
Spatial Bistability: A Chemical Idiosyncrasy?

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ABSTRACT: Spatial reactors allow the study of the true asymptotic states of dissipative structures in autocatalytic chemical systems in solution. They have permitted the experimental discovery of genuine Turing patterns. However, when reactions at work exhibit bistability between homogeneous steady states in a continuously stirred tank reactor, Turing structures remain elusive. A reason may lie in the existence for such reactions of the phenomenon of spatial bistability. A simple model for this effect is discussed here. © 2004 Wiley Periodicals, Inc. *Int J Quantum Chem* 98: 239–247, 2004

Key words: autocatalytic reactions; dissipative structures; gel reactors

Introduction

As mentioned by D'Arcy Thompson [1], people such as Leduc [2] already questioned, early in the 1900s, the possibility of generating stationary regular concentration patterns through the interplay of diffusion and chemistry when the study of symmetry-breaking instabilities was still in its infancy. It rests with Turing [3], 50 years ago, to have been the first to formulate the necessary conditions for the occurrence of a space symmetry breaking in such a context. Following the emergence of the Belousov–Zhabotinsky reaction [4, 5] in the mid 1960s, I. Prigogine and coworkers revived Turing's concept and put it on safe thermodynamic and

kinetic grounds [6–8]. This step opened up a whole new field of physical chemistry. Innumerable theoretical works followed, and the diffusive instability that generates such dissipative structures has popped up in many other fields relating to physics or chemistry. However, experiments in the chemical realm lagged behind, and it was only near the end of 1989 that the first experimental evidence was obtained by Castets et al. [9] using the Chlorite–Iodide–Malonic acid (CIMA) system in so-called “gel reactors.” A recent detailed status of Turing patterns and other symmetry-breaking instabilities in solution chemistry is presented in Ref. [10].

The Turing–Prigogine mechanism consists in the spontaneous instability of a homogeneous mixture of chemically reacting species, when some parameter threshold is crossed as one moves away from equilibrium conditions. It leads to a stationary, space-periodic pattern of the concentrations of re-

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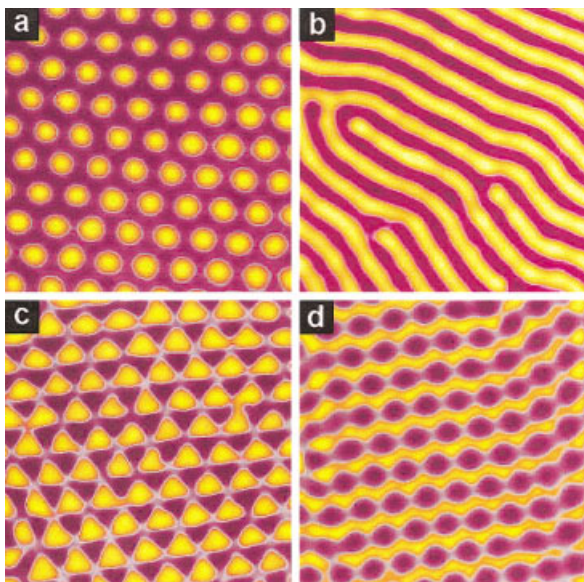


FIGURE 1. Turing structures of different symmetries obtained with the CIMA reaction. Dark and light regions, respectively, correspond to high and low iodide concentration. All patterns are at the same scale: view size, 1.7 mm \times 1.7 mm. (Courtesy of P. De Kepper, CRPP.)

actants (Fig. 1). To support such symmetry-breaking instability, the chemical kinetics must involve some type of positive feedback loop controlled by an activator species that reinforces its own changes, the latter being counterbalanced by an inhibitory process. Spatial structures can form when the inhibitory effects are transported by diffusion over a space range larger than that of the activatory mechanism. Moving further from equilibrium, the pattern may change its symmetry. In its minimal form, the description of all the systems that exhibit such diffusive instability can formally be cast in the common language of reaction–diffusion systems governed by the following set of equations:

$$\frac{\partial \mathbf{c}(\mathbf{r}, t)}{\partial t} = \mathbf{f}(\mathbf{c}, b) + D\nabla^2 \mathbf{c}(\mathbf{r}, t), \quad (1)$$

where $\mathbf{c}(\mathbf{r}, t) \equiv (\dots, c_i, \dots)$ is the local concentration vector, $\mathbf{f}(\mathbf{c}, b)$ is a vector function representing the reaction kinetics, b stands for a set of control parameters, and D is the matrix of constant diffusive transport coefficients. Appropriate initial and boundary conditions, in relation to the experimental setup (for the case discussed here, the chemical reactor used), are added to complete the mathematical formulation.

Theoretical work relies heavily on the use of nonlinear kinetic models for $\mathbf{f}(\mathbf{c}, b)$ with a limited number of chemical species, typically two or three. The models stand as a compromise between a minimum of chemical realism and mathematical tractability. For their part, the experimental kinetic schemes usually involve a large amount of species, often not yet unequivocally determined and therefore not amenable to a set of elementary reaction steps [11].

The outcome of analytical work that relies heavily on bifurcation theory [12, 13] allows one to determine which structures of given symmetry are stable for specific conditions (pattern selection). The calculated bifurcation diagrams help to organize the results obtained by straightforward numerical integration of the reaction–diffusion equations. Both data may finally be used to interpret the experimental results. The pattern selection problem was already on Turing’s mind. Indeed, in the final sections of his article [3] he stated: “Most of an organism, most of the time, is developing from one pattern into another, rather than from homogeneity into a pattern. One would like to be able to follow this more general process mathematically also.”

The experimental work takes place in so-called “open spatial reactors” [10] that are specifically designed to control the reaction and the structures that eventually develop at a fixed distance from equilibrium and allow one to probe the true asymptotic states of the reaction–diffusion systems. To this effect, they are constructed to avoid all perturbations induced by the hydrodynamic flows associated with the constant supply of fresh reactants. They must also enable the necessary diffusion differential between activator and inhibitor species to permit Turing instabilities to occur.

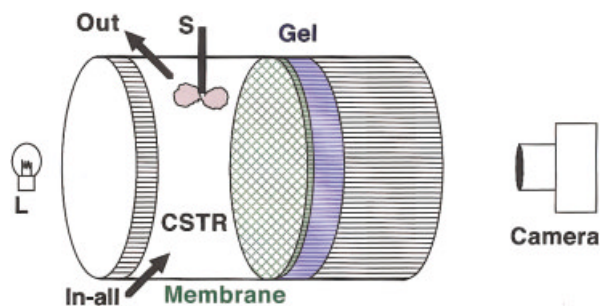


FIGURE 2. Schematic representation of open spatial reactors: disc-shaped OSFR; CSTR, Membrane (mineral disc, pore size 0.02 μm), Gel, In and Out (input and output ports of chemicals), L (light source), CCD camera (black and white or color).

Since the initial discovery, the experimental setup has undergone some modifications. Experiments are now usually performed in one-side-fed reactors (OSFR) sketched in Figure 2. The core of this kind of reactor is made of a piece of soft hydrogel (polyacrylamide, agarose, polyvinylalcohol [PVA]) fed by diffusion through one of its faces with chemicals contained in a continuous stirred tank reactor (CSTR), the contents of which are continuously renewed by pumps. The gel is used to prevent any fluid motion, so that the only processes at work within it are reactions and diffusion. The other faces of the piece of gel are pressed against impermeable transparent walls (Plexiglas). Often, an inorganic membrane is placed between the CSTR and the gel to maintain it rigidly. Viewing can be practiced both along the feeding axis or orthogonally to it. An advantage of such reactors is that they allow for direct correlations to be made between the dynamics of the CSTR, the bifurcation behaviors of which have been extensively studied in the past [11], and that of the gel. The dynamics of an OSFR is given by the following set of equations, respectively, for the CSTR and the gel

$$\begin{aligned} \frac{dc_o}{dt} &= f(c_o) + k_0(c_i - c_o) + \rho_v \frac{D}{L} \left(\frac{\partial c}{\partial x} \right)_{x=0} \\ \frac{\partial c}{\partial t} &= f(c) + D\nabla^2 c, \end{aligned} \quad (2)$$

where c_i , c_o , and c are the concentrations of the species, respectively, in the input flow of the CSTR, in the CSTR, and inside the gel; D is the corresponding diffusion coefficients matrix; k_0 , the inverse of the residence time of the CSTR; L , the thickness of the gel; ρ_v , the ratio of the volume of the gel to that of the CSTR; and x is the normal direction to the CSTR–gel interface. The f 's are the reaction rates. On the right side of the first of Eqs. (2), the second term represents the input and output flows of the species. It contains all the expandable control parameters of the system. The third term results from the diffusive flux of the species at the interface between the gel and the CSTR and represents the feedback of the gel contents on the CSTR dynamics. Because usually $\rho_v \ll 1$, the last term can be neglected so that the chemical state of the CSTR is independent of the state of the gel and the concentrations in the CSTR act as a Dirichlet boundary condition for the second Eq. (2) at $x = 0$ ($\forall y, z$) (in contact to the CSTR). No-flux boundary conditions are applied at $x = L$ ($\forall y, z$) along the opposite wall as well as on the other impermeable walls.

It is worthwhile to recall here a main characteristic of the CSTR. If the input flow is large, that is, if the residence time (k_0^{-1}) is much shorter than the typical reaction time, then the extent of the reaction is small and, in a stationary regime, the concentrations are close to the composition of the inflows (flow state F). On the contrary, if the residence time is much longer than the reaction time, then the extent of the reaction is large and the composition in the reactor is near that of the thermodynamic equilibrium that one would obtain in a closed reactor with the same initial composition (thermodynamic state T). In standard reactions, the branches of states F and T are smoothly connected at intermediate flow rates. However, when autocatalytic or similar nonlinear kinetic processes are present (as in the reactions we are interested in) the two states can coexist for a same set of flow rates (or feed concentrations): their stability domains overlap (hence, the bistability) over a range of control parameters, clearly defining two distinct branches F and T, and the transition from one state to the other occurs with hysteresis. The transition from the monostable to the bistable situation usually proceeds through a critical point where the transition from F to T, although smooth, is very sharp. Many examples of this behavior can be found in reference texts [11, 14]. Furthermore, reactions that are bistable in a CSTR exhibit “clock dynamics” in batch (closed reactor), that is, a sudden single switch to a state close to equilibrium after a well-defined induction period, characterized by a low conversion rate. The switch occurs when the concentration of some species involved in the positive feedback loop process reaches a critical level. Thereafter, the conversion rate considerably speeds up. In these reactions, after the dynamical switch, at least one of the major initial reactants is nearly totally consumed. It is therefore clear that chemical bistability between homogeneous steady states in a CSTR is the result of the interplay between a clock reaction mechanism and the mass fluxes of reactants and products through the reactor and is not already included, as in other fields, in the local kinetics function.

In the OSFR, because of such properties, it is convenient to distinguish systems that are monostable in a CSTR from those exhibiting bistability between two homogeneous stationary states.

MONOSTABLE REACTIONS IN CSTR

This case, the simpler, occurs with the CIMA reaction [15] that led to the discovery of the first Turing structures [9]. In this and the related Chlo-

rine Dioxide-Iodine-Malonic acid (CDIMA) reaction, iodide (I^-) and chlorite (ClO_2^-), respectively, play the role of the main activator and inhibitor species [16, 17]. In the experiments illustrated in Figure 1, the core of the reactor is made of agarose gel loaded with PVA, a macromolecule that plays two roles: (1) that of color indicator for the reaction. It forms a reddish purple complex in the presence of iodine and iodide species, and it is colorless in the absence of iodide; (2) consequently, this macromolecule of reduced mobility, by forming a fast reversible complex with these species, leads to an effective reduced diffusivity of the activator [18], a necessary condition for Turing pattern formation.

The piece of gel is usually very thin (typically a few tenths of a millimeter). Consequently, it is often considered that no significant concentration gradient would develop through the depth of the gel. Because this corresponds to a thickness of the order or less than the wavelength of the pattern, the reactors are often thought of as a good approximation of extended two-dimensional systems, irrespective of chemical feed concentrations. When the concentrations in the CSTR are in a steady state (because these reactions can there also exhibit temporal oscillations), semiquantitative agreement [19] can be obtained between experimental Turing patterns obtained in the gel (pattern symmetry, loci of bifurcations, e.g.) and the numerical integration of the reaction-diffusion for the CDIMA reaction for which a reasonable kinetic model exists [16, 17].

BISTABLE REACTIONS IN CSTR

A detailed analysis of pattern development in a bistable system has been undertaken in the framework of the Chlorine Dioxide-Iodide (CDI) reaction. The reaction belongs to the family of the CIMA and CDIMA reactions that lead to Turing patterns, as seen above. It is a "minimal" nonlinear chemical system [17, 20] for which a comprehensive kinetic mechanism has been proposed [21] and that accounts semiquantitatively for the batch and CSTR dynamical behaviors of the reaction. The prototypic bistable reaction system is less complex and has a much better established kinetic mechanism than that of the bistable Ferrocyanide-Iodate-Sulphite (FIS) reaction that has led to the observation of labyrinthine and other interacting front patterns [22, 23] in an OSFR slightly more intricate than the one described in Figure 2. A discussion of the origin of these labyrinthine patterns and that of Turing structures in systems with a bistable local kinetics (i.e., not arising from a clock reaction mechanism

and therefore outside the realm of chemistry in solution) is discussed in Ref. [10]. No sustained patterns have yet been obtained with the CDI reaction. However, the reaction allowed the discovery of an important concept that will be discussed in the next section.

Spatial Bistability

When the CSTR evolves in its bistable region, a first important aspect is the determination of the possible correlated states in the gel. Let us consider the situation along the direction orthogonal to the CSTR-gel boundary, that is, along the depth of the gel [direction x in Eq. (2)], as the feed is homogeneous along the two other directions. If the CSTR is on the F branch, fresh reactants are brought by diffusion from the feeding edge ($x = 0$), where the concentrations are kept fixed. Close to the edge, the extent of the reaction is small and the chemical composition remains close to that of the flow branch. As we move away from the edge, the extent of the reaction becomes larger, because the amount of fresh reactants that reaches the corresponding space point is limited by its transport through molecular diffusion. So, if the gel film is thick enough, the regions of the gel far from the feeding edge may eventually belong to a state lying on the T branch. In such a case, the composition changes from branch F to branch T, somewhere inside the gel in the region where the time for transport of the reactants overtakes the switching time of the clock reaction for the local conditions. Thus, for the same F state in the CSTR, one may observe two quite different composition profiles as a function of L , the thickness of the gel. If L is very small, the chemical composition in the gel stays near or in the direct continuity of the F state of the CSTR. By extension, we also call F this concentration profile in the gel. If L is large enough, the part of the gel close to the CSTR remains on branch F while the opposite part has the T composition. We call FT this mixed profile state of the gel. It can be shown experimentally and numerically (using the kinetic scheme for the CDI reaction) that there exist conditions for which the stability of the F and FT states of the gel can overlap for some finite range of L [24, 25]. Thus, two stable concentration profiles that fit the same homogeneous conditions at the CSTR-gel boundary can be observed in the gel. This is illustrated in Figure 3, obtained in a thin annular strip of gel fed along one edge (such geometry of the OSFR allows visualization in the depth of the gel). This multiplicity phe-

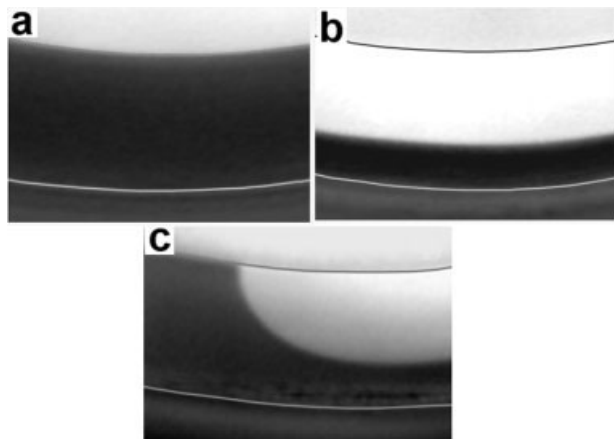


FIGURE 3. Spatial bistability for the CDI reaction in an annular OSFR. (a) State F. (b) State FT. (c) Interface between the F and FT states. Dark color correspond to high iodide concentration. The arc lines are the limits of the gel. The lower arc delineates the CSTR–gel interface; the upper arc delineates the impermeable wall. Distance between the two arc lines, $L = 1$ mm. (Courtesy of P. De Kepper, CRPP.)

nomenon has been dubbed “spatial bistability.” It is a characteristic property of clock reactions run in an OSFR: again, it results from the interaction of this particular kinetics with mass fluxes.

When the CSTR is on the T branch, the extent of the reaction is such that only a single stable concentration profile exists in the gel.

Although the concept of spatial bistability is well established, its numerical proof [24] from the integration of the reaction–diffusion equations for the eight-variables (if one includes the complexation with the color indicator) kinetic model for the CDI reaction offers little hope to apprehend the minimal conditions for its occurrence: Is it merely related to the specific boundary conditions, or do other dynamic effects play a role? Because we intend to use the concept of spatial bistability in relation to other problems, such as the transduction of chemical into mechanical energy in a gel sensitive to the involved chemistry, it seemed useful to try and find as minimal as possible a kinetic model, although still realistic, that exhibits the phenomenon.

Spatial Bistability in the Iodate–Arsenous Acid (IAA) Reaction

The iodate oxidation of arsenous acid in solution is another clock reaction [11], and when the latter compound is in excess, there exists a simple two-

variable kinetic scheme that allows a very precise study of its dynamics in a CSTR where it may but exhibit bistability between homogeneous states [26, 27]. No temporal oscillations ever come into the picture. The phase–space structure for the CSTR is thus of the simplest nature.

If $u = [\text{I}^-]$ and $v = [\text{IO}_3^-]$, the corresponding reaction–diffusion system in the gel part of the OSFR is

$$\frac{\partial u}{\partial t} = f(u, v) + D_u \nabla^2 u$$

$$\frac{\partial v}{\partial t} = -f(u, v) + D_v \nabla^2 v, \quad (3)$$

with $f(u, v) = (k_a + k_b u)uv$, where k_a and k_b are kinetic constants for which realistic values are given in the literature [11]. As discussed before, Eq. (3) must be solved with:

- Dirichlet boundary conditions at the gel–CSTR interface ($x = 0$)

$$u(0, y, z) = u_0; v(0, y, z) = v_0$$

- No flux boundary conditions at the impermeable walls in particular at $x = L$

$$\left(\frac{\partial u}{\partial x} \right)_{x=L} = \left(\frac{\partial v}{\partial x} \right)_{x=L} = 0,$$

where u_0 and v_0 are the concentrations in the CSTR.

Because the feed is uniform at the boundary of the gel, we may limit the discussion to one dimension along the x direction, as long as no transverse symmetry breaking becomes involved. In the discussion that follows we separately consider two cases.

EQUAL DIFFUSION COEFFICIENTS

Because all species involved in the IAA reaction are small ions, their diffusion coefficients may be taken as equal in absence of large-molecular-weight complexing agents. Then, as iodide and iodate are the only stoichiometric significant iodine-containing species, the following conservation law applies when the OSFR is working in regime: $u + v = u_0 + v_0 = u_i + v_i = s$. System (3) then reduces to a single-variable model governed by (after dropping all primes)

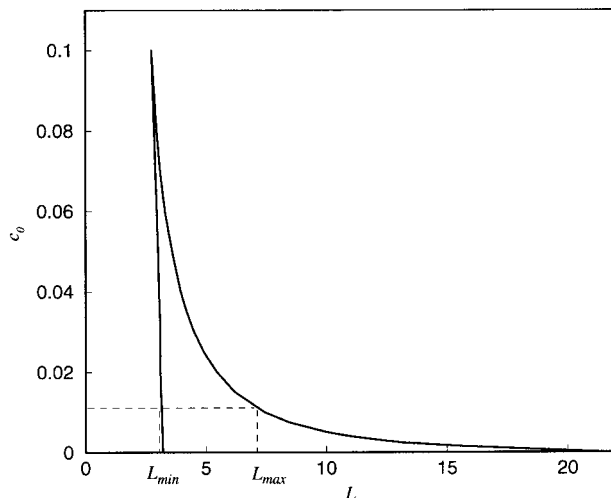


FIGURE 4. Spatial bistability between the F and FT states occurs inside the cusped region in the (c_0, L) parameters plane ($d = 0.0021$). Outside the cusp, only one of the profiles, either F (to the left) or FT (to the right), occurs.

$$\frac{\partial c}{\partial t} = c(1 - c)(c + d) + \frac{\partial^2 c}{\partial x^2}, \quad (4)$$

where $c = u/s, t' = t/\tau, x = x'/\sqrt{D\tau}$ with $d = k_a/k_b s$ and $\tau = 1/k_b s^2$. We also have $c(x = 0) = c_0$ and $(\partial c/\partial x)_{x=L} = 0$. Equation (4) has been used to describe a wave of conversion in a batch reactor with very satisfactory results [28]. Because of the normalization $0 < c < 1$. The values $c = 0$ and $c = 1$, respectively, pertain to no reaction at all or full conversion (thermodynamic equilibrium) and are, in an OSFR, unrealistic limiting cases corresponding to no feeding of the CSTR or infinite residence time of the CSTR. Because of the boundary conditions, there are no homogeneous steady states in the gel. An exact solution may be obtained for the stationary states by direct integration of

$$\frac{d^2 c}{dx^2} = c(c - 1)(c + d) + b.c. \quad (5)$$

to obtain

$$\int_{c_0}^{c_L} \frac{dc}{\sqrt{2(V(c) - V(c_L))}} = -L, \quad (6)$$

where $c_L = c(x = L)$ and

$$V(c) = \frac{c^4}{4} + \frac{(d - 1)}{3} c^3 - \frac{d}{2} c^2. \quad (7)$$

Unfortunately, this formal solution, which can be expressed in terms of elliptic functions, gives little insight, and we must resort to numerical integration, even in this simple case.

As simple as the model may be, we have various parameters at our disposal: the feeding concentrations of the CSTR and the residence time determine c_0 ; although it also depends on the feeding concentrations, d is an independent parameter function of the kinetic constants and the acidity of the solution. The third parameter is the thickness L of the gel slab. For sufficiently small d , numerical integration shows that there exists a region of spatial bistability bounded by the cusp in the (c_0, L) plane (Figure 4). For conditions inside the region, we may draw a usual bistability diagram (back-to-back saddle-node bifurcations) by representing the value of $c(L)$ as a function of L (Fig. 5). For a typical value the two stable coexisting concentration profiles, the F (almost flat) and FT states, are shown in Figure 6; they correspond to the chemical behavior that was discussed previously: when the gel becomes sufficiently thick, the system may grow "old" near the back impermeable barrier and transit to concentrations corresponding in the CSTR to the thermodynamic branch. Because this occurs for a one-variable model, the origin of the phenomenon does not lie with nonvariational effects as in other cases.

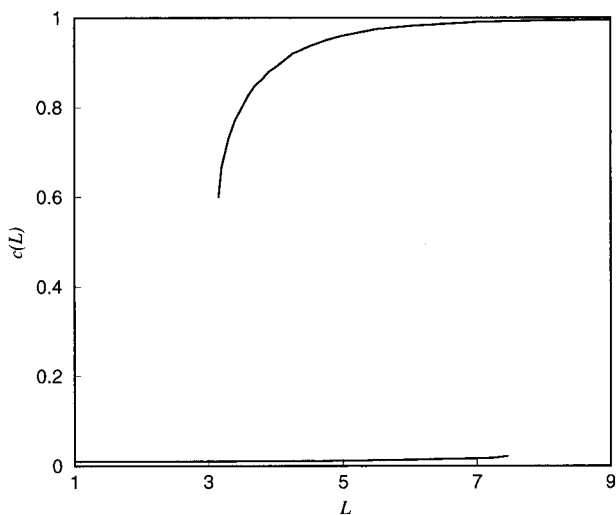


FIGURE 5. Bistability diagram exhibiting the two back-to-back saddle-node bifurcations. The concentration $c(x = L)$ at the impermeable boundary is represented as a function of L ; $c_0 = 0.05, d = 0.0021$.

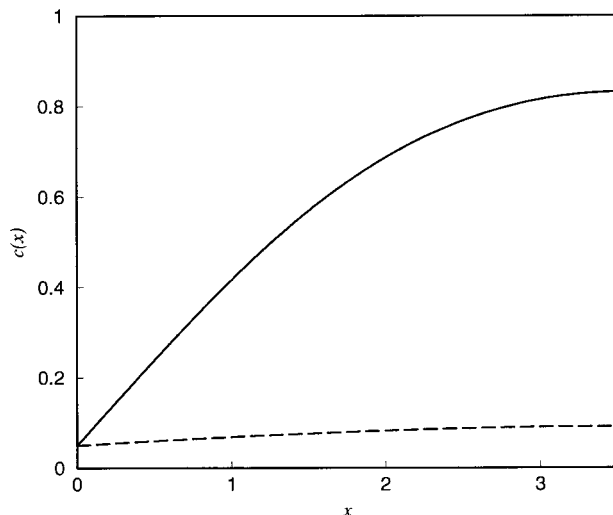


FIGURE 6. Coexisting concentration profiles $c(x)$ in the gel. The dotted and plain lines, respectively, correspond to the F and FT states; $c_0 = 0.05$, $d = 0.0021$, $L = 3.5$.

However, the precise origin remains unclear. Indeed, the roots of $f(c)$ are 1, 0, and $-d$. We have discussed above the meaning of the first two. The last, corresponding to a negative concentration, is unphysical. However, when d becomes too large, spatial bistability is lost. In the allowed region, $0 < c < 1$, $f(c)$ is a positive arc of a cubic. However, simpler models possessing the same zeros, such as the Fisher dynamics (also resulting in an elliptic integral) or a piecewise linear “tent” (which allows an analytic solution), do not give rise to spatial bistability.

The important result, however, is that, as in the CSTR, bistability is again generated through the competition of a clock reaction mechanism and the mass flux inside the gel. Because this flux varies through the gel from $2\sqrt{V(c_0)} - V(c)$ to zero, the coexisting states that are in play cannot be homogeneous.

UNEQUAL DIFFUSION COEFFICIENTS

When the diffusion coefficients of the two controlling antagonist species are different, one has to revert to the two-variables model [Eq. (3)]. Numerical results show that spatial bistability is still able to occur. Let us define $\varepsilon = D_v/D_u$. The selective control of this ratio can in some limits be achieved by binding the activator u or the inhibitor v to complexing agents, or eventually using other clock reactions. Two cases are therefore possible. For $\varepsilon >$

1 corresponding to long-range inhibition, either a Turing instability could occur for some conditions along the profiles or the profiles themselves could undergo a transverse morphological instability [29–33], leading to periodic patterns. The second instability could lie at the heart of the patterns observed with the FIS reaction [10, 22]. Neither has turned up in the search we have carried out so far with the IAA model.

For the reverse situation, long-range activation ($\varepsilon < 1$), we have recovered a result that was uncovered experimentally [34] using another clock reaction, namely, the tetrathionate-chlorite reaction. When ε becomes sufficiently small, in the region of stationary spatial bistability, there appears a Hopf bifurcation at ε_H (Fig. 7) of the FT profiles, the amplitude of which starts oscillating periodically in time while it remains locked to v_0 at $x = 0$. The oscillation in time of the amplitude of the FT profile at $x = L$ is shown in Figure 8. The oscillation is clearly the result of the differential diffusion, as the reaction never shows time periodic behavior in a CSTR.

When ε is further decreased, the oscillations vanish, possibly through a saddle-loop bifurcation at ε_H^* . To the left of this value on Figure 8, we have also

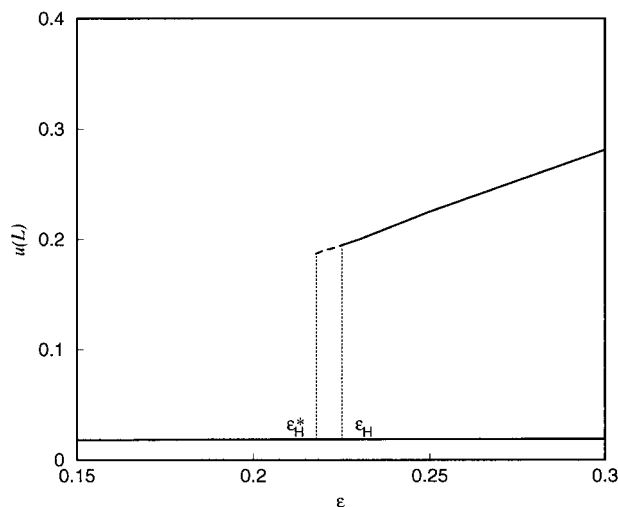


FIGURE 7. Bifurcation diagram for $u(L)$ as a function of ε the ratio of the diffusion coefficient of the inhibitor versus that of the activator in a region where spatial bistability occurs for $\varepsilon = 1$. The FT state [larger values of $u(L)$] undergoes a Hopf bifurcation at ε_H (≈ 0.225), below which its amplitude oscillates everywhere in the gel while being held at the fixed u_0 value at the CSTR–gel interface. The FT state is destroyed by another bifurcation at ε_H^* (≈ 0.218), a still lower value of ε . To the left of this point, the system exhibits excitability.

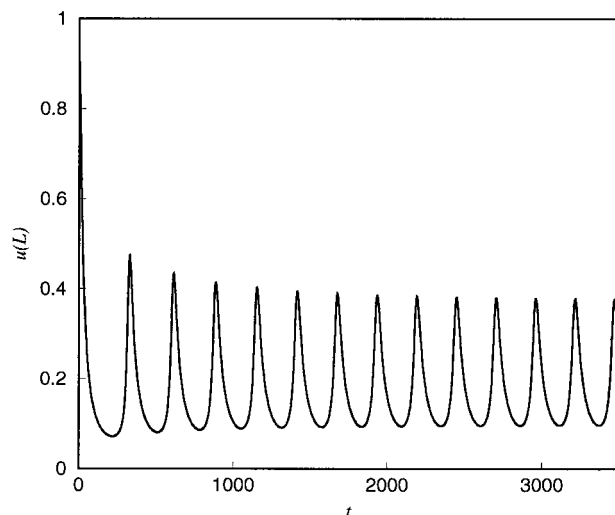


FIGURE 8. Periodic time oscillations (after the initial transient) of the FT state measured at the impermeable boundary [$u(L)$] for $\varepsilon = 0.22$; $u_0 = 0.01$, $v_0 = 0.99$, $d = 0.0021$, $L = 7.4$.

found a region of excitability (not discussed here) [34].

Conclusions

We have thus shown that spatial bistability can occur in a very simple realistic system that can be described semiquantitatively by one-variable dynamics. The origin of the phenomenon therefore does not lie in effects such as a nonvariational character but is most probably related to the boundary conditions related to the finite size of the system. Because of its complication, the analytical solution is of little value. Semianalytical methods (e.g., Galerkin expansion) are now being tested to reveal further characteristics. We have also in the simple case of the IAA reaction recovered the time periodic oscillations generated by a diffusion differential.

Autocatalytic chemistry in solution is particular as bistability between homogeneous steady states is never built in the kinetics alone. This is contrast with other fields, such as nonlinear optics, where the Turing pattern selection may then be studied along the usual lines if one takes into account the neutral modes pertaining to the bifurcations of homogeneous states [31].

Perhaps the most important point that remains to be explored in the chemical field is the importance of the existence of spatial bistability on spatial symmetry breaking, whether they arise from a mor-

phological transverse instability of fronts connecting the F and FT profiles (Fig. 3c) or from the Turing-Prigogine mechanism [10]. Spatial bistability also implies that the patterning problem becomes fully three-dimensional.

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