Chemical Chaos: From Hints to Confirmation

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Received March 16, 1987 (Revised Manuscript Received August 25, 1987)

1. Introduction

The term *chaotic*, as it is now widely used, describes nonperiodic behavior that arises from the nonlinear nature of *deterministic* systems, not noisy behavior arising from random driving forces.[1,2] Recent experiments on diverse nonlinear systems, including fluid flows and nonlinear electrical circuits, have revealed chaotic dynamics similar to that found in theoretical analyses. The intrinsically nonlinear properties of chemical kinetics suggest the possibility of chaos in chemical systems,[3] but there is a healthy skepticism regarding the actual existence of chaos in real well-controlled chemical reactions; for example:

"There certainly are experimental systems which exhibit 'chaotic' behavior in spite of heroic measures to control all recognized parameters. Such behavior does not prove that the chaos is inherent in the mechanism itself rather than due to unavoidable stochastic fluctuations."[4]

"In realistic models of the B. Z. [Belousov–Zhabotinskii] reaction, numerical computations, however, reveal only periodic patterns in both the continuous and discrete models."[5]

"...it is still an open question whether chaos arising from an homogeneous chemical mechanism has been obtained experimentally or whether it comes from the imperfect control of external features."[6]

Thus, it seems worthwhile to examine carefully the experimental and theoretical evidence for the existence of chemical chaos—that is the goal of this paper.

There is no question about the existence of *oscillations* in chemical reactions—many oscillating chemical reactions have been discovered in recent years.[7] Studies of oscillating reactions have focused primarily on the Belousov–Zhabotinskii (BZ) reaction,[8] in which bromate ions are reduced in an acidic medium by an organic compound (usually malonic acid) with or without a catalyst (usually cerous and/or ferrous ions). The mechanism of the BZ reaction was elucidated[9] in 1972 and elaborated later,[10] and it is generally accepted in spite of some recent discussions. Research on rate-determining steps indicated that many of the more than 20 species identified in the reaction were slaved in their time dependence to that of a few species. Hence, it was possible to develop a skeletal model, the "Oregonator", which had only three species.[11,12] This model (and another version with seven species[13]) was shown to be sufficient to reproduce qualitatively the main features of the BZ reaction known a decade ago, namely, bistability, excitability, and oscillations.

Thus, the theoretical understanding as well as experimental knowledge of the BZ reaction was far ahead of that for other oscillating chemical reactions. Therefore, when Ruelle[14] suggested in 1973 that chemical reactions might exhibit nonperiodic behavior, chemists turned naturally to the BZ reaction. The results dealing with nonperiodic behavior come primarily from studies of this reaction, and this Account will deal only with them.

2. First Qualitative Findings

Schmitz, Graziani, and Hudson[15] were the first to report observations of chaos in a chemical reaction. They conducted an experiment on the BZ reaction in a continuous flow stirred tank reactor, where the flow

Argoul, Richetti, and Roux are chemists at the Centre de Recherche Paul Pascal, which is a chemical laboratory that has for more than a decade pioneered in the study of chemical oscillations and chaos. Argoul and Richetti, who earned doctoral degrees from the Université de Bordeaux in 1986 and 1987, respectively, performed many of the recent experiments and analyses that are described in this Account. Arneodo, a theoretical physicist at the Université de Nice, switched fields from particle physics to dynamical systems in the early 1980s, and Swinney, an experimental physicist at the University of Texas, began to study instabilities in fluid dynamics in the mid-1970s. The French–Texas collaboration was initiated in 1980–1981, when Roux spent a year at the University of Texas at Austin as a visiting scientist in the nonlinear dynamics research program in the physics department. During that visit Roux discovered the now much-studied Texattractor shown in Figure 2.

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(1) See, for example, the following monographs: Bergé, P.; Pomeau, Y.; Vidal, C. *Order within Chaos*; Wiley: New York, 1986; Hermann: Paris, 1984. Thompson, J. M. T.; Stewart, H. B. *Nonlinear Dynamics and Chaos*; Wiley, New York, 1986. Schuster, H. G. *Deterministic Chaos*; Physik-Verlag: Weinheim, 1984.

(2) See, for example, the following collections of articles: Cvitanovic, P., Ed. *Universality in Chaos*; Hilger: Bristol, 1984. Holden, A. V., Ed. *Chaos*; Manchester University Press: Manchester, 1986. Bai-Lin, Hao, Ed. *Chaos*; World Scientific: Singapore, 1984. Shlesinger, M. F.; Cawley, R.; Saenz, A. W.; Zachary, W., Eds. *Perspectives in Nonlinear Dynamics*; World Scientific: Singapore, 1986.

(3) For an earlier discussion of chemical chaos, see: Swinney, H. L.; Roux, J. C. In *Nonequilibrium Dynamics in Chemical Systems*; Vidal, C., Pacault, A., Eds.; Springer: Berlin, 1984; p 124.

(4) Noyes, R. M. In *Stochastic Phenomena and Chaotic Behavior in Complex Systems*; Schuster, P., Ed.; Springer: Berlin, 1984; p 107.

(5) Schwartz, I. B. *Phys. Lett. A* **1984**, *102*, 25.

(6) Gray, P.; Scott, S. K. *J. Phys. Chem.* **1985**, *89*, 22.

(7) Field, R. J., Burger, M., Eds. *Oscillations and Travelling Waves in Chemical Systems*; Wiley: New York, 1985.

(8) See, for example: Field, R. J.; Noyes, R. M. *Acc. Chem. Res.* **1977**, *10*, 214.

(9) Field, R. J.; Körös, E.; Noyes, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 8649.

(10) Edelson, D.; Field, R. J.; Noyes, R. M. *Int. J. Chem. Kinet.* **1975**, *7*, 417.

(11) Field, R. J.; Noyes, R. M. *J. Chem. Phys.* **1974**, *60*, 1877.

(12) Field, R. J. *J. Chem. Phys.* **1975**, *63*, 2284.

(13) Showalter, K.; Noyes, R. M.; Bar-Eli, K. *J. Chem. Phys.* **1978**, *69*, 2514.

(14) Ruelle, D. *Trans. N.Y. Acad. Sci.* **1973**, *35*, 66.

(15) Schmitz, R. A.; Graziani, K. R.; Hudson, J. L. *J. Chem. Phys.* **1977**, *67*, 3040.

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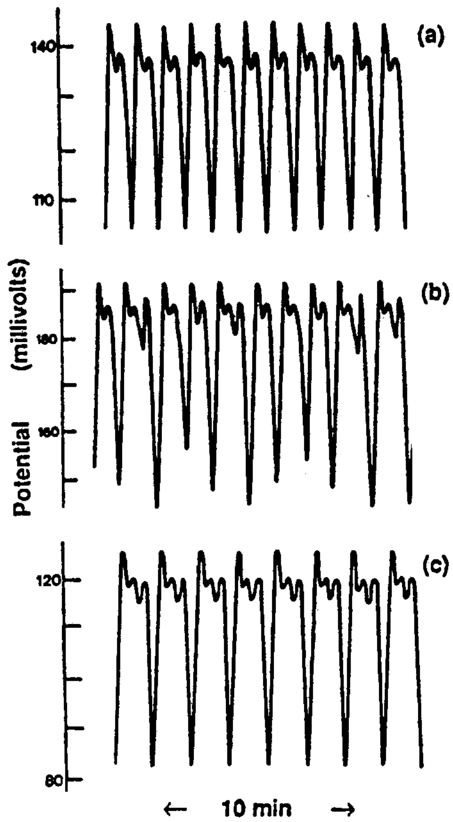

Figure 1. Time series records of the bromide ion electrode potential observed for periodic states that have (a) one large and one small oscillation per period and (c) one large and two small oscillations per period. (b) A chaotic state observed for conditions between those that yielded the periodic states (a) and (b). The residence time τ (the reactor volume divided by the total flow rate) was 0.104, 0.098, and 0.097 h in (a)–(c), respectively. From ref 16.

rate of the feed chemicals was maintained constant and the reaction behavior was monitored with bromide ion specific and platinum wire electrodes. For some range in flow rate, periodic oscillations in the concentrations were observed, as illustrated in Figure 1a. (This figure is from one of their later experiments.[16]) However, for another range in flow rate, chaotic (irregular) oscillations were observed, as illustrated in Figure 1b. The chaotic behavior persisted over about a 10% range in flow rate before there was a transition back to periodic oscillations.

Subsequent experiments on the BZ reaction[16–26] have shown that *periodic–chaotic* sequences are common. In these sequences two periodic states lie to either side (in flow rate) of a chaotic regime. Typically, one of the periodic states has m oscillations per period and the other has $m + 1$ oscillations per period, and the chaotic state that is bracketed by these two periodic states appears to be a random mixture of the two periodic states. Figure 1 illustrates this behavior: the chaotic state in (b) appears to be a mixture of periodic states with two oscillations per period (Figure 1a) and three oscillations per period (Figure 1c).

In the early experiments the term chaotic was used when (1) the time series looked irregular,[15,17,18] (2) the power spectra of the concentration time series contained broad-band noise that was well above the instrumental noise level found for the periodic states,[21,22] and (3) the autocorrelation function of the concentration decayed to zero for large times.[19,21] However, these measures could characterize random noise as well as chaos. In fact, the observed irregular behavior could plausibly be interpreted as arising from random fluctuations in the flow rate or other control parameters, which would result in a random switching of the system from one to another of the adjacent periodic states. Even though the range in flow rate in which the irregular behavior was observed appeared to be large compared to fluctuations in the pumping rate, this argument cast reasonable doubt on the existence of deterministic nonperiodic behavior in a well-controlled chemical system.

These experimental findings motivated numerical studies of models of the BZ reaction. However, these simulations yielded sequences involving only periodic states, but these states were found to be very similar to the ones observed in the periodic–chaotic sequence (see, e.g., ref 13). No chaos was observed in these simulations, at least through a visual inspection of the time series. (In section 4.2 we shall see the full significance of this remark.) Thus, a reasonable conclusion, reached in 1978, was that[13] "the difference between experiments and simulations suggests that the chaotic behavior observed experimentally may result from fluctuations too small to measure in any other way." Later work appeared to support this conclusion.[4–6,27,28]

3. Dynamical Systems Theory: Hints for Identifying Low-Dimensional Deterministic Chaos

Theoretical and numerical studies of deterministic chaos were a rapidly growing area of nonlinear physics by 1980, and the knowledge gained there provided new tools for experimentalists to use in the analysis and understanding of nonperiodic data.[1–3] We will describe two ideas that have proved to be especially fruitful.

3.1. Analysis of Experimental Data: Construction of Phase Space Portraits. Any dynamical system at an instant of time can be described by a single point in an appropriate multidimensional phase space. The temporal evolution of the system is then given by the trajectory of that point in phase space. Periodic behavior is given by a closed curve called a limit cycle. A chaotic state is described by an irregular trajectory, called a *strange attractor*.

For a chemical reaction with n species the n-dimensional phase space coordinates could be the concentrations of the n species. The measurement of the time

(16) Hudson, J. L.; Hart, M.; Marinko, D. *J. Chem. Phys.* **1979**, *71*, 1601.
(17) Rössler, O. E.; Wegmann, K. *Nature (London)* **1978**, *271*, 89.
(18) Wegmann, K.; Rössler, O. E. *Z. Naturforsch., A* **1978**, *33*, 1179.
(19) Bachelart, S. Bordeaux Thesis, 1981.
(20) Vidal, C.; Roux, J. C.; Rossi, A.; Bachelart, S. *C.R. Seances Acad. Sci., Ser. C* **1979**, *289*, 73.
(21) Vidal, C.; Roux, J. C.; Bachelart, S.; Rossi, A. *Ann. N.Y. Acad. Sci.* **1980**, *357*, 377.
(22) Vidal, C.; Bachelart, S.; Rossi, A. *J. Phys. (Les Ulis, Fr.)* **1982**, *43*, 7.
(23) Roux, J. C.; Turner, J. S.; McCormick, W. D.; Swinney, H. L. In *Nonlinear Problems: Present and Future*; Bishop, A. R., Campbell, D. K., Nicolaenko, B., Eds.; North-Holland: Amsterdam, 1982; p 409.
(24) Roux, J. C.; Swinney, H. L. In *Nonlinear Phenomena in Chemical Kinetics*; Pacault, A., Vidal, C., Eds.; Springer: Berlin, 1981; p 33.
(25) Turner, J. S.; Roux, J. C.; McCormick, W. D.; Swinney, H. L. *Phys. Lett. A* **1981**, *85*, 9.
(26) Simoyi, R. H.; Wolf, A.; Swinney, H. L. *Phys. Rev. Lett.* **1982**, *49*, 245.
(27) Ganapathisubramanian, N.; Noyes, R. M. *J. Chem. Phys.* **1982**, *76*, 1770.
(28) Rinzel, J.; Schwartz, I. B. *J. Chem. Phys.* **1984**, *80*, 5610.

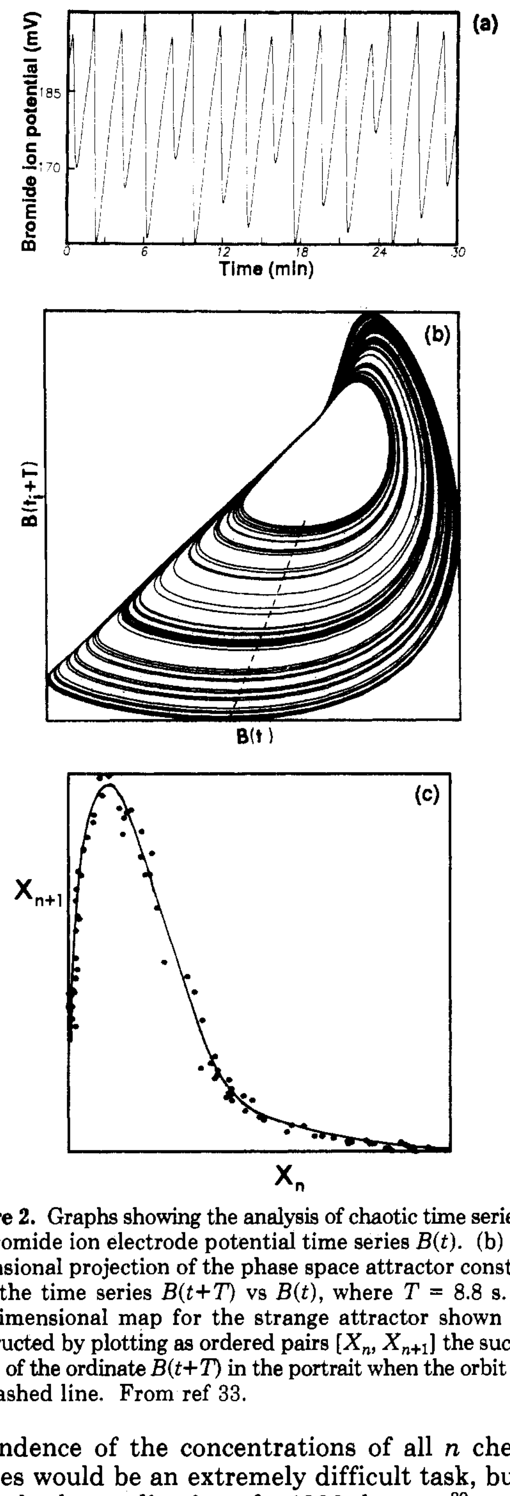

Figure 2. Graphs showing the analysis of chaotic time series data. (a) Bromide ion electrode potential time series $B(t)$. (b) A two-dimensional projection of the phase space attractor constructed from the time series $B(t+T)$ vs $B(t)$, where T = 8.8 s. (c) A one-dimensional map for the strange attractor shown in (b), constructed by plotting as ordered pairs $[X_n, X_{n+1}]$ the successive values of the ordinate $B(t+T)$ in the portrait when the orbit crosses the dashed line. From ref 33.

dependence of the concentrations of all n chemical species would be an extremely difficult task, but fortunately the application of a 1936 theorem[29] makes it possible to construct a multidimensional phase space portrait from time series measurements of a *single* variable, $B(t)$. The coordinates of a point in phase space are obtained from time delay values of the original time series:[30,31] $[B(t), B(t+T), B(t+2T), ...]$, where the time delay T is arbitrary for noiseless data. For real (i.e., noisy) data there is an optimum choice of T, as discussed by Fraser and Swinney;[32] the optimum delay is typically one-tenth to one-half the mean orbital period.

The time delay method was used to construct phase portraits for data obtained in Texas by Roux et al.[23-25] for another periodic–chaotic sequence, observed for similar chemical concentrations but much lower flow rates than in the experiments of Hudson et al.[16] Time series data for a chaotic state are shown in Figure 2a, and a two-dimensional projection of a phase space attractor constructed from these data is shown in Figure 2b. If the attractor is considered in three rather than two dimensions, the intersection of the orbits with a plane approximately normal to the orbits yields a set of points that, within the experimental resolution, lie along a smooth curve. Such a *Poincaré section* demonstrates the low-dimensional nature of this chaotic state—the orbits lie approximately on a two-dimensional sheet.

Further insight into the dynamics can be achieved by constructing a one-dimensional map: let the successive intersections of the ordinate $B(t+T)$ of the orbits with the dashed line in Figure 2b have values called X_1, X_2, ..., X_n, X_{n+1}, ... A plot of X_{n+1} vs X_n is shown in Figure 2c: the points fall on a smooth curve, a one-dimensional map. Thus, even though the behavior is nonperiodic and has a power spectrum with broad-band noise, the system is nevertheless completely (within the experimental resolution) *deterministic*!—for any X_n, the map gives the next value, X_{n+1}.

A hallmark of a strange attractor is exponential separation of nearby points on the attractor. Since a point on an attractor represents the entire physical system, exponential separation of nearby points on chaotic attractors means that systems that are initially nearly identical will inevitably evolve differently at long times. Hence, even though chaotic behavior is deterministic, long-term prediction of the state of the system is impossible! The quantity that characterizes the long-term separation rate of nearby points is the largest *Lyapunov exponent*; it is negative for a time-independent state of a system, zero for a periodic or multiperiodic state, and positive for a chaotic state.[1-3] A method has been developed for computing the largest Lyapunov exponent for time series data, and by use of this method the value of the exponent for the data in Figure 2 was found to be positive.[33,34] The exponential separation of nearby points cannot continue indefinitely (for example, none of the chemical concentrations can become infinite); therefore, the attracting set for strange attractors always has many folds. This folding, which results in a fractal (noninteger) dimension of the attractors, was directly observed for the data in Figure 2.[33]

3.2. Universal Dynamics. According to dynamical systems theory there are certain routes from regular to chaotic dynamics that are common in diverse systems. Some of these *universal* routes have been observed in recent experiments[1,2]—studies of convection, semiconductors, lasers, etc.—and these routes have also been found in chemical experiments.[3]

The best known and best understood route to chaos is through period doubling: the period of oscillation successively doubles in an infinite sequence of transitions that occurs as a control parameter is varied. The distance in control parameter between successive

(29) Whitney, H. *Ann. Math.* **1936**, *37*, 645.
(30) Packard, N. H.; Crutchfield, J. P.; Farmer, J. D.; Shaw, R. S. *Phys. Rev. Lett.* **1980**, *45*, 712.
(31) Takens, F.; *Lect. Notes Math.* **1981**, *No. 898*, 366.
(32) Fraser, A. M.; Swinney, H. L. *Phys. Rev. A* **1986**, *33*, 1134.
(33) Roux, J. C.; Simoyi, R. H.; Swinney, H. L. *Physica D (Amsterdam)* **1983**, *8*, 257.
(34) Wolf, A.; Swift, J. B.; Swinney, H. L.; Vastano, J. A. *Physica D (Amsterdam)* **1985**, *16*, 285.

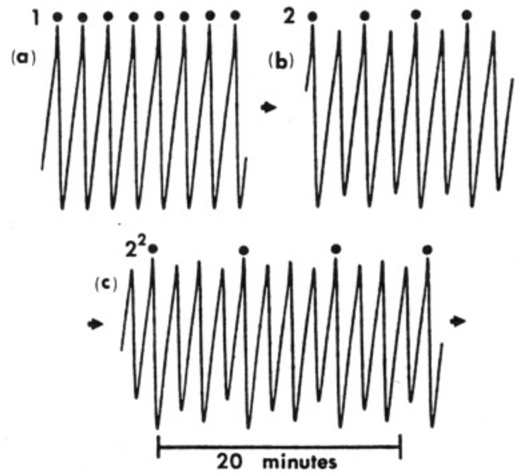

Figure 3. Bromide ion electrode potential time series illustrating a period doubling sequence. (a) The original periodic state (τ = 0.725 h). (b) The period has doubled; the waveform now repeats after every two oscillations (τ = 0.773 h). (c) The has doubled again; the waveform now repeats after every four oscillations (τ = 0.803 h). The dots above the time series are separated by one period. From ref 40.

transitions decreases geometrically at a universal rate; hence the sequence converges.[35-37] The accumulation point for the sequence marks the onset of chaos.

Period doubling is a generic property of systems described by a one-dimensional map with a single extremum.[38] The map in Figure 2c is of this type; therefore, it is not surprising (at least not now) that the chaotic state in Figure 2 is reached through a period doubling sequence.[26,39,40] Data illustrating this sequence are shown in Figure 3.

Another aspect of universality is the behavior found in the chaotic region beyond the end of a period doubling sequence. For a large class of mathematical models this chaotic regime contains an infinite number of periodic states (windows) that occur in a certain order—this is known as the *universal sequence*.[38] A large number of the distinct periodic states have been found in experiments on the regime that contains the chaotic state shown in Figure 2, and these periodic states have been found to have the same properties and occur in the same order as the states of the universal sequence.[33,40] The striking correspondence between the very complicated dynamics of the universal sequence and a sequence observed in experiments on the BZ reaction is alone strong evidence that deterministic chaos occurs in nonequilibrium chemical reactions.

Another kind of behavior often observed in nonlinear systems is intermittency, where regular oscillations are interrupted by occasional bursts of noise. At the onset of chaos these bursts are infinitely far apart in time, but as a control parameter is varied beyond onset, the bursts become more and more frequent. Pomeau and Manneville[41] have identified three distinct types of intermittency, and two types have been observed in experiments on the BZ reaction.[42,43]

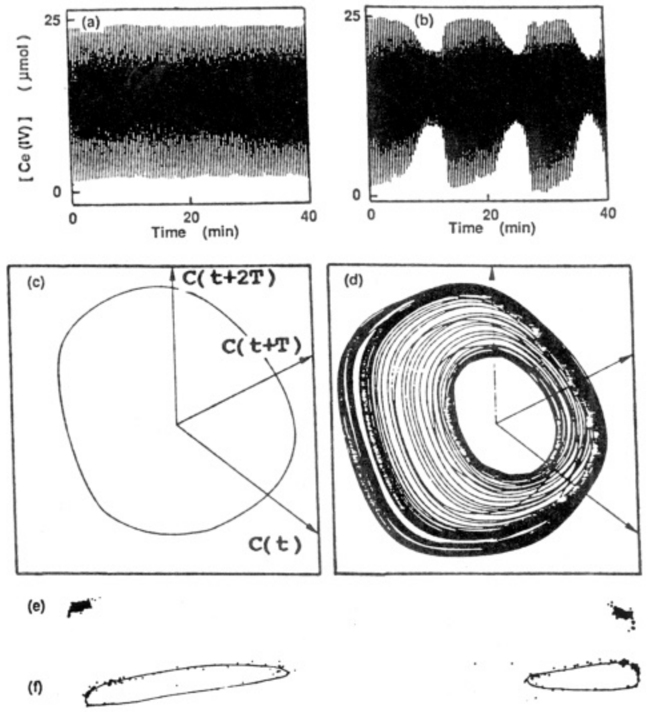

Figure 4. These laboratory data illustrate the transition from singly periodic behavior, where the phase space attractor is a limit cycle, to doubly periodic (quasi-periodic) behavior, where the attractor is a torus with frequency ratio $f_2/f_1 \cong 1/30$. Time series, phase portraits, and Poincaré sections are shown for two values of the residence time: τ = 0.44 h in (a), (c), and (e), and τ = 0.42 h in (b), (d), and (f). From ref 46.

Theoretical studies have shown that chaotic dynamics may also emerge from a regime with two incommensurate frequencies (frequencies whose ratio is an irrational number).[44] Recently, such two-frequency *quasi-periodicity* has been discovered in the BZ reaction.[45] It was found that, following a transition to a periodic state,[46] the resulting limit cycle underwent a secondary transition to a quasi-periodic state where the second frequency corresponded to a slow modulation of the amplitude of the initial periodic oscillations, as illustrated in Figure 4. With further change in the control parameter, the inner part of the toroidal phase space attractor shrank to a thin tube, and finally the torus disappeared, leaving a fixed point attractor on its axis.[46] For other experimental conditions, a transition to a chaotic state was observed to occur through a wrinkling of the torus.[47]

(35) Grossmann, S.; Thomae, S. *Z. Naturforsch., A* **1977**, *32*, 1353.
(36) Feigenbaum, M. J. *J. Stat. Phys.* **1978**, *19*, 25.
(37) Coullet, P.; Tresser, C. *J. Phys.* (*Les Ulis, Fr.*) **1978**, *39*, C5. Tresser, C.; Coullet, P. *C. R. Seances Acad. Sci.* **1978**, *287*, 577.
(38) Collet, P.; Eckmann, J. P. *Iterated Maps of the Interval as Dynamical Systems*; Birkhauser: Boston, 1980.
(39) Coffman, K.; McCormick, W. D.; Swinney, H. L.; Roux, J. C. In *Nonequilibrium Dynamics in Chemical Systems*; Vidal, C., Pacault, A., Eds.; Springer: Berlin, 1984; p 251.
(40) Coffman, K. G.; McCormick, W. D.; Noszitczius, Z.; Simoyi, R. H.; Swinney, H. L. *J. Chem. Phys.* **1987**, *86*, 119. Noszticzius, Z.; McCormick, W. D.; Swinney, H. L. *J. Phys. Chem.* **1987**, *91*, 5129.
(41) Pomeau, Y.; Manneville, P. *Commun. Math. Phys.* **1980**, *24*, 189.
(42) Pomeau, Y.; Roux, J. C.; Rossi, A.; Bachelart, S.; Vidal, C. *J. Phys., Lett.* **1981**, *42*, L271.
(43) Arneodo, A.; Kreisberg, N.; McCormick, W. D.; Richetti, P.; Swinney, H. L., in preparation.
(44) See, e.g.: the discussions in ref 1 and 2; Aronson, D. G.; Chory, M. A.; Hall, G. R.; McGehee, R. P. *Commun. Math. Phys.* **1982**, *83*, 303; MacKay, R. S.; Tresser, C. *Physica D* (*Amsterdam*) **1986**, *19*, 206.
(45) Argoul, F.; Roux, J. C. *Phys. Lett. A* **1985**, *108*, 426.
(46) Argoul, F.; Arneodo, A.; Richetti, P.; Roux, J. C. *J. Chem. Phys.* **1987**, *86*, 3325.
(47) Roux, J. C.; Rossi, A. In *Nonequilibrium Dynamics in Chemical Systems*; Vidal, C., Pacault, A., Eds.; Springer, Berlin, 1984; p 141.
(48) Hudson, J. L.; Mankin, J. C. *J. Chem. Phys.* **1981**, *74*, 6171.
(49) Nagashima, H. *J. Phys. Soc. Jpn.* **1980**, *49*, 2427.
(50) Hudson, J. L. In *Nonlinear Phenomena in Chemical Kinetics*; Pacault, A., Vidal, C., Eds.; Springer: Berlin, 1981; p 33.
(51) Turner, J. S. In *Self Organization in Dissipative Structures*; Schieve, W. D., Allen, P., Eds.; University of Texas Press: Austin, 1982; p 41.

The observations in experiments on the BZ reaction of routes to chaos that have been well-established in dynamical systems theory provide very strong evidence for the existence of low-dimensional deterministic nonperiodic behavior—*chaos*—in nonequilibrium chemical reactions. Despite this evidence, doubts about the existence of chaos persist, largely because chaotic states have not been found[61] in most simulations.[4-6,13,27,28] We will now describe some recent theoretical results that reconcile these legitimate doubts with the experimental observations.

4. Insights from Simulations

4.1. Simulations with Oregonator-Type Models. One reduction of the original 20-variable Field–Körös–Noyes model[9] of the BZ reaction leads to the skeletal scheme given by reactions R1–R9 with nine intermediate species,[53,54] where R· is an oxidized derivative of malonic acid (MA), P is an inert organic product, and BrMA is bromomalonic acid. The concentrations of both bromate and cerous ions are assumed to be constant in the reactor; only the input flow of Br^- is taken into account in the calculations.

$$BrO_3^- + Br^- + 2H^+ \xrightarrow{k_1} HBrO_2 + HOBr \quad (R1)$$

$$HBrO_2 + Br^- + H^+ \xrightarrow{k_2} 2HOBr \quad (R2)$$

$$HOBr + Br^- + H^+ \xrightarrow{k_3} Br_2 + H_2O \quad (R3)$$

$$BrO_3^- + HBrO_2 + H^+ \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} 2BrO_2\cdot + H_2O \quad (R4)$$

$$2HBrO_2 \xrightarrow{k_5} HOBr + BrO_3^- + H^+ \quad (R5)$$

$$BrO_2\cdot + Ce(III) + H^+ \xrightarrow{k_6} Ce(IV) + HBrO_2 \quad (R6)$$

$$HOBr + MA \xrightarrow{k_7} BrMA + H_2O \quad (R7)$$

$$BrMA + Ce(IV) \xrightarrow{k_8} Br^- + R\cdot + Ce(III) + H^+ \quad (R8)$$

$$R\cdot + Ce(IV) \xrightarrow{k_9} Ce(III) + P \quad (R9)$$

Although the numerical results presented in this paper have been obtained with this particular reaction scheme, we should emphasize that this particular model is only one among a number of reasonably realistic models that have been proposed to describe the dynamics of the BZ reaction.

Reactions R1–R9 translate into a system of seven ordinary differential equations, which when simulated on a computer[54] yield a periodic–chaotic sequence similar to the one observed in the Texas experiments; for example, the time series, attractor, and one-dimensional map shown in Figure 5 compare fairly well with the corresponding experimental ones shown in Figure 2. Furthermore, for the model as well as in the experiments the transitions from the periodic to the chaotic regimes all occur by period doubling,[39,54] and the successive periodic regimes[23,24] differ by the addition of one more small-amplitude oscillation per period of the time series. Simulations for a similar model, one with seven species,[13] have yielded a transition from periodic to quasi-periodic behavior,[55] just as was found in the experiments described in section 3.2 (see Figure 4).

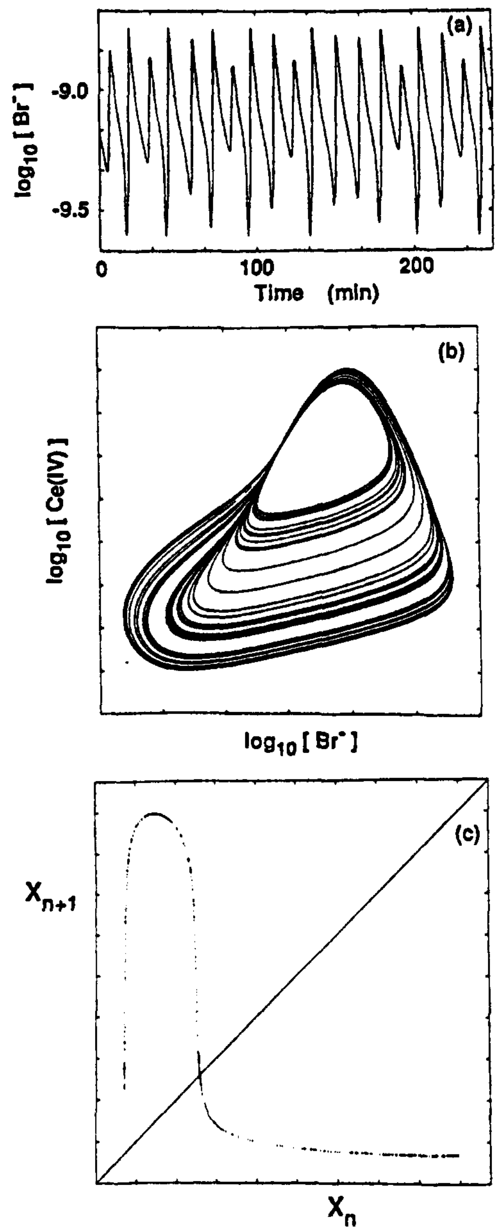

Figure 5. A chaotic state found in a numerical simulation of a 7-variable model (R1)–(R9) of the kinetics of the BZ reaction: (a) time series, (b) strange attractor, and (c) one-dimensional map with $X = \log\,[Ce(IV)]$. From ref 54.

4.2. Small-Scale Chaos. Experiments and simulations on the BZ reaction often yield, in addition to periodic–chaotic sequences and quasi-periodicity, sequences in which there appear to be abrupt transitions from one multipeaked periodic state to another. No chaos has been evident in experiments[46,54,56] on the latter sequences, and previous simulations[4-6,13,27,28] have also yielded transitions that appear to be directly from one periodic state to another without any intervening chaos. However, a new study[54] of the 7-variable model (R1)–(R9) shows that chaos *can* indeed occur in the

(52) Ringland, J.; Turner, J. S. *Phys. Lett. A* **1984**, *105*, 93.
(53) Richetti, P.; Arneodo, A. *Phys. Lett. A* **1985**, *109*, 359.
(54) Richetti, P.; Roux, J. C.; Argoul, F.; Arneodo, A. *J. Chem. Phys.* **1987**, *86*, 3339.
(55) Barkley, D.; Ringland, J.; Turner, J. S., *J. Chem. Phys.* **1987**, *87*, 3812.
(56) Maselko, J.; Swinney, H. L. *Phys. Scr.* **1984**, *52*, 269; *J. Chem. Phys.* **1986**, *85*, 6430; *Phys. Lett. A* **1987**, *119*, 403. Swinney, H. L.; Maselko, J. *Phys. Rev. Lett.* **1985**, *55*, 2366.

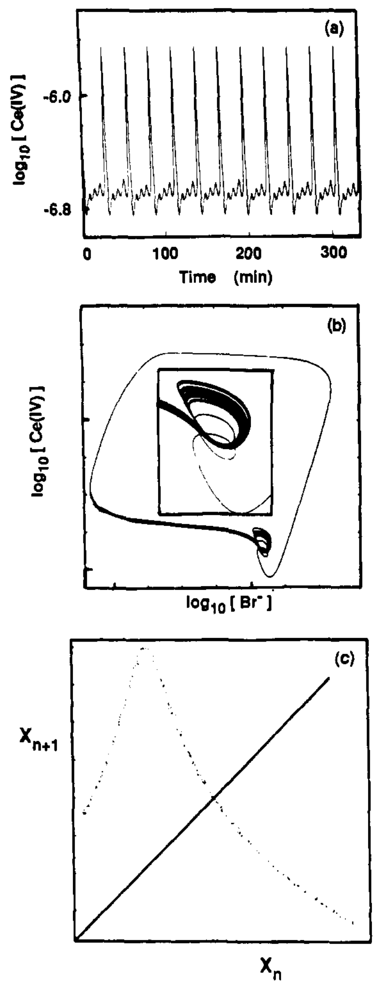

Figure 6. The possibility of chaos on a small scale, a scale too small to be observable in laboratory experiments, is illustrated by these results from a numerical study of a 7-variable model (R1)–(R9). The time series in (a), although apparently periodic, is actually chaotic: the one-dimensional map in (c), deduced from a Poincaré section for the attractor in (b), reveals the presence of a very small fluctuation in the value s of the ammplitude of the small-amplitude oscillation that immediately precedes the large-amplitude oscillation. The map demonstrates that these nonperiodic fluctuations in amplitude are *deterministic*: for any X_i, the map gives X_{i+1}, where X_i is the amplitude of ith occurrence of the third of three small-amplitude oscillations. From ref 54.

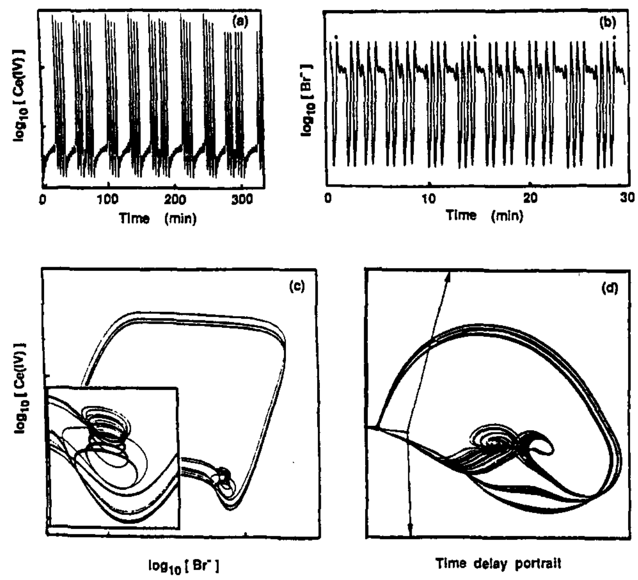

Figure 7. Waveforms in (a) and (b) and the phase portraits in (c) and (d) exhibit the spiraling in and spiraling out often observed for chaotic as well as periodic states in the BZ reaction: (a) and (c) illustrate a periodic state found in a numerical study of a 7-variable model (R1)–(R9); (b) and (d) illustrate respectively a periodic time series and a chaotic phase portrait obtained in experiments. (a) and (c) from ref 54, (b) from ref 56, and (d) from ref 46.

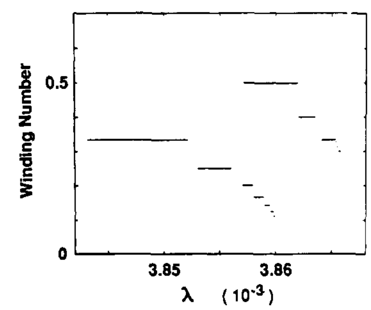

Figure 8. Devil's staircase obtained in a simulation of the 7-variable model (R1)–(R9). From ref 54.

neighborhood of the transition between different periodic states, but this chaos occurs on a very small scale, as Figure 6 illustrates: the time series in Figure 6a appears on first inspection to be periodic with four oscillations per period, but on closer inspection it can be seen that the amplitude of the small peaks that precede each large-amplitude oscillation varies irregularly by a very small amount. The one-dimensional map in Figure 6c, constructed from the phase portrait in Figure 6b, demonstates that the small irregularities are *deterministic*; as we have discussed, such a map is a hallmark of chaos. The *small-scale chaos* in Figure 6, in contrast to the large scale chaos in Figure 2, would be extremely difficult to observe directly in experiments, and even in simulations a definitive identification of the chaos is possible only by exploiting tools from dynamical systems theory.

Only one frequency is associated with the dynamics of the large-scale chaos shown in Figures 2 and 5,[53,57] but the states that have small-scale chaos are reminiscent of dynamics with two characteristic frequencies;[58] this is suggested by the convergent and divergent spiraling[46,48,54] that can be seen in time series and phase portraits such as those in Figures 6a,b and 7. However, this behavior, although characterized by two frequencies, is *periodic* rather than *quasi-periodic* (as in Figure 4a) because the two frequencies are locked together in rational ratios for finite ranges in control parameter; these frequency-locked states are readily apparent in the experiments and simulations. The frequency-locked states can be labeled by a *winding number*, which can be computed as follows:[54,58] in a periodic state with a total of N_t oscillations per period, and with N_l changes per period from a large-amplitude to small-amplitude oscillation, the winding number is N_l/N_t. Thus, for example, the periodic state in Figure 7b has a total of 26 oscillations per period and there are 6 changes per period from large to small amplitude, hence the winding number of 6/26.

A succession of frequency-locked periodic states was observed in experiments by Maselko and Swinney[56] and

(57) Argoul, F.; Arneodo, A.; Richetti, P. *Phys. Lett. A* **1987**, *120*, 269.

(58) Argoul, F. Bordeaux Doctoral Thesis, 1986.

(59) This winding number is defined differently from the firing number discussed in ref 56.

by Argoul et al.[46,54] and in simulations of the 7-variable model (R1)–(R9).[54] The winding numbers for sequences of frequency-locked states form a "devil's staircase"[44] when plotted as a function of a control parameter, as illustrated in Figure 8. In the simulations of the model[54] chaotic states were unambiguously observed, but only for very narrow control parameter ranges, and the chaotic nature of the state was localized on a very small part of the trajectory. However, observation of a devil's staircase with overlapping steps can be considered from dynamical systems theory to provide strong evidence for the existence of chaos in the experiments and simulations.[46,54,58]

In summary, it is now clear why chaos could have been present yet undetected in past experiments and numerical simulations that showed what appeared to be direct transitions from one periodic state to another: the domain of existence of chaos could have been too small to be seen, and moreover, small fluctuations in the amplitude of one (or more) of the many oscillations per period in a multipeaked waveform would naturally be interpreted as noise. For example, for a complex state like the one in Figure 7b, many full cycles of 26 oscillations per period would be required to determine the possible chaotic nature of the dynamics.

5. Conclusions

We have presented evidence for the existence of low-dimensional chaotic dynamics in the BZ reaction. Chemical kinetics is well-suited for studies of chaos because the behavior is often clearly nonperiodic. In fact, the first experimental strange attractor and one-dimensional map were extracted from laboratory data obtained in chemical experiments. Tools from dynamical systems theory and the observation of routes to chaos that are well-established theoretically have provided evidence for chaos in many chemical experiments.

Thus, the evidence for chaos when it occurs on a large scale is unequivocal. Surprisingly, our simulations have also revealed chaotic behavior even in situations that at first glance appear to be periodic: the chaotic dynamics occurs on a very small scale, a scale that could be very difficult to resolve in the laboratory. Although such small scale chaos was definitely proved for a time series obtained from a simulation, even in a simulation such chaos might easily go unnoticed or dismissed as round-off error; such nonperiodic behavior, if it were noticed, could not be understood without the recently developed tools of dynamical system theory. Thus, behavior identified as periodic in some past simulations may have in fact been chaotic.

All of the strange attractors that we have discussed, obtained from both simulations and experiments, can be considered to be embedded in a three-dimensional space. Furthermore, although space has not permitted a discussion here, we should at least mention the subject of *normal forms*,[60] which are the simplest nonlinear equations that describe the interaction of a few instabilities (for example, an oscillatory instability and the hysteresis instability that is associated with bistability). A recent analysis of normal forms has shown that a system of coupled differential equations with only three variables can describe most of the dynamics found in the BZ reaction, including quasi-periodicity and large- and small-scale chaos.[54] Thus, the reduction of the original Field–Körös–Noyes scheme involving some 20 species to some 3-variable skeletal mechanism (like the Oregonato) appears to be justified. But we have to be very careful at this point. The three variables in the normal form, unlike the three variables in the Oregonator, do *not* represent three species involved in the reaction. Rather, the normal form variables are nonlinear combinations of the original N species ($N \approx 20$). Thus, the normal form analysis specifies the appropriate three-dimensional subspace (in the N-dimensional phase space) on which the dynamics is confined asymptotically.

In conclusion, experimental, numerical, and theoretical evidence demonstrates the existence of chaos and that the chaos can be understood in terms of the chemical kinetics and the interaction of a few basic instabilities known to occur in the BZ reaction.

The research in Bordeaux is partially supported by a CNRS ATP Grant, and the research in Texas is partially supported by the Department of Energy, Office of Basic Energy Sciences.

(60) Arnold, V. I. *Geometrical Methods in the Theory of Ordinary Differential Equations*; Nauka: Moscow, 1978 (in English, Springer-Verlag: New York, 1983).

(61) A simulation of a 4-variable Oregonator-type model did exhibit chaos,[25,51] but this chaos was reached after a period doubling sequence from nearly sinusoidal oscillations,[52] while the chaotic states found in the experiments (e.g., see Figure 2) were reached through period doubling of relaxaton oscillations.