Crisis-Induced Intermittent Bursting in Reaction-Diffusion Chemical Systems

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We report on numerical evidence for intermittent bursting phenomena in a one-dimensional reaction-diffusion system that mimics spatiotemporal pattern formation in the Couette flow reactor. This bursting regime is attained via an interior crisis when decreasing the diffusion coefficient. The intermittent occurrence of spatially localized structures can be understood in terms of Shil'nikov's homoclinic chaos. This diffusion-induced chaotic bursting is likely to be observed in bench experiments.

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In recent years there has been a rebirth of interest in pattern-forming phenomena in chemically reacting and diffusing systems [1]. This interest has been mainly sparked by the technical development of open spatial reactors [2]. Among them, the Couette flow reactor [3,4] plays a privileged role since it provides a practical implementation of an effectively one-dimensional reaction-diffusion system with (i) well-defined boundary conditions, the fresh chemicals are fed at the two boundaries of the Couette reactor, and (ii) controlled turbulent diffusion process, the effective diffusion coefficient D is a tunable parameter that depends mainly on the rotation rate of the inner cylinder. The Couette flow reactor is remarkably well adapted to investigate the formation of sustained front patterns [4,5]. When considering a bistable chemical reaction, e.g., some variant of the chlorite-iodide reaction, stationary nonhomogeneous spatial patterns are easily obtained by imposing a concentration gradient from the boundaries. These spatial patterns are made of rather homogeneous regions corresponding to reduced or oxidized states, separated by sharp transition fronts caused by a fast switching process in the kinetics of the reaction. As documented in Ref. [5], when varying the chemical input concentrations or the transport rate D, these steady patterns usually destabilize into time-dependent states where the position of the fronts oscillates periodically in the Couette reactor. Thus far, no definite experimental evidence for chaotic spatiotemporal behavior has been obtained.

In a previous work [6] we have shown that the reported spatiotemporal patterns in the Couette flow reactor are characteristic of a wide class of reaction-diffusion systems. But our approach was mainly focused on the existence and stability of multifront patterns. The purpose of this Letter is to push this study further into the nonlinear regime. We elaborate on a very spectacular intermittent bursting phenomenon that is likely to be observed experimentally. More precisely, we elucidate a mechanism for the periodic and nonperiodic appearance of spatially localized bursts of reduced state in an oxidized medium imposed from the boundaries.

The reaction-diffusion system we will consider is a formal model that does not claim to describe faithfully the experimental situation encountered in the Couette flow reactor. It does not completely meet the experimental conditions and the requirements of chemical kinetics laws. However, it does retain the minimal ingredients necessary to reproduce most of the phenomena associated with the observed front patterns in the chlorite-iodide reaction [4–6]. This one-dimensional model reads

$$\frac{\partial u}{\partial t} = D\frac{\partial^2 u}{\partial x^2} + \epsilon^{-1}[v - f(u)]\,,$$
$$\frac{\partial v}{\partial t} = D\frac{\partial^2 v}{\partial x^2} - u + \alpha, \quad x \in [0,1]\,. \qquad (1)$$

The reaction term is a two-variable Van der Pol-like equation, which mimics the excitable character of the chemical reaction used in the experiments. This reaction term ensures the existence of an "S shaped" slow manifold $v = f(u) = u^2 + u^3$, consisting of three branches. Two of them attract the trajectories in a time $\sim\epsilon$ and account for the two families of reduced (upper branch) and oxidized (lower branch) steady states. The only steady state of the reaction term $[u_s = \alpha,\ v_s = f(\alpha)]$ is necessarily located on the slow manifold; it is unstable on the middle branch, the pleats of the slow manifold corresponding to supercritical Hopf bifurcations leading to oscillatory dynamics [7]. The diffusion term is given by a Fick law; the cross-diffusion terms are neglected and the diffusion coefficients are equal $(D_u = D_v = D)$, in order to mimic the turbulent mass transport in the Couette reactor. In agreement with the experimental observations [4,5], we consider Dirichlet boundary conditions: The system is fed symmetrically in an oxidized (lower branch) state, $v(x=0) = f(u(x=0)) = v(x=1) = f(u(x=1))$. For the sake of simplicity, α in Eq. (1) is set on the upper branch of the slow manifold, so that when switching off the diffusion process, all the intermediate cell points evolve asymptotically to the same reduced steady state [8].

The partial-differential equations (1) are solved numerically [6] through finite-difference approximation for the spatial derivatives and the method of line for time advancement. The model medium is represented by a discretized line with a resolution from 50 up to 200 points, i.e., of the same order of magnitude as the number

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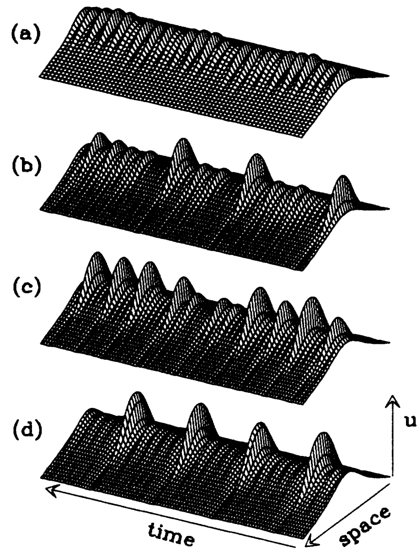

FIG. 1. Spatiotemporal pattern-forming phenomena in the reaction-diffusion system (1) for the model parameters $u(x=0)=u(x=1)=-2$, $\alpha=0.01$, $\epsilon=0.01$, and the slow manifold $f(u)=u^2+u^3$. (a) $D=0.0322560$, C_0^n oscillating pattern confined to the lower branch; (b) $D=0.0322550$, C_r crisis-induced intermittent bursting; (c) $D=0.0322307$, $C_1^{\{m\}}$ homoclinic intermittent bursting; and (d) $D=0.0322400$, P_1^4 periodic bursting. $x \in [0.3,0.7]$; $t \in [0,40]$ in (a), (b), and (c); $t \in [0,20]$ in (d).

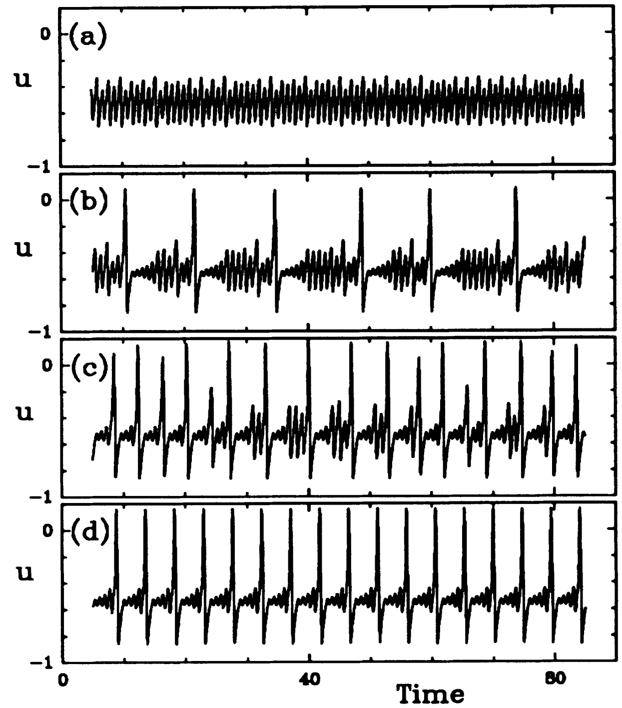

FIG. 2. Time series recorded at the central point $x=\frac{1}{2}$. (a)-(d) correspond respectively to the spatiotemporal patterns shown in Fig. 1.

of pairs of vortices (~50-100) in the Couette reactor. The resulting set of ordinary differential equations (ODEs) is integrated with a stiff ODE solver [6]. The following set of model parameters is considered: $\epsilon=0.01$, $u(x=0)=u(x=1)=-2$ (lower branch), $\alpha=0.01$ (upper branch), whereas D is taken as a control parameter. Even though there is no asymmetry in the feeding, there exists a concentration gradient close to the two boundaries. For $D \gg \epsilon^{-1}$, the diffusion term drives all the trajectories of the system towards a quasihomogeneous solution imposed from the boundaries: All the reactor cells are constrained to the lower branch. When D is decreased, this flat concentration profile transforms continuously into a two-front pattern: Two fronts separate a central region of reduced states (upper branch) from the two regions of oxidized states (lower branch) close to the two boundaries. The appearance of these two-front solutions is actually governed by a cusp instability. According to the chosen one-parameter path, the transition to the two-front profile solution can be either continuous (as considered in this paper) or discontinuous with hysteresis [6(b)]. Note that the experimental observation of spatial bistability between a quasiuniform state and a double-front state has been reported in Ref. [5].

When following our numerical path, D being decreased, the diffusion process carries less and less further the influence of the boundaries and a concentration gradient progressively settles in the system. The spatial profile of the variable $u(x)$ is no longer flat but it increases gradually from the edges to the center of the system. For some critical value of D, this symmetric pattern becomes unstable via a supercritical Hopf bifurcation [6(b)]. Among the one-dimensional array of coupled elementary reactor cells, the ones located at the center are no longer stabilized by the stable steady-state cells located close to the boundaries and the whole system starts oscillating periodically. When further decreasing D, this periodically oscillating nonhomogeneous state undergoes a cascade of period-doubling bifurcations leading to a chaotically oscillating pattern. The time evolution of the u variable spatial profile in the central part of the system is illustrated in Fig. 1(a). In Fig. 2(a) the time series recorded at $x=\frac{1}{2}$ corresponds to nonperiodic small-amplitude oscillations on the lower branch of the slow manifold. According to the nomenclature used in Ref. [9], we will label this chaotic state C_0^n, where the subscript and superscript denote, respectively, the number of large relaxational and small-amplitude oscillations in a basic motif of the time series. A two-dimensional projection of the phase portrait as reconstructed from the temporal evolution of the variables u and v recorded at an intermediate spatial cell point is shown in Fig. 3(a). The corresponding Poincaré map and 1D map obtained when using a (hyper)plane that intersects transversally all the trajectories are illustrated in Figs. 3(d) and 4(a). The fact that the Poincaré map is not a scatter of points but that all the points lie to a good approximation along a smooth curve indicates that the trajectories lie on a multi-

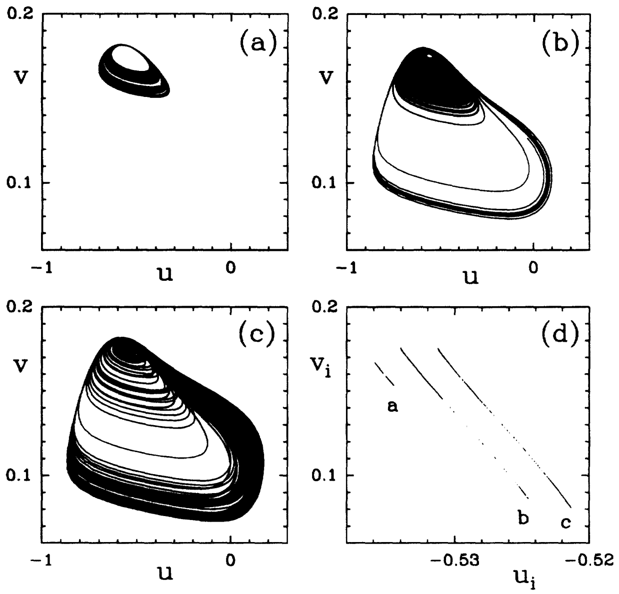

FIG. 3. (a)–(c) Two-dimensional projections of the phase portraits of the chaotic states C_0^n, C_r, and $C_1^{\{m\}}$, respectively. The corresponding first return maps obtained with the Poincaré (hyper)plane $u(x=\frac{1}{2})=-0.55$ are shown in (d); the three maps have been arbitrarily shifted for comparison.

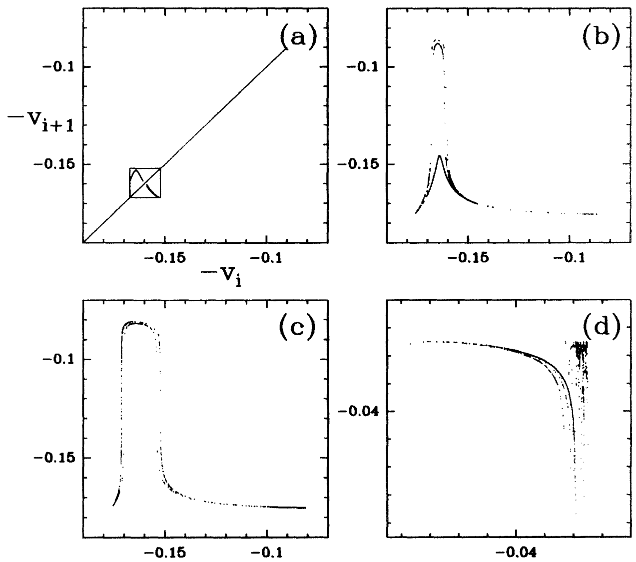

FIG. 4. (a)–(c) 1D maps of the chaotic states C_0^n, C_r, and $C_1^{\{m\}}$, extracted from the Poincaré maps in Fig. 3(d). The multibranched 1D map of $C_1^{\{m\}}$ in (d) is obtained when considering a Poincaré (hyper)plane $[u(x=\frac{1}{2})=0]$ which intersects only the trajectories involved in the reinjection process.

folded two-dimensional sheet in the phase space. The single-humped shape of the 1D map is the signature of low-dimensional deterministic chaos issued from a cascade of period-doubling bifurcations [10].

When D is decreased through a critical value D_c, a qualitative change is observed in the spatiotemporal evolution of the system as shown in Fig. 1(b). Sudden bursts of reduced states appear in an apparently erratic manner in the system. This intermittent appearance of a spatially localized two-front profile becomes more and more frequent when D is further lowered. As seen in the time series in Fig. 2(b), the dynamics at the central cell points is no longer confined to the lower branch of the slow manifold, and the chaotic regime C_0^n is interrupted once in a while by a large-amplitude relaxation oscillation corresponding to a very short visit to the upper branch. When comparing the phase portrait of this new regime C_r [Fig. 3(b)] with the one of C_0^n [Fig. 3(a)], one observes a sudden increase of the phase-space extent of the attractor. The term interior crisis [11] has been coined to describe this "explosion" of a strange attractor that occurs when it collides with an unstable coexisting periodic orbit or its stable manifold. The Poincaré map in Fig. 3(d) clearly shows that the attractor C_0^n is still embodied in C_r. The crisis mechanism is definitely elucidated when looking at the corresponding 1D maps: (i) Before the crisis all points of the map iterate within the invariant square sketched in Fig. 4(a); (ii) after the crisis some points fall outside this square and will escape this region [Fig. 4(b)]. The 1D map of C_r displays an additional large hump corresponding to the bursts, which ensures the return of the trajectories to the former chaotic region. Critical behavior near the interior crisis is generally characterized by the average time between bursts [11] which is predicted to scale as $\langle T\rangle \sim |D-D_c|^{-\gamma}$, where the exponent $\gamma=\frac{1}{2}$ is obtained in the limit of infinitely area contracting Poincaré maps (single-valued quadratic 1D map). In our system, due to finite dissipation rate and to the multivaluation of the 1D map in Fig. 4(b), a deviation from this value is expected [11]. We have checked that the probability distribution of times T between bursts decreases exponentially for large T. But, because computation time becomes prohibitively long in the vicinity of the crisis threshold, we have not been able to estimate accurately the value of γ. Very few clear experimental observations of crisis have been published thus far; a very convincing identification has been reported in the study of the Belousov-Zhabotinskii reaction in well-mixed media [9]. To our knowledge, the intermittent bursting phenomenon reported here is the first observation of a crisis in reaction-diffusion systems. This crisis-induced intermittency leading to macroscopic chaos is very likely to be observed experimentally in the Couette flow reactor.

When further decreasing D, the dynamics of the system ultimately loses the memory of the chaotic state C_0^n, and one witnesses an alternating sequence of chaotic ($C_1^{\{m\}}$) and periodic (P_1^{m}) bursting patterns. In Fig. 1(c), we show the chaotic-bursting regime $C_1^{\{m\}}$ that immediately follows C_r. When comparing the time series in Figs. 2(a), 2(b), and 2(c), respectively, C_r appears as a mixture of C_0^n and $C_1^{\{m\}}$. This is corroborated by the 1D map of C_r [Fig. 4(b)] which looks like the superposition of the small unimodal map of C_0^n [Fig. 4(a)] with the large hump with a flat tail of $C_1^{\{m\}}$ [Fig. 4(c)]. A careful examination of the time series in Fig. 2(c) shows that its basic motif is made of a large-amplitude relaxation oscillation and m' small-amplitude quasiharmonic oscillations, where m' belongs to the finite set $\{m\}$. This basic motif is characteristic of the chaotic dynamics that exists in the neighborhood of a "spiraling out" homoclinic orbit of Shil'nikov type [12]. This interpretation is strengthened by the multibranched structure of the 1D map [Fig. 4(d)] obtained when considering a Poincaré plane which only intersects the large-amplitude relaxation oscillations ensuring the reinjection process. This 1D map is strikingly similar to the theoretical 1D map predicted for "spiral-type" attractors in nearly homoclinic conditions [12]. Each branch of this 1D map corresponds to a number of small-amplitude oscillations in between two bursts. The intermittent bursting in Fig. 1(c) is thus governed by a deterministic iteration scheme that satisfies the symbolic dynamics of Shil'nikov homoclinic chaos. Theoretically a double cascade of saddle-node (originating P_1^m) and subharmonic (leading to $C_1^{\{m\}}$) bifurcations should accumulate at the locus of homoclinicity [12,13]. The bending at the top of each branch of the 1D map in Fig. 4(d) suggests the existence of some folding effect in the reinjection mechanism [12]. In this case, cusp bifurcations with bistability and hysteresis phenomena exist locally near the onset of homoclinicity [13(b)]. This feature is likely to explain the concurrency between periodic and chaotic bursting patterns observed along our one-parameter path. A periodic bursting pattern P_1^4 is shown in Fig. 1(d). Let us mention that, nearby in the parameter space, bursting patterns with up to $m=7$ small-amplitude oscillations in between two successive bursts can be attained. For lower values of D, this sequence of periodic (P_1^m) and intermittent ($C_1^{\{m\}}$) bursting patterns, with m decreasing progressively, ends on a periodically oscillating two-front pattern (P_1^0) which ultimately stabilizes in a stationary two-front pattern. This succession of periodic and chaotic bursting patterns is the counterpart of the alternating sequences of periodic and chaotic oscillations that exhibits the Belousov-Zhabotinskii reaction when conducted in a well-mixed medium [9,12,14]. The so-called chemical chaos and its homoclinic nature was shown to arise from the nonlinear complexity of the chemical kinetics [12,14]. The remarkable feature of the homoclinic intermittent bursting described in this paper is that it results from the interaction of the diffusion process with a chemical reaction, which itself would proceed in a stationary manner if diffusion were negligible. In a forthcoming publication we hope to demonstrate the existence of a Shil'nikov homoclinic orbit using nonlinear Galerkin projection techniques [15].

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[1] *Waves and Patterns in Chemical and Biological Media,* edited by H. L. Swinney and V. I. Krinski [Physica (Amsterdam) **49D** (1991)].

[2] J. Boissonade, in *Dynamic and Stochastic Processes. Theory and Applications,* edited by R. Lima, L. Streit, and R. Vilela-Mendes, Lecture Notes in Physics Vol. 355 (Springer-Verlag, Berlin, 1990), p. 76.

[3] W. Y. Tam, J. A. Vastano, H. L. Swinney, and W. Horsthemke, Phys. Rev. Lett. **61**, 2163 (1988); W. Y. Tam and H. L. Swinney, Physica (Amsterdam) **46D**, 10 (1990).

[4] Q. Ouyang, J. Boissonade, J. C. Roux, and P. De Kepper, Phys. Lett. A **134**, 282 (1989); J. Boissonade, Q. Ouyang, A. Arneodo, J. Elezgaray, J. C. Roux, and P. De Kepper, in *Nonlinear Waves in Processes in Excitable Media,* edited by A. V. Holden, M. Markus, and H. G. Othmer (Plenum, New York, 1991), p. 47.

[5] Q. Ouyang, V. Castets, J. Boissonade, J. C. Roux, P. De Kepper, and H. L. Swinney, J. Chem. Phys. **95**, 351 (1991).

[6] (a) A. Arneodo and J. Elezgaray, Phys. Lett. A **143**, 25 (1990); (b) J. Elezgaray and A. Arneodo, J. Chem. Phys. **95**, 323 (1991).

[7] According to the specific shape $f(u)$ of the slow manifold, the Hopf bifurcation can be either supercritical or subcritical. See W. Eckhaus, in *Asymptotic Analysis II,* edited by F. Verhulst, Lecture Notes in Mathematics Vol. 985 (Springer, Berlin, 1983), p. 449.

[8] A more realistic model should take into account a spatial dependence of the parameter α, with $\alpha(x=0)=\alpha(x=1)=u(x=0)=u(x=1)$, but the effective implementation of this spatial constraint does not have much meaning in this formal approach since it should strongly depend on the specific kinetics of the reaction, as debated in Ref. [6(b)].

[9] P. Richetti, P. De Kepper, J. C. Roux, and H. L. Swinney, J. Stat. Phys. **48**, 977 (1987).

[10] P. Collet and J. P. Eckmann, *Iterated Maps of the Interval as Dynamical Systems* (Birkhaüser, Boston, 1980).

[11] C. Grebogi, E. Ott, and J. A. Yorke, Phys. Rev. Lett. **48**, 1507 (1982); Physica (Amsterdam) **7D**, 181 (1983); Phys. Rev. Lett. **57**, 1284 (1986); C. Grebogi, E. Ott, F. Romeiras, and J. A. Yorke, Phys. Rev. A **36**, 5365 (1987).

[12] F. Argoul, A. Arneodo, and P. Richetti, Phys. Lett. A **120**, 269 (1987); in *A Chaotic Hierarchy,* edited by G. Baier and M. Klein (World Scientific, Singapore, 1991), p. 79.

[13] (a) P. A. Glendenning and C. Sparrow, J. Stat. Phys. **35**, 645 (1983); (b) P. Gaspard, R. Kapral, and G. Nicolis, J. Stat. Phys. **35**, 697 (1984).

[14] F. Argoul, A. Arneodo, P. Richetti, J. C. Roux, and H. L. Swinney, Account Chem. Res. **20**, 436 (1987).

[15] M. Marion and R. Teman, SIAM J. Numer. Anal. **26**, 1139 (1989).