Controlling Chemical Chaos

Bo Peng, Valery Petrov, and Kenneth Showalter

Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506-6045
(Received: April 24, 1991)

The long-term unpredictability associated with chaos may be undesirable in certain settings. Ott, Grebogi, and Yorke (Phys. Rev. Lett. 1990, 64, 1196) have recently proposed a method by which any of the infinite number of unstable periodic orbits embedded within a strange attractor can be, in principle, stabilized through small, controlled perturbations of a system constraint. This method is applied to a prototype model for isothermal chemical chaos to stabilize period-1, period-2, and period-4 unstable limit cycles out of chaotic behavior. The method reduces to a simple geometrical algorithm when the strange attractor is described by a 1-D map.

Introduction

Chemical systems may exhibit chaotic behavior if they contain certain elements of dynamical feedback. While chaos is intriguing, it is not clear what role it plays in real chemical processes, in living systems, and otherwise. One suggestion is that chaotic systems possess a virtually unlimited wealth of dynamical behavior, and this behavior can be brought under control in a deliberate and selective manner.

Chaotic dynamics can be visualized in terms of the asymptotic trajectory in phase space, tracing out a strange attractor. For continuous dynamical systems, there is an infinite number of unstable limit cycles embedded in such an attractor, each characterized by a distinct number of oscillations per period. Ott, Grebogi, and Yorke (OGY) have demonstrated that the unstable periodic orbits can be stabilized by introducing small, controlled perturbations to a system constraint. The method has been successfully applied to the Hénon map and to an experimental system of buckled magnetoelastic ribbon. It is of interest to examine the OGY method in a chemical context and to explore its implications to chemical and biological systems.

The Model System

We recently proposed a three-variable model, an offspring of the two-variable autocatalator, that is capable of exhibiting asymptotic chaos under isothermal, open conditions and transient chaos under isothermal, closed conditions. The scheme consists of six reaction steps, each with rates given by law-of-mass-action kinetics:

\[ P \rightarrow A, \quad \text{rate} = k_A p_0 \]  
\[ P + C \rightarrow A + C, \quad \text{rate} = k_{AC} \]  
\[ A \rightarrow B, \quad \text{rate} = k_A a \]  
\[ A + 2B \rightarrow 3B, \quad \text{rate} = k_{AB^2} \]  
\[ B \rightarrow C, \quad \text{rate} = k_B b \]  
\[ C \rightarrow D, \quad \text{rate} = k_C c \]

where the concentration of the precursor reactant P is treated as a constant, \( p_0 \), for the open system considered here. The rate equations for the above scheme can be written in a convenient dimensionless form:

\[
\frac{dx}{dt} = \mu(x + \gamma) - \alpha - \alpha \beta^2 \quad (4)
\]
\[
\sigma(\frac{dy}{dt}) = \alpha + \alpha \beta^2 - \beta \quad (5)
\]
\[
\delta(\frac{dz}{dt}) = \beta - \gamma \quad (6)
\]

where \( \alpha = (k_A k_0 / k_0)^{1/3} a \), \( \beta = (k_0 k_j / k_j)^{1/2} b \), \( \gamma = (k_0 k_j / k_j k_2)^{1/2} c \)

are dimensionless concentrations
\( \tau = k_d t \)

is dimensionless time, and

\[ \mu = (k_0 / k_0) p_0, \quad \kappa = (k_0 k_3 / k_3)(k_1 / k_0)^{1/2} \]

\[ \sigma = k_d / k_2, \quad \delta = k_d / k_3 \]

are dimensionless parameters. We choose \( \mu \) corresponding to the concentration of the precursor P, as the controlling parameter, the other parameters being \( \kappa = 65, \sigma = 5 \times 10^{-3}, \) and \( \delta = 2 \times 10^{-2} \) throughout the study. The behavior of the system as a function of \( \mu \) has been examined for both open and closed conditions. As \( \mu \) increases (from zero), the asymptotic behavior changes from steady state to oscillatory through a supercritical Hopf bifurcation at \( \mu = 0.016 \) and exhibits a period-doubling sequence beginning at \( \mu = 0.143 \). For 0.153 < \( \mu < 0.1551 \), chaotic behavior is exhibited. The system then goes through a reverse period-doubling cascade with period-1 oscillations appearing again at \( \mu = 0.157 \), and steady-state behavior is restored through another supercritical Hopf bifurcation at \( \mu = 0.175 \).

For the present study, we focus on the strange attractor at \( \mu = 0.154 \). Applying the Grassberger–Procaccia algorithm, with 30000 data points obtained from a constant-time-interval numerical integration, a correlation dimension of 2.2 ± 0.1 is calculated for this attractor. A Poincaré section defined by \( \gamma = 15 \) and \( \gamma > 0 \), visualized as an opaque sheet in Figure 1, gives the unimodal 1-D map shown by the middle curve in Figure 2. The intersection of the map and the bisectrix, defined by \( \beta_{\text{sat}} = \beta_{\text{ps}} \) corresponds to the period-1 unstable limit cycle. Unstable limit cycles with higher periodicity are easily located by plotting \( \beta_{\text{sat}} \) vs \( \beta_{\text{ps}} \), \( \beta_{\text{sat}} \) vs \( \beta_{\text{ps}} \), etc. Also shown in Figure 2 are maps generated with slightly larger and smaller values of the control parameter \( \mu \).

Controlling Chaos

Due to extreme sensitivity to initial conditions, the long-term behavior of a chaotic system is unpredictable. However, in the vicinity of an unstable point on a Poincaré section, corresponding to an unstable limit cycle of a continuous system, the evolution can be readily predicted. The basis of the OGY method is to take advantage of this local predictability: the unstable point is deliberately shifted such that the system falls on the stable manifold

1.4
1.0
0.6
0.2

Figure 1. Phase portrait of eqs 4-6 with \( \kappa = 65, \sigma = 5 \times 10^{-3}, \delta = 2 \times 10^{-3}, \) and \( \mu = 0.1540. \) Poincaré section defined by \( \gamma = 15.0, \gamma > 0, \) shown by opaque sheet.

1.0
0.0
-1.0
-2.0
-3.0
-4.0

Figure 2. 1-D return maps constructed from Poincaré section shown in Figure 1 for \( \mu = 0.1544 \) (lower), 0.1540 (middle), and 0.1536 (upper). The intersection of each map with the bisectrix \( (\beta_{n+1} = \beta_n) \) corresponds to the period-1 unstable limit cycle for the corresponding value of \( \mu. \)

Poincaré section defined by \( y = 15.0. \) Shown by opaque sheet.

\[
\beta_{n+1} = f(\beta_n) + \beta_n \quad (7)
\]
or near any particular unstable point if there are several (e.g.,

Figure 3. Maps in the local vicinity of the unstable fixed points for \( \mu = 0.1539 \) (a), 0.1540 (b), and 0.1541 (c). Solid lines are least-squares fits to the data points of each curve bounded by figure. By shifting the map from (b) to (c), \( \beta_n \) is directed to the original unstable fixed point \( \beta_s \) on the next return.

As illustrated in Figures 2 and 3, the map is shifted by changing the parameter \( \mu. \) Suppose that the horizontal distance of the
shifted map from the original unstable point is \( \Delta \beta \) for the perturbation \( \Delta \mu \), as shown in Figure 3. If the perturbation is small, then the ratio \( \Delta \beta / \Delta \mu \) is approximately constant:

\[
\Delta \beta / \Delta \mu = g \approx \text{constant} \quad (8)
\]

A chaotic system is bound to fall in the vicinity of any given unstable point at some point in time (unless the chaos is not fully developed, for example, as in the logistic map shortly beyond the accumulation point\(^4\)). Suppose \( \beta \) is close to \( \beta \). If one introduces a perturbation to \( \mu \) such that the map is shifted to coincide with line \( a \), then the next return to the section, giving \( \beta_{n+1} \), falls very close to the original unstable point \( \beta \). The effect of the perturbation is to move \( \beta \) vertically to the new map, as shown in Figure 3. With no further perturbations, any deviation from the unstable point will cause the system to move away from that point on successive returns according to the original map. To stabilize the system in the vicinity of \( \beta \), the appropriate perturbation \( \Delta \mu \) is applied on each return, easily calculated from the current value of \( \beta \):

\[
\Delta \mu = (\beta - \beta_0) / g \quad (9)
\]

Thus, to stabilize a particular unstable period-\( k \) orbit, the proportionality factor \( g \) is first determined by monitoring the system at two slightly different values of the control parameter, \( \mu \) and \( \mu + \Delta \mu \); it is then only necessary to measure the difference \( \beta - \beta_0 \) on each \( k \)th return to the section in order to apply the appropriate stabilizing perturbation. Although conceptually it is useful to imagine the perturbation being switched off after the \( k \)th return to the section (so the system is described by the original map), the algorithm is most efficiently applied by simply adjusting the perturbation according to eq 9 on each \( k \)th return.

For the period-1 unstable limit cycle at \( \mu = 0.154 \), the unstable point in Figures 2 and 3 occurs at \( \beta_0 = 40.568 \) (shown on the middle curve where \( \beta_{n+1} = \beta_n \)). The value of \( g \) is determined by constructing the map for a slightly different value of \( \mu \), shown by curve \( a \) in Figure 3, and calculating the ratio \( \Delta \beta / \Delta \mu = -4.5 \times 10^4 \). The corresponding quantities for period-2 and period-4 unstable limit cycles are determined in an analogous manner. The perturbation on \( \mu \) is arbitrarily limited to \( \pm 4 \times 10^4 \); i.e., the perturbation is not turned on unless \( |\beta - \beta_0| < 1.8 \) according to eq 9. (Notice that although the value of \( \mu \) remains within the chaotic region, this is not a requirement of the method.)

![Figure 4](image-url)  
*Figure 4.* Values of \( \beta \) on Poincaré section shown in Figure 1 vs time \( T \) indicating successive stabilizations of period-1, period-2, period-4, and period-1 unstable limit cycles as controlling begins and changes accordingly. Control feedback is switched on at \( T = 40.0 \) for period-1, \( T = 70.0 \) for period-2, \( T = 100.0 \) for period-4, and \( T = 130.0 \) for period-1. Values of \( (\beta, g) \) in period-1, period-2, and period-4 stabilizations are \((40.568, -4.5 \times 10^4), (77.0, -1.5 \times 10^4), \) and \((85.0, -1.25 \times 10^4)\).

Figure 4 shows the results of applying the stabilization algorithm. The period-1 unstable limit cycle is stabilized shortly after control is switched on; the system is then stabilized in period-2 and period-4 orbits and back again to period-1. The initial transient period, as well as the switching period between the stabilization of different periods, typically lasts from 5 to 10 oscillations. The transient period is due primarily to the time required for the system to appear near the unstable point, at which time the stabilization algorithm is first applied. Once the system is within the controlling range \( |\Delta \beta| < 1.8 \), it is stabilized in a few oscillations to the close neighborhood of the unstable point and the subsequent stabilizing perturbations are very small \( |\Delta \mu| \approx 10^{-5} \). Very little transient would occur if an additional algorithm were applied: the system could be deliberately moved to near the unstable point from any place on the attractor by applying a targeting algorithm proposed by Shinbrot et al.\(^5\) We chose to rely on the natural evolution of the system in order to make the algorithm as simple as possible.

An important feature of the method is that the map only needs to be single valued near the unstable point of interest; the global features of the map are unimportant. We also stabilized unstable limit cycles using a Poincaré section defined by \( \gamma = 0, \beta > 0 \) (a plane defined by the minima in \( \gamma \)), even though the resulting map is not globally single valued. Another important feature is that the proportionality factor \( g \) can be determined with maps constructed either from Poincaré sections in the phase space of the dynamical variables or from sections in a time-delay phase space reconstructed from a single variable.

**Conclusion**

Chemical systems may exhibit chaotic behavior, and this behavior could be of special importance to living systems, chemical reactor processes, etc. When deliberately controlled via feedback, chemical chaos offers a vast reservoir of accessible dynamical behavior. Of course, limits will be encountered in any practical setting, as higher periodicities are increasingly difficult to access and consequently control. In the context of chemical processing, it should be noted that the model used here is a close relative of three-variable autocatalator models based on thermal feedback,\(^9,10\) and control of chaos in nonisothermal systems could easily be demonstrated with these models. An especially intriguing hypothesis is that controlled chaos might be important in the self-regulation of living systems, where behavior is selected by subtle feedback mechanisms.

Nonlinearity of the map, limited precision in measurement, and uncontrollable random perturbations on the variables and parameters can cause inaccuracies in targeting the unstable point. However, small inaccuracies in determining \( \beta \) and/or \( g \), as well as slight nonlinearities in the map near the unstable point, result only in the system being stabilized at a nearby point on the section. It should also be noted that, while the perturbation is small due to an imposed upper limit, limited precision in an experimental system would impose a lower limit. The method, however, can easily accommodate a wide variety of situations; for example, the nonlinearities of the map could be readied taken into consideration by utilizing a nonlinear fitting function in place of eq 9, thereby enhancing the accuracy and range of the stabilizing perturbation. If the entire map were stored, either as an analytical function or numerically, and if the features of the map were relatively independent of the control parameter over the required range, a particular unstable orbit could be targeted and almost immediately stabilized from any point on the chaotic attractor.

**Acknowledgment.** This work was supported by NATO (Scientific Affairs Division, Grant 0124/89) and the National Science Foundation (Grants CHE-8920664 and INT-8822786). K.S. thanks Stephen K. Scott of the University of Leeds for many enlightening discussions of double-feedback autocatalator and Vilmos Gáspár of Kossuth Lajos and West Virginia Universities for critically reading the manuscript.

---

