Relaxation to Equilibrium Can Be Hindered by Transient Dissipative Structures

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Relaxation processes in a closed chemical reaction-diffusion system which can potentially form Turing-like patterns during the transient are investigated to address the question given by the title. We find that when certain conditions are fulfilled the relaxation process is indeed drastically hindered, once the pattern is formed. This slowing down is shown to be due to stepwise relaxation, where each plateau in the relaxation process corresponds to residence at a certain spatial pattern. Mechanism and universality of the phenomena are discussed.

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In open systems far from equilibrium, organized structures are well-known phenomena [1]. Such "dissipative structures" include temporal rhythms and spatial patterns in chemical reaction-diffusion systems, hydrodynamical systems, optical systems, and so forth [1,2,10]. Among others, biologically complex structures can also be maintained by nonequilibrium conditions [3,4].

In the study of dissipative structures, systems are generally prepared in far-from-equilibrium states by imposing certain constraints. For example, concentrations of some chemicals are fixed at higher or lower levels by supplying or removing them from the outside. On the other hand, in biological systems, nonequilibrium conditions are maintained autonomously, at least when considering long time spans. As a first step for understanding the autonomous sustainment of biological nonequilibrium conditions, it is of interest to investigate the possibility that the longevity of the conditions for dissipative structures is extended by the formation of the structures themselves.

In closed systems, of course, equilibrium states without any structures are reached eventually. However, oscillatory behaviors or spatial pattern formations can be observed as transient phenomena during the course of relaxation to equilibrium [5–9,11,12]. Here, we address the following question: Can the formation of (transient) dissipative structures make far-from-equilibrium conditions last significantly longer by slowing down the relaxation process to equilibrium? To answer this question, we study the relaxation behaviors of a closed coupled chemical reactor that can potentially form transient Turing-like patterns during the relaxation process.

Here, in contrast to most studies in reaction-diffusion systems, we need to take the changes in the concentrations of all chemicals into account, instead of keeping the concentrations of some chemicals constant. Thus we consider the following reaction-diffusion system consisting of the reactions (I) $A + v + 2u \rightleftharpoons_{k_{BA}}^{k_{AB}} B + 3u$, (II) $u \rightleftharpoons_{k_{vu}}^{k_{uv}} v$, and (III) $A + u \rightleftharpoons_{k_{vu}}^{k_{uv}} A + v$, and also diffusion. Considering the limiting case $k_{AB} = 1 \gg k_{BA}$, the evolution of the chemical concentrations is given by

$$\dot{u}_i = A_i v_i u_i^2 - (1 + A_i)(u_i - v_i), \tag{1}$$

$$\dot{v}_i = -A_i v_i u_i^2 - (1 + A_i)(v_i - u_i) + D_v(v_{i+1} + v_{i-1} - 2v_i), \tag{2}$$

$$\dot{A}_i = -A_i v_i u_i^2 + D_A(A_{i+1} + A_{i-1} - 2A_i). \tag{3}$$

Here, u_i, v_i, and A_i denote the concentrations of the chemical components (activators, inhibitors, and resources) and i denotes the index of each site in a one-dimensional space (N sites), where periodic boundary conditions are adopted for i. Here we use $k_{uv} = k_{vu} = 1$, but the behaviors to be reported are preserved even if $k_{uv} \neq k_{vu}$, and for a wide range of parameter values. Each chemical diffuses to neighboring sites with a diffusion coefficient D_X ($X = u$, v, or A). Although we adopt a spatially discrete system for simplicity, the conclusions drawn do not change even when the continuum-limit (partial differential equation) is taken. The diffusion coefficient D_u is assumed to be slow, and we mostly study the case with $D_u = 0$ as in Eq. (1) since this will not affect our findings qualitatively as long as $D_u \ll D_v$.

This model is a variant of the Gray-Scott [9,10] or Brusselator [1,11] models so that changes of the resources A_i are included. Note that the value $\frac{1}{2N}\sum_i (u_i + v_i) = S$ is conserved due to the system being closed.

While relaxation to a unique equilibrium state satisfying $A = 0$ and $u_i = v_i = S$ is assured for $t \to \infty$ in this model, if we fix $A_i = Ao \gg 1$ in order to maintain the nonequilibrium condition, this system shows the following bifurcation of the attractor, depending on S. (I) If $S \leq 0.75$, a unique uniform state with u_i and v_i constant over i and time exists that is stable against small perturbations. (II) If $S > 0.75$, the uniform state is unstable against perturbations with some range of wave number. With this Turing instability, the attractor is replaced by a nonuniform pattern of u_i and v_i, which is constant in time. This Turing instability of the uniform states is straightforwardly obtained by linear stability analysis.

In order to study the relaxation process from a nonequilibrium state to the homogeneous equilibrium state, we now investigate the effects of changing A_i as in Eq. (3) for the case $S > 0.75$. Here, depending on the initial configurations of u_i, spatial patterns can be formed during relaxation to the homogeneous equilibrium state. We study typical relaxation behaviors by varying initial configuration of $u_i = u_i^0$ and the initial condition $A_i = A_{\text{ini}}$ and $v_i = S$. We control spatial inhomogeneity of u_i^0 by taking an initial condition $S + \delta \times rnd_i$, with rnd_i as a uniform random number over $[-1, 1]$ $(0 \le \delta \le S)$.

Two sets of typical temporal evolutions of u_i and A_i with $S = 4$ and $A_{\text{ini}} = 100$ are displayed in Figs. 1(a) and 1(b), where $\delta = 0.1$ in (a) and $\delta = 4.0$ in (b) with $D_v = 250$ and $D_A = 0$. The pattern is plotted at time $0.05n$ (n are integer numbers) until it has nearly reached the equilibrium state. The corresponding time evolution of $\langle A \rangle$ $(= \frac{1}{N}\sum_i^N A_i)$ is plotted in Fig. 1(c).

When δ is small, u_i remains almost flat with only minor fluctuations, and no structure is formed as in Fig. 1(a). In this case, $\langle A \rangle$ decreases smoothly with time as the solid curve in Fig. 1(c). On the other hand, when δ is large, the initial inhomogeneity in u_i is amplified leading to the formation of a nonuniform spatial pattern that is sustained over some time span until it is reorganized into a different pattern, as shown in Figs. 1(b) and 1(d). In this case, the relaxation of $\langle A \rangle$ exhibits some plateaus, as shown in Fig. 1(c), and requires much more time as compared to the case when δ is small. Each plateau corresponds to a specific spatial pattern as shown in Fig. 1(d) [13]. Such plateaus in relaxation always appear for δ larger than a critical value as mentioned after.

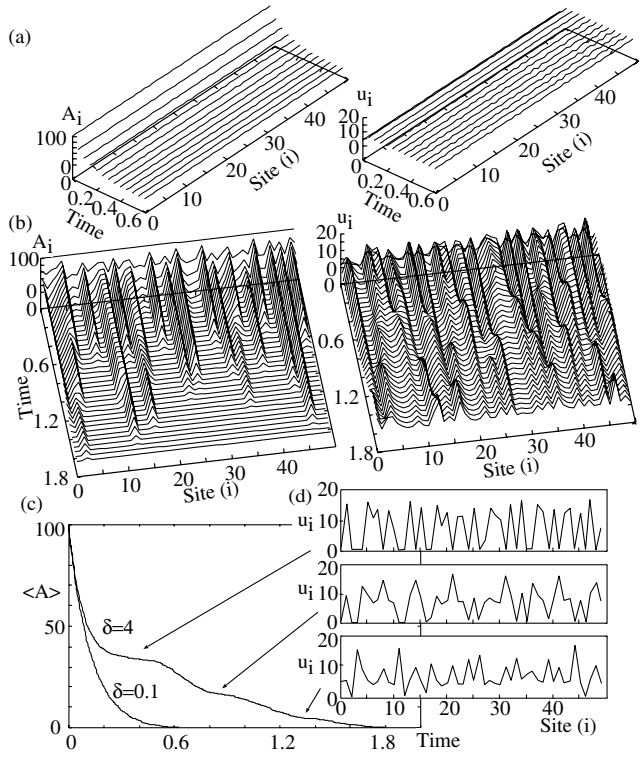

FIG. 1. Typical temporal evolutions of A_i (left) and u_i (right) for $D_v = 250$, $D_A = 0$, and $S = 4$. The patterns are plotted through the time course, until $\langle A \rangle$ becomes smaller than $0.001A_{\text{ini}}$ per $\Delta t = 0.05$. (a) $\delta = 0.1$ and (b) $\delta = 4.0$ plotted. (c) The time evolutions of $\langle A \rangle$ corresponding to (a) and (b). (d) Three typical snapshots of the spatial patterns of u_i in (b) which are plotted at the time step shown by the arrows.

Hence, we have found an explicit example in which the formation of a dissipative structure slows down the relaxation process. This behavior is rather general in our model, as long as S and D_v are large enough to allow for the formation of spatial patterns [14].

In order to obtain insight into the relationship between pattern and relaxation, we have measured the spatial inhomogeneity of u_i defined by $F(t) = \frac{1}{N}\sum_i^N |u_{i+1} - u_i|^2$. In Fig. 2, we plot the decay rate of $\langle A \rangle$ defined by $\langle A \rangle' = \frac{d \log\langle A \rangle}{dt}$, as a function of $F(t)$. As can be seen, the system alternates between structure formation where A_i is consumed and residence at the formed nonuniform structure where consumption of A_i is suppressed. Indeed, the decrease of $\langle A \rangle'$ is highly correlated with the increase of F. Thus, the slowing down of the relaxation process by the spatial structure is confirmed.

Next, we study the conditions for this slowing down of the relaxation process. We investigate the dependence of the relaxation time on the initial inhomogeneity. Figure 3(a) shows the sample average of the relaxation time T as a function of the initial heterogeneity δ, computed up to the time when $\langle A \rangle$ has decreased to $0.1A_{\text{ini}}$. Here, the parameters are set to $D_v = 250$, $S = 4$, $A_{\text{ini}} = 100$, and $N = 200$, while the diffusion constant D_A is chosen to be 0, 0.25, and 25. As can be seen, there is a critical inhomogeneity δ_c (≈ 0.5), beyond which the relaxation time increases, when D_A is small. Indeed, δ_c is nothing but a threshold for the inhomogeneity above which the reorganization of the spatial structure is possible. For large D_A, however, the reorganization of the structure is even then not possible, and the relaxation time is insensitive to the initial fluctuations. The threshold δ_c

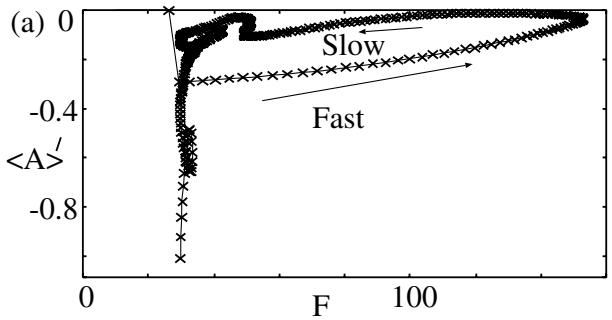

FIG. 2. Time course of $[\langle A \rangle'(t), F(t)]$ obtained from the same simulation of Fig. 1(b). See the text for the definition of $\langle A \rangle'$ and F.

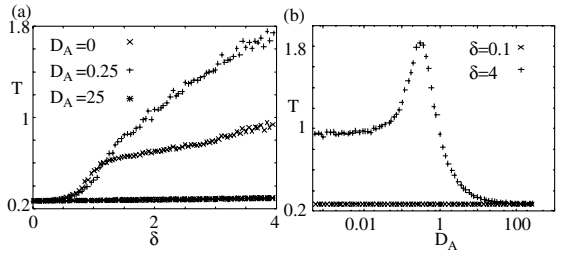

FIG. 3. (a) The average relaxation time T, plotted as a function of δ, for $D_A = 0$, 0.25, and 25, and (b) T as a function of D_A for $\delta = 0.1$ and 4. $D_v = 250$.

exists for $D_A \lesssim 20$, while the value of δ_c itself is insensitive to the value of D_A within this range.

The dependence of the relaxation time on D_A, on the other hand, is plotted in Figure 3(b) where $\delta = 0.1$ or 4. When δ is smaller than δ_c, the relaxation time remains short. In contrast, it shows a peak around $D_A \sim 0.3$, when δ is larger than δ_c, while for smaller and larger D_A, it approaches constant values. The relaxation time for smaller D_A remains large, while it is quite small for larger D_A [see Fig. 3(a)].

Now, we study the mechanism for the observed drastic enhancement of the relaxation time. When A_i is initially large, the Turing instability can introduce an inhomogeneous pattern for u_i with some wavelength. However, if initial inhomogeneity in u_i is not large, A_i is consumed before such a pattern is formed, and then the Turing instability is lost. As shown in Fig. 1(a), A_i is then consumed almost uniformly through the entire system.

On the other hand, if u_i has large spatial variations, the Turing instability amplifies the spatial fluctuations soon, leading to some pattern in u_i, before A_i is consumed, as shown in Fig. 1(d). Now we discuss how such a pattern formation slows down the relaxation of A.

First, we discuss the time regime during pattern formation. In this regime, for sites with growing u_i, A_i is consumed rapidly, since the reaction progresses with the rate $\sim A_i v_i u_i^2$. Soon, however, this consumption of A_i at the sites stops since A_i therein is consumed out. On the other hand, at sites with small u_i, the reaction between u and v consuming A (whose rate is $A_i v_i u_i^2$) is always highly suppressed, even if A_i therein is large, because u_i^2 is much smaller. Then A_i at such sites is always consumed only little by little.

When A_i at sites with large u_i is almost consumed, the plateau in the relaxation appears, because, the consumption of A_i no longer progresses there, while for other sites with small u_i, the consumption of A_i is slow as mentioned above. Hence, in this regime the consumption of A_i is suppressed for all sites. The suppression of the decrease of $\langle A \rangle$ here gives a plateau that appears in the relaxation of $\langle A \rangle$. Here, the decrease of u_i there mainly progresses by the reaction $u_i \rightleftharpoons v_i$, whose rate is given by $\sim u_i$, which is much smaller than $A_i u_i$, when $\langle A \rangle \gg 1$ [15].

This hindrance of relaxation continues until the decrease of u_i at the site with large u_i is completed. Then, u_i at some other site that still keeps large A_i starts to be amplified, by the Turing instability, and starts to consume A_i. During this fast relaxation process, A_i at such a site is again consumed, and then the relaxation is hindered, leading to another plateau in the relaxation. This process corresponds to the reorganization of the spatial structure of u_i as described in Figs. 1(b) and 1(d). In this way, several plateaus appear successively.

Once the initial inhomogeneity is large enough to assure the pattern formation before the consumption of A_i, then the the consumption is suppressed by the above mechanism. Hence there appears threshold initial inhomogeneity beyond which the relaxation is hindered drastically. This is nothing but δ_c.

Next, we explain the D_A dependence of the relaxation time in Fig. 3. With the above mechanism, u_i increases at a certain site i, and A_i is consumed at such site. Then, the resource A diffuses into this site from adjacent sites if $D_A > 0$. This fact leads to the further acceleration of the increase of u_i, by consuming A_j at the sites adjacent to i. Consequently, the peak height of u_i can be much higher than that of the case with $D_A = 0$. Then, it takes more time before u_i at such a site is consumed by the slow reaction process $u_i \rightleftharpoons v_i$. Thus, the time intervals between reorganizations of u_i become larger, resulting in the increase of the relaxation time.

On the other hand, if $D_A \gg 1$, the resource A is consumed faster due to the diffusion of A. In this case, the speed of the flow of A_i is higher than that due to the reaction $u_i \rightleftharpoons v_i$ for sites with large u_i. Therefore, the resource A_i is consumed continuously by sites with large u_i, and a reorganization of the spatial structure u_i no longer occurs. In this case, the consumption speed of A_i goes up to the level for the relaxation from a homogeneous pattern. Hence, the relaxation time to equilibrium for the case $D_A \gg 1$ is much smaller than for the case with $D_A < 1$, even when $\delta > \delta_c$. The peak of the relaxation time in Fig. 3(b) is thus explained.

The mechanism for the slowing down of relaxation processes proposed here is general. Take any reaction-diffusion system in which dissipative structures are formed by constraining the concentrations of some resource chemicals in such a way that their values are larger than their equilibrium values. [i.e., (0) the presence of Turing instability when the nonequilibrium condition is fixed to a high level]. Now consider the corresponding closed system, where the dynamics of the resource chemical(s) is incorporated. The proposed mechanism for slowing down the relaxation is possible if the following two conditions are fulfilled.

(1) The reaction-diffusion processes of the chemicals that give the nonequilibrium conditions are not too fast compared to those of the other chemicals. The diffusion constants as well as the reaction rates for the consumption

of the resource chemicals should be smaller than the others. This leads to differences in the time scales of the concentration changes and thus, when the pattern formation progresses fast enough, the consumption of resource chemicals to support the nonequilibrium conditions slows. The resource chemical concentrations work as slow variables (or parameters) of the system.

(2) The consumption of resources slows down due to feedback from the spatial structure. In the example here, the consumption of resources is completed soon at sites with higher u_i, while for other sites it progresses only slowly. Hence the overall depletion of resources slows down by the spatial pattern. In general, it is not so difficult to satisfy these two conditions, and indeed we have confirmed the present mechanism by studying some variants of the present reaction-diffusion system.

If only the second condition is satisfied but not the first, some increase in the relaxation time is still observed, but the relaxation does not have several plateaus. As an example, consider the reaction systems (i) $a_i + v_i + 2u_i \rightleftharpoons^{1}_{k} a'_i + 3u_i$, (ii) $b_i + u_i \rightleftharpoons b'_i + v_i$, (iii) $e_i + u_i \rightleftharpoons e'_i + c_i$, and (iv) $f_i + v_i \rightleftharpoons f'_i + d_i$, with diffusion. If we set $e_i = e'_i = 0$ and $c_i = c(= \text{const})$, this model is equivalent to a Brusselator [1,11] with the reversible reactions, while it corresponds to the Gray-Scott model [9,10] with the reversible reactions, if $b_i = b'_i = 0$ and $d_i = d(= \text{const})$. In this model, Turing patterns are formed if the concentrations a_i of resource and waste chemicals are suitably fixed with $k \ll 1$. By including the dynamics of a_i and by choosing a large a_i initially, a structure is formed if the initial inhomogeneity δ is not too small, in the same way as for our model above. Again, some amplification of the relaxation time is observed. However, since the ratio among b_i, b'_i, and a_i determining the growth speed of spatial fluctuations changes drastically in time, the condition (1) cannot remain to be satisfied. Once the initially formed structures are destroyed, the reorganization of novel structures is not easy [though it is still possible if b_i and b'_i are highly correlated to a_i as in Eqs. (1)–(3)]. Hence, the enhancement of the relaxation time in this case is not as significant as in the previous case.

In this Letter, the relaxation process to equilibrium is investigated through a closed coupled chemical reactor system. Under certain conditions, we have found that the relaxation is drastically hindered once a Turing-like pattern is formed. In addition, we have observed repeated formations of patterns, with which the relaxation is further slowed down as compared to the case without the structure formation. Extension of the present result to other dissipative structures such as oscillatory or excitable states is an important future problem.

In experimental studies of dissipative structures, the system under consideration is usually set to be open in order to sustain the nonequilibrium condition. Still, even in closed systems, dissipative structures are often observed as transients which may last for rather long time spans (recall, for example, the Belousov-Zhabotinsky reaction in a petri dish). By choosing a suitable reaction system, it is possible to demonstrate the present enhancement of the relaxation time due to the transient dissipative structure. In an experiment, the initial inhomogeneity can be introduced, for example, by a perturbation or transient process before the system is closed [16].

In complex reaction systems, with more chemical components, the relaxation process could further be slowed down. For example, assume that A and B in our model are synthesized by lower-level resources A' and B', and that these reactions also satisfy the mechanism demonstrated here. By a hierarchy of such reactions, the relaxation time is expected to be further increased. This may provide some insight into why a cell system can maintain a nonequilibrium state over a huge time span.

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[13] The patterns observed in such closed systems tend to be disordered because A_i is consumed before starting the pattern ordering process, differently from open systems.
[14] By taking a larger D for all chemicals, or by choosing initial conditions with a longer scale fluctuation, one can get a pattern with a longer wavelength. In this case again, the relaxation is slowed down by the pattern formation.
[15] Note that for a stationary homogeneous state, $v_i u_i^2 \sim u_i - v_i$ is satisfied if $A_i \gg 1$. When the locally conserved quantity $u_i + v_i = 2S$ is large, this stationary solution satisfies $v_i \sim 1/u_i$. Then, the consumption speed of A_i can be approximated by $\sim A_i v_i u_i^2 \sim A_i u_i$.
[16] The threshold δ_c is decreased by increasing initial A_i.