One-Dimensional Dynamics in a Multicomponent Chemical Reaction

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(Received 10 May 1982)

Experiments on the Belousov-Zhabotinski reaction in a stirred flow reactor reveal behavior that is strikingly similar to that generated by one-dimensional maps with a single extremum. In particular, a period-doubling sequence is observed that leads to a regime containing both chaotic and periodic states. Within the experimental resolution the ordering of the periodic states is in accord with the theory of one-dimensional maps.

PACS numbers: 05.70.Ln, 47.70.Pw, 64.60.-i, 82.20.-w

We have conducted experiments on a complex chemically reacting system (with about 25 chemical species) which exhibits, as a function of the flow rate of the chemicals through the reactor, a sequence of periodic and chaotic states that is in good agreement with that exhibited by unimodal (single-extremum) one-dimensional (1D) maps. From the data we have constructed 1D maps that correspond to the different periodic and chaotic states.

A decade ago Metropolis, Stein, and Stein showed that unimodal maps, $x_{n+1} = \lambda / x_n$, exhibit universal (map-independent) dynamics as a function of the bifurcation parameter $\lambda$. Analysis of higher-dimensional systems has led to the conjecture that, if such a system were to exhibit a period-doubling sequence, then the dynamics of the system would be similar to that of a 1D map. Indeed, period-doubling sequences have been discovered in recent experiments on a variety of physical systems, and the observed behavior for at least the first few doublings has been in accord with the theory for 1D maps. However, 1D maps were not obtained in any of those experiments, and the rich dynamical structure that 1D maps exhibit beyond the period-doubling sequence has been observed only in the experiments of Testa, Pérez, and Jeffries on the simplest nonlinear physical system that has been studied, an electrical oscillator with three degrees of freedom. We will now review the properties of 1D maps and then present the results of our experiments.

1D maps. — A method called symbolic dynamics can be used to show that the dynamics of unimodal 1D maps of the interval $[0, 1]$ is exhausted by the periodic states of the “U (universal) sequence” of Metropolis, Stein, and Stein and the chaotic states of the “reverse bifurcation sequence” of Lorenz. The theory uses only the unimodal property of the map to deduce the nature of the states and the order in which they appear as a function of the bifurcation parameter $\lambda$. Feigenbaum and others, making the additional assumption that the map has a quadratic extremum, have obtained detailed predictions for the scaling of various dynamical quantities. We will confine our discussion to the results of symbolic dynamics theory since it is the ordering and nature of the states and not their scaling properties that have been determined in our experiments.

We begin with the mechanics of map iteration. For a given value of $\lambda$ one picks any initial condition (except for a set of measure zero) and iter-
lates the map until transient behavior disappears. Further behavior of the sequence \( \{x_n\} \) can be either periodic or chaotic. For the purpose of categorizing periodic states we may restrict our attention to the iterates of the point \( \bar{x} \), where \( f(\bar{x}) \) is the extremum of the map.\(^1\) If the \( n \)th iterate of \( \bar{x} \) falls to the right of \( \bar{x} \), then the \( n \)th character of a descriptive character string is set to "R"; otherwise it is set to "L." Thus, for example, the 4-cycle in Fig. 1 is described by the string "RLR" where a character for the initial condition \( \bar{x} \) (neither R nor L) is omitted. Periodic states may be uniquely classified also by the order in which points on the \( x_n \) axis are visited. For the example in Fig. 1 the iteration pattern can be seen to be 2-0-3-1.

Consider the dynamics of a map as a function of \( \lambda \). For small \( \lambda \) the map has a fixed point (1-cycle). If \( \lambda \) is increased the 1-cycle eventually loses its stability to a 2-cycle in a pitchfork bifurcation. There exists an infinite sequence of such period-doubling transitions that converges to a \( 2^n \)-cycle at finite \( \lambda = \lambda_c.\)\(^2\)

The dynamics past \( \lambda_c \) is very complex.\(^3,4,5\) Fundamentals of all integer periods (the first fundamental was the 1-cycle) appear and undergo their own complete period-doubling sequences. Thus, for example, there is a 3-cycle and its "harmonics" (\( 3 \times 2^n \)-cycles for all positive \( n \)) for some interval in \( \lambda \). The larger the integer, the larger the number of allowed states; for example, there are three distinct 5-cycles (RLRR, RLLR, and RLLL) and 27 distinct 9-cycles. In Table I we list in order of increasing \( \lambda \) some of the periodic states of period less than 11, along with their "RL..." strings and iteration patterns. The full U sequence consists of the extension of this table to all allowed periodic states. Each allowed pattern occurs only once, and at any given \( \lambda \) not more than one periodic state is stable.

Additional structure in the region past \( \lambda_c \) was described by Lorenz.\(^6\) In any system of finite resolution there exist gaps between various period-doubling sequences. These contain chaotic (intrinsically noisy) "reverse bifurcation sequences" which appear at the end of each period-doubling sequence; these sequences show period halving with increasing \( \lambda \) back down to the appropriate fundamental. While the chaotic states do not exist for intervals in \( \lambda \), there is a finite probability of encountering a chaotic state.\(^5\)

**Experimental methods.**\(^7\) We have conducted experiments on the Belousov-Zhabotinskii reaction in a well-stirred reactor as a function of the flow rate of the chemicals through the reactor (with input chemical concentrations held fixed). The time dependence of the concentration of one of the chemicals, the bromide ion, was measured with a specific ion probe, as described previously.\(^7\)

**Results.**—The states listed in Table I are in fact the observed states. Time series records for several of the states are shown in Fig. 2. Presumably, unobserved U-sequence states exist over flow rate ranges too small to resolve in our experiments; indeed, our data files contain many short segments corresponding to U-sequence states not included in Table I—the table lists only states that were observed in several runs.

The ordering of the states in Table I was difficult to determine definitively because the pump had to be recalibrated for each run and not every

![Image](image-url)

**FIG. 1.** The map \( x_{n+1} = \lambda x_n (1 - x_n) \) with \( \lambda = 3.4985617 \) exhibits a 4-cycle of the type RLR.

<table>
<thead>
<tr>
<th>Period</th>
<th>Sequence</th>
<th>Pattern</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>...</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>R</td>
<td>0-1</td>
</tr>
<tr>
<td>2\times2</td>
<td>RLR</td>
<td>2-0-3-1</td>
</tr>
<tr>
<td>2\times2</td>
<td>RLR(^2)LR</td>
<td>2-6-0-4-3-7-5-1</td>
</tr>
<tr>
<td>10</td>
<td>RLR(^2)RLR</td>
<td>2-8-6-0-4-3-9-7-1</td>
</tr>
<tr>
<td>6</td>
<td>RLR(^3)</td>
<td>2-0-4-3-5-1</td>
</tr>
<tr>
<td>5</td>
<td>RLR(^2)</td>
<td>2-0-4-3-1</td>
</tr>
<tr>
<td>3</td>
<td>RL</td>
<td>2-0-1</td>
</tr>
<tr>
<td>2\times3</td>
<td>RL(^2)RL</td>
<td>2-5-3-0-4-1</td>
</tr>
<tr>
<td>9</td>
<td>RL(^2)RL(^2)</td>
<td>2-8-5-3-0-6-4-7-1</td>
</tr>
<tr>
<td>5</td>
<td>RL(^3)R</td>
<td>2-3-0-4-1</td>
</tr>
<tr>
<td>4</td>
<td>RL(^3)</td>
<td>2-3-0-1</td>
</tr>
<tr>
<td>2\times4</td>
<td>RL(^3)RL</td>
<td>2-6-3-7-4-0-5-1</td>
</tr>
</tbody>
</table>
state was observed in a given run, and because even with our high signal-to-noise ratio, a state identified as periodic in records of finite length could in some cases be its reverse-sequence counterpart (our data are consistent with the identification of all states as being periodic).

Also, a slow drift in flow rate, characteristic of peristaltic pumps, resulted in data files that sometimes contained two (occasionally more) different periodic states; however, the periodic states observed in the same file were always found to be close together in the U sequence—this in itself is strong evidence for the existence of the U sequence in the chemical system.

The data taken as a whole support the ordering given in Table I. Further confirmation of the U sequence is provided by the 1D maps described in the following section.

Phase portraits and 1D maps.—The well-stirred Belousov-Zhabotinskii reaction may be described by the instantaneous concentrations of about 25 chemicals. It is not feasible to monitor all these quantities and thus determine the phase-space behavior of the system. For many purposes, however, embedding theorems justify the use of a single chemical concentration, \( B(t_i) \) \( (i = 1, \ldots, \infty) \), to construct an \( m \)-dimensional phase portrait with the vectors \( \{B(t_i), B(t_{i+T}), \ldots, B(t_{i+(m-1)T})\} \), for sufficiently large \( m \) (and for almost any time delay \( T \)).

In Fig. 3(a) we show a 2D projection of a 3D phase portrait constructed with the third axis normal to the page. Our studies of the resulting strange attractor (an attracting set in phase space with the property that infinitesimally separated trajectories exponentially diverge on the average) suggest that it is essentially two-dimensional and that a 3D construction of the phase portrait is adequate for our system.\(^{7,9} \) The connection between continuous motions on the attractor and a unimodal map is provided by the Poincaré section, the intersection of an \( (m-1) \)-dimensional hypersurface with "positively" directed orbits in \( m \) space. The intersections of our sheetlike attractor with a plane normal to the page (through the dashed line in Fig. 3(a)) lie approximately along a parametrizable curve, not on a higher-dimensional set.\(^{10} \) Thus within this resolution the parameter values at successive intersections provide a sequence \( \{x_n\} \) which defines a 1D map, as shown in Fig. 3(b). The shape

FIG. 2. Observed bromide-ion potential time series with periods \( \tau \) (115 s), 2\( \tau \), 2\( \times 2 \tau \), 6\( \tau \), 5\( \tau \), 3\( \tau \), and 2\( \times \)3\( \tau \); the dots above the time series are separated by one period.

FIG. 3. (a) A 2D projection of a 3D phase portrait for a chaotic state. (b) A 1D map constructed from the data in (a) (see text). (c) A 1D map for the nearby 6-cycle RLR\(^3 \). In (b) and (c) the curves are drawn to guide the eye.
of the map evolves slowly with flow rate, and so its shape in the periodic regions is known from the chaotic maps for nearby flow rates. For example, the map for a 6-cycle is shown in Fig. 3(c). The iteration pattern, 2-0-4-3-5-1, can be read from the map.

Conclusions.—In the parameter range studied here the Belousov-Zhabotinskii reaction exhibits the U sequence of 1D maps. The iteration patterns and, within the experimental resolution, the order of occurrence of the periodic states are in accord with the theory for 1D maps. To our knowledge these observations provide the first example of a physical system with many degrees of freedom that can be modeled in detail by a 1D map.

We acknowledge collaboration with J. C. Roux (who discovered the period-doubling sequence described here), J. S. Turner, W. D. McCormick, M. Kilgore, and J. Swift, and helpful discussions with M. J. Feigenbaum. This research was supported by National Science Foundation Grant No. CHE79-23627 and Robert A. Welch Foundation Grants No. F-805 and No. F-767.

10Strictly speaking, the Poincaré section for a chaotic strange attractor in a 3D construction must have dimension greater than unity because of the fractal nature of the attractor [see B. Mandelbrot, Fractals, Form, Chance, and Dimension (Freeman, San Francisco, 1977)].