Experimental study of the dimensionality of black-eye patterns

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The spatial structure of one type of Turing pattern named ''black eyes'' is studied in experiments using the chlorite–iodide–malonic acid reaction in spatial open reactor. The purpose of the work is to verify (or falsify) two possible theoretical interpretations of black-eye pattern formation: the projection of a body-centered-cubic (bcc) structure onto the plane vertical to the body diagonal and the spatial resonance of larger wave vectors with the fundamental ones. The latter happens when the mode of the larger wave vectors becomes linearly unstable, as the system goes far beyond the onset of Turing bifurcation. Our experimental results give evidence that black-eye patterns are not a projection of the bcc structure, so that the interpretation of a three-dimensional structure can be ruled out. The observations in the experiment also suggest another possible mechanism for the formation of black eyes.

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I. INTRODUCTION

Stationary and spatially periodic structures of chemical concentrations, known as Turing patterns [1], may appear in a spatially extended system as a result of the interplay between diffusion and chemical reactions. General pattern selection theories predict that, depending on the dimensionality of the pattern forming system, different patterns may appear at the onset [2,3]. In a three-dimensional (3D) system, the first structure that grows from a homogeneous background is body-centered cubic (bcc). It gives way to a pattern of hexagonal columns as a control parameter passes a critical point beyond the onset; then the hexagonal columns give way to walls as the control parameter passes another threshold value [2–4]. In a 2D system, a structure of hexagonal spots will appear at the onset, followed by a pattern of stripes as a control parameter is varied across another critical point beyond the onset [5].

In recent years, Turing patterns have been observed in experiments in two types of spatial open reactors using the chlorite–iodide–malonic acid (CIMA) reaction [6,7]. In both types of reactor, the reaction medium was a piece of gel. Two opposite faces of the gel were each kept in contact with a permanently refreshed reservoir. Different reactants were supplied in different reservoirs, so that multiple gradients of reactant concentrations were built up in the direction orthogonal to the faces, and a continuous change of reactant concentrations existed inside the gel. When the conditions for Turing pattern formation were met in a region inside the reaction medium, a regular chemical pattern with an intrinsic wavelength formed. The typical wavelength of an observed Turing pattern was about 0.2 mm. In the first type of reactor, the size of the gel in the gradient direction was about 3 mm, the visualization was perpendicular to the feeding direction; and a few successive rows of spots emerged when control parameters were varied across a given threshold. A qualitative analysis identified the observed pattern as a body-centered-cubic structure [8]. In the second type of reactor, the size of the gel in the gradient direction could be as thin as 0.4 mm; the visualization was parallel to the gradient direction; and hexagonal or striped patterns appeared at the onset of Turing instability [7]. These patterns were proved to be quasi-two-dimensional [9]. Beyond the onset, more complex patterns, such as rhombic structures, zigzags, and black eyes, would appear to replace the previous patterns [10]. Similar concentration patterns of black eyes were also reported by Steinbock and co-workers in another reaction-diffusion system [11].

When the observation of black-eye patterns was first reported, a possible mechanism of the black-eye pattern formation was given based on the assumption that the system was quasi-two-dimensional [10]. The Fourier transform provided in [10] report revealed that black eyes consisted of a superposition of two hexagonal lattices with different wavelengths: a larger lattice with white spots and a smaller lattice with black ones. The ratio of the wavelengths was $\sqrt{3}:1$, so that the smaller lattice could be considered as spatial harmonics of the larger lattice. The authors proposed that, as the system was driven far from the onset, the secondary mode, corresponding to the lattice of black spots would become linearly unstable. This unstable mode could be reinforced by spatial harmonics generated by nonlinear interactions of the basic mode (lattice of white spots). Nonlinear coupling between the two modes was responsible for the formation of black-eye patterns. An alternative to the above mechanism of black-eye pattern formation is a 3D effect. Recently, Gomes used three-dimensional Euclidean symmetries to propose a theory for the formation of black-eye patterns [12]. The author considered a 3D effect in the reaction-diffusion system constructed by Ouyang and co-workers [9]. Taking into account the focal depth of the observation lens, the geometry of patterns along the observation direction was difficult to resolve precisely, so that experimental pictures might correspond to projections of an actual three-dimensional structure. The black-eye pattern was expected to be a slice of a particular sinusoidal bcc planform, which was the most favored structure in a 3D system [13].

The purpose of this paper is to clarify one issue: whether a black-eye pattern is a quasi-two-dimensional structure or a

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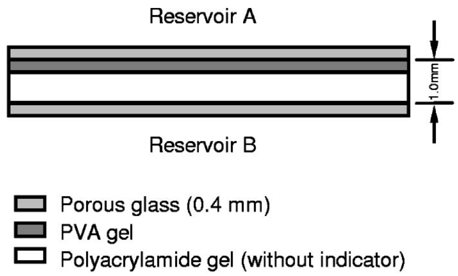

FIG. 1. A sketch of the spatial open reactor and the arrangement of gels in the experiment.

slice of a 3D bcc planform. By observing black eyes in a thin enough gel, the possibility of the second suggested mechanism can be excluded. The black-eye pattern is quasi-two-dimensional. In view of some discrepancies with the mechanism suggested in [10], we propose that the black-eye pattern may occur in the boundary layer of the reaction medium. This hypothesis is partly supported by our experimental observations.

II. EXPERIMENTAL SETUP

Our experiments were conducted in a spatial open reactor, which was basically the same as that described in the early studies [10]. The CIMA reaction was used in the investigation of black-eye pattern formation. A major modification of the reactor was that the reaction medium, which was sandwiched between two porous glass disks, consisted of two gel disks rather than one: a very thin disk of polyvinyl alcohol (PVA) gel and a disk of polyacrylamide gel. A sketch of the reactor is shown in Fig. 1. The diameter of the reaction medium is 24.8 mm; the thickness of the porous glass disks is 0.4 mm; and the total thickness of the gel disks is 1.0 mm. The outer flat surface of each porous glass disk is in contact with a reactant reservoir, in which the concentration of chemicals and the temperature are maintained constant.

Unlike previous work, in this experiment the polyacrylamide gel was not preloaded with starch or other color indicators of tri-iodide (I_3^-). Since slowing down the effective diffusion rate of tri-iodide is a necessary condition for Turing pattern formation in the CIMA reaction [14,15], no Turing instability can take place in this gel. On the other hand, the PVA gel is ready to react with tri-iodide to form a complex, thus slowing down the effective diffusion rate of tri-iodide. As a result, in this setup Turing patterns can appear only in the layer of PVA gel when the other conditions for Turing instability are satisfied there. The patterns can be visualized because the PVA–tri-iodide complex gives a red color, and tri-iodide is one of the variable species in the CIMA reaction. The depth field of our camera lens is about 1 mm.

In the experiments, we chose the feeding concentration of malonic acid in reservoir A ($[CH_2(COOH)_2]_0^A$) as the control parameter, and varied the thickness of the active reaction medium, the PVA gel disk. Three PVA gel disks with different thicknesses were prepared. The thicknesses of the gel disk were 0.144, 0.10, and 0.09 mm. The thickness of the polyacrylamide gel disk was adjusted accordingly to make the total thickness of the gels 1.0 mm. Because of technical difficulties, a PVA gel thinner than 0.09 mm was hard to make, and the medium became too inhomogeneous as the thickness went below 0.09 mm. To make sure the observed patterns were not transients, for each set of experimental conditions, enough time (more that 2 h) was given to allow the system to relax to its asymptotic state.

III. EXPERIMENTAL RESULTS AND ANALYSIS

We repeatedly conducted the experiments using the PVA gels with different thicknesses. In all the experiments, as the concentration of malonic acid was varied across a critical value, we observed black-eye patterns that emerged and stayed in the system as a stable asymptotic state. The observed patterns were the same as described in the earlier study [10]. In fact, changing the thickness of the disk of PVA gel had no quantitative effect on the formation of black eyes, except that the wavelength of the pattern might change very slightly, and the concentration of malonic acid in reservoir A had to be adjusted in order to bring the system into the black-eye regime. In our experiments, a black-eye pattern could emerge from a background of a hexagonal or striped pattern. In the first case, as the control parameter was varied, a black spot gradually appeared in the middle of each white spot; in the second case, as the control parameter was varied, a regular array of black spots first gradually appeared in the middle of white stripes, forming a beanlike structure. Then the beanlike structure broke to form black eyes. In both cases, transitions to black-eye patterns were continuous as a function of the control parameter. This observation was consistent with the earlier findings [10]. In the narrow window of black eye formation, the wavelength of black-eyes is constant. We also monitored the transient process when the control parameter was put immediately in the black-eye regime. Half an hour after the control parameter was switched into the black-eye regime, a hexagonal pattern appeared first from a uniform state. Then the hexagons changed into stripes within about 1 h. In about 5 h, black eyes gradually emerged from the stripes and the system attained the asymptotic state. Figure 2 shows some typical examples of black-eye patterns (a)–(c) and a mixed state (d) observed in the experiments. The wavelength of the white hexagons (the principal wavelength) in Figs. 2(a), 2(b), and 2(c) is, respectively, 0.22, 0.23, and 0.21 mm. They were measured both in physical and in Fourier space.

As discussed in the Introduction, there are two alternative mechanisms for black-eye pattern formation, proposed, respectively, by Gunaratne and co-workers [10] and Gomes [12]. The paper of Gomes suggests that a particular sinusoidal bcc structure, the most stable Turing pattern at the onset in a 3D system [13], is expected to form in the experiments where black-eye patterns are observed. We reason that the necessary conditions for a bcc structure to appear as a black-eye pattern are that the body diagonal of the bcc structure must be parallel to the gradient direction; and that the focal depth of the observation lens is no more than two monolayers. A monolayer is defined in Ref. [12] as the inte-

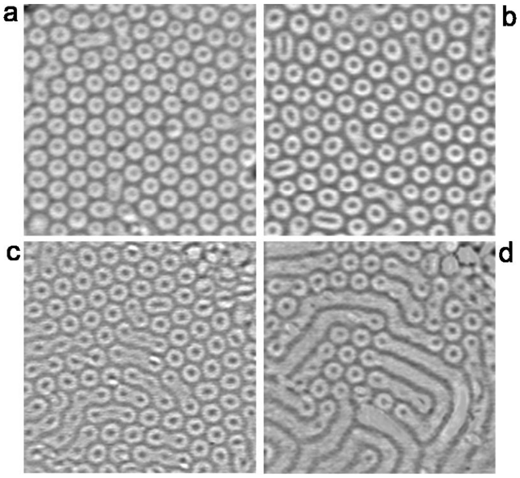

FIG. 2. Examples of black-eye patterns observed in the spatial open reactor using the chlorite–iodide–malonic acid reaction. The thickness of the PVA gel is (a) 0.14 mm, (b) 0.10 mm, (c) 0.09 mm, (d) 0.09 mm. (d) shows a mixed state of black eyes and stripes. The wavelengths of the two patterns are the same. The malonic acid concentration in reservoir A is (a) 14.0 mM, (b) 14.5 mM, (c) 13.5 mM, and (d) 15.0 mM. Other control parameters were held fixed: $[I^-]_0^{A,B}=3.0$ mM, $[Na_2SO_4]_0^{A,B}=4.5$ mM, $[NaOH]_0^B=1.0$ mM, $[H_2SO_4]_0^A=20.0$ mM, $[H_2SO_4]_0^B=2.0$ mM, $[ClO_2^-]^A=0.0$ mM, $[ClO_2^-]^B=22.0$ mM. The temperature is 4 ± 1 °C.

gral between two adjacent lattice planes vertical to the body diagonal. To demonstrate the second condition, we produce an artificial bcc pattern using a sinusoidal function with a computer, and integrate one, two, and three monolayers in the direction of the body diagonal. The results are shown in Figs. 3(a), 3(b), and 3(c), respectively. One observes that a black-eye pattern appears only in the situation of one monolayer. When two or more monolayers are involved, the black-eye structure disappears. Even in the case of one monolayer, in order to observe a black-eye pattern projection, the center of the monolayer must be located in a narrow range of special points of focal depth. For example, if we put the center of the integral around a lattice plane of the bcc structure, the projection does not look like a black-eye pattern, as shown in Fig. 3(d). From Ref. [12], we know that the ratio of the wavelength of a bcc pattern and the thickness of the monolayer is $2\sqrt{6}:1$. Therefore if the observed black-eye patterns shown in Fig. 2 was the result of a bcc projection, the thickness of one monolayer should be, respectively, 0.046, 0.048, and 0.043 mm in Figs. 2(a), 2(b), and 2(c). Thus the thickness of the gel should equal approximately three monolayers in (a) and two monolayers in (b) and (c). Even more monolayers would exist in the setup of former experiments [10]. From the experiments conducted by De Kepper *et al.* [8], we know that a bcc pattern should form at least a few monolayers, not only one; and as mentioned in Sec. II, the depth field of our observation lens is about 1 mm, containing many more monolayers. Putting all the above arguments together, we conclude that a black-eye structure cannot be observed in our experiment even if a sinusoidal bcc pattern appears.

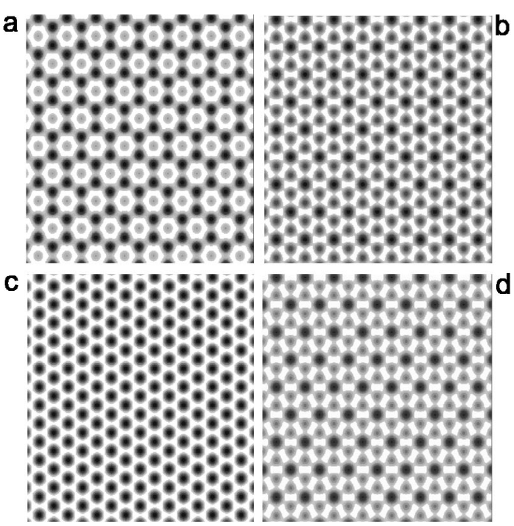

FIG. 3. The integral of a thin domain of bcc pattern. (a) One monolayer; (b) two monolayers; (c) three monolayers; (d) the integral of a monolayer whose center passes only one lattice plane of a bcc structure.

The situation will not improve with the assumption that the black-eye pattern is a projection of a nonsinusoidal bcc structure. In this case, although black eyes might appear with a bcc projection of more than one monolayer, the range of the integral must be special. We know from experiments that as the control parameters change the position of the patterned layer will migrate in the gradient direction of the reaction medium [9]. Thus with the change of the control parameter, we should expect to observe certain complex patterns [as in Fig. 3(d) for example] in the vicinity of black eyes. We did not observe such patterns in the experiments.

There is another discrepancy in the interpretation of black eyes with the bcc projection. Pattern formation theories predict that at the onset of Turing instability the wavelength of a Turing pattern is determined by a dispersion relation that is independent of the dimensionality of the system. Thus a bcc pattern in a 3D system or a hexagonal or striped pattern in a 2D system should have the same wavelength at the onset. All previous experimental work conducted in gels using the CIMA reaction gave a Turing pattern wavelength around 0.2 mm. In our experiments, the measurements show that the principal wavelength of black-eye patterns is about 0.22 mm. If we assume that a black-eye pattern ia a slice of a bcc planform, the wavelength of the bcc pattern should be around 0.11 mm, since the wavelength of bcc structure and its apparent wavelength as black eyes should have a ratio of $1:2$. In the experiments, we observe the coexistence of black eyes and stripes near a transition point [Fig. 2(d)], and the principal wavelength of the black-eye pattern and that of the stripes is almost the same. If the observed black-eye pattern in Fig. 2(d) were a projection of a bcc structure, the pattern formation theory would fail in explaining why the wavelength of the Turing pattern suddenly doubles as the system undergoes a transition from a bcc pattern to a striped pattern.

From the above arguments, we believe that the black-eye patterns observed in this and previous experiments [10] are not a special 2D projection of a 3D bcc structure, so that the observed patterns should be quasi-two-dimensional. Then according to the theory of spatial harmonics, the scenario of the black-eye pattern formation might be as follows. At the onset of Turing instability, only the primary mode becomes linearly unstable. As a result hexagonal patterns with white spots or stripes appear. As the system is driven far from the onset, the band of unstable mode broadens so that the second mode, corresponding to the smaller lattice of black spots, also becomes linearly unstable. Since this mode is a spatial harmonic of the primary mode [10], the two modes can have a nonlinear coupling, which causes the formation of a black-eye pattern. Our experimental results are not in conflict with this interpretation, although they add no evidence to this theory of black-eye pattern formation.

IV. DISCUSSION AND CONCLUSION

Although our experimental results support the interpretation of spatial harmonics proposed by Gunaratne and coworkers in Ref. [10], there are still discrepancies between the experiments and the mechanism. As pointed out by Gomes [12], the major problem is that, since pattern formation and pattern selection processes are considered as universal phenomena which are, to a large degree, determined by symmetry considerations, black-eye patterns have not been reported in other prototype pattern forming systems, such as convection or surface reactions [16]. There must be a special feature in our reaction-diffusion system, which other pattern forming systems, such as Bénard-Marangoni convection, do not have. The answer to this question by Gomes [12] is that the reaction-diffusion mechanism has an intrinsic isotropy that introduces 3D symmetries. Since our experimental results basically rule out the 3D effect, other special effects must account for the black-eye pattern formation.

By reconsidering our experimental setup, we propose the following tentative interpretation. The relation between the wavelength of a Turing pattern and the diffusion coefficients of chemical species in primary Turing bifurcation is determined by the linear term of the reaction-diffusion system. It has the following form:

$$\lambda_c = \sqrt{2\pi PD},$$

where λ_c is the critical wavelength of the Turing pattern, P is a constant related to reaction properties, and D is the geometric mean of the diffusion coefficients of the inhibitor and the activator of the reaction in the isoconcentration plane of the reaction medium. A former experiment [17] showed that the diffusion coefficient of chemical species in a porous glass medium is about 3 to 4 times smaller than that in a polyacrylamide gel medium. Supposing that the diffusion coefficients of reactants in the PVA gel and in the porous glass are in a range around the ratio of $3:1$, at the onset of Turing pattern formation, two different wavelengths will be selected in the plane of the boundary between the PVA gel and porous glass disks; their ratio will be around $\sqrt{3}:1$, which is the ratio for spatial resonance between the two modes. If we further suppose that the pattern on the PVA side of the interface is H_0 (white spot hexagons), while the pattern on the porous glass side of the interface is H_π (black spot hexagons), due to certain nonlinear pattern selection processes, the two linear modes may have a spatial coupling in the boundary region, so that the wavelengths of the two types of hexagonal patterns are locked in the ratio of $\sqrt{3}:1$, constructing black-eye patterns. Thus black-eye patterns may emerge near the onset of Turing patterns in the boundary layer, rather than far from the onset. In the experiment, if we start from a regular hexagonal or striped pattern (white spots or stripes) and change the control parameter, the patterned layer will move along the direction of the concentration gradient. When it is situated on the boundary between the PVA and porous glass disks, a black-eye pattern will appear because of the formation of black spots on the surface of the porous glass disk. Preliminary numerical simulation (not shown) partially supports the above interpretation. However, much more work is needed to reveal the detailed mechanism.

To test this line of thinking experimentally, we added another thin layer of polyacrylamide gel to separate the PVA gel and the porous glass. This gel was not preloaded with starch and had nearly same diffusion coefficient as the PVA gel. We observed normal hexagons and stripes in this setup. However, black-eye patterns were never obtained. This result indirectly supports the above assumption.

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