Resolving an Experimental Paradox in Open Spatial Reactors: The Role of Spatial Bistability

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The interpretation of numerous experiments on spatial and spatiotemporal nonequilibrium chemical patterns performed in continuous gel reactors fed from one side leads to an apparent paradox. We show that this paradox can be resolved with the concept of spatial bistability. We illustrate this theory by numerical simulations with a model related to the Belousov-Zhabotinsky reaction. [S0031-9007(98)07754-0]

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The study of spatial and spatiotemporal reaction-diffusion patterns in chemical systems kept far from equilibrium by a permanent feed of fresh reactants has become a major field in nonlinear science [1]. These developments were favored by the use of open spatial reactors, among which one-side-fed gel reactors (hereafter called OSFR), first introduced by Tam *et al.* [2], are very popular. They are made of a thin film of gel (often disk shaped), one side of which is in contact with the reactive contents of a continuous stirred tank reactor (CSTR) that sustains the nonequilibrium conditions. The reactants diffuse into the gel where they can develop concentration patterns resulting from the sole interplay between reaction and diffusion. The volume of the gel is generally very small in regard to the volume of the CSTR so that the concentrations in the latter are practically independent of the dynamics inside the gel. The local chemical state of the gel is monitored by light transmission in the direction orthogonal to the faces, averaging concentrations over the gel thickness. These reactors have been extensively used in the study of spiral waves [2,3], stationary Turing patterns [4–7], and front dynamics [8–10].

Theoretical interpretations generally assume that, since the gel is thin, it can be considered as two dimensional and that, since the contents of the CSTR are homogeneous, the nonequilibrium parameters are uniform; but these assumptions lead to a paradox. Onto the interface between the gel and the CSTR, all species should have the same uniform concentration they have in the CSTR, i.e., there is a uniform Dirichlet boundary condition. For gels that are thin enough for the 2D approximation to be valid, the effect of the boundary condition should extend through the whole thickness of the gel, thus hindering the development of patterns that would imply nonuniformity of concentrations in the planes parallel to the faces. Accordingly, for a given composition of the CSTR, only one type of uniform concentration domain should be allowed in the gel in order to achieve continuity and uniformity at the interface. However, there are experimental situations where it was possible to observe different states of the gel for a same state of the CSTR [9]. Also, stationary or nonstationary domains, characterized by different concentrations and separated by steep fronts, can coexist over times much longer than one would expect from the diffusion time of the CSTR species into the bulk of the gel [8,10].

To resolve this paradox one can invoke the presence, in some experimental devices, of an additional intermediate membrane that breaks the continuity of concentrations between the CSTR contents and the gel [6,7,11]. Then, for appropriate chemical kinetics, the Dirichlet boundary condition can be replaced by a mixed boundary condition that serves to bypass the problem [6,7]. In another limit, if one assumes that the membrane can be described by a local flow term and that the gel is infinitely thin, one can use the so-called CFUR approximation ("continuous flow unstirred reactor"), as it is done in calculations of Ref. [9]. Nevertheless, we are going to show that, in a number of cases, the solution can be found in the system dynamics itself, without introducing an external element or disputable approximations. This approach relies on the concept of spatial bistability.

Although the argument can be applied to different types of patterns, we shall illustrate our approach on a classical simple case, namely the dynamics of fronts connecting the two stationary states of a bistable system [12–15]. We shall first show that the system can actually exhibit several states for a same state of the CSTR, resolving the experimental paradox. The basic idea is the following. Bistability in a CSTR generally results from the competition between a "clock reaction" driven by an autocatalytic species, say X, and the input flow [16]. In the following, we note the species by X and its concentration by X. In a batch reactor, X evolves slowly in time, until it suddenly jumps to a value close to its equilibrium value X_{eq}. In a CSTR, at high flow rates, the feed dominates the reaction and X remains close to its value X_0 in the input ("flow state," further referred to as F); at low flow rates, the reaction dominates the feed and X approaches the value X_{eq} it would eventually take at equilibrium in a closed vessel ("thermodynamic state," further referred to as T). In a range of intermediate flows, both states can be stable with hysteresis. The selected state depends on the former history of the system. Let us now assume that the CSTR is in state F and coupled to a gel as described above. In the vicinity of the interface, one expects that X remains close to X_0 but the amount of fresh reactants transported by diffusion from the interface with the CSTR decreases with the distance to this interface so that, far away, X must approach a value corresponding to a T state. If the gel is thick enough for this transition to occur, the temporal concentration jump of the clock reaction gives rise to a stiff concentration change in space. This steep change forms a stationary front parallel to the interface, so that a part of the gel remains in state T. This type of spatial profile will be referred to as FT. In some respects, the diffusion plays the same role as the flow terms in the CSTR. Thus, one has the intuition that, as for the CSTR, there is perhaps a range of parameters for which there are two different stable profiles depending on the initial state of the gel. If the system is initially in state T, a front forms, starting from the CSTR boundary, until the final spatial profile corresponds to the FT state is attained; but, if it is initially in state F, the whole gel can remain in state F. Such a system exhibit a *spatial bistability* between F and FT states. A similar spatial bistability has actually been experimentally observed some time ago with the $(\mathrm{ClO}_2^-, \mathrm{I}^-)$ reaction in a quasi-one-dimensional system where the molecular diffusion was replaced by a tunable turbulent hydrodynamic diffusive transport, used as the control parameter [17,18]. We believe that this is a prevailing phenomenon in OSFRs. We have checked this point by numerical simulation of several models of classical bistable reactions. For the sake of simplicity, we limit this presentation to the oxidation of Ce(III) by acidic bromate with a feedstream of bromide (a subset of the Belousov-Zhabotinsky reaction) that has been shown, experimentally and theoretically, to be bistable in a CSTR [19–21].

The rate equations of the model in the CSTR are [19,20]

$$\dot{X} = k_1 A Y - k_2 X Y + (k_3 A - 1/\tau) X - 2 k_4 X^2, \quad \text{(1a)}$$

$$\dot{Y} = -k_1 A Y - k_2 X Y - (Y - Y_0)/\tau, \quad \text{(1b)}$$

where $A = [\mathrm{BrO}_3^-]$, $X = [\mathrm{HBrO}_2]$, $Y = [\mathrm{Br}^-]$, k_1-k_4 are rate constants found in the literature [22], and τ is the residence time of the reactor. The bromate is injected in large excess, so that A can be considered as constant and takes a fixed value in the CSTR (and further also inside the gel). Bromous acid is only a product ($X_0 = 0$). One can show analytically that this system exhibits bistability for 1.4×10^{-7} M $< Y_0 < 6.3 \times 10^{-4}$ M, where Y_0 is the concentration of bromide in the input flows [20] (Fig. 1). Now, let us consider the CSTR coupled with a gel of thickness $e = 1$ mm, a typical experimental value. To study the distribution of concentration in the depth of the gel, one adds the diffusion terms $D_x \nabla_{\mathbf{r}}^2 X$ and $D_y \nabla_{\mathbf{r}}^2 Y$, respectively, to Eqs. (1a) and (1b) and solves the resulting one-dimensional PDEs by numerical simulation. We assume that the diffusion coefficients D_X and D_Y take the archetypal value for small inorganic species $D = 10^{-5}$ cm^2 s^{-1}. The system is found to exhibit spatial bistability between a F state and a FT state for 4.97×10^{-6} M $< Y_0 < 1.74 \times 10^{-3}$ M. In Fig. 2, we

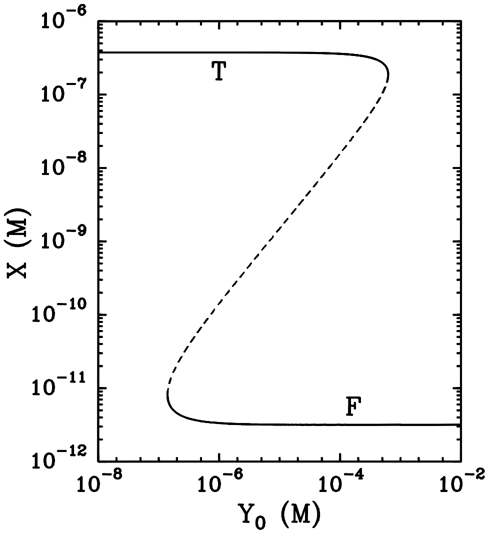

FIG. 1. Bistability in the CSTR: $k_1 = 4.25$ M^{-1} s^{-1}, $k_2 = 3 \times 10^9$ M^{-1} s^{-1}, $k_3 = 1.5 \times 10^4$ M^{-1} s^{-1}, $k_4 = 4 \times 10^7$ M^{-1} s^{-1} (all constants for $[\mathrm{H}^+] = 1.5$ M at $T = 25$ °C), $A_0 = 2 \times 10^{-3}$ M, $1/\tau = 4.5 \times 10^{-3}$ s^{-1}; solid lines: Stable states T (thermodynamic branch) and F (flow branch); dotted line: Unstable states.

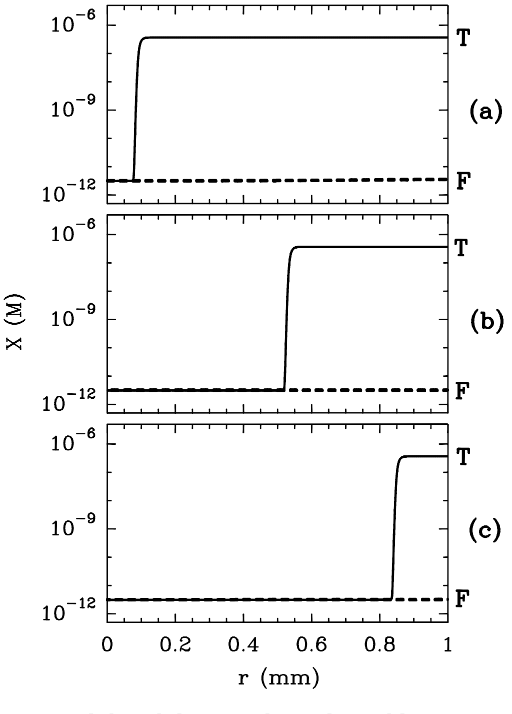

FIG. 2. Spatial bistability in the gel: Stable concentrations profiles of X in the depth of the gel ($0 \leq r \leq e$). The CSTR is located at $r = 0$. Solid line: State FT; dotted line: State F. Same constants as in Fig. 1. (a) $Y_0 = 2 \times 10^{-5}$ M; (b) $Y_0 = 2.5 \times 10^{-4}$ M; (c) $Y_0 = 1 \times 10^{-3}$ M.

TABLE I. Lower and upper limits of bistability range as a function of e. Same constants as in Fig. 1.

e (mm)	Lower Y_0 (M)	Upper Y_0 (M)
0.015	1.4×10^{-7}	5.2×10^{-7}
0.020	1.4×10^{-7}	1.2×10^{-6}
0.030	1.4×10^{-7}	3.0×10^{-6}
0.050	1.4×10^{-7}	6.9×10^{-6}
0.1	1.4×10^{-7}	1.7×10^{-5}
0.25	2.0×10^{-7}	5.7×10^{-5}
0.5	5.6×10^{-7}	1.9×10^{-4}
0.8	2.1×10^{-6}	7.3×10^{-4}
1.0	4.9×10^{-6}	1.7×10^{-3}
1.5	4.4×10^{-5}	2.0×10^{-2}

have represented the two stable spatial profiles of species X for three different values of Y_0. When Y_0 is increased, which favors the flow term, the front shifts away from the CSTR until it reaches the opposite side of the gel where the FT state and the spatial bistability vanish. Thus the bistability range obviously depends on the gel thickness e (Table I). Spatial bistability actually disappears when $e < 1.12 \times 10^{-2}$ mm. Since the average of X over the gel thickness is clearly different for states F and FT, they can be distinguished unambiguously by light transmission, which resolves the apparent paradox.

The simplest pattern for which our approach is relevant, is a unique propagating front that connects the two stable states of a bistable system. In order to show that it can actually be studied in an OSFR, we shall now consider our model as a purely formal one and relax the experimental kinetics constants to make the system less stiff and the computations easier. In the CFUR approximation, where all points of an infinitely thin gel exchanges matter with the surrounding at rate $1/\tau$, the states F and T are connected in space by an "Ising front" (in the terminology of Ref. [15]) that propagates into the less stable state according to the input concentrations. A similar behavior is observed in the CSTR-gel system except that the competition now occurs between states F and FT, since the CSTR is kept in state F. After a short transient, the front profile between states F and FT is independent of the way it is initiated: either a part of the system is initially prepared in state F and the other part in state FT, or one starts from a front profile obtained in a former numerical experiment and changes the value of the control parameter Y_0. In Fig. 3, we have represented the distribution of X within the depth of the gel when the front moves in one direction or the other according to the value of Y_0. The location of the steep concentration change exhibits a strong curvature at the junction between the leading edge of the propagating front and the stationary front of the FT state. The sign of this curvature does not change with the direction of propagation. In Fig. 4, we compare the front velocity as a function of Y_0 for two different values of e with the velocity in the CFUR. In contradiction with a naive intuition, the shift of the critical point that corresponds to zero velocity ("coexistence point") is the largest in the thinnest system, which indicates that the dynamical behavior in the limit of small thicknesses does not fit with the two-dimensional CFUR approximation.

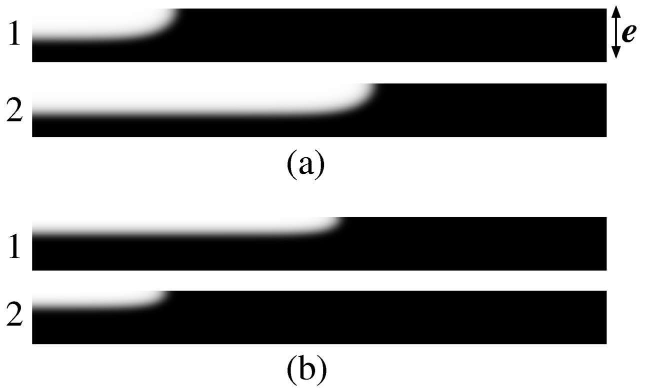

FIG. 3. Propagating fronts: Plane sections of the gel orthogonal to the faces (CSTR is located at the bottom of each section). The gray scale is proportional to the concentration X (full scale: minima in black, maxima in white). $k_1A_0 = 4 \times 10^{-3}$, $k_2 = 1$, $k_3A_0 = 10$, $k_4 = 2.5$, $D_X = D_Y = 1$, $e = 10$, system length $= 100$ (all constants in arbitrary units). (a) Front propagating to the right for $Y_0 = 500$ (section 1: $t = t_0$; section 2: $t = t_0 + 200$); (b) front propagating to the left for $Y_0 = 800$ (section 1: $t = t_0$; section 2: $t = t_0 + 200$).

We have shown that, because of spatial bistability, the dynamics of patterns that relies on the existence of two stable states, can actually be studied in the OSFR, in spite of the sustained uniformity onto the CSTR boundary. However, the implied mechanism is basically tridimensional so that the dynamics explicitly depends on the gel thickness and two-dimensional approximations are generally no longer valid, even in thin systems. In particular, the instability of propagating fronts should be driven, not only by their local curvature in planes parallel to the faces [15], but also by the strong curvature that

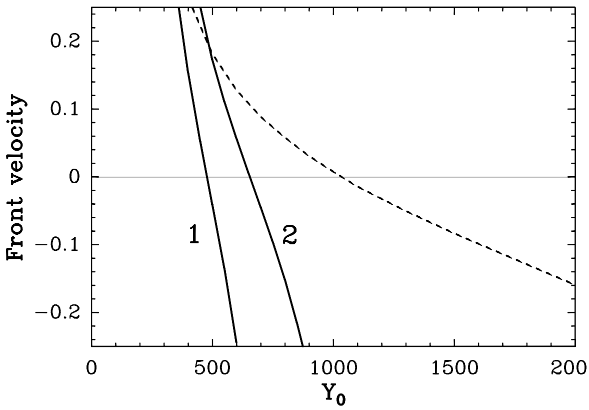

FIG. 4. Front velocity. Same constants as in Fig. 3; dotted line: CFUR approximation; solid line 1: $e = 1$; solid line 2: $e = 0.75$.

exists in the system depth at the leading edge. Finally, let us mention that all these results can be trivially extended to the case of *two-sided* fed reactors where the gel is fed *symmetrically* from the opposite faces. This approach has also been successfully applied to a realistic model of the (ClO_2, I_2) reaction and is supported by preliminary experimental results [23].

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