



Light-Modulated Intermittent Wave Groups in a Diffusively Fed Reactive Gel

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Abstract: Inspired by the biological growth that takes place in time-varying external fields such as light or temperature, we design an open reaction-diffusion system in order to investigate growth dynamics. The system is composed of the Belousov–Zhabotinsky (BZ) oscillatory reaction coupled with a copolymer gel consisting of NIPAAm and a photosensitive ruthenium catalyst. When subject to a unidirectional flow of the BZ reactants, the system displays groups of chemical waves whose structure depends upon the period and amplitude of illumination. Simulations of a modified six-variable Oregonator model exhibit all the complex wave groups found in our experiments. Studying this growth structure may aid in understanding the influence of periodic environmental variation on complex growth processes in living systems.

As an organism grows, it experiences environmental variations, such as the annual cycle of the seasons and the alternation between day and night.^[1] This observation suggests that growth morphology may be related to periodic external stimulation, e.g., light or temperature. Furthermore, the growth process also depends upon the supply of nutrients and neural signals. As internal growth is subjected to external perturbations, organisms can develop different morphologies: for example, the complex outline of leaves (Figure 1c),^[2] the tree of neural synapses,^[3] pigmentation patterns on sea shells.^[4] Developing morphologies may be modeled and studied in the spatiotemporal pattern formation occurring in dissipative systems subject to time-dependent forcing.^[5]

The Belousov–Zhabotinsky (BZ) reaction,^[6] which exhibits spatiotemporal phenomena, was discovered in a search for an inorganic analog of the tricarboxylic acid cycle,^[7] a key metabolic process in living systems. Yoshida^[8] has synthesized a copolymer gel consisting of *N*-isopropyl acrylamide

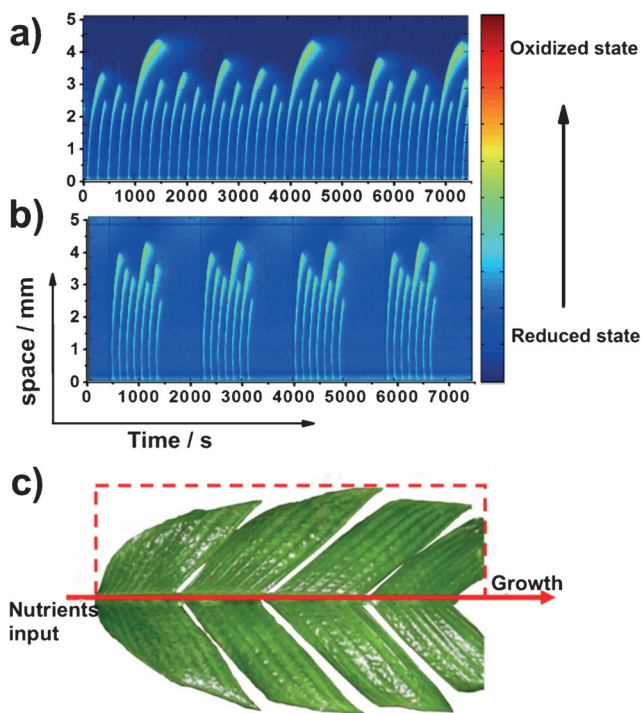


Figure 1. Chemical pulse waves and leaf pattern. a) Time-space plot of reaction-diffusion wave under constant illumination. b) Time-space plot under periodic illumination. Chemicals are introduced at $x=0$ in (a) and (b). $[MA] = 30 \text{ mM}$, $[NaBrO_3] = 90 \text{ mM}$, $[HNO_3] = 0.6 \text{ M}$, $T = 22^\circ\text{C}$. $T_F = 1800 \text{ s}$, $\Phi_{\min} = 0.054 \text{ mWcm}^{-2}$, $\Phi_{\max} = 0.925 \text{ mWcm}^{-2}$. c) Pinnatisect-shaped *Pinanga discolor* burret leaf.

(NIPAAm) and a photosensitive ruthenium-based catalyst of the BZ reaction. When this gel is placed in a solution containing the BZ reactants, pulse waves and periodic volume changes are generated. In previous work,^[9] we modified the copolymer gel with a higher concentration of cross-linker before synthesis to obtain a Ru-copolymer NIPAAm gel that supports chemical waves but does not exhibit volume changes. When confined to a capillary into which the BZ reactants (but not the catalyst) diffuse from one end, this gel makes an ideal system for investigating diffusion-fed spatiotemporal dynamics and its response to external stimulation.

The effect of light on the homogenous form of the Ru-catalyzed BZ reaction has been extensively examined.^[10] Periodic perturbation of chemical oscillators can produce phase shifts, synchronization, an excitable response with a time delay, signal communication and collective behavior.^[11] Periodic light is more effective than constant light with the same average light intensity.^[12] Recently we found a non-

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monotonic relationship^[13] between oscillation frequency and illumination intensity, indicating that photopromotion and photoinhibition occurred under low and high light intensities, respectively. In the present work, we couple a unidirectional diffusion-fed system with external periodic light perturbation in order to mimic biological growth structures. The results indicate that external periodic forcing can induce the growth of wave groups analogous to certain growth patterns in living organisms.

The experiments, as described in part 1 and Figure S1 of the Supporting Information, were initiated by illumination for 12 h under constant white light intensity, $\Phi_{\min} = 0.054 \text{ mW cm}^{-2}$. Then, the gel was exposed to a periodic intensity (period T_F) that varied between Φ_{\min} and Φ_{\max} .^[11b]

Figure 1a shows a time–space plot of pulse waves under constant illumination at low light intensity (Φ_{\min}) in the gel-filled capillary. The chemical pulse waves originate spontaneously at one end and propagate toward the other end. Over about 10 h, a series of spatial period-doubling bifurcations^[9,14] occurs starting from a period-1 pattern and ending with the stable period-16 pattern shown in Figure 1a. When the applied light intensity is periodically modulated, Figure 1b shows intermittent wave groups, denoted I^7 , in the time–space plot. A stable wave group appears in the first portion of each period followed by an interval of quiescence. The period of

this state is equal to that of the periodic light perturbation, indicating that I^7 is entrained to the forcing. As can be seen in Movie S1 (Supporting Information), I^7 spreads intermittently from right to left in the diffusion-fed gel system. Its group structure can be clearly seen in the space–signal intensity plot shown in Movie S2 (Supporting Information), in which the blue curve shows the chemical waves propagating in the capillary gel for about three periods. One-dimensional maps of pulse propagation–distance for Figures 1a and 1b also characterize the transition from period-doubling waves to intermittent wave groups (Figure S2 of Supporting Information).

In Figure 2a, we observe the sequence of chemical waves groups I^2, \dots, I^9 as the illumination period increases from 400 s to 2800 s. When the period is less than 400 s, the wave pattern shows a period-16 structure, which is same as under constant illumination at intensity Φ_{\min} as shown in Figure 1a. When the period exceeds 3000 s, the wave pattern is quasiperiodic without intermittent groups. We obtain the same sequence of patterns in simulations of a modified six-variable light-perturbed reaction-diffusion model, as shown in Figure 2b.

The experimental local dynamics are shown in Figure 3. When $T_F = 400$ s, the gray value oscillates twice and then becomes nearly constant (Figure 3a), in agreement with the time–space plots under the same conditions. As shown in

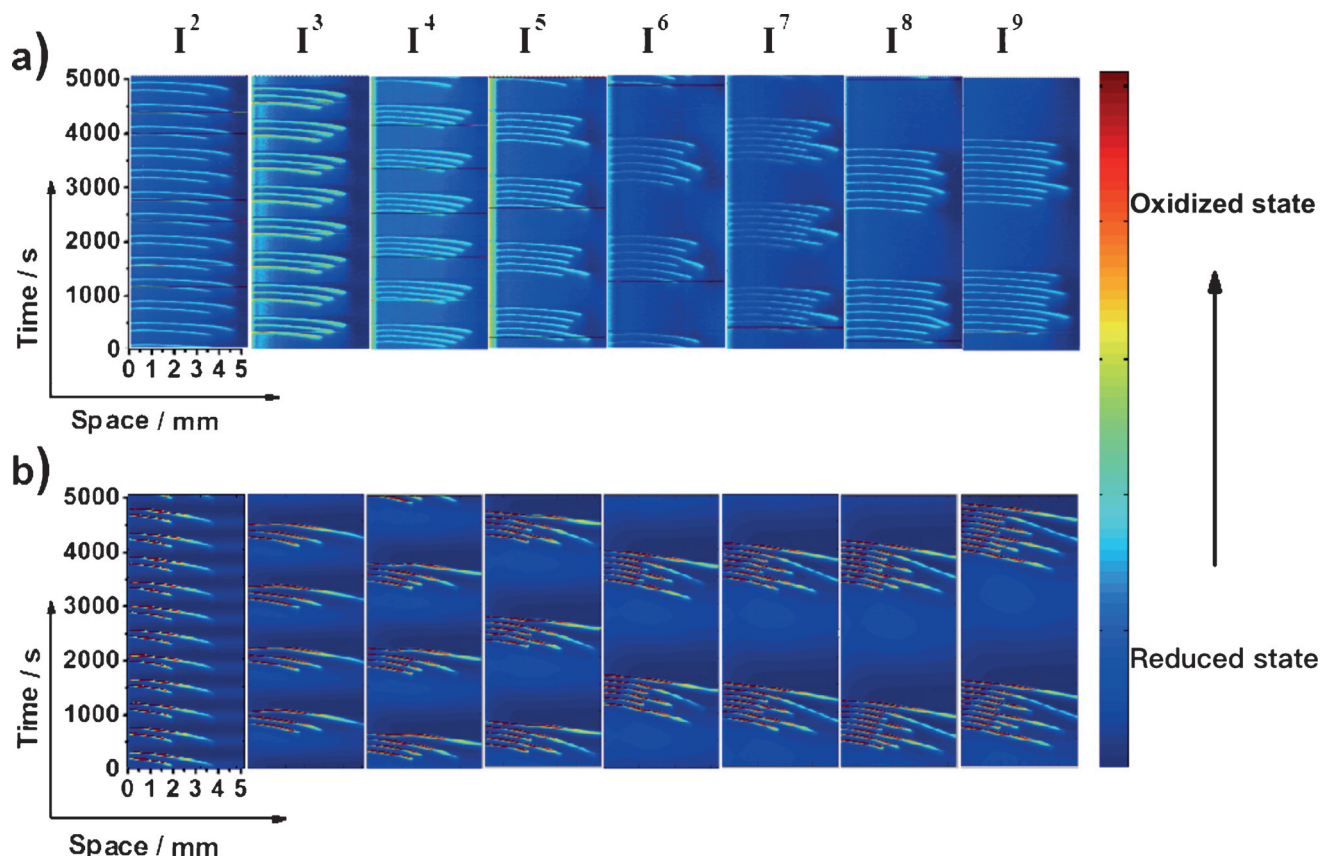


Figure 2. Effect of light perturbation period on space–time patterns of waves propagating in a diffusion-fed gel. a) Experimental results. Illumination periods from left to right: $T_F = 400$ s; 600 s; 800 s; 1200 s; 1400 s; 1800 s; 2400 s; 2800 s. $\Phi_{\min} = 0.054 \text{ mW cm}^{-2}$, $\Phi_{\max} = 0.925 \text{ mW cm}^{-2}$, $[MA] = 30 \text{ mM}$, $[NaBrO_3] = 90 \text{ mM}$, $[HNO_3] = 0.6 \text{ M}$, $T = 22^\circ\text{C}$. b) Simulated results ($\Phi_{\min} = 1 \times 10^{-8} \text{ M s}^{-1}$, $\Phi_{\max} = 1 \times 10^{-6} \text{ M s}^{-1}$). The system consists of 1024 grid points (length = 5 mm). Each plot consists of 1000 horizontal data lines at 5 s intervals (i.e., the span of each space–time plot is 1.39 h).

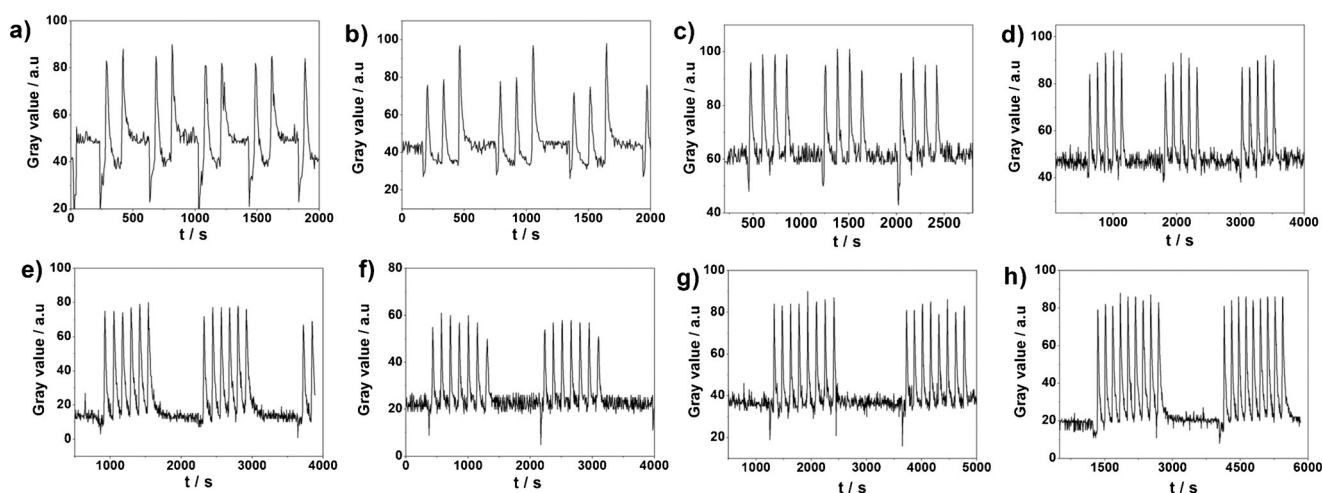


Figure 3. Experimental local dynamics corresponding to I^2, \dots, I^9 intermittent wave groups with increasing illumination period. Experimental conditions as in Figure 2a.

Figure 3a–h), the structure of the intermittent oscillatory pattern changes from I^2 to I^3 , I^4 , I^5 , I^6 , I^7 , I^8 and I^9 with increasing T_F . The simulated results for the local dynamics, shown in Figure S3, are consistent with the experiments. Thus the wave group structure originates from the local complex dynamics modulated by the periodic illumination.

We performed further experiments to investigate the effects of varying the maximum light intensity from 0.145 mW cm^{-2} to 2.0 mW cm^{-2} . The results are shown in Figure 4a. To simulate the wave structure in this diffusion-fed gel system (Figure 4b), we used an eight-step modified photosensitive BZ mechanism to simulate the time-dependent light-perturbed reaction-diffusion waves. Details are given in the Supporting Information.

The phase diagram can be divided into five regions: (1) non-synchronization; (2) weak perturbation; (3) frequency-locked; (4) non-locked; and (5) steady state. In the first region, the light intensity changes quickly, and the gel system is unable to follow the light oscillations. The forcing fails to induce synchronization of the gel system. The system experiences the average light intensity, and its behavior resembles that observed under steady illumination with the average light intensity. In the second region, the maximum light intensity is close to the minimum intensity: i.e., the variation of light intensity from Φ_{\min} to Φ_{\max} is relatively small. In this region, the effects are similar to those observed under constant illumination.

In the frequency-locked region, the oscillations of the gel system couple to the periodic light perturbation to create the intermittent wave groups described above. The higher light intensity produces more of the inhibitor, bromide, which ultimately suppresses the oscillations. At shorter forcing periods, the extra bromide is generated more rapidly, causing the oscillation to terminate sooner, resulting in simpler wave groups, e.g., I^2 . At a given forcing period, higher Φ_{\max} results in a more rapid buildup of bromide, leading to simpler wave groups. This region is divided into eight subregions, from (I) to (VIII), corresponding to I^2, \dots, I^9 .

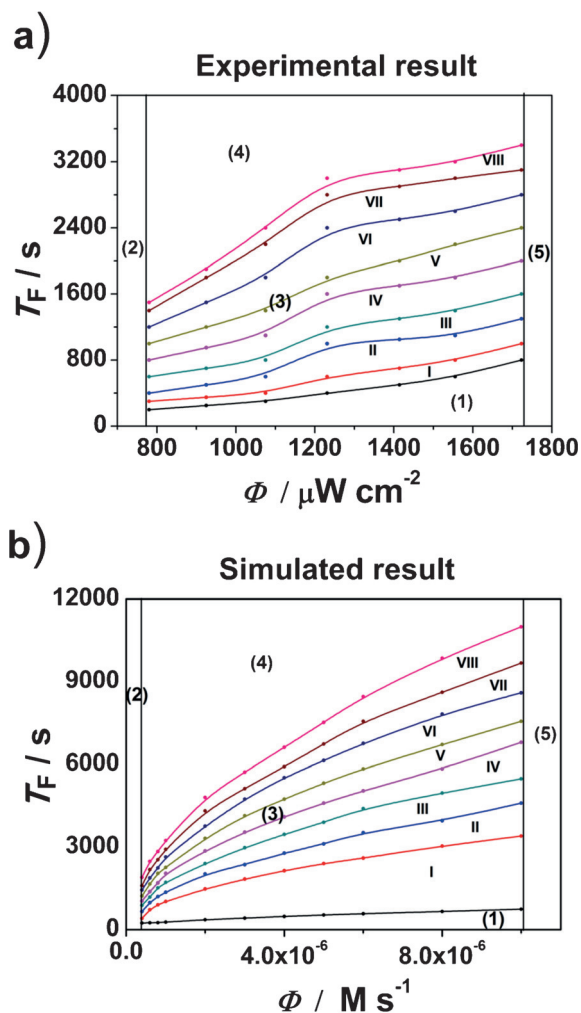


Figure 4. Phase diagrams showing the behavior of the system as a function of forcing period and maximum light intensity. a) Experiments. b) Simulations. (1) Non-synchronization; (2) weak perturbation; (3) frequency-locked; (4) non-locked; (5) steady state. Regions between curves (I)–(VIII) correspond to intermittent wave groups I^2 to I^9 in turn. Other parameters and conditions as in Figure 2.

In the fourth region, T_F is large enough to allow the system to consume the extra bromide produced by illumination, so the oscillations are never completely inhibited. The system displays quasiperiodic oscillations in local dynamics and undulating wave groups (Figure S5a in the Supporting Information) in a time–space plot. Finally, in the last region, the light intensity is high enough to inhibit oscillations completely, and the system displays a steady state.

The above space–time plots describe the evolution of pulse lengths in time, just as Meinhardt^[4] depicted the development of patterns on sea shells, where the passage of time is reflected in the growth direction of the patterns. Also in plant growth, nutrients are diffusion-fed from the trunk and branched to leaf veins at multiple levels, where photosynthesis then transforms nutrients and CO_2 to biomolecules, resulting in new lateral veins with multiple length scales.^[2] In a previous report,^[9] we observed a similar multiple length instability of wave propagation in a diffusion-fed BZ gel.

Both BZ oscillations^[13a] (see Figure S4 in the Supporting Information) and photosynthesis^[15] can transition from photopromotion to photoinhibition with increasing light intensity. Plants must cope with several orders of magnitude change in light intensity during a single day. Superimposed on the daily and annual cycles are oscillations or fluctuations with frequencies ranging from seconds to years. Plants may respond to variations of frequency and amplitude via development of shape changes and leaf movements.^[16] In this work, periodic changes of illumination intensity on a diffusion-fed BZ gel induced the transition from regular waves to wave groups or undulating waves. These new wave structures may share a basic underlying dynamics, i.e., coupling between diffusive transport and chemical reaction, with different leaf morphologies such as pinnatisect-shaped, lobe-shaped and crena-shaped leaves^[17] (see Figure 1c and Figure S5 of the Supporting Information) resulting from growth of lateral veins via group or undulating waves. This periodically forced, diffusively-fed reaction wave mechanism may provide an alternative to the deformation theory of mechanical buckling and cracking,^[18] at least in some cases. It would be instructive to perform experiments aimed at determining whether periodic variations of temperature or light intensity with periods quite different from the length of a day might lead to structural variations in the development of some simple organisms. Finally, it is important to note that the wave groups studied in this work can further combine and interact with other wave dynamics^[4] such as branching, rotating, superposing and crossing of propagation waves, in addition to elastic deformation,^[18] for understanding the more complex developmental structure that may arise in living matter.

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