

# Reversible Control of Chemical Reaction Systems

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Starting from an algorithm for continuous chaos control, a reversible control method based on mutual diffusive coupling of chemical reactors is developed. With sufficient coupling strength, the proposed mutual coupling leads to control even if both reactors are of similar size. The controlling and controlled reactor exchange their roles at a certain size ratio. Insufficient coupling can lead to a more complex dynamics than that of the uncoupled reactors. This method for control via reversible coupling of chemical reactors should be implementable on a purely microscopic level.

**Key words:** Chaos control, Diffusive coupling, Synchronization, Molecular dynamics.

## Introduction

Chaos control methods can be used to enhance the flexibility of chaotic [1] and arbitrary [2] systems by switching between different dynamics of the system at the same set of parameters with only small control signals. They may be involved in natural processes as well, e.g. in information processing in the brain [3]. One approach to chaos control was introduced by Ott, Grebogi, and Yorke (OGY) [1]. It requires explicit information about the dynamics of the system to be controlled. Such information can in principle be obtained by analyzing the time series of some measured signal, but this information extraction cannot be performed in physical and chemical systems *on a molecular level*. Thus the applicability of this method is restricted to systems on a macroscopic level, since it typically demands measuring some system variables (such as concentration of a chemical species), computing the control signal and imposing control by changing macroscopic variables (e.g. the flow of some species). It is not clear how to tackle this required “information flow” physically, since the resulting controlled system is far too complex to be described on a molecular level. In order to estimate whether chaos control methods may play a role in natural systems, it would thus be desirable to have implementations of such methods on a microscopic physical level.

The mechanism for continuous chaos control and synchronization of chaotic systems originally proposed by Pyragas [4, 5] seems promising in this context, since it does not require explicit knowledge of the dynamics of a system except minimal information about the target orbit. In this case the controlling system is coupled to the controlled system via a kind of diffusion term which is, however, still unphysical because it acts only unidirectional on the controlled system.

We suggest a reversible control method for nonlinear systems based on Pyragas’ approach from which the latter can be rederived as a limit. This leads to a control mechanism which can be implemented on a molecular dynamics level, e.g. on a Hamiltonian basis. By means of such a mechanism the principles of chaos control may become applicable for chemical reaction systems in a most natural way.

## Synchronization of Chemical Reaction Systems

The external force control method for chaotic systems [4] considers a dynamical system described by a (potentially unknown) set of ordinary differential equations and assumes that one is able to add a control signal  $F(t)$  to at least one variable of the system:

$$\dot{x} = f(x) + F(t). \quad (1)$$

For the control of systems with a chaotic attractor one needs to know explicitly one component,  $x_i'(t)$ , of the orbit to be stabilized ( $x'(t)$ ). The control signal which

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is applied to the dynamics of the  $i$ -th component is the difference between the desired and the actual system output in this variable,  $D(t)$ , multiplied by a real parameter  $K > 0$ :

$$F_i(t) = K [x'_i(t) - x_i(t)] = K D(t). \quad (2)$$

This method can also be used to synchronize two chaotic systems [5]. In this case an output of the second system ( $x'$ ) is used as a control input to the first system ( $x$ ) according to (2), leading to synchronization.

In a chemical system, the variables have to be identified with the concentrations of the chemical species. In this context the control term specified in (2) can be interpreted as diffusive coupling acting on the first system. Since there is no impact of the control on the second system, the control algorithm leads to a violation of mass conservation in the first system and is thus not applicable in a closed coupled microscopic system. We would like to find a coupling between two systems which both obeys mass conservation and results in effective control of one of the systems.

Mass conservation implies a flow of particles between the two systems. This means that in the above picture control signals have to be added to *both* systems, which results in mutual coupling of the cells. However, mutual coupling, e.g. by diffusive exchange, in general leads to a new system with new dynamical features instead of the desired control. One can expect, however, that control is successful in mutually coupled systems when the impact of the first system on the second is made negligible. We thus demand that the relative impact of mass flow on both systems can be regulated, and that the external force control is a limit of this coupling.

One means to achieve this is to couple chemical reactors of different sizes. The impact of a given transfer of mass is then smaller for the larger reactor and vanishes as the reactor size approaches infinity. Assuming  $\sigma$  to be the volume of the second reactor, setting the volume of the first reactor to unity and defining the absolute number of molecules in the two reactors as  $z' = \sigma x'$  and  $z = x$ , respectively, diffusive coupling of the two reactors leads to the following dynamics:

$$\begin{aligned} \dot{z} &= f(z) + F(z, z'/\sigma), \\ \dot{z}' &= \sigma f(z'/\sigma) - F(z, z'/\sigma). \end{aligned} \quad (3)$$

Here  $f$  denotes the kinetics of the uncoupled system, while  $F$  is the mass flow between the systems. In our

case mass flow is allowed to take place for one variable only ( $z_i$  and  $z'_i$ , respectively):

$$F_i(z, z'/\sigma) = K [z'_i/\sigma - z_i]. \quad (4)$$

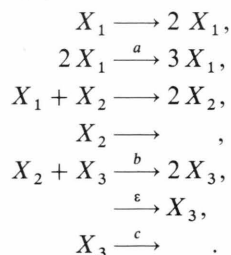
In this description it is obvious that the coupling, (3), does not violate mass conservation. The scaling factor  $\sigma$  appearing with  $z'$  indicates that the kinetics of the system as well as the diffusive mass exchange is governed by the concentration of the species rather than by the absolute number of molecules. Thus (3) is simplified by using the concentrations as variables:

$$\begin{aligned} \dot{x} &= f(x) + F(x, x'), \\ \dot{x}' &= f(x') - \frac{F(x, x')}{\sigma}, \\ F_i(x, x') &= K [x'_i - x_i]. \end{aligned} \quad (5)$$

The derived equations show that reversible diffusive coupling of chemical reaction systems can in principle be used to implement Pyragas' external force control algorithm. Thus we can expect to find all aspects of chaos control, such as synchronization of chaotic systems or stabilization of unstable periodic orbits, in suitable coupled chemical reactors. As a consequence, it should also be possible to achieve chaos control in reversible microscopic systems described by a molecular dynamics simulation.

### Application to a Chaotic Chemical Reaction System

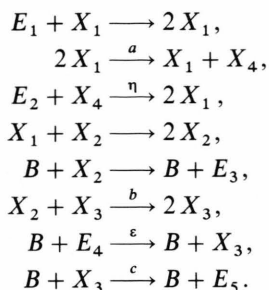
We consider the following sequence of chemical reactions [6]:



Here,  $X_j$  denotes chemical species. Species  $X_3$  is supplied at constant rate, and species  $X_2$  and  $X_3$  are assumed to decay in a first-order reaction. The nonlinearities stem from the autocatalytic reactions which are assumed to be second-order reactions. The initial conditions of species  $X_1$  and  $X_2$  have to be non-zero.

In order to apply the reversible control technique by means of a molecular dynamics simulation, this reaction system has to be slightly modified in order to

allow reversible formulation. First, the reaction mechanism is changed into a sequence of elementary bimolecular reactions. For this purpose, the quadratic autocatalysis is divided into two steps by introducing a new intermediate  $X_4$ . In addition, the three first order reactions are interpreted as being pseudo-first order. The constant input of variable  $X_3$  can either be thought of as the result of the reaction of a pool species or it can be implemented as a constant flow from the outside. The first possibility has the advantage that it can be implemented in an exactly reversible way. These considerations lead to the following sequence of molecular reactions:



In a first approximation the pool species  $E_1$  through  $E_5$  can be identified. Species  $B$  is considered to be an arbitrary collision partner. Thus, by means of colour coded reaction rules and an exactly time symmetric integration method [7, 8] the above reaction schema can be performed reversibly.

Numerical problems with a microscopic treatment of this system may arise because the time scales of the oscillations of the chemical species and of the molecular collision events differ by several orders of magnitude. A common way to avoid these problems is to introduce stochastic methods [9, 10]. This implies that the time reversibility of a Newtonian treatment is lost. However, it was shown by Heinrichs and Schneider [11] that a Hamiltonian treatment of second order reactions is possible. In combination with the exactly reversible algorithm [8] (as used to check Boltzmann's theory for a monomolecular gas) this allows a reversible treatment of the reactive case as well. In our context this means that it should be possible to apply the modified chaos control algorithm of (5) to the proposed chemical reaction system by means of coupling two reactors of different sizes and with slightly different parameters in an exactly reversible molecular dynamics simulation.

To understand the chemical reaction system and the reversible control mechanism proposed, we study the

dynamics of the present system on a macroscopic level. Applying the laws of mass-action and assuming the concentrations of the pool substances ( $E_i$ ,  $B$ ) to be unity, the dynamics of the proposed reaction scheme is described by the following set of ordinary differential equations:

$$\begin{aligned} \dot{x}_1 &= x_1 - x_1 x_2 - a x_1^2 + 2\eta x_4, \\ \dot{x}_2 &= x_1 x_2 - x_2 - b x_2 x_3, \\ \dot{x}_3 &= \varepsilon + b x_2 x_3 - c x_3, \\ \dot{x}_4 &= a x_1^2 - \eta x_4. \end{aligned} \quad (6)$$

With coupling of the first variable according to (5), the coupled system is then given by

$$\begin{aligned} \dot{x}_1 &= x_1 - x_1 x_2 - a x_1^2 + 2\eta x_4 + K(x'_1 - x_1), \\ \dot{x}_2 &= x_1 x_2 - x_2 - b x_2 x_3, \\ \dot{x}_3 &= \varepsilon + b x_2 x_3 - c x_3, \\ \dot{x}_4 &= a x_1^2 - \eta x_4, \\ \dot{x}'_1 &= x'_1 - x'_1 x'_2 - a' x'^2_1 + 2\eta x'_4 + \frac{K}{\sigma}(x_1 - x'_1), \\ \dot{x}'_2 &= x'_1 x'_2 - x'_2 - b x'_2 x'_3, \\ \dot{x}'_3 &= \varepsilon + b x'_2 x'_3 - c x'_3, \\ \dot{x}'_4 &= a' x'^2_1 - \eta x'_4. \end{aligned} \quad (7)$$

In the following, we set  $K=0.4$  and  $b=10$ ,  $c=20$ ,  $\varepsilon=0.01$ ,  $\eta=100$  for both systems, unless stated otherwise. A different dynamics of the individual systems can be generated by choosing different parameters  $a$  and  $a'$ . The uncoupled system of (6) possesses a spiral-like chaotic attractor for  $a=0.24$  and a period-three orbit for  $a=0.25$ . Since the stable period-three orbit emerges in a crisis of the chaotic attractor at  $a=a_c \approx 0.2478$ , both a period-three UPO and a chaotic saddle should be present in the vicinity of the point of crisis.

For  $\sigma \rightarrow \infty$ , the second (primed) subsystem controls the first (unprimed) subsystem according to the synchronization by external force control described in [5]. Choosing  $a=0.24$  and  $a'=0.25$  (case 1), the unstable period-three orbit within the chaotic attractor of the first subsystem is approximately stabilized for  $K \geq 0.097$ . Since the stable period-three orbit at  $a'=0.25$  differs slightly from the unstable period-three orbit at  $a=0.24$ , the orbit stabilized is a compromise between the stable and the unstable orbit of the uncoupled systems, approaching the stable one for growing  $K$ . With  $a=0.25$  and  $a'=0.24$  (case 2), the second (chaotic) subsystem can control the first (periodic) subsystem and stabilize the chaotic saddle. This is

possible because the continuous chaos control methods from [4] do not rely on the presence of a chaotic attractor [2]. In both cases the temporal mean of  $D^2(t) = [x'_1(t) - x_1(t)]^2$  ("error signal"  $\langle D^2 \rangle$ ) is very small and indicates a successful control.

Now we study finite values of the parameter  $\sigma$ . We find that in case 1 mutual coupling results in successful control of the period-three orbit in the first subsystem for  $\sigma \geq \sigma_c \approx 3.72$ . For  $\sigma < \sigma_c$ , the chaotic saddle in the second subsystem is stabilized by the first subsystem. Figure 1 shows the two largest Lyapunov characteristic exponents (LCEs) of the coupled system as functions of  $\sigma$ . The switching between the two control states can clearly be seen. For  $\sigma > \sigma_c$ , the chaotic subsystem is forced on a periodic orbit, which leads to the vanishing of the positive LCE. For  $\sigma < \sigma_c$ , the chaotic subsystem controls the periodic one. This, however, does not lead to the occurrence of two positive LCEs, since the forced chaos in the second subsystem is synchronized with the "original" chaos of the first subsystem. In this case the behaviour is intermittent as  $\sigma$  approaches  $\sigma_c$ . For both control states, the stabilized orbits remain nearly unchanged as  $\sigma$  approaches  $\sigma_c$ . Thus not only synchronization but also control in the original sense is successful for nearly all values of  $\sigma$ . Closer inspection indicates that the value of  $\sigma_c$  depends approximately on the distance of the parameters  $a$  and  $a'$  from the point of crisis  $a_c$ . In addition to this simple switching behaviour we found a small range of parameters in the vicinity of  $\sigma = 0.06$  (not shown in the figure) for which a higher periodic orbit is stabilized instead of the chaotic one. This phenomenon remains to be analyzed in more detail.

Figure 2 shows the dependence of the error signal  $\langle D^2 \rangle$  on  $\sigma$ .  $\langle D^2 \rangle$  remains small ( $< 10^{-3}$ ) for all values of  $\sigma$ , indicating successful synchronization of the two subsystems. For  $\sigma \rightarrow \infty$ , the error signal approaches the value obtained with unidirectional control (0.00061). For  $\sigma \rightarrow 0$ , the error signal converges to 0. This is due to the fact that the control algorithm of (5) is not symmetric with respect to controlling and controlled system. When the first subsystem controls the second one (i.e. for  $\sigma \rightarrow 0$ ), the effective coupling is  $K/\sigma$ , which goes to infinity when  $\sigma$  approaches zero. In order to inspect the results of this inverse control with constant effective coupling  $K$ , one has to exchange the two subsystems. Then, for  $\sigma \rightarrow \infty$  in case 2, the error signal again approaches the respective value for unidirectional control (0.00057). In both cases we observe that with constant  $K$  the error signal decreases when

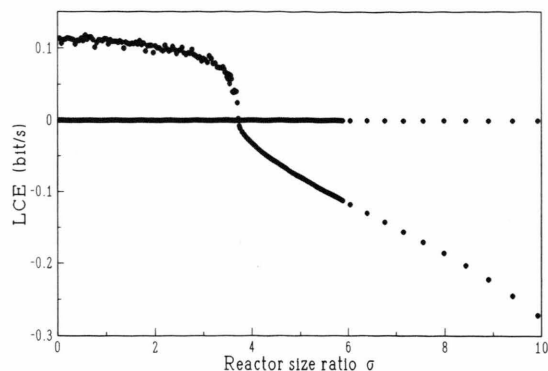


Fig. 1. Dependence of the two largest LCEs of the coupled system (7), case 1, on  $\sigma$ .

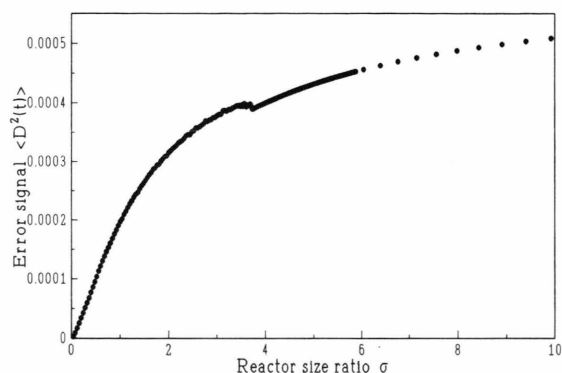


Fig. 2. Dependence of the error signal  $\langle D^2 \rangle$  for the coupled system (7), case 1, on  $\sigma$ .

$\sigma$  decreases from  $\infty$  to  $\sigma_c$ . Thus, in the case of reversible coupling the quality of synchronization improves compared to the unidirectional case. The described effects (namely, the switching between the two control states and the improvement in quality of control when  $\sigma$  decreases towards  $\sigma_c$ ) were also found in other chaotic systems including the Lorenz system.

Next we consider the effect of  $K$  on the reversible control. Figure 3 shows the three largest LCEs of the coupled system as functions of  $K$  for  $\sigma = 5$  in case 1. The desired control of the period-three UPO is successful for  $K \geq 0.12$ . For vanishing  $K$  ( $K \leq 0.004$ ), both subsystems retain their respective original dynamics. For intermediate values of  $K$  ( $0.004 < K < 0.09$ ), the coupled system is hyperchaotic. A similar occurrence of hyperchaos with insufficient coupling strength is found in case 2.



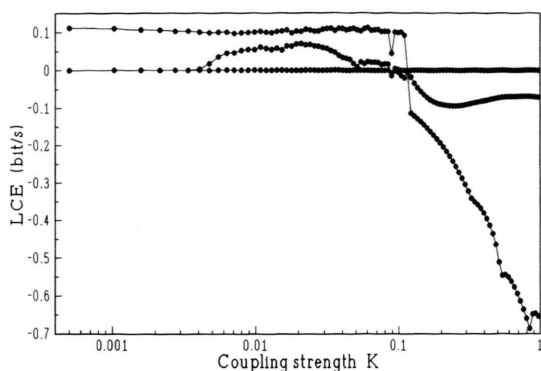


Fig. 3. Dependence of the three largest LCEs of the coupled system (7), case 1 ( $\sigma = 5$ ), on  $K$ .

In all cases considered we have assumed the diffusive exchange to be restricted to a single variable, i.e. we have thought of a semipermeable membrane between the two reactors. If we allow diffusive coupling of all variables (a hole between the reactors), the control works even better. Leaving all other parameters unchanged, the error signal  $\langle D^2 \rangle$  is smaller when coupling all variables instead of only one, indicating a stronger coupling.

## Discussion

We have demonstrated that the external force control method proposed by Pyragas [4] can be used with only slight changes in an exactly reversible manner and may easily be implemented in chemical reaction systems by diffusive coupling of reactors of different sizes. Thus chaos control can be applied in all its facets to microscopic systems without any macroscopic influence on the system. Especially, a chaotic reaction system can be synchronized with a periodic reaction system at a slightly different parameter value.

In combination with the recent findings that Pyragas' algorithms can be used to control unstable periodic orbits and chaotic saddles even in the absence of a chaotic attractor [2] the proposed diffusive coupling of similar chemical reaction systems leads to even more flexibility in the control of chemical reactors than previously assumed. The application of this method is only restricted by the fact that in order to stabilize a UPO in the first reactor the stable dynamics of the second reaction system used for control has to be similar to this UPO. This condition is fulfilled

best in the vicinity of a point of crisis, as in the example shown in this paper, or near any bifurcation point which turns a stable orbit unstable. But since Pyragas' external force control method works quite well with distorted information [2, 3], it should be possible to stabilize UPOs by diffusive coupling with stable orbits at considerably different parameter sets as well. It could even be feasible to stabilize a UPO using a totally different set of chemical reactions in the second system, as long as the resulting stable dynamics of the coupled species is similar to the corresponding one in the UPO.

It was already shown by several authors that the *delayed feedback* control method [4] can be applied to experimental chemical reactions like the Belousov-Zhabotinsky reaction [12] and the peroxidase-oxidase (PO) reaction [13]. However, delayed feedback control of chemical systems requires some analysis of the system, e.g. the measurement of oxygen concentration during the PO reaction and the tuning of the oxygen input according to the measured value. Thus the use of non-reversible chaos control methods is characterized by a systems analysis on a higher hierarchical level, which is then followed by a triggering of the microscopic system.

We found that reversible coupling of chemical reactors with slightly different parameters and qualitatively different dynamics leads to a synchronization of both systems to the stable orbit of one of the subsystems. Two requirements have to be met in order to achieve this result: First, unstable periodic or chaotic orbits have to be present in each subsystem in addition to the attractor. If the shape of the unstable orbit differs slightly from the attractor in the other subsystem, the error signal is finite but control is still possible. Second, the coupling has to exceed a threshold value below which there is no synchronization. Above this threshold the desired behaviour can be selected by means of the reactor size. We would like to point out that the reversible control leads to error signals which are smaller than those of the unidirectional coupling. This could be a result of the fact that reversible coupling leads to a bidirectional compromise in shape between the attractor on one hand and the unstable orbit at a different parameter value on the other hand. Combining our results with the previous finding that the external force control also works with incomplete or distorted information [3], we expect that our procedure will enhance the robustness of the control with respect to external noise. It is therefore plausible that

the internal noise introduced by a molecular dynamics simulation of the system will not destroy the control features of the diffusively coupled system.

With the reversible control method proposed and the possibility of achieving chaos control by mutual coupling of reactors, a systems analysis on a higher hierarchical level is no longer needed for chaos control. The only requirement left is simple diffusive exchange of particles between the two reactors. One might suspect that with the reversible chaos control method the controlling reactor has to be much larger than the controlled reactor. As our results show, however, reversible control is even successful with reactors of similar size. In the example presented, the chaotic reactor controls the periodic one even when it has only one-third of the controlled reactor's size (see Figure 1). We also found that changing the parameters of the subsystems leads to a considerable variation of  $\sigma_c$ , so that it should be possible for applications to choose parameter values with which the control is most efficient.

A point which demands further consideration is the bifurcation diagram of the reversibly coupled system as a function of the coupling strength  $K$ . We found a regime where the effect of coupling can be neglected, and a broad regime with effective mutual control of the subsystems. In between we observed a regime with hyperchaotic dynamics, i.e. an attractor with a fractal dimension higher than that of each coupling partner (see Figure 3). From the fact that control is successful we conclude that there is a chaotic saddle present in the period I three subsystem. It appears that weak coupling exploited the unstable manifolds of this saddle. It is open so far whether this is an accidental case or whether there is a more general mechanism behind it. Another open question concerning Pyragas'

method is how to choose correct parameters  $K$  and (in our case)  $\sigma$  in order to achieve successful control. One main criticism of this algorithm compared to OGY's method is that it is not possible to obtain the required control parameters analytically. However, for the original external force control method numerical evidence suggests that control is always successful when  $K$  is chosen large enough. Analytical work concerning this topic is in preparation.

## Outlook

Synchronization of chemical reaction systems can be achieved by mutual diffusive coupling on a strictly microscopic level. While the occurrence of chaotic dynamics in natural systems is already well known [14–16], the proposed reversible control algorithm shows a way for using chaos control and especially synchronization in nature. Speculations on possible applications in natural systems up to now deal mostly with the idea of exploiting chaos control for information processing in the brain [3, 17]. They make use of the fact that the presence of different hierarchical levels in the brain could allow the use of non-reversible chaos control methods in this case. We expect that the reversible algorithm will allow broader applications in natural systems, in particular in the context of information processing in the brain.

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