Controlling chaos in the Belousov–Zhabotinsky reaction

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DETERMINISTIC chaos is characterized by long-term unpredictability arising from an extreme sensitivity to initial conditions. Such behaviour may be undesirable, particularly for processes dependent on temporal regulation. On the other hand, a chaotic system can be viewed as a virtually unlimited reservoir of periodic behaviour which may be accessed when appropriate feedback is applied to one of the system parameters[1]. Feedback algorithms have now been successfully applied to stabilize periodic oscillations in chaotic laser[2], diode[3], hydrodynamic[4] and magnetoelastic[5] systems, and more recently in myocardial tissue[6]. Here we apply a map-based, proportional-feedback algorithm[7,8] to stabilize periodic

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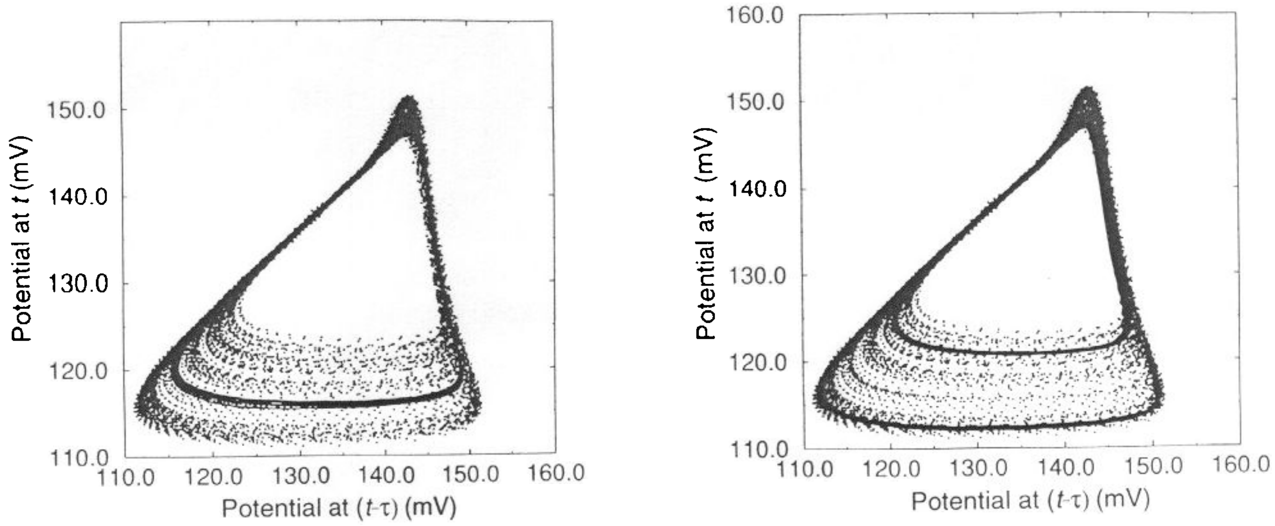

FIG. 1 Stabilized period-1 and period-2 limit cycles embedded in strange attractor of the BZ reaction. Scattered points show chaotic trajectory in time-delay phase space ($\tau = 13$ s) with a reactor residence time of 2.8×10^3 s and concentrations, after mixing, of [malonic acid] $= 2.22 \times 10^{-1}$ M, $[Ce_2(SO_4)_3] = 4.50 \times 10^{-4}$ M, $[NaBrO_3] = 1.02 \times 10^{-1}$ M and $[H_2SO_4] = 0.200$ M. Solid curves show (*a*) period-1 limit cycle stabilized by using $A_s = 33.0$ mV and $g = 18.0$ in equation (1) and (*b*) period-2 limit cycle stabilized by using $A_s = 26.9$ mV and $g = 33.4$. Reaction was carried out in a continuously stirred tank reactor (volume 34.0 ml, stirring rate 1,800 r.p.m.) maintained at 28.0 ± 0.1 °C and fed with separate solutions of malonic acid, cerous sulphate and sodium bromate. Two peristaltic pumps were used, with the malonic acid solution delivered at a fixed flow rate by one, and the cerium and bromate solutions (acidified with sulphuric acid) delivered by the other at a rate regulated by a computer. The potential of a bromide-ion-selective electrode was monitored and collected at a frequency of 10 Hz by a 16-bit data-acquisition board. Moving averages of 10 values were calculated and stored each second, and these values were numerically filtered using a 5-s characteristic period.

behaviour in the chaotic regime of an oscillatory chemical system: the Belousov–Zhabotinsky reaction.

The dynamical behaviour of a chaotic system can be visualized by the strange attractor (an attractor in which the trajectory never exactly repeats itself) traced out by its trajectory in phase space. An infinite number of unstable periodic orbits are embedded in such an attractor, each characterized by a distinct number of oscillations per period. In low-dimensional systems, these orbits are simple saddle-type limit cycles with an attracting stable manifold and a repelling unstable manifold. A general algorithm for stabilizing such orbits, based on targeting the stable manifold of the limit cycle by applying perturbations to a system constraint, has been developed by Ott, Grebogi and Yorke[1] (OGY). The stable manifold is found in a particular Poincaré section in the phase space, and it is targeted in this section each period of oscillation. For systems exhibiting low-dimensional chaos characterized by effectively one-dimensional maps, the OGY method can be reduced to a simple map-based algorithm[7,8]. The simplified method is more convenient in experimental applications because it minimizes the targeting procedures, and it has been used to control chaos in laser[2] and diode[3] systems.

The best-studied example of an oscillatory chemical system is the Belousov–Zhabotinsky (BZ) reaction, in which Ce(IV)/Ce(III) catalyses the oxidation and bromination of $CH_2(COOH)_2$ (malonic acid) by BrO_3^- in H_2SO_4. If the reaction is carried out in a continuous-flow stirred-tank reactor, the flow rate of the reactants into the tank ultimately determines whether the system exhibits steady-state, periodic or chaotic behaviour. Here we use conditions similar to the low-flow-rate Texas experiments[9-11], which ensure that the system is maintained within the chaotic regime (see Fig. 1). An important difference in our experiment is that we apply feedback to the system by perturbing the rate at which the cerium and bromate solutions are fed into the tank (the flow rate of the malonic acid being fixed), permitting the targeting and stabilization of periodic behaviour within the chaotic regime.

Figure 1*a* shows the strange attractor and the stabilized period-1 limit cycle for the BZ reaction. The time-delay phase portrait was reconstructed *in situ* from smoothed values of the potential of a bromide electrode. Except for small positive and negative perturbations to the flow rate of the bromate and cerium reactant stream, the operating conditions were identical for the chaotic and periodic behaviour. Figure 1*b* shows the stabilized period-2 limit cycle embedded in the strange attractor, again obtained with the same average reactant-stream flow rate. The oscillatory behaviour can be switched between period-1, period-2 and chaos by simple adjustments of the proportional feedback. Each time the controlling experiment was repeated (more than 10 times), a bifurcation diagram was first constructed to locate a suitably wide range of chaotic behaviour arising from a period-doubling cascade. The flow rate of the bromate and cerium reactant stream was chosen as the bifurcation parameter, as this choice gave the widest range of period-doubling chaos.

The control algorithm takes advantage of the predictable evolution of a chaotic system in the vicinity of a fixed point in the next-amplitude map, corresponding to a particular unstable periodic orbit. Shown in Fig. 2*a* is the next-amplitude map for the strange attractor and the period-1 orbit shown in Fig. 1*a*. The position of the period-1 fixed point is given by the intersection of the map with the bisectrix, where system state $A_{n+1} = A_n$. As the chaotic system traverses the attractor, the region near the fixed point is eventually visited, and the control algorithm is then activated. Control is achieved by perturbing a system constraint such that the fixed point is targeted on each return.

A shift of the map occurs on varying a system constraint, and this shift can be used to target any particular fixed point. Shown in Fig. 2*b* is a next-amplitude map constructed from the Györgyi-Field[12] model of the BZ reaction with concentrations and residence time similar to the experimental values for Fig. 2*a*. The inset shows a blowup of the map around the period-1 fixed point (right) and the shifted map (left) obtained at a slightly different value of the bifurcation parameter μ (the flow rate of the bromate and cerium reactant stream). For small perturbations, the shift in the linear region around the fixed point is directly proportional to the variation in μ. The map can therefore be shifted to target the fixed point by applying a

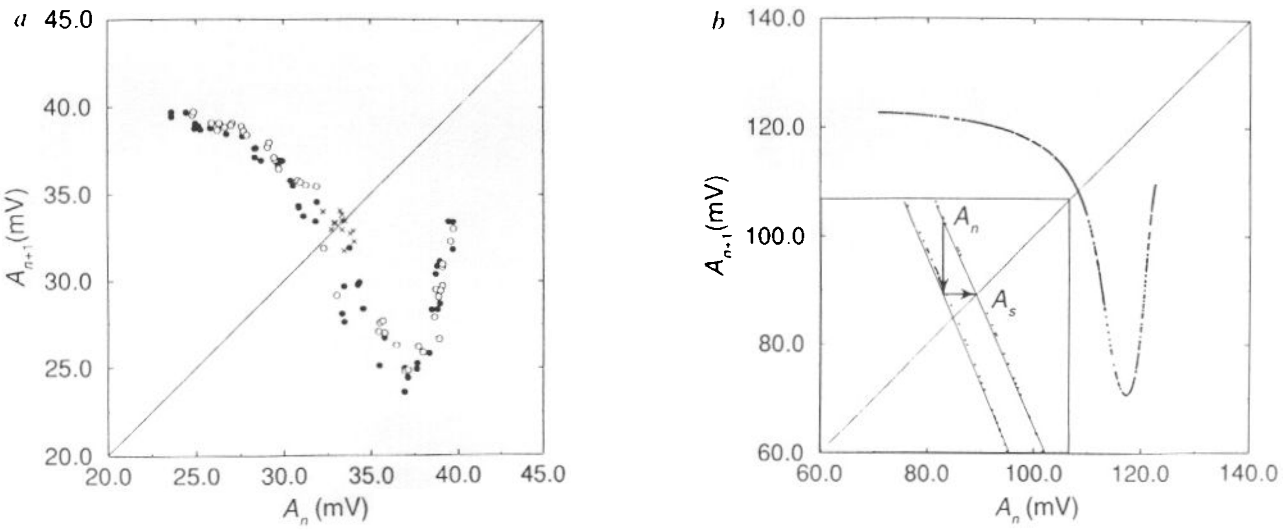

FIG. 2 *a*, Next-amplitude map before (●) and after (○) controlling period-1 and period-2, respectively, as shown in Figs 1 and 3*a*. Also shown are values (×) near fixed point during control corresponding to period-1 limit cycle trajectory in Fig. 1*a*. *b*, Next-amplitude map calculated from three-variable Györgyi–Field model of the BZ reaction with rate constants and residence time (2.17×10^3 s) the same as in ref. 12, and concentrations as in Fig. 1 except [malonic acid] = 0.24 M. Inset shows a 40-fold enlargement of map around fixed point (right) and shifted map (left) resulting from a 0.2% change in the flow rate of the bromate and cerium reactant stream. The system at state A_n is directed to A_s on the next return by varying μ according to equation (1) to shift map[7,8].

perturbation to the bifurcation parameter according to the difference between the system state A_n and the fixed point A_s

$$\Delta\mu = (A_n - A_s)/g \qquad (1)$$

where g is a constant. The current amplitude A_n is measured and with the value of A_s obtained from the map, the value of $\Delta\mu$ necessary for the fixed point to be targeted is calculated. The value of the proportionality constant g can be determined by measuring the horizontal distance between two maps constructed at slightly different values of μ (refs 7, 8), as shown in Fig. 2*b*. Various period-*k* limit cycles can be similarly stabilized by using the corresponding values of A_s and g (obtained from the appropriate maps of A_{n+k} against A_n) to determine $\Delta\mu$ in equation (1). The control algorithm may be implemented in several variations; for example, the perturbation determined every *k*th return may be applied for the entire period or for only a fraction of the period. In the stabilization of period-1 and period-2 shown in Fig. 1, the perturbation was applied for 15 s on each return.

Experimental fluctuations in the measured bromide potential result in significant scatter in the next-amplitude map, as shown in Fig. 2*a*. To reduce experimental noise, next-amplitude maps were used in the control algorithm rather than next-return maps; similar results were obtained with slightly more noise using

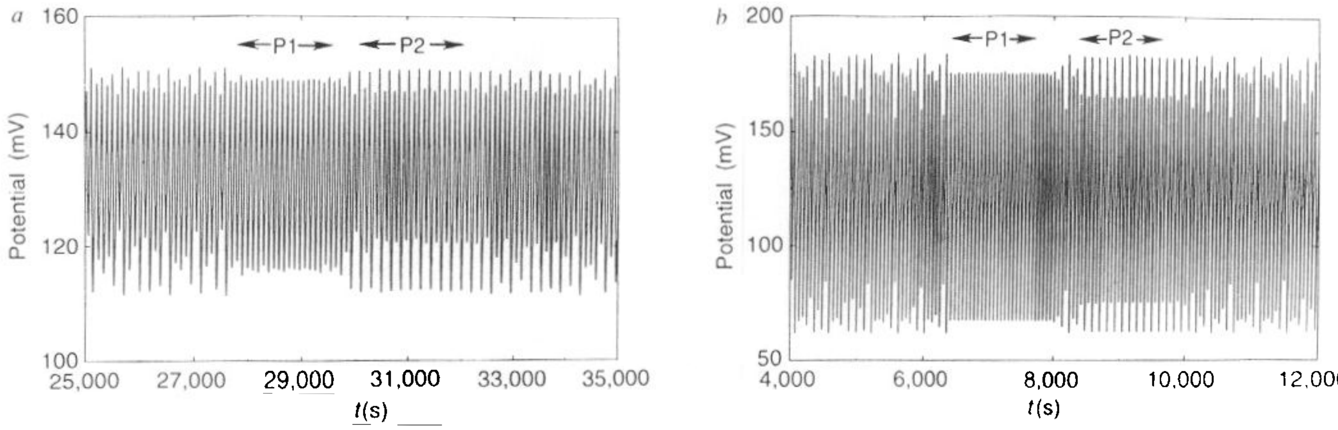

FIG. 3 *a*, Potential of bromide electrode as a function of time in BZ reaction with conditions given in Fig. 1. The control algorithm was switched on to stabilize period-1 at $t = 27{,}800$ s and switched off at $t = 29{,}500$ s, with the parameters corresponding to Fig. 1*a*. The parameters were changed at $t = 30{,}000$ s to stabilize period-2, with values corresponding to Fig. 1*b*, until $t = 32{,}100$ s when control was switched off. The control range was set at ±3.0 mV for both period-1 and period-2. *b*, Oscillations in bromide potential calculated from Györgyi–Field[12] model showing chaos, stabilized period-1 and period-2, and the reappearance of chaos. Potential calculated from the Nernst equation and bromide concentration assuming an Ag/AgCl reference electrode potential of 197 mV. Period-1 limit cycle stabilized by using $A_s = 108.25$ mV and $g = -9.0 \times 10^4$ and period-2 limit cycle stabilized by using $A_s = 90.235$ mV and $g = 7.0 \times 10^4$ in equation (1). Controlling algorithm was applied on each return for 25 s and the control range was set at ±5.0 mV. In both calculation and experiment, the flow rate of the bromate and cerium reactant stream was varied during control; a residence-time decrease of 1.0% therefore gives rise to an increase in these concentrations of 0.5% and a decrease in the malonic acid concentration of 1.0%. The typical residence-time variation during control was ~1.0% in experiment and ~10^{-5}% in calculation.

next-return maps. Although the experimental uncertainty seems to be comparable to that in previously reported maps for chaos in the BZ reaction[9,10], the scatter prevented the direct measurement of the proportionality constant g. The value of g was therefore estimated from the shift of A_s with variation of μ in the bifurcation diagram, and the final value was determined by adjustments around the initial estimate. Once the values for the fixed points and corresponding proportionality constants had been determined, the system could be switched between period-1 and period-2 behaviour and chaos by appropriately changing the values. Figure 3*a* shows the effect of the control algorithm, with the stabilization of the period-1 limit cycle followed by the period-2 limit cycle and the reappearance of chaotic behaviour when control was switched off. Transient aperiodic oscillations appear between period-1 and period-2 as the system leaves the period-1 orbit to arrive eventually at the control range of the period-2 orbit. When control was switched off, the chaotic behaviour was much the same as before the application of the feedback algorithm (Fig. 2*a*). Calculated behaviour using the Györgyi–Field[12] model is shown in Fig. 3*b*, with the stabilization of period-1 followed by period-2 and then a return to chaotic behaviour.

The stabilization of periodic orbits in chaotic systems by imposed feedback was first proposed by Ott, Grebogi and Yorke[1], and implications for biological self-regulation as well as practical uses such as convenient waveform generation have been pointed out[1-6]. The quenching techniques of Sørensen and Hynne[13-15] for targeting the unstable stationary state following a supercritical Hopf bifurcation are closely related to the OGY method. These authors have also successfully targeted the period-1 orbit in the BZ system following the initial period-doubling bifurcation, resulting in the transient appearance of these oscillations[15]. The map-based algorithm is more convenient than the OGY method for some experimental settings. (The OGY method has successfully been applied to stabilize period-1 in our BZ experiment, with results similar to those shown in Fig. 1*a*.) The map-based algorithm is especially useful in controlling high-frequency chaos, such as in laser[2] and diode[3] systems. In these applications, as well as in our present experiments, it is advantageous to apply the controlling perturbation for only a fraction of the oscillatory period. The system is attracted by the stable manifold of the unstable limit cycle during the perturbation-free fraction, thereby reducing the targeting error by ensuring that it resides effectively on the unstable manifold on its next return.

An important feature of both the OGY method and the map-based algorithm is that no knowledge of the underlying dynamics of a system (that is, the governing differential equations) is necessary for stabilizing any particular periodic orbit. This feature can be exploited to characterize experimentally the bifurcation behaviour of a chaotic (or periodic) system by tracking the unstable orbits as a bifurcation parameter is varied. The technique is similar to the computational algorithm AUTO[16] for exploring the bifurcation behaviour of model systems.[17] The tracking algorithm based on stabilizing periodic orbits, however, does not depend on model descriptions. We have made preliminary investigations of the BZ reaction using this technique with promising results; period-1 can easily be tracked after the first period-doubling bifurcation. □

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