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Flower Patterns in a Growing Active Chemical Medium

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A simple experimental model on the basis of the Belousov−Zhabotinsky (BZ) reaction was produced for the study of wave patterns in a spatially growing excitable medium. A drop of sulfuric acid, placed onto a millipore filter soaked with low-acid BZ solution, expanded with time and made the system excitable. New patterns of flower-like propagation were observed at the frontier of a growing excitable spot. Initially plain circular wave fronts, when expanding, changed to a crown of petal-like propagating fragments of excitation waves. The overall symmetry of the system spontaneously changed with time.

Introduction

The ability of living systems to grow and create various forms starting from one cell is an exciting phenomenon.[1−5] A few general mechanisms are suggested to describe patterns of growth in biological systems: reaction−diffusion processes (Turing structures),[1,2,5] population dynamics coupled with single-unit mobility,[5−12,21,22] and cellular automata and topological approaches.[5] Few of these are understood and reproduced in physicochemical systems. The most famous are dendritic growth in physics and Turing structures in chemical systems.[2,13,14] On the other hand, there are well-known excitation patterns arising in biological[1,15−22] and physicochemical systems,[23−29] although there is a complete lack of knowledge concerning what can happen in growing excitable systems.

We have observed pattern formation induced by growth and excitation waves in an active chemical system. Propagating chemical waves in the Belousov−Zhabotinsky (BZ) reaction are known as a picturesque example of self-organized pattern.[23−29] They provide a clear and manageable experimental model for study of excitation propagation, structures, and patterns, especially related to the biological active media.[1] A simple experimental model of a growing system on the basis of BZ reaction has shown new patterns of flower-like propagation. Circular wave fronts in a growing excitable medium changed to a crown of petal-like propagating fragments of excitation waves. The overall symmetry of the system spontaneously changed with time.

Results

The experiments were made in a batch reactor.[23,24,29] An approximately 3 cm × 3 cm piece of millipore filter (pore size 0.5 m) was soaked with BZ solution with initial concentrations: $NaBrO_3$, 0.142 M; NaBr, 0.025 M, H_2SO_4, 0.142 M; $CH_2(COOH)_2$, 0.14 M; $Fe(phen)_3$, 3.6 mM. A 0.5 μL drop of 6 M sulfuric acid was placed (with micropipette Gilson) at the surface of the millipore filter and absorbed into the filter during 30−40 s. After that the filter was covered by a 2 mm layer of transparent chemically inert oil in order to prevent drying and oxygen influence on the reaction.[29] The use of a thin (0.12) millipore filter as a support for the excitable medium precluded hydrodynamic motion and three-dimensional effects, such as 3D wave propagation, concentration gradients etc. The concentrations in the medium were chosen in order to make the medium excitable only when an additional amount of sulfuric acid was provided. Thus, the drop of sulfuric acid formed a blue circular spot (diameter about 3 mm) on the red background (Figure 1), expanding with time due to diffusion of the acid. All of the medium was distinctly divided into two major parts: an active part, influenced by additional acid, where excitation (oxidation waves) was possible and an inactive part, remaining in reduced state. In a central area of the blue oxidized spot, no wave propagation was observed and the medium permanently remained in the oxidized blue state.

The oxidized core emits periodic, circularly expanding waves, in a pacemaker fashion. At the beginning of experiment, the propagating waves could be seen only in a narrow band, encompassing the permanent blue zone. The waves originated at the oxidized area and propagated toward the unexcitable, inactive part of the medium, Figure 1a,b. When they reached the unexcitable region they died down and disappeared, while the medium remained bluish where the wave passed through it. The picture of the frontier of the excitable spot underwent alternatively the sharp border and a diffusive smooth border. The sharp border is observed when a wave is propagating; see Figure 1a. A diffusive smooth border is observed after the wave disappears; see Figure 1c. Thus, in an early stage of the development of the wave pattern, the active area, periodically pulsating (with the period 30−40 s), slowly expanded with time.

After 5−6 pulsations the shape of the wave front usually changed. In Figure 1c one can see that a small fragment of wave number 6 (at the left bottom part of the frame) did not disappear simultaneously with the rest of the wave, but protruded slightly more, forming a triangular petal-like trace. On the contrary, the next propagating wave (number 7) underwent a wave break at the same place, Figure 1d. Again wave number 8 formed the petal, Figure 1e. Further, each even wave formed the petal, and each odd wave formed the break in the front at the same place. With time alternative petal−wave break defects arose also in other places, forming a flower-like structure, Figure 1e,f. This structure expanded with time, accumulating more defects. It disappeared only with exhaustion of the medium, normally about 60 min after the start of the experiment.

With slightly changed concentrations (increased concentration of malonic acid to extend the lifetime of the reaction[26,29] and increased amount of sulfuric acid placed on the filter), it is possible to observe transition to another flower structure with petals-waves propagating in a ring-shaped band of the excitable medium, Figure 2. The radial direction of the wave propagation spontaneously changed to a circular propagation. The waves were moving around the central unexcitable spot. This blue spot (in the middle of Figure 2b) might be formed by the fast exhaustion of the excitable medium in the region of increased

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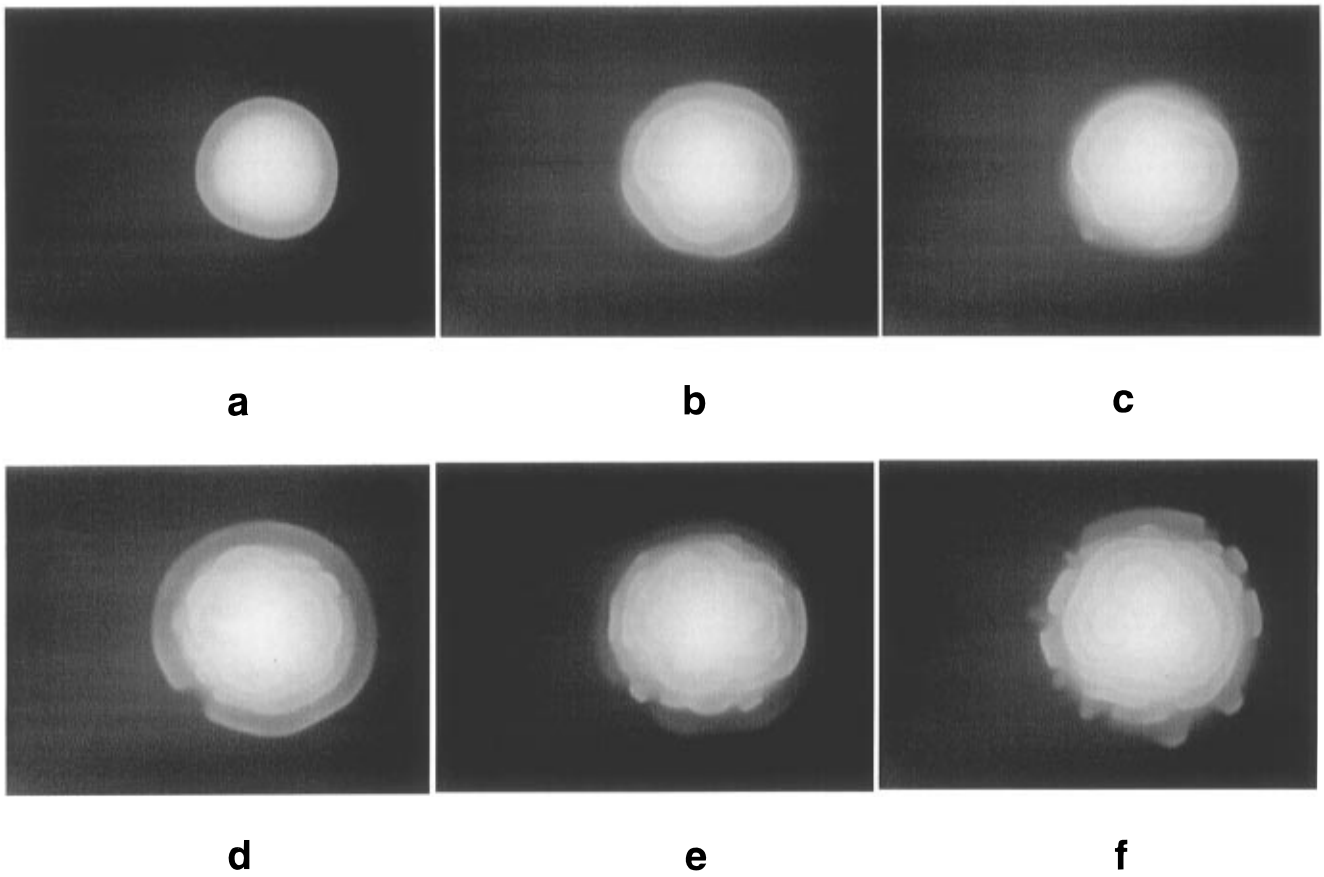

Figure 1. Wave propagation in the diffusively expanding drop of sulfuric acid. (a) At the beginning of the experiment (the first wave). The white spot is the oxidized area with strong acidity (formed by a 0.5 μL drop of 6 M sulfuric acid); it is encompassed by the wave (a light band with sharp boundary), propagating toward the unexcitable part of the medium. Frame size: 17.3 mm × 12.7 mm. (b) 3.25 min after the biginning of the experiment (wave number 6). The oxidized and excitable area expands. (c) 4 min after the beginning. Wave number 6 has died down except for a small fragment of the wave front, at the left bottom part of the picture. The propagating fragment leaves a triangular petal-like trace. (d) 4.20 min, wave number 7. The wave number 7 is broken at the same place where the fragment of the wave number 6 protruded further than the rest of the wave. (e) 5.30 min, wave number 8. Wave number 8 died down, leaving the petal at the place where wave number 7 had been broken. Also the new petal-like fragments of wave front appear (e.g. at the right bottom part of the frame). (f) 7.30 min. Wave number 10 has multiple wave breaks. The excitable area is surrounded by petal-like propagating fronts.

acidity, or it might be a region that is permanently in the oxidized blue steady state. This oxidized steady state produces brominated products continuously that can inhibit the reaction in the dark ring surrounding the blue spot. (In the dark ring the acid concentration should be lower than in the center; thus, the brominated products diffusing out of the center can keep the system permanently in the reduced steady state there.) Finally there is a third ring of excitability surrounding the dark ring. A self-oscillatory pacemaker close to the "North Pole" sends waves on this excitable ring in both directions. The clockwise and counterclockwise waves finally meet and annihilate close to the "South Pole" of the figure.

In order to study the mechanism of the blooming of an initially plain circular structure, we changed composition in the inactive part of the medium. With the decrease of acidity, in general, the flower structure appeared at the later stages (more than 10−12 pulsations, when sulfuric acid was completely excluded from basic solution) and the length of the petals decreased. On the contrary, with increased acid concentration, it was possible to observe the defects of the wave front at the beginning of the experiment, as early as at the second pulsation. If further increased, the acidity was sufficient to activate the inactive part of the medium with propagating waves. In the latter case the observed picture was very similar to that described in ref 30.

We have measured the radius r of the flower structure with time, Figure 3, lower curve. The dependence of r^2 on time is very close to linear, as it should be for a diffusion process (the diffusion of sulfuric acid). But it slightly deviates from linear probably because of the overall change of the concentrations in a batch reactor due to the aging of the solution.[31] We also studied the expansion of the oxidized blue spot in a single switch system, showing no periodic waves but only one transition from the reduced to the oxidized state. For this purpose, we excluded malonic acid and the basic solution contained only bromate and ferroin. In this case the initial blue circular spot was slowly growing in size (the upper curve on the Figure 3), always surrounded by a sharp border. The border between the blue and the red color clearly showed the concentration level of the sulfuric acid, sufficient for the triggering of the autocatalitic process. From Figure 3 one can see that the measured size of the flower structure and the radius of this spot are very close. The main difference is that in the system without recovery we never observed the fragmentation of the propagating front and any petal-like structures.

Discussion

Formation of moving and stationary patterns in reaction−diffusion systems is an area of current interest. Since the publication of the first open spatial reactor,[33] the annular gel reactor, research in this area focused mainly on patterns appearing in asymptotic or steady states. The present Letter reports an angular symmetry breaking in a transient state: on the perimeter of an expanding spot of higher acidity in a BZ

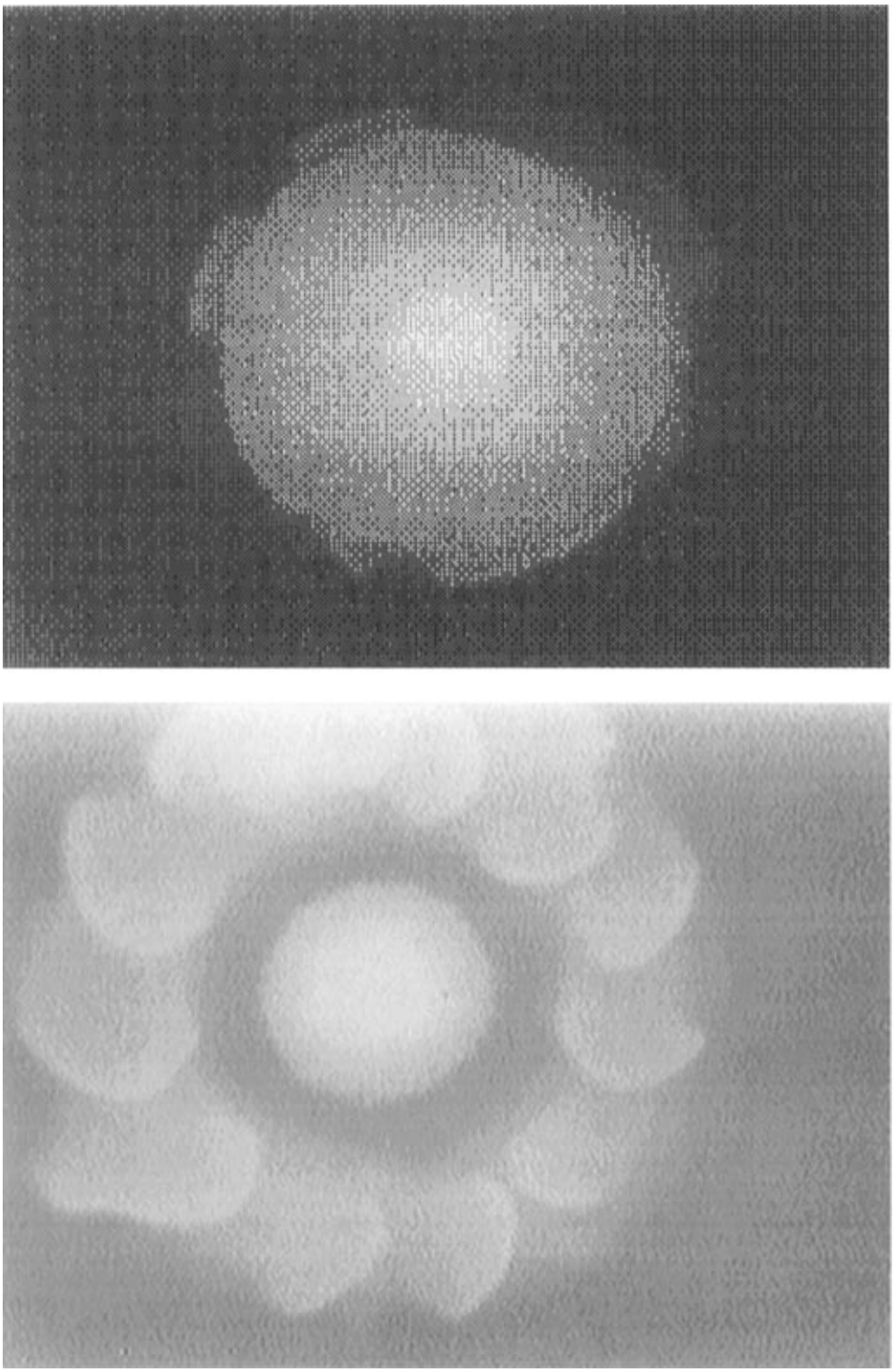

Figure 2. Transition from radial to circular wave propagation. (a, top) The expanding excitable area, formed by a 2 μL drop of 6 M sulfuric acid, 8.30 min after the beginning of the experiment. (b, bottom) The waves, propagating in the circular excitable band, spontaneously formed in the medium. 48 min after the beginning of the experiment.

medium. The ring-shaped reaction zone is similar to that in ref 33 but with a major difference: due to the ever changing chemical gradients in the expanding spot the present system is always in a transient state. It is rather probable that the breaking of the perfect angular symmetry of the initial target patterns is caused by just those acidity gradients that are changing in space and time and that are characteristic of the transient state.

Figure 4 explains the chemical "anatomy" of the flower structure. The acid distribution creates three zones in the medium: (1) an overoxidized unexcitable zone, formed at the central part of the structure where a strong acid solution was introduced in the medium; it always remains blue; (2) an excitable zone, encompassing zone 1, where the amount of diffused sulfuric acid was sufficient to trigger the wave propagation; (3) a reduced unexcitable zone, surrounding all the structure. With time, sulfuric acid diffused into zone 3, expanding zone 2 and decreasing the steepness of the concentration distribution. The boundary between zones 1 and 2 serves as a source for periodically emitting waves. At the boundary between zones 2 and 3 the waves die, undergoing damped propagation.

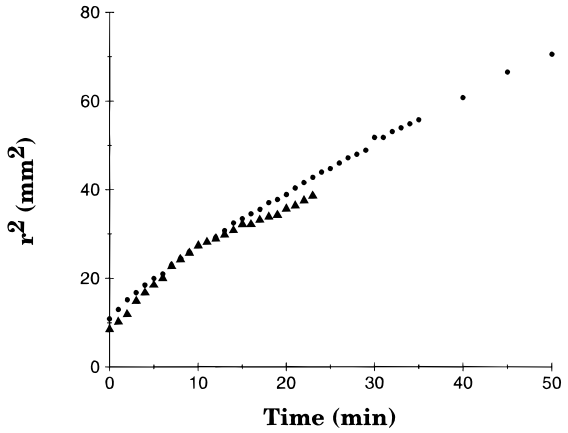

Figure 3. Radius (r^2) of the excitable area versus time. Circles, the size of the oxidized area in the nonoscillating trigger system (without recovery). Triangles, the size of the excitable area in the oscillating system. The volume of the drop of 6 M sulfuric acid is 0.5 μL.

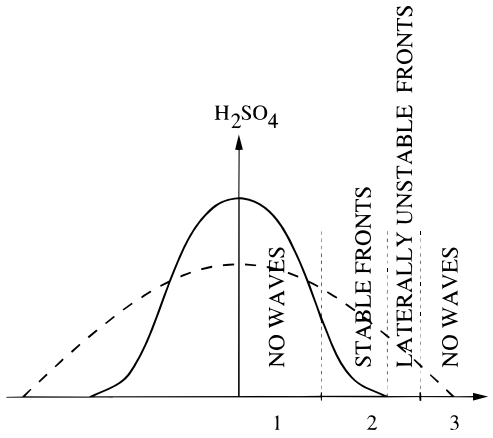

Figure 4. Schematic representation of the expanding excitable area. 1, overoxidized unexcitable zone where wave propagation is impossible. 2, excitable zone where wave propagation occurs. 3, unexcitable zone to which excitable zone expands. Expanding of the whole structure with time is shown by the dashed curve.

How do front defects arise, giving birth to petal structures? Are they generic for such a system? Evidence is provided by the observation of a propagating oxidation front in the system with excluded malonic acid. We never observed petal-like growth in this system. Expanding oxidation fronts always remained plain and smooth without any deviations. So, we can conclude that petal instability appears only for the waves propagating in oscillating growing system. Unfortunately there is no well-developed theory for the growing excitable systems.

The process of the accumulation of petal defects seems clearer. It is based on the dynamic memory of the system. Once it appears, the defect of the wave front is memorized by the medium. The protruded fragment of the propagating front leaves a distinct trace of bluish nonrecovered medium. The next wave reaches this trace and breaks down. Then there appears a "hole" in the wave front, Figure 1d. This hole provides the conditions for the protrusion of a fragment of the next wave, Figure 1e. Thus the defect of the wave front alternatively appears as the hole or the petal. Once is formed it does not disappear. With time, new defects arise and form flower structures. Finally, to explain the circulating petals-waves structure shown in Figure 2, we refer to ref 34 where it was shown that such structures are generic for a ring-shaped reactor.

A seed of excitable medium developing with time and expanding into surrounding area is a very general phenomenon. Growing and spatially expanding microbial populations often give similar flower-like structures.[8,11] A plasmodium of the cellular slime mold Physarum polycephalum expands by periodic pulsations.[20] The growth of biological tissues,[1,5,7] the processes of early morphogenesys,[1,2] and the structure of annual rings of woody plants can all be described by similar dynamic models. We hope that development of simple experimental models featuring these processes will provide new ground for understanding.

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