Clustering of Arrays of Chaotic Chemical Oscillators by Feedback and Forcing

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(Received 14 December 2000)

Feedback and external forcing are applied to an array of chaotic electrochemical oscillators through variations in the applied potential. We see transitions from intermittent clusters to stable chaotic clusters to stable periodic clusters to synchronized states as the feedback gain and forcing amplitude, respectively, are varied. With forcing up to four clusters are observed in stable states. The transition to synchronization with feedback occurs by the increase in the size of one cluster at the expense of the others.

DOI: 10.1103/PhysRevLett.86.4954 PACS numbers: 82.40.Np, 05.45.Xt

The synchronization of small sets of chaotic oscillators (usually two) has been investigated theoretically [1] and in chemical experiments [2]. The collective dynamics of larger sets of coupled oscillators, however, encompasses a greater variety of possible dynamics, including turbulent, partially ordered, ordered, and coherent states [3]. Simulations on coupled maps [4] and differential equations [5–7] have shown the rich behavior of sets of chaotic oscillators. However, condensation has only recently been seen in experiments. In a recent paper on arrays of globally coupled chaotic electrochemical oscillators [8] we have shown the existence of both stable and intermittent cluster states.

In this Letter we explore the effects of adding feedback and periodic forcing to the arrays. The feedback and the forcing are applied to the potential, which affects all oscillators. Both effects influence the dynamics of the oscillators and thus the resulting behavior differs from that obtained with the global coupling of the resistors. We show here the types of cluster formation that occur with forcing and feedback, and we describe the similarities and differences among the three types of interactions.

The experiment is carried out with an array of electrodes as shown in Fig. 1a.

A standard electrochemical cell consisting of a nickel working electrode array (64 1-mm diameter electrodes in an 8×8 geometry), $Hg/Hg_2SO_4/K_2SO_4$ reference electrode, and a platinum mesh counter electrode (not shown in the figure) was used. Experiments were carried out in 4.5 M H_2SO_4 solution at a temperature of 11 °C. The working electrodes are embedded in epoxy, and reaction takes place only at the ends. The potential applied to all electrodes $(V_{app}(t))$ is the sum of a constant potential ($V_0 = 1.355$ V) and a perturbation $[\delta V(t)]$ due to forcing or feedback. The currents of the electrodes are measured independently at a sampling rate of 100 Hz. Since the currents of all the individual electrodes are measured, the rate of reaction as a function of position and time is obtained. The array can be a good approximation to a continuous system in electrochemistry at space scales larger than that of the electrode size [9]. Thus discrete measurements also augment previous experimental studies on forcing and feedback of nonchaotic chemical reaction-diffusion systems [10].

The uncoupled chaotic state is reached via a period-doubling bifurcation sequence as the applied potential is changed. An attractor reconstructed by the use of time delays from the time series of one of the elements is shown in Fig. 1b. The information dimension is 2.2. A power spectrum made from the time series is shown in Fig. 1c; the dominant frequency is 1.3 Hz. The currents from all 64 electrodes taken under conditions in which the coupling is weak (without added coupling, feedback, or forcing) are shown in a space/time plot in Fig. 2a.

As a reference for the feedback and forcing studies to be discussed below, we first show some behavior obtained with the application of global coupling to the behavior of Fig. 2a. We have developed a method of altering the strength of global coupling while holding all other parameters constant [8]. We employ a series resistor, R_s, and a set of parallel resistors, R_p, and hold the total resistance,

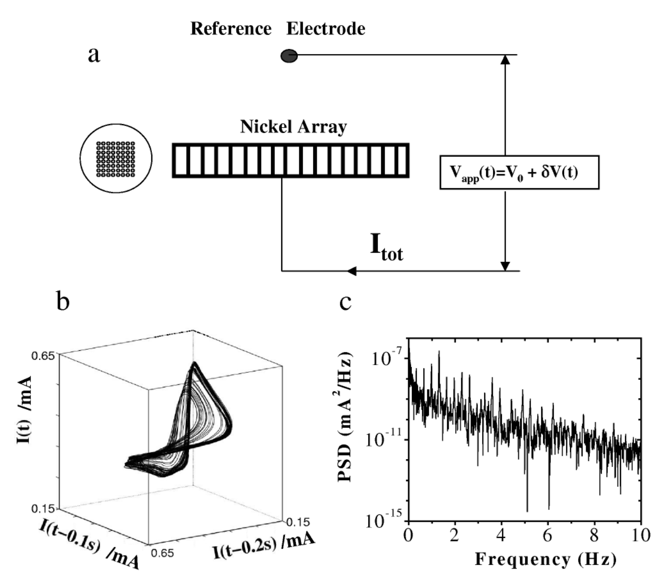

FIG. 1. (a) Schematic of the apparatus. (b) Reconstructed chaotic attractor of the current of one of the uncoupled oscillators. (c) The corresponding power spectrum.

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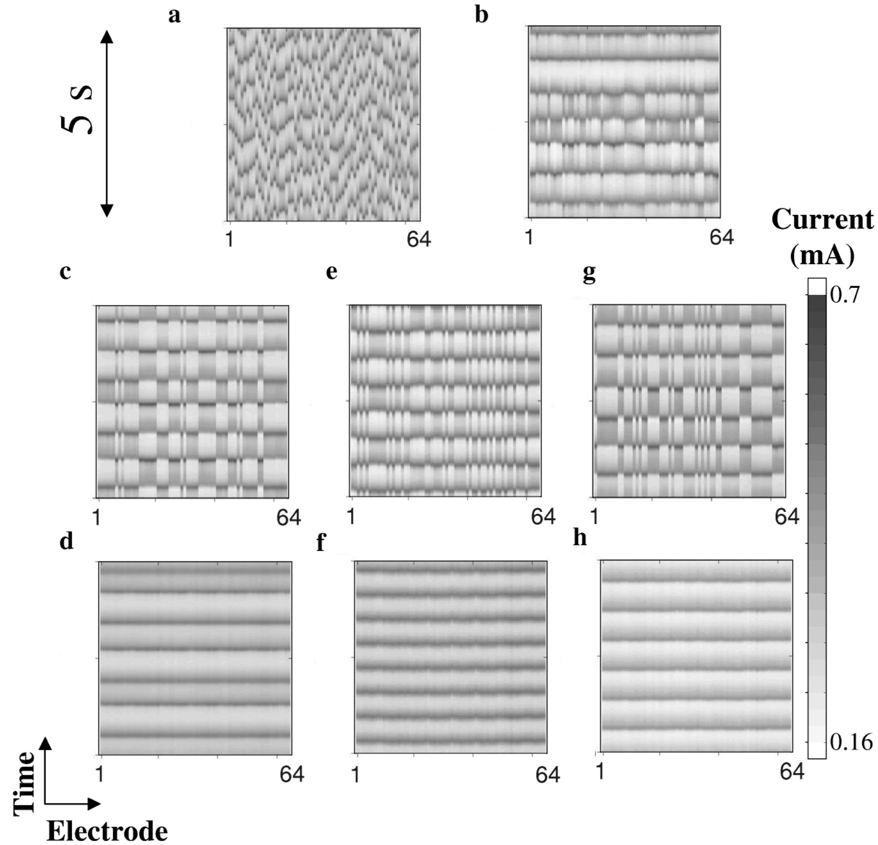

FIG. 2. Space/time plots of local current. Clustering and synchronization obtained through three types of coupling. (a) Uncoupled oscillators, $\varepsilon = 0.0$. (b) Base case, $\varepsilon = 0.56$. (c) Global coupling, $\varepsilon = 0.725$. (25, 39) cluster configuration. (d) Synchronized chaotic oscillations via global coupling. $\varepsilon = 1.0$. (e) (29, 35) cluster configuration with feedback. $K = 2.2$ mV/mA, $\varepsilon = 0.56$. (f) Synchronized periodic oscillations via feedback. $K = 3.8$ mV/mA, $\varepsilon = 0.56$. (g) (26, 38) cluster configuration with forcing. $A = 30$ mV, $\omega = 1.3$ Hz, $\varepsilon = 0.56$. (h) Synchronized periodic oscillations via forcing. $A = 50$ mV, $\omega = 1.3$ Hz, $\varepsilon = 0.56$.

R_t, constant. A global coupling parameter, defined as $\varepsilon = R_s/R_t$ where $R_t = R_s + R_p/64 = 14.2\ \Omega$, takes on values from zero to one as the coupling strength is increased. The behavior of the 64 elements is shown in Fig. 2b at $\varepsilon = 0.56$; although the turbulent nature of the uncoupled case (Fig. 1a) is no longer seen, the state is not quite synchronized or clustered.

As the global coupling is increased, condensation occurs. In Fig. 2c a space/time plot of a stable chaotic state with two clusters obtained at $\varepsilon = 0.725$ is shown. Many stable cluster configurations have been seen in our experiments. We have obtained stable chaotic clusters with as few as 18 elements. A (25, 39) cluster configuration is shown in Fig. 2c. (There are 25 and 39 elements in each of the two clusters, respectively.) On either side of the cluster state intermittent cluster states (not shown) occur in which clusters form and fall apart in a transient manner. The synchronized state seen in Fig. 2d undergoes a chaotic motion that is approximately the same as that of a single, uncoupled element.

We now investigate the effects of adding feedback and periodic forcing to the chaotic array. They are applied to a base state in which some global coupling is present, that is, to the behavior seen in Fig. 2b. There are two reasons for applying the feedback and forcing to a state in which some coupling is already present rather than to the very weakly coupled state of $\varepsilon = 0$. First, we note that the feedback and forcing at any feedback gain or forcing amplitude are not strong enough to synchronize the turbulent state ($\varepsilon = 0$) under the conditions of these experiments. Second, we compare the transitions into and through the cluster states of the feedback and forcing with the globally coupled case and thus start the sets of experiments at a base case just below the stable cluster region. The initial state for all experiments is that shown in Fig. 2b. After application of feedback or forcing a transient occurs in which the system tends to synchronize; this transient synchronized state then breaks up. Only the final, stationary behavior is shown here.

The feedback is affected by perturbation of the circuit potential according to the relationship $V_{\text{app}}(t) = V_0 + \delta V(t)$, $\delta V(t) = K[I(t) - I_{\text{mean}}]$, where K is a feedback gain, I is the total current (sum of the local currents), and I_{mean} is the mean of the total current.

Results with feedback are shown in Figs. 2e and 2f. As in the case with global coupling we see a transition through a series of states as the control parameter (K) is increased. The observed states are the following:

$K < 1.8$ mV/mA, intermittent chaotic clusters; 1.8 mV/mA $< K <$ 2.6 mV/mA, chaotic clusters; 2.6 mV/mA $< K <$ 3.2 mV/mA, periodic clusters (p4); 3.2 mV/mA $< K <$ 3.6 mV/mA, periodic clusters (p2); $K >$ 3.6 mV/mA, periodic (p1) synchronized state.

An example of the chaotic clustered behavior [a (29, 35) cluster configuration] obtained at a feedback gain of $K =$ 2.2 mV/mA is shown in Fig. 2e. In the chaotic cluster states only configurations containing two clusters were observed. The specific cluster configuration depends, of course, on the initial conditions. However, in the chaotic region the numbers of elements in the two clusters are approximately evenly balanced; the numbers in the two clusters ranged from (32, 32) to (28, 36). In the periodic region, however, the imbalance among cluster sizes became greater as the control parameter was increased. As the synchronized region is approached, one of the clusters dominates; thus, for example, at $K =$ 3.2 mV/mA a configuration of (6, 10, 48) is seen; additional increases in K (to 3.8) lead finally to synchronization. Thus there appears to be, to the resolution of the experiments, a continuous change from a clustered to a synchronized state with increasing K. In addition, the length of the transient before the attainment of a stationary state also increases as the value of K is increased into the synchronization region. The synchronized state obtained at $K =$ 3.8 mV/mA is seen in Fig. 2f. The periodic behavior can be contrasted to the dynamics of the globally coupled oscillators where a chaotic synchronized state occurs.

Clustering and synchronization can also be affected via periodic forcing if the forcing frequency is chosen to be close to the dominant frequency. We applied forcing of the circuit potential through $V_{\text{app}}(t) = V_0 + \delta V(t)$, with $\delta V(t) = A \sin(2\pi \omega t)$. With increasing values of the forcing amplitude the system goes through the following sequence: intermittent chaotic clusters; stable chaotic clusters; periodic clusters; periodic synchronized state. Examples of the resulting behavior are shown in the third column of Fig. 2. A stable (26, 38) chaotic cluster state is seen in Fig. 2g. With further increase in forcing amplitude, the system reaches a periodic clustered state. Larger values lead to periodic synchronization (Fig. 2h).

In order to point out more clearly the differences obtained with the application of global coupling and with forcing and feedback, we present in Fig. 3 some examples of the cluster configurations obtained with the latter two methods.

The configurations obtained with four values of the forcing amplitudes are shown in Figs. 3a1–3a4. Of course, as always, these are only representative configurations and many others are possible depending on initial conditions. The four example configurations shown are chaotic two-cluster, periodic four-cluster, periodic two-cluster, and periodic synchronized state. Some configurations obtained with feedback are shown in Figs. 3b1–3b3 with increasing feedback strength. The sequence shown is chaotic two-cluster, periodic three-cluster, and synchronized periodic state; note that as the feedback strength is increased one of the clusters grows until it dominates the entire region.

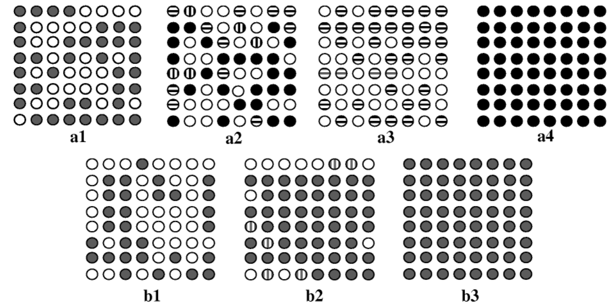

FIG. 3. Representative stable cluster arrangements with increasing amplitude of forcing [(a1)-(a4), $\omega =$ 1.3 Hz] and strength of feedback (b1)-(b3). Forcing: (a1) Two (26, 38) chaotic clusters, $A =$ 30 mV. (a2) Four (23, 25, 11, 5) periodic clusters, $A =$ 35 mV. (a3) Two (26, 38) periodic clusters, $A =$ 45 mV. (a4) Periodic synchronization, $A =$ 50 mV. Feedback: (b1) Two (29 + 35) chaotic clusters, $K =$ 2.2 mV/mA. (b2) Three (6, 10, 48) periodic clusters, $K =$ 3.2 mV/mA. (b3) Synchronized periodic state, $K =$ 3.8 mV/mA.

We have calculated the average pair distances in three-dimensional state space between each electrode pair of the 64 elements as a function of time. An order parameter is defined as the fraction of the number of pairs whose distance in three-dimensional state space is less than some value [7], here taken to be 0.06 mA (Fig. 4).

The mean order parameter has a value of near zero without coupling (not shown) and one in the synchronized case. The order parameter for feedback is shown at the top of the figure. As the feedback gain is increased, the order parameter reaches a plateau of somewhat above 0.5 in the stable chaotic cluster region in which the two clusters are approximately the same size. The order parameter increases to 1.0 with further increase in the gain since one of the clusters grows and dominates the system. In contrast, in the case of external forcing shown in the center panel, the order parameter drops as the forcing amplitude is increased over that of the stable cluster region because of the existence of a four-cluster configuration for which the order is lower. Additional increases in the forcing amplitude lead to a synchronized state with order parameter of one. In the globally coupled case shown at the bottom, the stable chaotic cluster region is also at a maximum of the order parameter because it is bordered on both sides by regions of intermittent clusters that are less ordered.

Detailed studies of globally coupled ordinary differential equation models showing clustering and synchronization can be found in the literature [7]. We carried out some limited simulations using two kinetic models for electrochemical reactions that have been previously used to show chaotic behavior of a single oscillator [11]. We present here the coupled forms of these models in order to point out more clearly the three types of coupling that have been used in the experiments. In addition, they might act as a

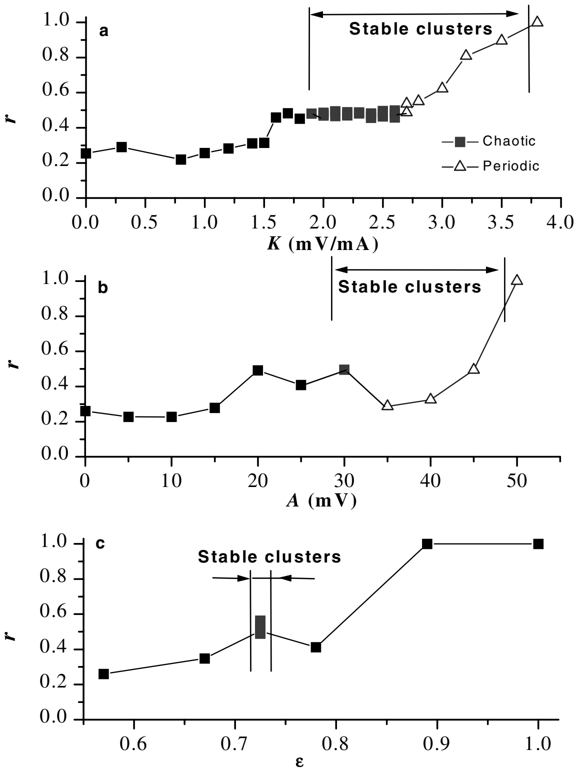

FIG. 4. Order parameter r based on mean distance as a function of global coupling strength. (a) Feedback. (b) Forcing. (c) Global coupling.

guide for future theoretical studies on this type of reaction system.

$$\frac{de_k}{dt} = \frac{V_0 - e_k}{nR_{\rm tot}} - i_{\rm F}(e_k, c_{1,k}, c_{2,k}) + \frac{1}{nR_{\rm tot}}\left(\frac{\varepsilon}{1-\varepsilon}(e_{\rm mean} - e_k) + \delta V(t)\right), \quad (1)$$

$$\frac{dc_{1,k}}{dt} = f_1(e_k, c_{1,k}, c_{2,k}), \quad (2)$$

$$\frac{dc_{2,k}}{dt} = f_2(e_k, c_{1,k}, c_{2,k}). \quad (3)$$

e_k and $c_{j,k}$ are variables corresponding to the double layer potential and the concentrations of chemical species at the kth electrode, respectively. The forms of $i_{\rm F}$ (Faradaic current) and f_j (reaction and transport) are given in the original papers. We have coupled these equations through the addition of the last term in Eq. (1); it consists of contributions due to the global coupling [12] and to feedback or forcing. Equations (2) and (3) describe the evolution of species concentrations at individual electrodes. Behavior similar to that seen in the experiments (chaotic and periodic clustering, synchronization, etc.) can be obtained. For example, up to four periodic clusters are obtained with forcing as in the experiments. However, a complete quantitative description of all the transitions and states obtained in experiments with feedback and forcing is still not available. Recently the effect of noise on globally coupled chaotic oscillators has been shown to play an important role [6]. Heterogeneities among the elements are likely also to be important in simulating experimental systems.

We have seen in our experiments that many of the features previously seen with the addition of global coupling through factors such as transport and electric fields appear also with the application of feedback and forcing. All three types of interactions bring discrete chaotic oscillators to a synchronized state. These transitions to ordered states are not monotonic, however, and the details depend on coupling type. Similar collective dynamics involving stable and intermittent clustering may arise in a variety of other types of discrete chaotic systems.

This work was supported by the National Science Foundation.

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