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ARTICLES

Dancing Waves in Reaction−Diffusion Systems

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The mechanism of pattern formation in reaction−diffusion systems is treated as an interesting subject, generally for understanding self-organization observed in living systems and natural phenomena. Several spatial patterns appear in the reaction−diffusion systems where an activator and an inhibitor coexist as an intermediate, as represented by a traveling wave, a stationary wave called a Turing structure, etc. Here, we show new kinds of waves in reaction−diffusion systems, which exhibit reciprocating motion without colliding into each other or blinking periodically. These patterns have never been observed in the conventional numerical models, although experimentally oscillating spots have been often observed. Our model demonstrates that other than the ratio of diffusion coefficients for both intermediates, the thickness of reaction media acts to generate inhibitory effect. The spatial factor of the medium contributes to new pattern formation in reaction−diffusion systems. For the design of new functional materials, the concept might be useful as a simple controlling method for pattern dynamics.

Introduction

Pattern dynamics in reaction−diffusion systems has been widely studied both theoretically and experimentally. As examples of waves observed in reaction−diffusion systems, it is known that the following patterns appear: "traveling wave", which propagates in the media at constant rate, "breezing wave (pulsating wave)", which expands and shrinks, and "stationary wave", which does not move.[1,2] Traveling waves can be typically observed in the Belousov−Zhabotinsky (BZ) reaction.[3] When the ratio of the diffusion coefficient for the inhibitor to the activator's is enough large, stationary waves (well-known as "Turing structure") often appear. By the experiment using acrylamide gel membrane as a medium for the CIMA (chlorite−iodide−malonic acid) reaction, such stationary waves were actually observed.[4,5] Turing structure is recognized as the significant model for explaining pattern dynamics on animal's skin. Kondo et al.[6,7] showed the hypothesis that the pattern formation on the angelfish is due to the Turing structure and recently succeeded in exhibiting experimental data to support this hypothesis by artificially causing the reaction−diffusion waves on the skin of mutant mouse. When the ratio of diffusivities is large, it is also demonstrated from the Gray−Scott model that a self-replicating pattern like cell division can be obtained.[8,9] Lee et al.[8,10] experimentally observed such a self-replicating pattern in acrylamide gel membrane by causing FIS (ferrocyanide−iodate−sulfite) reaction using a continuous-flow stirred tank reactor (CSTR) and showed a coincidence with the simulation by the model.

Typically the ratio of diffusivities is set to 2 in the Gray−Scott model for the numerical simulation of the FIS reaction. In this condition, all of the patterns obtained from the simulations for two-dimensional media finally result in stationary waves as an equilibrium state. The stationary wave and the pulsating wave then do not coexist. In the experiments using gel membrane, however, periodical motions such as oscillating spots and shrinking rings are often observed as steady-state wave motion.[11] This result suggests that the factor other than the ratio of diffusivities affects the pattern formation. Spatial factor of the medium must be primarily considered to control the patterns because the characteristics of the reaction medium as an open system will vary with the change in inside conditions. For example, although the gel membrane is regarded as a two-dimensional medium in simulation, the thickness of gel is often not negligible. The new condition then appears that there is no effect of the convective flow inside the gel. Therefore, we consider the spatial effect on pattern formation as a practical model.

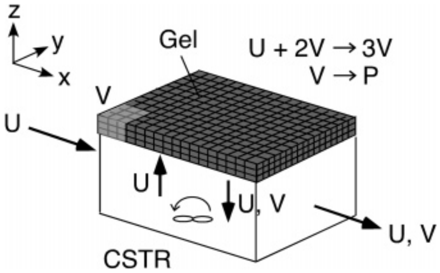

Figure 1. The physical situation of the reaction−diffusion model.

Model

The Gray−Scott model represents the following autocatalytic reaction.

$$U + 2V \rightarrow 3V \qquad (1)$$

$$V \rightarrow P \qquad (2)$$

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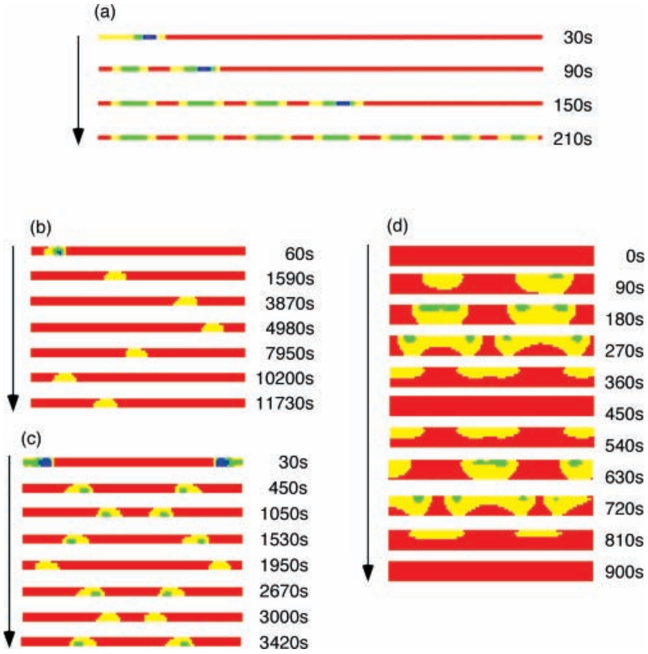

Figure 2. Cross-sectional view of patterns formed in the linear reaction media. The size for numerical calculations (length × width × thickness) is (a) 100 × 1 × 3, (b, c) 100 × 1 × 5, (d) 100 × 1 × 10. As the initial condition, the local domain (length = 10) with the uniform concentration $U = 0.5$ and $V = 0.25$ was given at one or both ends. The diffusion coefficients of inhibitor and activator are set to be $D_U = 2.0 \times 10^{-5}$ and $D_V = 1.0 \times 10^{-5}$, respectively. The other parameters used for calculation are (a) $F = 0.04$, $k = 0.05$, (b) $F = 0.07$, $k = 0.04$, (c) $F = 0.08$, $k = 0.04$, (d) $F = 0.02$, $k = 0.01$. The color represents the concentration of V as follows: red (lower than 0.1), yellow (0.1−0.2), green (0.2−0.25), blue (higher than 0.25).

Here, we consider the model as represented by Figure 1. The gel sheet is in contact with a CSTR that supplies the reactants and carries away the reaction products. U is fed to the CSTR, and U and V are forced to excrete from the reactor. The reaction occurs only in the gel phase. The pattern due to the reaction−diffusion mechanism is created in the gel, and the outer CSTR phase is negligible in the simulation. The pattern dynamics, which is created in the gel, can be simulated via the following equations.

$$\partial U/\partial t = -UV^2 + F(1 - U) + D_U \nabla^2 U \tag{3}$$

$$\partial V/\partial t = UV^2 - (F + k)V + D_V \nabla^2 V \tag{4}$$

Here, F and k represent the feed rate to CSTR and the rate constant of eq 2, respectively. In addition to this conventional model, we newly consider that the flow has no effect inside the gel. The equations can then be reduced as follows.

$$\partial U/\partial t = -UV^2 + D_U \nabla^2 U \tag{5}$$

$$\partial V/\partial t = UV^2 - kV + D_V \nabla^2 V \tag{6}$$

The equations were solved by finite difference method. In the simulation, we assume a cell as a minimum dimensionless space unit. The gel is considered as an assembly of the cells. (When the mesh is considered, one mesh point represents a cell.) The gel size is expressed by the number of cells that are arranged in the direction of x, y, and z; that is, $N \times 1 \times 1$ means one-dimensional gel, $N \times N \times 1$ means two-dimensional gel, and $N \times 1 \times N$ means linear gel with some thickness. As a result of the simulation only using eqs 5 and 6, no pattern is formed in any two-dimensional media. This means that no flow region inside the medium acts to disturb the pattern formation on the surface that is affected by flow. Coupling of inside and surface conditions might have some effects to generate new pattern

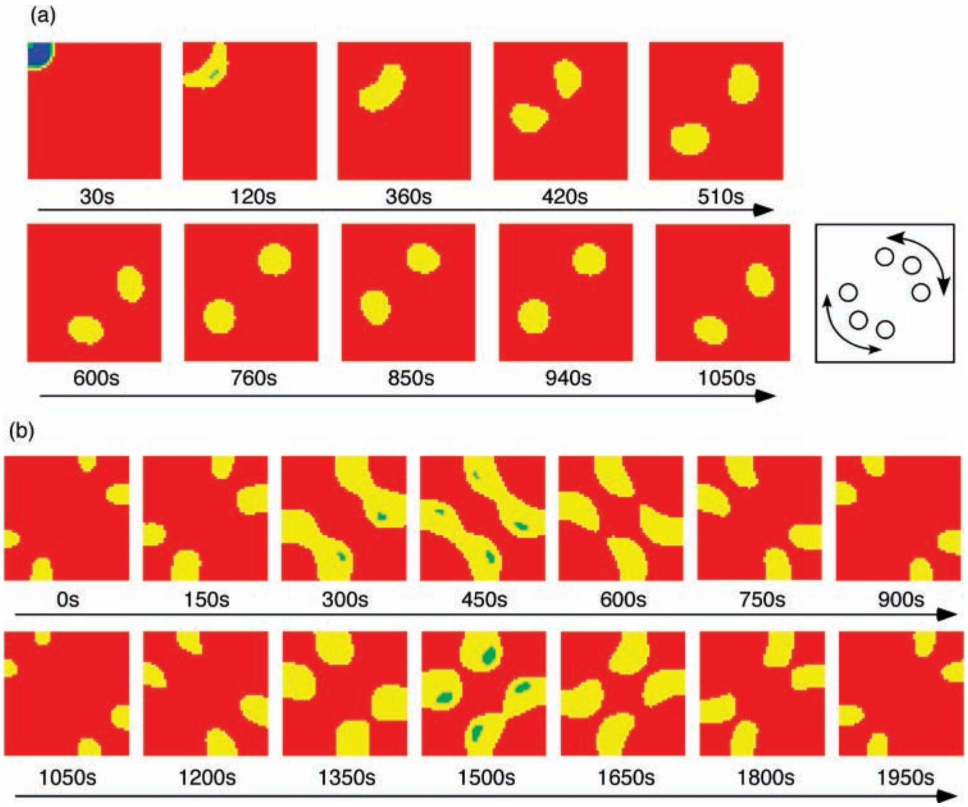

Figure 3. Top view of patterns formed in the square medium with the size of 50 × 50 × 5 for (a) $F = 0.02$, $k = 0.03$, and (b) $F = 0.02$, $k = 0.02$. D_U and D_V are the same values as in Figure 1. The domain (5 × 5 × 5) with $U = 0.5$ and $V = 0.25$ was given at the corner as the initial condition.

formation. Therefore, here we give the spatial condition that eqs 3 and 4 are applied only at the surface (the outermost layer that contacts to the solution in CSTR), while eqs 5 and 6 are applied inside the gel. Under this condition, pattern formations in different reaction media with several sizes were simulated by numerical calculation.

To evaluate the artifacts, the same simulations were attempted by decreasing the mesh size and increasing the cell number for the same gel size. When the mesh size is changed, the other parameters that are affected by the changes of the cell size (e.g., the amount that is fed to the cell) are adjusted in the simulation.

Results and Discussion

Figure 2 shows the cross-sectional view of pattern dynamics in linear media with different thickness. In the thinner medium (Figure 2a), the stationary wave finally covers all the medium as the Turing structure. In the thicker medium, however, the traveling wave that turns back at the end and keeps on moving is observed (Figure 2b). When the initial domains are given at both ends, two waves that start from both ends move to the center, but turn back before collision and keep on moving (Figure 2c). These traveling waves do not collide with the right and left boundaries. It is well known that the Turing structure has an intrinsic wavelength that does not depend on the size of the system. Similarly in our model, the length of closed structure does not affect the pattern formation. Only the thickness affects the pattern formation. Actually, as a result of simulation for a longer medium with the same thickness (300 × 1 × 5), the same reciprocating waves as shown in Figure 2b and c were obtained. In the much thicker medium, the blinking pattern that repeats appearance and disappearance periodically is observed (Figure 2d). Here, both making and erasing mechanisms seems to act in pattern formation. As the thickness increases furthermore (e.g., 100 × 1 × 100 size), such a blinking pattern appears only near the surface; that is, the thickness has no influence over a certain value. These results suggest that increasing thickness has some effect as an inhibitor.

In the simulation, the equations were solved by finite difference method. To confirm that these results are not due to artifacts, we have attempted the simulation by decreasing the mesh size and increasing the cell number for the same gel size. As a result of decreasing the mesh size 5 times, the dynamic behaviors of pattern formation, for example, generation of dancing waves, do not change, although the spot size changes somewhat as the effect that the surface layer becomes thinner. This suggests that the results are not due to artifacts.

In a conventional two-dimensional medium, stationary wave was formed by the interaction of local chemical dynamics and diffusive transport; the inhibitor diffuses faster, and it disturbs the activator's diffusion. In our model, on the other hand, the concentration difference between the surface and inside also seems to play another important role to form spatial patterns. Because U is force-fed to the reactor at constant rate, the concentration of U at the surface is always higher than that inside the medium. On the other hand, V is force-excreted from the reactor without a feed. As a result, concentration gradient must be formed inside the medium; the concentration decreases toward the inside for U but increases for V. The formation of concentration gradient leads to diffusive transport toward the opposite direction from each other; U migrates inside, while V migrates to the surface. This apparently has the same effect as the reaction of $U \rightarrow V$ occurring at the surface. Actually, the same kinds of patterns can be obtained by the model simulation for two-dimensional medium in which $U \rightarrow V$ is newly added to the kinetics as the other reaction process. From this result, it is found that the new mechanism is spontaneously established in our model.

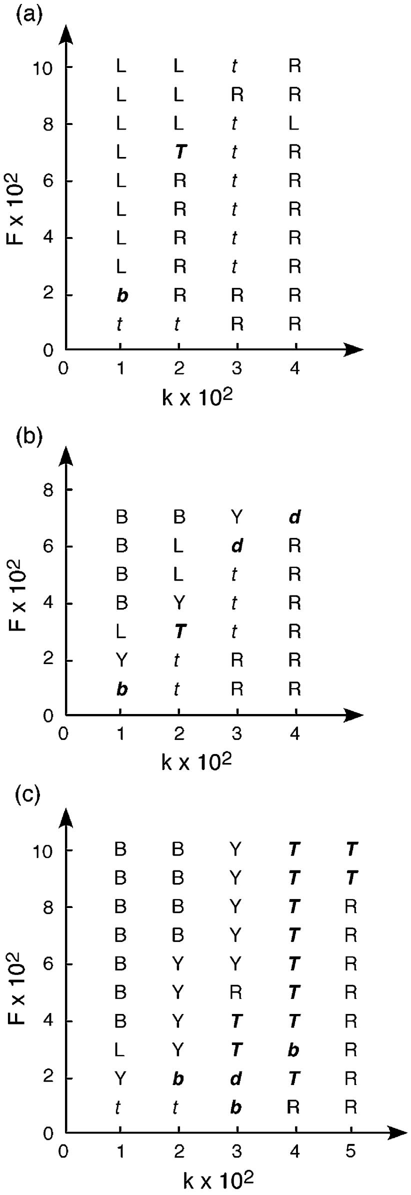

Figure 4. Phase diagram of the pattern formation with the changes in parameters F and k for several media with different sizes: (a) 100 × 1 × 10, (b) 100 × 1 × 5, (c) 50 × 50 × 5. Each character indicates the observed patterns as follows: L, layer structure; B, homogeneous blue state; R, homogeneous red state; Y, homogeneous yellow state; T, Turing pattern; d, dancing wave; b, blinking wave; t, single trigger wave.

Figures 3 shows the top view of pattern formation in the square media with a certain thickness. The two traveling spots that reciprocate with drawing of an arc symmetrically to each other are observed on the surface (Figure 3a). They never collide and continue dancing as a steady state wave motion. Under the other flow conditions, the arc-shaped waves that repeat division and fusion periodically are observed (Figure 3b). These patterns are also formed by the same mechanism as considered in Figure 2. According to our model considering the thickness of medium, the patterns change as if D_U/D_V changes, although the ratio is fixed actually. In experiments using gels, it is difficult to control the ratio of diffusivities. Yet the result obtained here demonstrates that the same effect can be easily obtained only by changing the thickness of gels as a control parameter.

Figure 4 shows the phase diagram of the pattern formation when *F* and *k* are changed. Actually, several kinds of patterns including the stationary wave appear with the change in *F* and *k*. In general, the region where static and dynamic periodical patterns appear (corresponds to *T*, *d*, and *b*) becomes smaller as the thickness of the medium increases. It is a tendency that the pattern formation is disturbed by increasing thickness. The two-dimensional extent of surface area leads to an increase in Turing structure region.

Our model not only suggests the mechanism of actually observed oscillating spot in FIS reaction, but also shows a possibility of new kinds of spatial patterns such as dancing and blinking waves in experiments. These patterns are created by the double inhibitory mechanism due to the spatial factor. Other new patterns that have various properties may be possible by coupling the inhibitory mechanisms and the geometry factor of the reaction medium. Although there are few studies on the design of functional materials utilizing reaction−diffusion waves at present, the concept demonstrated here would be useful for control of pattern dynamics and development of new functional materials with the self-organizing function.

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