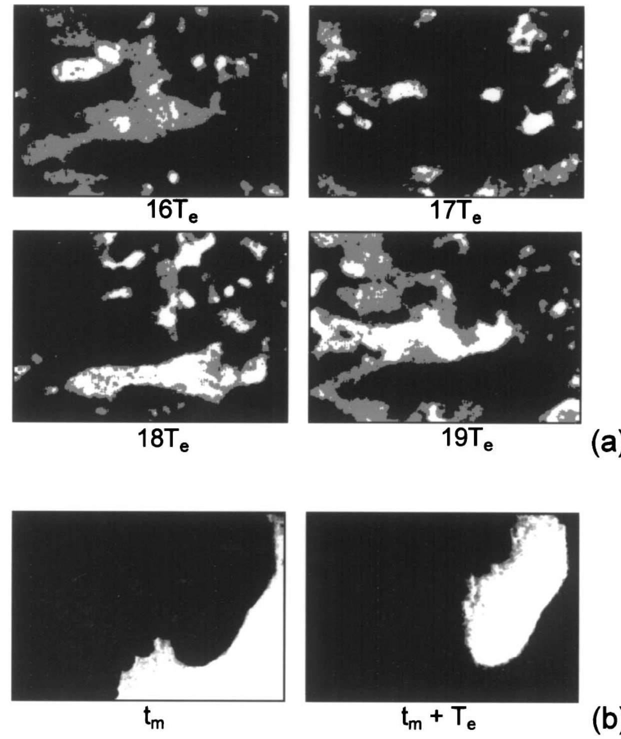

FIG. 3. (a) Irregular clusters, $T_L = 2$ s, $T_D = 7.5$ s. (b) Localized clusters, $T_L = 7$ s, $T_D = 10$ s.

Irregular clusters [see Fig. 3(a)] are found in the right and left lower vertices of the cluster triangle. The resolution of our experiment allows us to see that different "white" subdomains of IC actually have different amplitudes. There is zero overlap between the white domains of consecutive snapshots separated by T_e.

Localized clusters [Fig. 3(b)] are found only in the right portion of the cluster triangle, where $T_e \approx T_0$. The white domains of two consecutive snapshots of LC (separated in time by T_e) are in antiphase. The left portion of the gel does not oscillate or oscillates with small amplitude. Patterns resembling the bubble patterns in the Texas experiments are also found in our experiments near the top of the cluster triangle. They appear to be a combination of pairs of modes, such as waves and SC or high amplitude bulk oscillations and SC. Bubbles are transition patterns to SC. We failed to observe the labyrinthine standing wave patterns found in the Texas experiments.

Decreasing the gel thickness (from 0.41 to 0.24 mm) or the concentration of $Ru(bpy)_3{}^{2+}$ (from 1.5 to 0.5 mM) or increasing the light intensity I_{act} (from 3 to 15 mW/cm^2) all lead to a shift to the left of the boundary between the wave and cluster zones in the T_L-T_D plane.

High amplitude bulk oscillations ["+" in Fig. 1(b)] arise from the normal bulk oscillations of the BZ reaction, like those in Fig. 1(c). Small amplitude oscillations ["−" in Fig. 1(b)] result from photochemical reactions R1 and R2 [15,16],

$$Ru(bpy)_3{}^{2+} + h\nu \rightarrow [Ru(bpy)_3{}^{2+}]^*, \qquad (R1)$$

$$[Ru(bpy)_3{}^{2+}]^* + \text{Br-org} \rightarrow Ru(bpy)_3{}^{3+} + Br^- + \text{products}, \qquad (R2)$$

where Br-org is bromomalonic acid (BrMA) or dibromomalonic acid. When the light is turned on, the concentration of $Ru(bpy)_3{}^{3+}$ increases. When the light is turned off, $[Ru(bpy)_3{}^{3+}]$ decreases [see Fig. 1(c) at 60 s < time < 70 s] owing to the reaction of $Ru(bpy)_3{}^{3+}$ with BrMA. The normal oscillations of the BZ reaction, which are associated with the autocatalytic process, are suppressed.

To analyze the scenario of cluster-cluster bifurcations, we focus on two "directions," the lines $T_D + T_L = T_0$ and $T_D/T_L = (I_{act}/I_2 - 1)$. Note that in the Texas experiments [12], the vertical direction $T_L = \text{const}$ was explored. Moving along the line $T_D + T_L = T_0$ from the top vertex to the lower right vertex of the cluster triangle is analogous to increasing the feedback coefficient in the Brandeis experiments, since the average light intensity increases and the frequency of external illumination remains constant. Along the second line, the frequency changes but the average light intensity I_{av} is constant. Following the line $I_{av} = \text{const}$, we find cluster-cluster bifurcations in the sequence SC-3pC-IC. Along the line $f_e = \text{const}$ ($T_D + T_L = T_0$), the scenario SC-3pC-IC-LC is observed.

We conclude that the average light intensity and the frequency of external illumination are important parameters for cluster-cluster transitions, which obey the following fundamental scenario: SC(or two-phase clusters)-3pC-IC-LC. The same scenario was found with increasing feedback strength in our experiments [14] and was confirmed by simulations of the BZ reaction with global feedback [17]. A simple model system consisting of three identical Oregonator oscillators globally coupled by negative feedback also exhibited a similar scenario: two-phase regime ↔ three-phase regime ↔ chaos ↔ localized regime [14]. It thus appears that the scenario for cluster-cluster transitions is determined by global influences on the system through external periodic forcing or through autonomous global coupling, and local (reaction-diffusion) coupling plays only a secondary role.

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