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Chaos Via Mixed-Mode Oscillations

Raima Larter and Curtis G. Steinmetz

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Chaos via mixed-mode oscillations

By Raima Larter and Curtis G. Steinmetz

Department of Chemistry, Indiana University – Purdue University at Indianapolis, 1125 E. 38th Street, Indianapolis, Indiana 46205, U.S.A.

The route by which chaos arises from mixed-mode periodic states in a model of the peroxidase enzyme catalysed oxidation of NADH is described. The specific model studied displays a rich variety of exotic dynamical behaviour including simple oscillations, quasiperiodicity, bistability between periodic states, complex periodic oscillations (including the mixed-mode type) and chaos. The route to chaos in this system involves a torus attractor which becomes destabilized and breaks up into a fractal object, a strange attractor. The mixed-mode states correspond to phase-locking on this fractal attractor and are arranged in staircases according to the complexity of the state. In this paper, we investigate the sequence leading from a mixed-mode periodic state to a chaotic one in the staircase region and find a familiar cascade of period-doubling bifurcations, which finally culminate in chaos.

1. Introduction

Chaos is one of the more exotic of the exotic phenomena displayed by nonlinear systems. It is likely that examples of chaos are widespread in homogeneous chemical kinetics, but only two such examples have been extensively studied. In this paper we describe one of these examples, the chaotic behaviour observed (Olsen & Degn 1977) during the horseradish peroxidase enzyme-catalysed oxidation of nicotinamide adenine dinucleotide (NADH), a common biochemical substrate. The second well-studied example of chemical chaos is the acid-catalysed bromination of a carboxylic acid, which has come to be known as the Belousov–Zhabotinskii (BZ) reaction, after its discoverers (see Field & Burger 1985 for leading references). Other occurrences of chemical chaos are known, but most have not been as extensively studied as these two examples.

The study of chaotic behaviour often involves determining the 'route to chaos', i.e. the ordered sequence of time-dependent states that arise as a control parameter is varied through a set of critical, or bifurcation, values. This sequence of states can involve only periodic states or both periodic and quasiperiodic states, before the aperiodic behaviour known as chaos arises. The 'chaotic' state (a misnomer in some sense) is actually quite ordered, and retains some characteristics of the periodic states from which it arises. Studying the route to chaos in a particular system has proven to be a valuable approach to unravelling the mechanism which underlies the chaotic behaviour. Also, it can be very difficult to distinguish between highly complex, yet periodic, states on the one hand, and chaotic states on the other. Demonstrating that a suspected chaotic state is associated with a known route to chaos is important evidence that the state is, indeed, chaotic.

In a recent paper (Steinmetz & Larter 1991), we described the transition to chaos which occurs in a simple four-variable model of the peroxidase oscillating reaction

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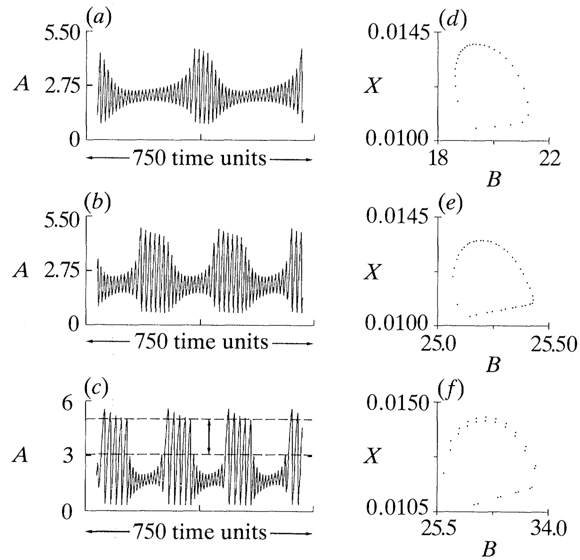

Figure 1. Phase-locked and mixed-mode oscillations. The values of k_1 are: (*a*) 0.193762205, (*b*) 0.1621, and (*c*) 0.1033 (this is the $5^{11}5^{10}$ state discussed elsewhere). The surfaces of section in (*d*), (*e*) and (*f*) correspond to the time series in (*a*), (*b*) and (*c*) respectively. The dashed lines in (*c*) show the gap between the largest small oscillation and the smallest large oscillation. This gap is about the size of the small oscillations themselves. There is no such gap in (*a*) and (*b*). The other parameters (other than k_1) are: $k_2 = 1250$, $k_3 = 0.046875$, $k_4 = 20$, $k_5 = 1.104$, $k_6 = 0.001$, $k_7 = 0.89$, $k_{-7} = 0.1175$, and $k_8 = 0.5$. Throughout this paper these are the values used for all parameters other than k_1.

(Degn *et al.* 1979). Chaos becomes possible in this system when a two-dimensional torus attractor (a 2 torus) becomes unstable, being replaced by a fractal torus attractor. The fractal nature of this attractor is found to become more highly developed as the chaotic region is penetrated until the fractal torus finally breaks up, forming a banded structure called a broken torus. The broken torus can support mixed-mode oscillations as well as chaotic states. The former are complex periodic states in which a clear distinction can be made between large-amplitude peaks and small-amplitude peaks. These are found to be arranged in staircases according to the number of large-amplitude peaks in each cycle of the oscillation. Within each staircase the steps are arranged according to a Farey sequence. Chaotic states are found to occur between the steps of the staircase. The sequence of changes in the torus attractor found to occur in this system along its route to chaos are similar to those found in the BZ reaction as well as in other chaotic systems.

It is the purpose of this paper to describe in more detail the sequence by which chaos arises out of the mixed-mode oscillations, i.e. the 'route to chaos' from mixed-mode states. Briefly, we find a familiar cascade of period-doubling bifurcations (Devaney 1989; Schuster 1988) leading from the mixed-mode oscillations into chaotic states within the broken torus region. The period-doubling route is well known from extensive studies of iterated maps such as the logistic map and has been observed in different types of experimental systems as well. This study reports the first example in which the route to chaos from mixed-mode oscillations has been determined. It is hoped that our extensive study of this simple model system will encourage other investigators to look for similar behaviour in other experimental systems displaying mixed-mode oscillations.

2. The model

In the peroxidase–oxidase reaction a peroxidase enzyme (which, as its name implies, normally utilizes hydrogen peroxide as the electron acceptor) catalyses an aerobic oxidation:

$$2YH_2 + O_2 + 2H^+ \rightarrow 2YH^+ + 2H_2O,$$

where YH_2 is a general electron donor. In the most widely studied version of this reaction *in vitro* (the peroxidase–oxidase reaction is also thought to occur *in vivo* in plants (Pantoja & Willmer 1988)) YH_2 is NADH and the enzyme is horseradish peroxidase. After the discovery (Yamazaki *et al.* 1965) of damped oscillations in the concentrations of O_2 and NADH during the course of this reaction, the reaction was studied in an open system and sustained oscillations were found (Nakamura *et al.* 1969). It was also found (Olsen 1981) that by decreasing the enzyme concentration one could observe three distinct oscillatory modes: (*a*) high-frequency simple oscillations with a single amplitude; (*b*) chaotic oscillations consisting of mixtures of amplitudes with no repeating pattern; and (*c*) low-frequency bursting oscillations.

Various models of the peroxidase–oxidase reaction have been proposed (see Aguda & Larter 1990 for a review), some quite detailed and some with as few as four variables. The earliest four variable model is the Degn, Olsen and Perram (DOP) model (Degn *et al.* 1979), which consists of the following eight step mechanism:

$$\left.\begin{array}{l} \mathrm{A+B+X} \xrightarrow{k_1} 2\mathrm{X},\ 2\mathrm{X} \xrightarrow{k_2} 2\mathrm{Y},\ \mathrm{A+B+Y} \xrightarrow{k_3} 2\mathrm{X},\ \mathrm{X} \xrightarrow{k_4} \mathrm{P} \\ \mathrm{Y} \xrightarrow{k_5} \mathrm{Q},\ \mathrm{X_0} \xrightarrow{k_6'} \mathrm{X},\ \mathrm{A_0} \underset{k_{-7}}{\overset{k_7'}{\rightleftharpoons}} \mathrm{A},\ \mathrm{B_0} \xrightarrow{k_8'} \mathrm{B}, \end{array}\right\} \tag{1}$$

where A is dissolved O_2, B is NADH and X and Y are intermediates. In a recent report, we have proposed (Aguda & Larter 1990) that X may correspond to $NAD^{\bullet}$ radical and Y to compound III (a radical form of the enzyme). The first step in the above mechanism is the autocatalytic production of X. The second step is a branching step in which X is converted to Y, and in the third step one Y is converted to 2 Xs. Steps 2 and 3 together constitute a second route for the autocatalytic production of X, and these two routes are coupled by step 2. Steps 4 and 5 are termination steps for X and Y, while step 6 is the spontaneous generation of X. Steps 4, 5 and 6 are consistent with the hypothesis that X and Y are free radicals. Step 7 is the equilibration of gaseous O_2 with the liquid phase, and step 8 is the slow constant inflow of NADH. In the experimental system, no outlet exists and any volume change which occurs is very small, so step 8 is taken to be irreversible. From this mechanism we can use the laws of mass action kinetics to derive the following system of four coupled nonlinear differential rate equations:

$$\dot{A} = -k_1 ABX - k_3 ABY + k_7 - k_{-7} A, \tag{2a}$$

$$\dot{B} = -k_1 ABX - k_3 ABY + k_8, \tag{2b}$$

$$\dot{X} = k_1 ABX - 2k_2 X^2 + 2k_3 ABY - k_4 X + k_6, \tag{2c}$$

$$\dot{Y} = -k_3 ABY + 2k_2 X^2 - k_5 Y. \tag{2d}$$

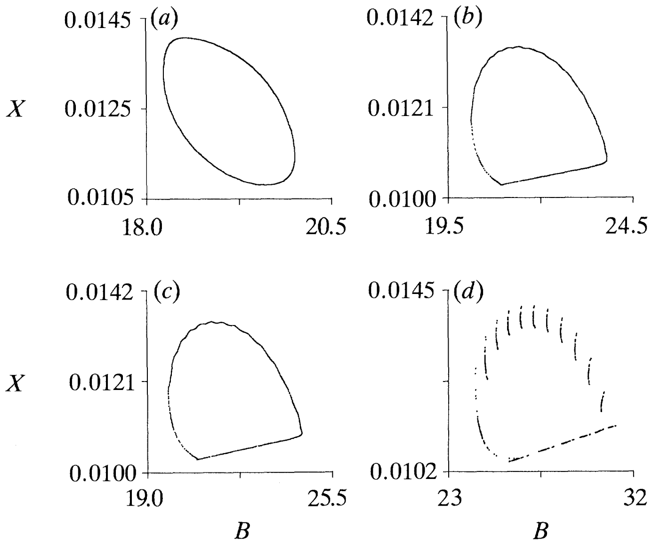

Figure 2. The four stages of the torus: (*a*) the undistorted torus, (*b*) the wrinkled torus, (*c*) the fractal torus, and (*d*) the broken torus. The values of k_1 are (*a*) 0.205, (*b*) 0.17, (*c*) 0.1634 and (*d*) 0.1178; other parameters are as given in figure 1. The Poincaré sections in figures 1 and 2 were generated by taking the intersections of the trajectory with the plane $Y = Y^*$ (the Y value of the unstable steady state); this plane cuts through the hole of the torus.

Although highly simplified, the DOP model is able to reproduce the three modes of simple, chaotic and bursting oscillations (Larter *et al.* 1987, 1988) found in experiments as the enzyme concentration is decreased. This sequence is observed in calculations with equations (2) when k_1 is decreased; k_1 is, thus, thought to be directly related to the enzyme concentration. In addition to the three types of experimentally observed oscillations the DOP model is also known to display complex periodic oscillations with repeating patterns of large and small amplitude peaks (see figure 1). It is these latter 'mixed-mode' states, which are our main concern in this paper.

3. The transition to chaos

As explained in more detail in a previous paper (Steinmetz & Larter 1991), the chaotic dynamics in the DOP model are governed by a torus which evolves through four distinct stages as the parameter k_1 is varied. These four stages are: (i) the undistorted torus; (ii) the wrinkled torus; (iii) the fractal torus; and (iv) the broken torus. The time series and surfaces of section shown in figure 1 correspond to phase-locked states on the wrinkled torus (parts *a*, *b*, *d* and *e*) and on the broken torus (parts *c* and *f*). The latter is an example of a mixed-mode oscillation, in which a clear distinction is possible between large-amplitude peaks and small-amplitude peaks. Figure 2 is reproduced from our earlier paper (Steinmetz & Larter 1991) and shows the Poincaré sections of the torus in each of its four stages. The transition from stage (ii), figure 2*b*, to stage (iii), figure 2*c*, occurs when a horizontal inflection point develops in the circle map associated with the section. It is known that a 2 torus must have a circle map that is invertible, i.e. it must be monotonic. So, the development of such an inflection point in the circle map heralds the death of the 2 torus. However, the 2 torus is immediately reborn as a fractal torus, a strange attractor

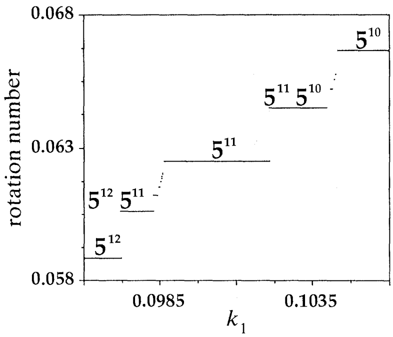

Figure 3. Staircase formed by the rotation numbers of mixed-mode states with five large oscillations (the '5-sequence'). For a mixed-mode oscillation of the form $(L^S)^m(L^{(S+1)})^n$ the rotation number is given by $\rho = (m+n)/[m(L+S)+n(L+S+1)]$. Note that this formula is completely equivalent to the one used by Richetti *et al.* (1987) (see their equation 26). The primary states (unconcatenated) and secondary states (only one concatenation) are labelled, while the tertiary states (two or more concatenations) are shown but not labelled. Notice the absence of tertiary states to the right of the secondary states ($5^{11}5^{10}$ and $5^{12}5^{11}$). When comparing this figure with fig. 8*d* in Steinmetz & Larter (1991) note that here the abscissa is k_1 rather than k_1', thus the staircase goes up (from left to right) instead of down. Also note that the state we call $5^{11}5^{10}$ here is the same as that labelled $5^{10}5^{11}$ in Steinmetz & Larter (1991), the difference in labelling being due to the different orientations of the staircase with respect to k_1 and k_1'.

that can support chaotic as well as periodic dynamics. This bifurcation also corresponds to a distinct change in the nature of the rotation number. The rotation number is defined by the following limit:

$$\rho = \lim_{n\to\infty} \frac{\theta(i+n)-\theta(i)}{2\pi n}, \tag{3}$$

where $\theta(i)$ is the angle at which the ith point appears in the Poincaré section. On a 2 torus this limit is always well defined. For a strange attractor, the limit can be undefined in one of two senses: (*a*) either the limit does not converge at all; or (*b*) it is dependent upon initial conditions. The first case corresponds to chaos while the second yields bistability. The limit is not always undefined in this region, however; in some intervals within this region, there is a single periodic attractor associated with a well-defined rotation number. Hence, the development of a horizontal inflection point in the circle map signals a global transition to the region in which chaos is now a possibility, but other non-chaotic states occur in this region as well.

While the fractal torus is difficult to distinguish from the wrinkled torus, the broken torus (stage (iv)) is immediately recognizable from its surface of section. Once the transition from fractal torus to broken torus occurs (iii to iv), we immediately see the appearance of mixed-mode oscillations. The mixed-mode states can be grouped according to the number of large oscillations in a given state. The rotation numbers of the states with a given number of large oscillations form a monotonically increasing sequence (see figure 3), which we have called an L-sequence (where L is the number of large oscillations). Within each L-sequence, there are relatively small intervals of hysteresis over which two oscillatory states coexist. In figure 3, the steps corresponding to 5^{11} and $5^{11}5^{10}$ overlap, resulting in an interval of hysteresis, i.e. bistability, between 5^{11} and $5^{11}5^{10}$. Another region of hysteresis is found between 5^{12} and $5^{12}5^{11}$. The L-sequences also overlap each other, so that significantly larger

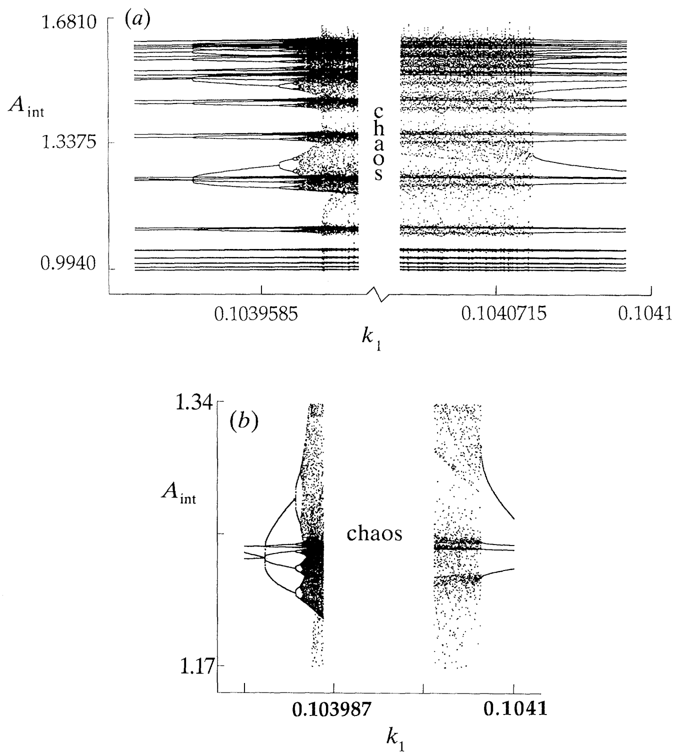

Figure 4. Bifurcation diagram. (*a*) In this diagram k_1 goes from 0.10393 to 0.1041. The periodic state to the left of the chaotic region is the $5^{11}5^{10}$ state (shown in figure 1*c*), and it undergoes a cascade of period doubling bifurcations into the chaotic region. The periodic state on the right is the $5^{11}5^{10}5^{10}$ state (shown in figure 4) which undergoes a sudden bifurcation to chaos reminiscent of a crisis associated with type I intermittency (as discussed in the text). (*b*) This is a close up of part (*a*) in which a horizontal strip has been expanded (compare the ordinate ranges of the two plots).

intervals of hysteresis also exist in which states with different numbers of large oscillations coexist.

Within a given L sequence chaotic states alternate with mixed-mode states in a manner similar to that seen experimentally in the BZ reaction and other systems. Between the 5^{10} and $5^{11}5^{10}$ states shown in figure 3, a small staircase consisting of highly complex mixed-mode states of the form $5^{11}(5^{10})^n$, where n is an integer, can be found alternating with chaotic states. Figure 4 shows a bifurcation diagram corresponding to a small interval between $5^{11}5^{10}$ and $5^{11}5^{10}5^{10}$. The bifurcation diagram is constructed by plotting the value of one of the concentration variables (A) in the Poincaré section as a function of the bifurcation parameter k_1. The $5^{11}5^{10}$ state can be seen to go through a series of period-doubling bifurcations before the chaotic state finally appears. At the other end of the chaotic region, the $5^{11}5^{10}5^{10}$ state abruptly appears, with no evidence of a reverse period-doubling cascade. Figure 5 shows a three-dimensional phase portrait of the $5^{11}5^{10}5^{10}$ state, illustrating that the mixed-mode states are, indeed, phase-locked trajectories on a broken torus.

The abrupt transition from chaos to the $5^{11}5^{10}5^{10}$ state may be an example of a ‘crisis’ in which the strange attractor collides with its basin boundary and the system

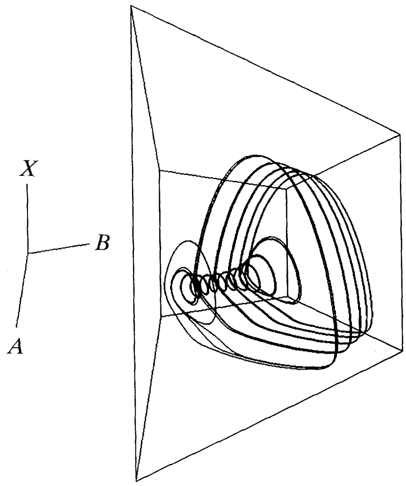

Figure 5. Three-dimensional phase portrait for the $5^{11}5^{10}5^{10}$ state, with $k_1 = 0.1041$ (since the system is four dimensional, this is, in fact, a projection out of 4-space).

moves to a coexisting limit cycle attractor. A tangent bifurcation may be responsible for this 'crisis' and is often associated with Type I intermittency (Schuster 1988). In a tangent bifurcation, the one-dimensional map associated with the limit cycle approaches very close to, eventually becoming tangent to, the identity line. We find that the above sequence appears to be common throughout the mixed-mode region: the transition to chaos from mixed-mode oscillations is characterized by a cascade of period-doubling bifurcations; at the other end of the chaotic interval the chaos is abruptly replaced by a new mixed-mode state.

4. Conclusions

Five distinct bifurcations are encountered along the route to chaos in the DOP model of the peroxidase reaction: (*a*) a Hopf bifurcation leading from steady state to simple periodic oscillations; (*b*) a secondary Hopf bifurcation leading from simple limit cycle behaviour to quasiperiodicity; (*c*) the bifurcation of the 2 torus to a fractal torus via loss of invertibility in the associated circle map; (*d*) the destabilization of periodic states on the fractal or broken torus via a cascade of period doubling bifurcations; and (*e*) a tangent bifurcation leading from the strange attractor to a new mixed-mode state. The third bifurcation characterizes the global nature of the transition to a region in parameter space in which chaos is possible. The fourth and fifth bifurcations occur many times throughout the region in which the broken torus exists and characterize the local nature of the transition to chaos in the DOP system.

Mixed-mode oscillations have been found experimentally in the BZ reaction (Argoul *et al.* 1987; Maselko & Swinney 1986), other chemical oscillators (Orbán & Epstein 1982) and the electrodissolution of copper (Albahadily *et al.* 1989), as well as in models of the BZ reaction (Richetti *et al.* 1987; Barkley 1988). Also, quasiperiodicity has been found experimentally in the BZ reaction (Argoul *et al.* 1987; Roux & Rossi 1984) and the electrodissolution of copper (Albahadily *et al.* 1989; Basset & Hudson 1989), and in models of the BZ reaction (Barkley *et al.* 1987; Barkley 1988). All of this suggests that the route to chaos found in the DOP model could have application to other reactions and may constitute a universal route to chaos for chemical oscillators. This route involves both of the best-understood pathways which lead to chaotic behaviour: (i) the quasiperiodic route involving wrinkling and breakup of a torus; and (ii) the route involving a cascade of period-doubling bifurcations. The former sets the stage for the *possibility* of chaos, while the latter shows how phase-locked states on the broken torus can become destabilized, giving rise to the actual *observation* of chaos.

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