Is relaxation to equilibrium hindered by transient dissipative structures in closed systems?

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Dissipative structures are generally observed when a system relaxes from a far from equilibrium state. To address the reverse question given by the title, we investigate the relaxation process in a closed chemical reaction-diffusion system which can potentially form Turing-like patterns during the transient. 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. Universality of the phenomena as well as their biological relevance is briefly discussed.

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In open systems far from equilibrium, organized structures are well-known phenomena. Such “dissipative structures” include temporal rhythms and spatial patterns in chemical reaction-diffusion systems, hydrodynamical systems, optical systems and so forth. Among others, biological complex structures can also be maintained by non-equilibrium conditions.

In the study of dissipative structures, systems are generally prepared in far from equilibrium states by imposing certain constraints. For example, the concentrations of some chemicals are fixed at (compared to the equilibrium state) higher or lower levels by supplying or removing them from the outside. On the other hand, in biological systems, non-equilibrium conditions are maintained autonomously, at least when considering long time spans. As a first step for understanding the autonomous sustenance of biological non-equilibrium conditions, it is of interest to investigate the possibility that the longevity of the conditions for the 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. 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) \( A + v + 2u \xrightarrow{k_{BA}} B + 3u \), II) \( u \rightleftharpoons v \), and III) \( A + u \rightleftharpoons A + v \), and also diffusion. Considering the limiting case \( k_{AB} = 1 \gg k_{BA} \), the evolution of the chemical concentrations is given by

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

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

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

Here, \( u_i \), \( v_i \), and \( A_i \) denote the concentrations of the chemical components and \( i \) denotes the index of each site in a one-dimensional space, where periodic boundary conditions are adopted for \( i \). Each chemical diffuses to neighboring sites with a diffusion coefficient \( D_X \) (\( X = u, v, \text{or} A \)). 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 \( D_u \ll D_v \). The chemicals \( u_i, v_i \) and \( A_i \) can be regarded as activators, inhibitors and resources respectively.

This model is a variant of the Gray-Scott or Brusselator models such that we additionally include changes in the resources \( A_i \). Note that the value \( \frac{1}{N} \sum_i (u_i + v_i) = S \) is conserved due to the system being closed (\( N \) is the number of sites.).

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 \( A_i = A_0 \gg 1 \) in order to maintain the non-equilibrium 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, and the attractor is replaced by a non-uniform 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 non-equilibrium 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 $u_i = u_i^0$ with $S = 4$ and the initial condition $A_i = A_{ini} = 100$ and $v_i = S = 4$. We control initial spatial inhomogeneity of $u_i^0$ by taking an initial condition $S + \delta \times N2_i$, with $N2_i$ as a uniform random number over $[-1, 1]$ ($0 \leq \delta \leq S$).

Two types of typical temporal evolutions of $u_i$ and $A_i$ 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 until it has nearly reached the equilibrium state. The corresponding time evolution of $<A>$ ($= \frac{1}{N} \sum_i A_i$) is plotted in Fig. 1(c).

When $\delta$ is small, $u_i$ remains almost flat with only minor fluctuations, and no structure is formed as in Fig. 1(a). In this case $<A>$ decreases smoothly with time as indicated by the solid curve in Fig. 1(c). On the other hand, when $\delta$ 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 re-organized into a different pattern, as shown in Figs. 1(b) and (d). In this case, the relaxation of $<A>$ exhibits some plateaus as shown in Fig. 1(c), and requires much more time as compared to the case when $\delta$ is small. In general, several plateaus are observed during the relaxation process, each of which corresponds to a specific spatial pattern, as shown in Fig. 1(d).

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.

In order to obtain insight into the relationship between pattern and relaxation, we have measured the spatial inhomogeneity of $u_i$ defined by $F(t) = \frac{1}{N} \sum_i |u_{i+1} - u_i|^2$. In Figure 2 we plot the decay rate of $<A>$ defined by $<A>' = \frac{\log A'}{dt}$, 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 non-uniform structure where consumption of $A_i$ is suppressed. Indeed, the decrease of $<A>'$ 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 inhomogeneity $\delta$, computed up to the time when $<A>$ has decreased to $0.1A_{ini}$. Here, the parameters are set to $D_v = 250$, $S = 4$, $A_{ini} = 100$ 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 $\delta_c$ ($\approx 0.5$), beyond which the relaxation time increases, when $D_A$ is small. Indeed, $\delta_c$ is nothing but a threshold for the inhomogeneity above which the re-organization of the spatial structure is possible. For large $D_A$, however, the re-organization of the structure is even then not possible, and the relaxation time is insensitive to the initial fluctuations. The threshold $\delta_c$ exists for $D_A \approx 20$, while the value of $\delta_c$ 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 $\delta$ is smaller than $\delta_c$, the relaxation time remains short. In contrast, the relaxation time shows a peak around $D_A \approx 0.3$, when $\delta$ is larger than $\delta_c$, while for smaller and larger $D_A$, it approaches constant values. Here the relaxation time for smaller $D_A$ remains large, while it is quite small for larger $D_A$, as already shown in Fig. 3(a).

Now, we study the mechanism for the observed drastic enhancement of the relaxation time, by exploring the mechanism behind the dependence of the relaxation process on the spatial fluctuations in the case of small $D_A$. In Fig. 1. If $u_i$ is distributed almost uniformly, $A_i$ is consumed almost uniformly through the entire system as in Fig. 1(a). On the other hand, if $u_i$ has large spatial variations, $A_i$ is consumed locally at the sites with large $u_i$, resulting in an amplification of the spatial fluctuations, as shown in Fig. 1(d). Then, at sites with large $u_i$, $A_i$ is consumed rapidly so that the reaction $A + v + 2u \leftrightarrow k_{AB} A + 3u$ hardly occurs at these sites ($k_{AB} = 1 >> k_{BA}$). The decrease of $u_i$ there mainly progresses by the reaction $u_i \leftrightarrow v_i$ which does not consume $A_i$.

On the other hand, with this spatial structure, at several sites that do not belong to the peaks in the pattern, $u_i$ and $v_i$ are suppressed. Then, the reaction between $u$ and $v$ with the consuming $A$ (whose rate is $A_i u_i v_i^2$) is highly suppressed, even if $A_i$ therein is large. $A_i$ at such sites with small $u_i$ is consumed only little by little. Hence, a plateau appears in the relaxation of $<A>$. After the decay of $u_i$ at the site with large $u_i$ is completed, $u_i$ at some other site that keeps large $A_i$ starts to be amplified by consuming $A_i$. This process corresponds to the re-organization of spatial structure of $u_i$, as described in Fig. 1(b) and Fig. 1(d). In this way, several plateaus appear successively during the relaxation process.

Based on the above argument, the drastic increase in the relaxation time by the increase of the initial inhomogeneity $\delta$ is explained by comparing the speed of the reaction consuming $A_i$. With the reaction $u_i \leftrightarrow v_i$. Note that for a stationary state, $v_i u_i^2 \sim v_i$ is satisfied (by disregarding diffusion) if $A_i >> 1$. 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 \( \sim A_i v_i u_i^2 \sim A_i u_i \), according to the estimate for the steady state. On the other hand, the order of the speed of the reactions \( u_i \equiv v_i \) is given by \( \sim u_i \), which is much smaller when \( \angle A > \gg 1 \). Accordingly, the relaxation process of \( \angle A > \) with the re-organizations of \( u_i \) involve fast and slow processes, with reaction speeds \( \sim A_i u_i \) and \( \sim u_i \). Thus, the relaxation of \( \angle A > \) has several bottlenecks corresponding to the slow processes with speeds in the order of \( \sim u_i \), leading to plateaus. In contrast, the relaxation from a state with little inhomogeneity involves only a fast process with a reaction speed \( \sim A_i u_i \), since the inhomogeneity in \( u_i \) is not amplified to form a structure. Hence, the relaxation time is small when \( \delta < \delta \).

Next, we explain the \( D_A \)-dependence of the relaxation time in Fig. 3. As \( u_i \) increases at a certain site \( i \), the resource \( A_i \) diffuses into this site from adjacent sites as \( A_i \) is consumed at site \( i \). Thus the increase of \( u_i \) is further accelerated by the use of \( A_j \) at the sites adjacent to \( i \). Consequently, the peak height of \( u_i \) can be much higher than the case when \( D_A = 0 \). With such increases of the spatial amplitudes, the time intervals between re-organizations of \( u_i \) become larger, resulting in an 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 \( u_i \equiv v_i \) for sites with large \( u_i \). Therefore, the resource \( A_i \) is consumed continuously by sites with large \( u_i \), and a re-organization 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 that for the case with \( D_A < 1 \), even when \( \delta > \delta \). The peak of the relaxation time in Fig. 3(b) is thus explained.

Note that the mechanism for the slowing down of relaxation processes proposed here is rather 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. Then consider the corresponding closed system, where the dynamics of the resource chemicals(s) is incorporated. Now the proposed mechanism for slowing down the relaxation process is possible if the following two conditions are fulfilled.

First, the reaction and diffusion processes of the chemicals that give rise to the non-equilibrium conditions should not be 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 those for 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 non-equilibrium conditions slows. Then, the changes of resource chemical concentrations work as a kind of slow variables (or parameters) of the system.

Second, the consumption of resources should slow down due to feedback from the spatial structure. In the present example, the consumption of resources is completed soon at sites with higher \( u_i \) and for other sites with very small concentrations of \( u \), the consumption reaction progresses only slowly. Hence the overall depletion of resources is much slower than in the case with a homogeneous concentration of \( u \).

In general, it is not particularly 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 condition, some increase in the relaxation time is still observed, but it is neither drastic nor does the relaxation have several plateaus. As an example we consider the reaction system i) \( a_1 + v_i + 2u_i \rightleftharpoons \frac{1}{2} a'_1 + 3u_i \), ii) \( b_i + u_i \rightleftharpoons b_i + v_i \), iii) \( e_i + u_i \rightleftharpoons e_i + c_i \), iv) \( f_i + v_i \rightleftharpoons f_i + d_i \), with diffusion. If \( u_i = 0 \) and \( c_i = c(= \text{const}) \), this model is equivalent to a Brusselator model with the reactions reversed, while it corresponds to the Gray-Scott model, again with the reactions reversed, if \( b_i = 0 \) and \( d_i = d(= \text{const}) \). In this case too, Turing patterns are formed if the concentrations of resource and waste chemicals are fixed as \( a_1 = a_0 \) with \( k < < 1 \) in order to keep the non-equilibrium condition. By including the dynamics of \( a_i \) and by choosing a large \( a_i \), initially, a structure is formed if the initial inhomogeneity \( \delta \) is not too small, in the same way as for our model above. Indeed, some amplification of the relaxation time is observed here. However, once the initially formed structures are destroyed, new large structures are not produced. 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 pattern is formed. In addition, we have observed repeated formations of patterns. With this itinerary over patterns, the relaxation is further slowed down as compared to the case without the structure formation.

In experimental studies of dissipative structures, the system under consideration is usually set to be open in order to sustain the non-equilibrium 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 will be possible to demonstrate the present enhancement of the relaxation time due to the transient dissipative structure. In relationship with the possibility of an experimental observation, it should be noted
that the slow relaxation process we studied here does not progress gradually, but repeats residence at several quasi-stationary states corresponding to certain structures. The quasi-stationary states associated with the successive spatial structures act as bottlenecks for the relaxation process.

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 in the present paper. By a hierarchy of such reactions, the relaxation time is then expected to be further increased. This may provide some insight into why a cell system can maintain a non-equilibrium state over a huge time span.

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

FIG. 2: Time course of ($<A>^\prime(t), F(t)$) obtained from the same simulation of Fig. 1(b). See text for the definition of $<A>^\prime$ and $F$. 
FIG. 3: (a) The average relaxation time $T$, plotted as a function of $\delta$, for $D_A = 0$, $= 0.25$, and $= 25$, and (b) $T$ as a function of $D_A$ for $\delta = 0.1$ and $= 4$. $D_v = 250$. 