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Multiplicity in a Chemical Reaction with One-Dimensional Dynamics

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Measurements on the Belousov-Zhabotinskii reaction in a stirred flow reactor reveal, beyond a period-doubling cascade, a sequence of periodic states that is different from the "U (universal) sequence" found in recent experiments on diverse systems. Particular periodic states occur in *three* different parameter ranges rather than one range as in the U sequence. However, the order of periodic states found here *is* in accord with a one-dimensional single-parameter map constructed from the laboratory data.

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Experiments in the past few years have demonstrated that systems far from equilibrium often exhibit sequences of instabilities that have *universal,* that is, system-independent, properties.[1] The best understood transition sequence is the period-doubling cascade, which has been observed in a variety of systems: At a critical value of a control parameter, a system makes a transition from one periodic state to another which has twice the period of the original state. Further variation of the control parameter leads to a sequence of such period-doubling transitions; the interval between transitions decreases geometrically at a universal rate. Beyond the accumulation point for the period-doubling sequence there is chaos. Within the chaotic region there is an ordered sequence of distinct periodic states, each of which occurs for some range of the control parameter. Metropolis, Stein, and Stein[2] (MSS) have called this sequence the U (universal) sequence since the ordering of the states is system independent for a large class of systems.

The period-doubling sequence and the subsequent chaotic region which contains the U sequence of periodic states can be understood by the study of one-dimensional (1D) maps, $X_{n+1}=f(X_n)=\lambda g(X_n)$, which have a single extremum and a multiplicative control parameter λ. Each periodic state of the map can be labeled by a symbol sequence of R's and L's that give the location (to the right or left of the extremum) of the successive iterates of the map that follow an initial point near the map extremum.[3] For example, the only states with period 5 allowed by the theory are RLR^2, RL^2R, and RL^3, and these states occur in the order given as λ is increased. Each allowed periodic state is predicted to occur for only a *single* parameter range. Remarkably, even systems with many degrees of freedom, including continuum fluids[4] and homogeneous chemical reactions with large numbers of chemical species,[5] have been found to exhibit dynamical behavior that is described well by this 1D map theory.

In experiments on an oscillating homogeneous chemical reaction in a stirred flow reactor we have found a period-doubling sequence followed by a sequence of periodic states that occur for *multiple* parameter ranges. When the control parameter (the flow rate of the chemicals) is varied monotonically, a particular state will appear, disappear, and then reappear in another control-parameter range. Recently Beyer, Mauldin, and Stein[6] reported the first study of multiplicity of the periodic states of 1D maps. Although the U sequence has only been proved to occur for parabolic and trapezoidal maps and conjectured for concave maps, they nevertheless found it surprising that a map as simple as a piecewise-linear "indented trapezoid" exhibited multiplicity. A single-parameter family of indented-trapezoid maps fitted to our data yields the *same* multiplicity that we observed in our experiments.

We will first describe the experimental results and then discuss the mathematical models. The experiments were conducted with a refined version of the

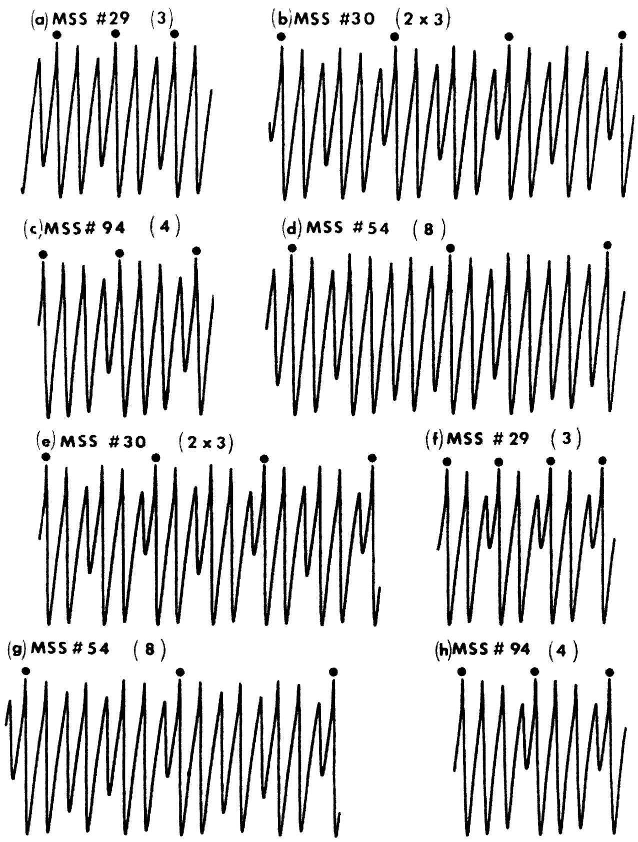

FIG. 1. Time series for the bromide-ion potential at increasing values of the residence time τ: (a) 0.764 h (state RL), (b) 0.766 h (RL^2RL), (c) 0.779 h (RL^2), (d) 0.799 h (RL^2R^3L), (e) 0.808 h (RL^2RL), (f) 0.815 h (RL), (g) 0.821 h (RL^2R^3L), and (h) 0.824 h (RL^2). The symbol sequences can be determined directly from the time-series data, as described previously in Ref. 5. The states are labeled by their MSS numbers and (in parentheses) the number of oscillations per period. The dots above each time series are separated by one period; the time per oscillation is about 115 s.

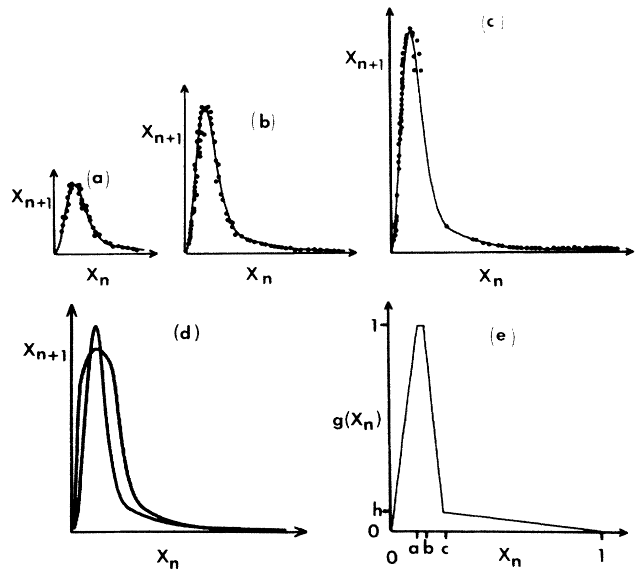

FIG. 2. (a)–(c) One-dimensional maps constructed from successive time-series minima X_n for three chaotic states which correspond to $\tau = 0.757$, 0.769, and 0.817 h, respectively; the three maps are on the same scale, which is arbitrary. The curves through the data points in (a)–(c) show cubic spline fits by $f(X) = \lambda g(X)$ with the *same* $g(X)$ [with $\lambda = 0.220$, 0.472, and 0.713 for (a)–(c), respectively]. (d) $g(X)$ obtained in the present experiment (narrow peak) compared to a map (broad peak) obtained in a previous experiment (Ref. 5) that yielded the U sequence; both maps illustrate chaotic states observed for about the same value of τ. (e) Indented-trapezoid map giving a sequence of periodic states that is in accord with the observed sequence for the following map parameters: $a = 0.13$, $b = 0.16$, $c = 0.25$, and $h = 0.09$.

apparatus used in our earlier studies of periodic and chaotic behavior in the Belousov-Zhabotinskii reaction in a well-stirred flow reactor.[5,7] The flow rate was controlled with precision piston pumps, while the chemical feed concentrations were held fixed. We express the control parameter as the chemical residence time $\tau = V/f$, where V is the reactor volume and f is the total flow rate. The concentrations in the reactor were $0.25M$ malonic acid, $0.10M$ bromate, $0.00083M$ cerous sulfate, and $0.20M$ sulfuric acid. Surprisingly, an earlier experiment with essentially the same chemical concentrations yielded the U sequence rather than the sequence reported here.[5] We will discuss later how very small amounts of impurities in malonic acid can result in qualitatively different transition sequences.

Figure 1 illustrates the observed multiplicity by showing the time series for two occurrences of each of the four states. Note that the time series for states with the same symbol sequence are not identical [e.g., cf. Figs. 1(a) and 1(f)].

Metropolis, Stein, and Stein have enumerated all 209 allowed states of the U sequence that have period $k \leq 11$. The "MSS number" provides a convenient parameter for indicating the position of a state in the U sequence, even though there is an infinite number of U-sequence states with $k > 11$ between any two adjacent states in the MSS table. The MSS numbers would of course be different if the U-sequence states were tabulated for a different maximum value of k. However, states with large k (say $k > 9$) are quite difficult to observe since the parameter range in which a state occurs decreases extremely rapidly with increasing period.

Chaotic as well as periodic states have been observed. Presumably our system, like the parabolic map, has no intervals of chaos, but the chaotic points (between the periodic windows) have positive measure. Figures 2(a)–2(c) show for three chaotic states the next-amplitude maps X_{n+1} vs X_n constructed from successive amplitude minima in the time series. In each case the data are well described by a smooth 1D map with a single extremum. The height of the maps was found to be a smooth monotonically increasing function of the residence time τ. To make comparison with the models we use the map height λ rather than τ as the bifurcation parameter.

We will compare the observed sequence with the sequences given by two model maps: (i) a smooth curve obtained from a cubic spline fit to the data and (ii) a piecewise-linear indented-trapezoid map [shown in Fig. 2(e)]. The former represents the data more accurately, but the latter simple map provides, through the variation of a single parameter, insight into the origin of the multiplicity. The smooth map will be described first.

Maps obtained at different residence times τ were fitted by

$$f(X) = \lambda g(X), \tag{1}$$

where $g(0) = g(1) = 0$ and $g_{max} = 1$. The *same* $g(X)$ was found to fit all the data, as the examples in Figs. 2(a)-2(c) illustrate.

Figure 3 compares the sequence of periodic states given by (1) with the sequence observed in the experiments; the agreement is very good.[8] In particular, for both the map and the experiment the periodic states with MSS numbers from about 29 to 100 occur in *three* different ranges of λ.

Further confirmation of the model is provided by examination of the way in which a given periodic state gains and loses stability. Each fundamental periodic state in the U sequence gains stability at a tangent bifurcation and loses stability by period doubling (a pitchfork bifurcation).[3] Similarly, in the sequences given by (1) that exhibit multiplicity, a periodic state in its first and third appearances as a function of λ gains stability at a tangent bifurcation and loses stability by period doubling. However, the second appearance of the state is *preceded* by a reverse period-doubling sequence and followed by a tangent bifurcation. This reverse period-doubling behavior was observed in the experiment, as Fig. 1 illustrates for the period-3 state: The period doubling is in the forward direction from (a) to (b) and in the reverse direction from (e) to (f).

Consider now another form for $g(X)$, the indented trapezoid shown in Fig. 2(e). This simple map, similar to one studied by Beyer, Mauldin, and Stein,[6] illustrates how a map can evolve from one that yields the U sequence to one that exhibits multiplicity.

We have studied the dynamics of the indented trapezoid for different heights h of the map at the point of the indentation; a, b, and c were held fixed at the values given in Fig. 2. Figure 4 shows the onset values of λ for three periodic states as a function of h. For $h > 0.89$ the map is concave and it gives the U sequence, as expected, but there is also a range in h,

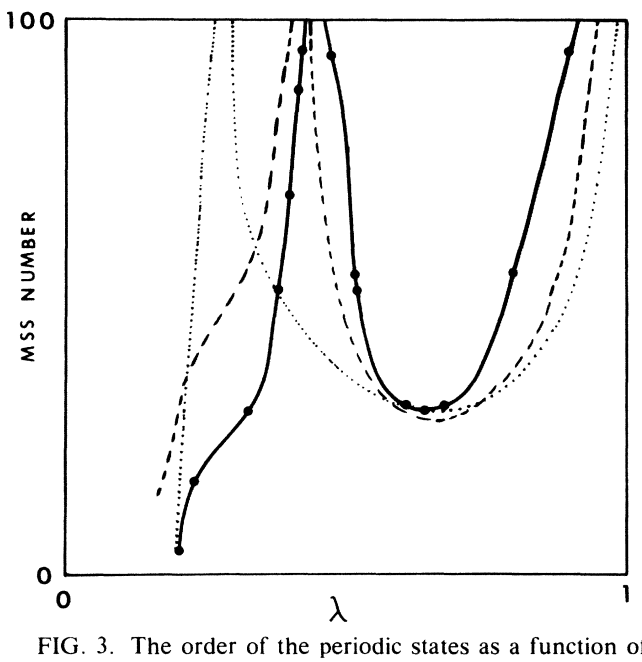

FIG. 3. The order of the periodic states as a function of the map height λ for (i) the experimental data (the points connected by a solid line drawn to guide the eye), (ii) the function $g(X)$ shown in Figs. 2(a)-(c) (dashed curve), and (iii) the indented-trapezoid map of Fig. 2(e) (dotted curve). The U sequence would be given (by definition) by any monotonically increasing curve. In contrast, the periodic states here that have MSS numbers greater than about 29 occur for *three* ranges of λ.

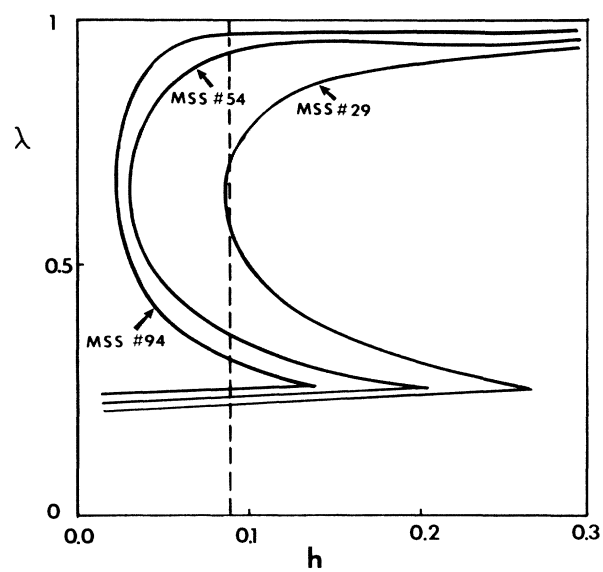

FIG. 4. The onset values of λ for three of the periodic states (see Fig. 1) as a function of the indented-trapezoid map parameter h. The vertical dashed line shows the value of h for which this map yields a sequence in accord with the observed sequence.

$0.62 < h < 0.89$, in which the *indented* map yields the U sequence—all of the periodic states occur for only a *single* range in λ. However, for $h < 0.62$, some states occur for *three* ranges in λ. For example, as can be seen in Fig. 4, for $h < 0.27$ the state RL (MSS No. 29) occurs for three ranges in λ. For a deeper indentation, $h = 0.09$, each of the MSS states between about 29 and 100 occurs for three distinct ranges in λ; in fact, for this h, the order of the periodic states for the indented trapezoid is in complete accord with that observed in the experiments, as is shown by the dotted curve in Fig. 3.

Thus the indented-trapezoid map demonstrates that multiplicity occurs if the map has too deep an indentation. Beyer, Mauldin, and Stein[6] emphasize that the appearance of multiplicity is a consequence of the indentation and not of other map properties such as differentiability, magnitude of the Schwarzian derivative, etc.

Now we return to the question of the difference between the sequence described here and the U sequence reported previously for ostensibly the same experimental conditions. Figure 2(d) illustrates the striking differences between the maps obtained previously and those reported here. This difference arises from trace amounts of impurities in high-purity ($> 99.5\%$) malonic acid. Extensive chemical analysis has revealed a number of different impurities at the parts-per-million level, but most impurities have been found to have *no* significant affect on the dynamics. However, iron dramatically changed the dynamics, while the other inorganic impurities had no significant effect at the parts-per-million level. For example, when 3 ppm of ferrous iron was added to iron-free malonic acid, the onset of period doubling was shifted by about 2% in τ (about 25% of the width of the U sequence), and with 10 ppm of ferrous iron the width of the entire periodic sequence was reduced to less than 0.5%! Ferric iron also had a striking affect on the dynamics, even at a level of only 10 ppm, where the period-3 state alone was more than 2% wide. The malonic acid used in the experiment here contained 4 ± 1 ppm of iron, with about equal amounts in the ferrous and ferric states. We tested malonic acids from seven different vendors, including several lot numbers from the same vendor, and found iron impurities ranging from 4 to 50 ppm, except for one sample that contained less than 0.1 ppm. Each of these samples yielded different 1D maps.

Iron is not the whole story, however, for there are also traces of organic impurities present in the malonic acid, and at least one of these, an ester of malonic acid, significantly affects the dynamics. A systematic detailed study of the effect of impurities is now underway and will be reported elsewhere.

In summary, each periodic state that we have observed is an allowed state of the U sequence, but the ordering of the observed states as a function of control parameter is different from the U sequence. Moreover, some of the observed states occur in more than one interval of the control parameter. Nevertheless, the order of the observed sequence of states is in complete accord with that given by a simple piecewise-linear 1D map model, and this map describes the qualitative change in the transition sequence that occurs for small changes in the chemistry. Thus, even though the Belousov-Zhabotinskii reaction involves more than thirty chemical species, it exhibits rather complex behavior that is modeled well by 1D maps. The present study illustrates that purely mathematical studies of maps[6] can provide surprising insight into the dynamics of nonequilibrium physical systems with many degrees of freedom.

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[8]It should be mentioned that for some λ there are some initial values X_0 (at very large or very small X) for the indented trapezoid that are not attracted to the periodic states discussed in this paper.