Recurrence quantification analysis of spatio-temporal chaotic transient in a closed unstirred Belousov–Zhabotinsky reaction

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We analyse the transient spatio-temporal chaos that we observe in the Belousov–Zhabotinsky reaction performed in a closed unstirred batch reactor by recurrence quantification analysis (RQA). We characterize the chaotic transient by measuring the Lyapunov exponent and the Kaplan–Yorke dimension. The latter shows the fractality of the attractor. The importance of the coupling between hydrodynamics and kinetics for the onset of chaos is also shown.

1 Introduction

The oscillatory behaviour of chemical and biochemical systems is well understood and many theoretical and experimental works have been done in this field.[1,2] The Belousov–Zhabotinsky (BZ) reaction[3] represents the most widely studied nonlinear chemical system. In perfectly stirred open systems a great variety of dynamical behaviours are observed.[4,5] As parameters (i.e. reagent concentration and/or residence times) are varied, the system can switch through different dynamical regimes. Each behaviour corresponds to an attractor in the phase space and the system 'jumps' from one attractor to the other: these jumps are known as bifurcations.[5]

Moreover, it is well established that closed chemical systems can exhibit various dynamic regimes in spite of the fact that the system will reach thermodynamic equilibrium. Transient behaviour may be sustained for significant periods of time, and the chemical mixture can be considered to evolve in consecutive different pseudo-steady states by spontaneous transitions. Therefore, with some special considerations it is possible to study the dynamic states and the relative transition scenarios also for closed chemical systems. Not only simple oscillations but also bistability and chaotic behaviour can take place in a closed BZ system.[6–8] Sensitivity to initial conditions has been pointed out in such systems at transient conditions both theoretically and experimentally.[9–12] Transient scenarios in the BZ system have also been the object of investigation.[6,13] For example, Wacker et al. showed the existence of a transient spatio-temporal chaos for a reaction diffusion system.[14] In 1980, Nagashima proved the existence of a chaotic state for the well-stirred and temperature-controlled batch BZ reaction under nitrogen.[15] Wang et al. showed experimental evidence of successive transient period doubling and torus oscillations to transient chaos in a closed well-mixed BZ system.[16]

We focus our attention on a closed unstirred BZ system, where not only simple oscillations but also aperiodic behaviours take place. Using suitable initial concentrations of reagents, this system shows various dynamic regimes despite the inevitable continuous drift to ultimate thermodynamic equilibrium. We proved that the aperiodic pattern shows evidence of sensitivity to initial conditions, which is considered to be the major feature of chaos.[9] We also showed that, during the chemical evolution, the system spontaneously gives the following sequence of dynamic behaviour before reaching equilibrium: period-1 → quasi-periodicity → chaos → quasi-periodicity → period-1. Two transition scenarios were observed: at the onset of chaos and at its end. One appeared as the mirror image of the other.[17,18] The sequence of the first two bifurcations is known as the Ruelle–Takens–Newhouse (RTN) scenario.[4,18] The last two bifurcations are described as the inverse RTN scenario. The sequence of attractors in the phase space that corresponds to each dynamical behaviour is: limit cycle → torus → strange attractor → torus → limit cycle. Clearly during the chemical evolution of the reaction the system spans the whole parameter space by successive bifurcations so that in reality the topology of the phase space is ever changing. For example, to the periodic regime there will correspond not a limit cycle but a slowly winding spiral. We also showed that the medium viscosity is a bifurcation parameter of the unstirred BZ system; a chaotic attractor appears or disappears when the polyethylene glycol concentration (i.e. the solution viscosity) decreases or increases.[19]

In other words the chaos appears as a result of the interplay between kinetics, diffusion and convection. Similar results were obtained when we modified the viscosity of the solution with non-ionic-micelle-forming surfactants.[20] We also observed that temperature is a bifurcation parameter of the closed unstirred BZ reaction.[21]

In this paper in order to quantify transient chaos we apply the recurrence quantification analysis (RQA).[22–25] We demonstrated that, in a short time interval, the evolution can be considered pseudo-stationary and we can apply the pool chemical approximation: for a given interval of time the reagent concentrations are considered constant and so the system lies on an attractor. This approximation implies that we can look at the system as a coarse-grained succession of dynamical behaviours—i.e. the topology of the phase space does not change continuously but by discrete leaps between well-defined attractors. Here we introduce the basics of recurrence quantification analysis and we outline the features of the chaotic region for an unstirred BZ system.

2 Experimental

2.1 Recurrence quantification analysis

Recurrence quantification analysis was first introduced as a set of analyses that quantify the structure appearing in a recurrence plot (RP). Webber and Zbilut applied it to the study of nonstationary data sets particularly in the area of physiology[22–24] and Trulla *et al.*[24] used it to identify transition points in nonstationary data sets. RPs were introduced by Eckmann, Kamphorst and Ruelle[26] in a 1987 paper as a graphical tool for measuring the time constancy of dynamical systems. To obtain the RP of an experimental time series $Y = (y_1, y_2, ..., y_N)$ one applies the delay-coordinate reconstruction of the unobserved multidimensional phase space. At a particular time delay τ and an embedding dimension d_e, the resultant trajectory in $\Re^{d_e}$ is

$$X = (x_1, x_2, \ldots, x_m) \qquad (1)$$

where $m = N - (d_e - 1)\tau$ and

$$x_j = (y_j, y_{j+\tau}, y_{j+2\tau}, \ldots, y_{j+(d_e-1)\tau}) \qquad (2)$$

for $j = 1, 2, \ldots, m$. By the Takens[27] theorem, the topology of this multidimensional phase space is equivalent to that of the real unknown phase space underlying the observed dynamics. Recurrence plots are based upon mutual distances between points on a trajectory. An $m \times m$ recurrence matrix is defined as

$$R(i, j) = D(x_i, x_j) \qquad (3)$$

where $D(x_i, x_j)$ is the maximum norm between points, defined as

$$\max_{1 \leqslant k \leqslant d_e} \|x_{i+(k-1)\tau} - x_{j+(k-1)\tau}\| \qquad (4)$$

We choose to use this norm and not the Euclidean norm because it is less sensitive to the embedding dimension used.[28] Then a cut-off radius r is chosen and points lying within it will be black coloured, while the others will be white. Again an $m \times m$ *thresholded recurrence matrix* is generated

$$T(i, j) = \begin{cases} 1 & \text{if } 0 < D(x_i, x_j) < r \\ 0 & \text{otherwise} \end{cases} \qquad (5)$$

To perform RQA on a recurrence plot one computes statistical values acting directly on the thresholded recurrence matrix T [eqn. (4)]. We are interested particularly in four of these quantifiers: The percent *recurrence* (*rec*) is the percentage of points darkened in the RP above the diagonal—*i.e.*, given s the number of 1s in T, then $rec = 100 \times (s/m^2 - m)$. Usually periodic dynamics have higher *rec* values than aperiodic dynamics. The percent *determinism* (*determ*) is the percentage of recurrent points that form lines parallel to the main diagonal. Lines consist of two or more (s_l) points that are diagonally adjacent with no intervening blank space; thus $determ = 100 \times (s_l/m^2 - m)$. It is clear that this quantifier measures how an RP is 'organized'. During a transition, *rec* is more affected than *determ*. We then introduce a new variable: *ratio* $= determ/rec = s_l/s$: it addresses nonstationarity characteristics in RP and increases substantially during a transition and settles down when a quasi-steady state is achieved. Finally, *entropy* measures the Shannon entropy of the diagonal line segment distribution; in general it is high within periodic windows (large diversity in diagonal line lengths) but low within chaotic windows (small diversity in diagonal line lengths).

The fifth and final RQA statistic is called *div*: it is the reciprocal of the longest line length found in the computation of *determ*. According to Eckmann, Kamphorst and Ruelle it is directly related to the largest Lyapunov exponent: in a periodic signal, lines tend to be very long so that *div* is small. On the other hand, high values of *div* are indicative of chaotic behaviour. RQA has been applied to nonstationary simulated and experimentally observed systems by taking subsets of the time series and calculating the cited quantifiers. These subsets are called 'epochs'. Successive subsets displace each other by a quantity called *displacement* so that the intersection among them is not null. Then *rec*, *determ*, *ratio*, *entropy* and *div* are plotted against the point (*start*) in the time series where an epoch begins. Transitions between different dynamical regimes are observed by studying the features of these plots.

2.2 Reagents and apparatus

All experiments were performed isothermally at $25\,°C$ in a batch reactor (spectrophotometer cuvette, $1 \times 1 \times 4$ cm^3). A thermostat has been used in order to keep the temperature constant in the cuvette. The dynamics were monitored by the solution absorbance at 320 nm using quartz UV grade spectrophotometer cuvettes. A double beam spectrophotometer (Varian, series 634) was used. All chemicals were of analytical quality and were used without further purification. The following concentrations of reactant stock solutions were used: $Ce(SO_4)_2$ 0.004 M, malonic acid 0.30 M, $KBrO_3$ 0.09 M; each stock solution was 1 M H_2SO_4. The oscillator was started by mixing equal quantities of reactants in a flask. The solution was stirred for 3 min with a 1 cm length Teflon-coated magnetic stirrer, at a constant high stirring rate, and was then poured into the cuvette until the sample reached the top, when measurement of the signal began. The cross sectional area of the spectrophotometer light beam was 30 mm^2. The volume spanned by the beam was 300 mm^3 (7.5% of the total volume) and was located 2 cm away from the liquid–air interface, 1 cm away from the bottom of the cuvette and about 0.4 cm away from the sides. The spectrophotometer was connected to an IBM compatible PC for data acquisition by an analog to digital board converter with a 16 bit resolution. The absorbance was recorded with a $\tau_s = 0.5$ s sampling time. Time series points were recorded and stored in the computer for data analysis. Recurrence quantification analysis and time series analysis were applied in order to characterize the signal. Two software packages were used: RQA52[29] and TISEAN.[30,32]

3 Results and discussion

A 5 h acquisition was divided in to epochs of 2800 points (*ca.* 23′ 20″) and *ratio*, *div*, *entropy* and *determ* values were calculated for each epoch. The whole time series were analysed using a *displacement* of 100 points. A time delay of 38, an embedding dimension of 5 and a cut-off radius of 6 were used. In Fig. 1 the transition from the periodic regime to chaos and from chaos to periodicity is clearly observed by the sudden change in all the quantifiers. The chaotic region lies in the interval 2000–15 000 points (1000–7500 s). In this region *determ* is low and *div* is high. At a first analysis of the *div* values, it seems that the chaotic interval could be divided into three regions: two with higher Lyapunov exponents and one with a lower one. For the sake of clarity we introduce the concept of chaoticity of a time interval: it is the measure of orbit divergency in the reconstructed attractor. The higher the Lyapunov exponent (or any quantifier related to it), the higher is the chaoticity of that interval. In Fig. 1 it seems that the chaoticity of the aperiodic region rises at the beginning, then decreases in the middle of the interval, then increases again and finally goes down until the behaviour turns to periodic. We isolated the interval 2000–15 000 and performed a finer recurrence analysis taking epochs of 3600, 3200, 2800, 2400, 2000, 1600 and 1200 points. It is meaningless to use shorter epochs because the study would be made on little pieces of dynamic evolution and we could not catch enough points for good statistics. Moreover, as shown in Fig. 2, the structure of the chaotic zone is fully unfolded using epochs of 1200 to 2000
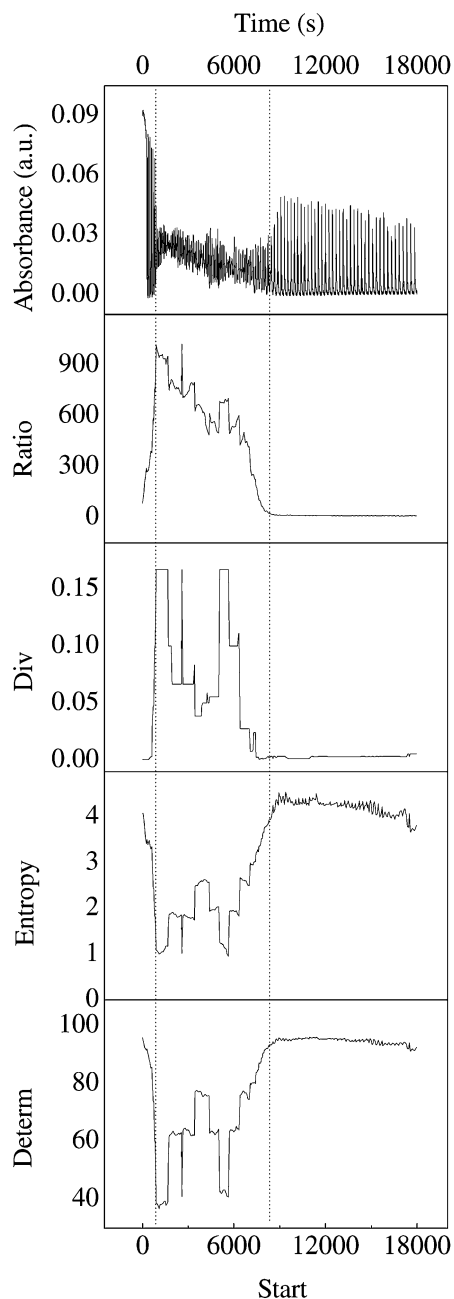
Fig. 1 Spectrophotometric signal (top panel) and RQA quantifiers (lower four panels). Epochs of 2800 points and a displacement of 100 points were used. The chaotic region lies between the two vertical dotted lines as evidenced by abrupt change in the four RQA statistics.

Fig. 2 (a) The 6500 s evolution of the chaotic region. Lower panels show *div* values calculated using epochs of 3600 (b), 3200 (c), 2800 (d), 2400 (e), 2000 (f), 1600 (g) and 1200 (h) points. In these, α and β denote regions that have highest *div* values and ζ, the region with lower *div*. The extension and qualitative features of these regions remain almost the same in the last three panels.

points. We do not analyse longer epochs because we could lose information by studying intervals that can no longer be approximated as pseudo-stationary. This refinement clearly shows the emergence of a more complex structure of the chaotic transient. We can distinguish windows of higher Lyapunov exponents (higher *div* values in regions α and β) between regions of lower ones (region ζ). It is worth noting that the zone ζ is shorter when we use shorter epochs than when we use longer ones; it is simply because when we use long epochs we span regions with different dynamical behaviours and their statistical weights influence the values of *div*. As the behaviour of *div* does not change a lot using epochs shorter than 2000 points, it is reasonable to assume that those points lie on the same chaotic attractor and the system jumps from one to the other by successive bifurcations.

Given this approximation, we can calculate the correlation dimension of each attractor: as suggested by Kaplan and Glass
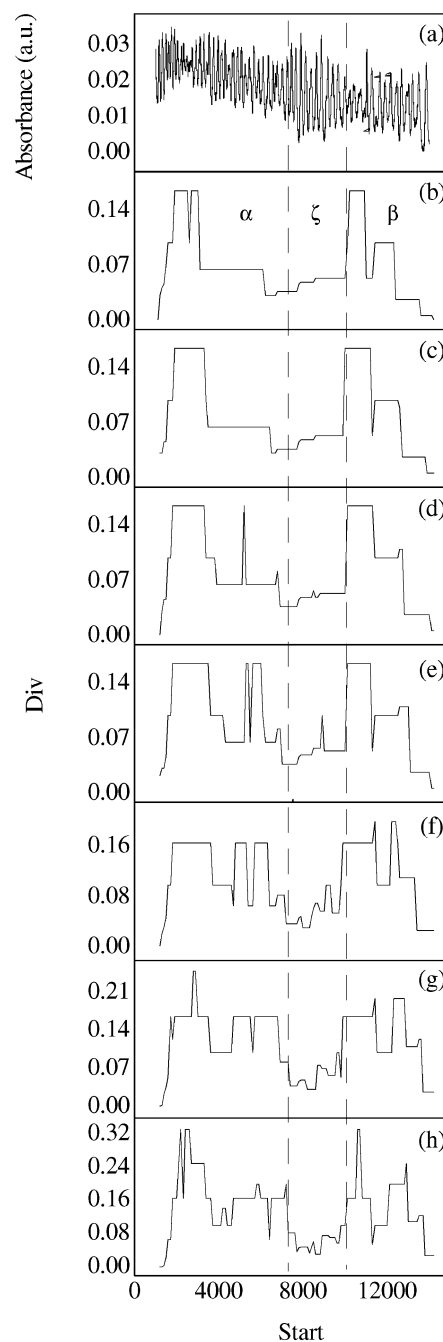
we calculate *rec* in an interval for increasing values of the cut-off radius. The slope of the linear region in the *rec versus* radius plot (Fig. 3) is defined as the correlation dimension of that data set.[33] We took 12 epochs of 2000 points with a *displacement* of 1000 points and calculated the correlation dimension of the reconstructed attractor in each interval. The behaviour of the estimated dimension [Fig. 4(a)] mimics exactly that of *div*. Furthermore, with a time series analysis software (TISEAN), we calculated the Kaplan–Yorke dimension of the attractor by estimating the spectrum of Lyapunov exponents.[34] As for the correlation dimension, the Kaplan–Yorke dimension characterizes the fractality of an attractor. As can be seen in Fig. 4(b), the Kaplan–Yorke dimension behaves exactly like the correlation dimension, giving further proof that every attractor
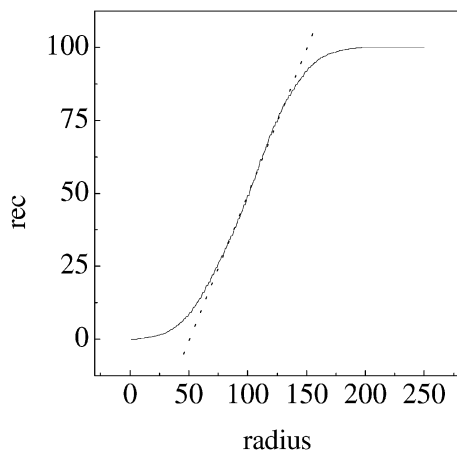
Fig. 3 Plot of *rec versus* radius for the interval 2000–4000. The slope of the linear part of this graph (0.97519 ± 0.005 908) gives the correlation dimension for that interval. Similar plots are obtained for the 12 epochs into which the chaotic region was divided.

has a different behaviour. Another proof of this trend is given by the asymptotic value of the highest Lyapunov exponent of each epoch [Fig. 4(c)]. Similar results are obtained on a sample of 10 acquisitions performed with the same experimental conditions.

In previous works we suggested and proved that the coupling of nonlinear chemical kinetics, diffusion and convection is responsible for the observed transition to chaos in the BZ reaction in a batch unstirred reactor. We observed that internal and external parameters such as medium viscosity and temperature affect the dynamical evolution of the reaction. In particular, in conditions of high viscosity[19] or low temperature,[21] the chaotic transient disappears and the evolution is fully periodic. The periodic evolution has been well studied by means of fast fourier transforms;[18] it has been observed that, because of reagent consumption, it shows a regular decrease in time both of frequencies and of amplitude. We expected the chaotic evolution to follow such a trend: in fact the intensity of convection should be stronger when higher concentration gradients are created by the local nonlinear kinetics. Thus the intensity of the coupling between kinetics and hydrodynamics is expected to decrease regularly in time with the oscillation amplitude—*i.e.* the reagent concentration. Moreover, because the chaotic behaviour is related to this coupling, we expected a regular trend for the chaoticity evolution of the system. In contrast, the results described above prove that the intensity of the coupling follows a complex irregular behaviour: all the invariant measures of the successive attractors of the system change without regularity. The system dynamics jumps between attractors with different chaoticity. It is obvious that, in addition to the reagent concentration, other parameters affect the intensity of the coupling between kinetics and hydrodynamics. The coupling is also influenced by the exothermicity of the reaction (density gradients due to thermal gradients cause the onset of convection), which depends locally on the distribution of chemical species and their ratio. In numerical simulations it is observed that, during the periodic evolution of the reaction, the ratio between the intermediates varies periodically too. On the other hand, when the oscillations are aperiodic, the ratio changes irregularly as a consequence of the underlying chaotic dynamics.

Our hypothesis is that an important bifurcation parameter is the reagent ratio: it should be responsible not only for the onset of chaos during the evolution of the BZ reaction, but also for the observed transition between attractors of different
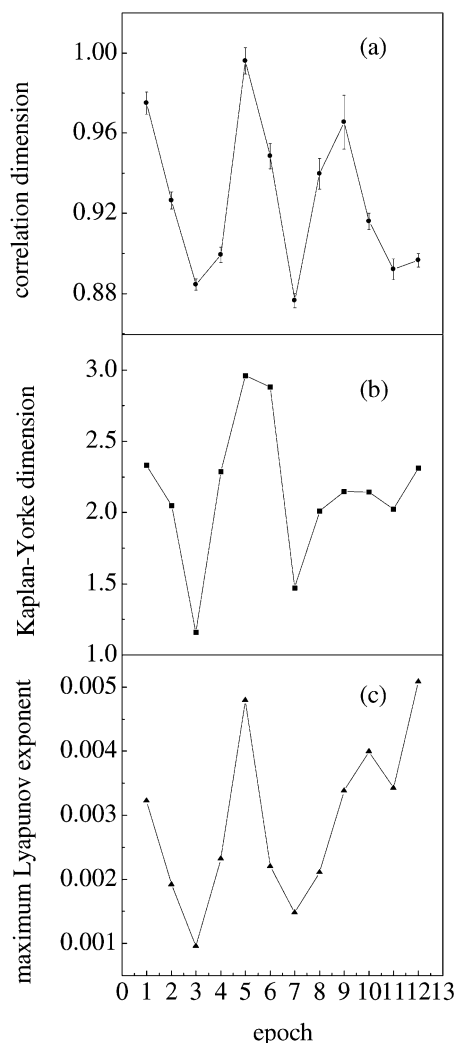

Fig. 4 (a) Correlation dimension *versus* epoch in the chaotic region. The error bars come from the error in the interpolation of the linear region (Fig. 3). (b) Kaplan–Yorke dimension *versus* epoch in the chaotic region; the behaviour is similar to that found in (a) for the correlation dimension. (c) Highest Lyapunov exponent *versus* epoch in the chaotic region; qualitatively we find the same behaviour as the correlation dimension (a) and the Kaplan–Yorke dimension (b).

chaoticity. Preliminary observations show that, when we vary the ratio of the initial reagent concentrations, the reaction evolves in a different way. After a critical value of this ratio, the initial periodic evolution disappears and the chaotic behaviour lasts for longer time intervals.

4 Conclusion

Our work confirms that a transition to chaos occurs when the Belousov–Zhabotinsky reaction is performed in a closed unstirred batch reactor. Furthermore we prove that the chaotic transient can be characterized, and information about the basin of attraction and its time evolution (during the drift to equilibrium of the reaction) can be obtained by a recurrence quantification analysis of experimental time series. Our analysis strengthens our previous hypothesis that the coupling of hydrodynamics to nonlinear kinetics is responsible for the onset of chaos. The techniques used in this work should be a useful tool in the study of the features of the Belousov–Zhabotinsky reaction when performed in different experimental conditions.

Acknowledgements

References

1 S. K. Scott, in *Oscillations, Waves and Chaos in Chemical Kinetics*, Oxford Chemistry Primers, Oxford University Press, Oxford, 1994.

2 R. J. Field and M. Burger, in *Oscillations and Travelling Waves in Chemical Systems*, Wiley, New York, 1985.

3 A. M. Zhabotinsky, *Chaos*, 1991, **1**(4), 379.

4 P. Bergè, Y. Pomeau and C. Vidal, *L'Ordre dans le Chaos*, Hermann, Paris, 1984.

5 G. Nicolis, in *Introduction to Nonlinear Science*, Cambridge University Press, Cambridge, 1995.

6 P. Ruoff and R. Noyes, *J. Phys. Chem.*, 1985, **89**, 1339.

7 P. Ruoff, *J. Phys. Chem.*, 1992, **96**, 9104.

8 P. Ruoff, *J. Phys. Chem.*, 1993, **97**, 6405.

9 M. Rustici, M. Branca, C. Caravati and N. Marchettini, *Chem. Phys. Lett.*, 1996, **263**(3/4), 429.

10 S. K. Scott, B. Peng, A. S. Tomlin and K. J. Showalter, *J. Chem. Phys.*, 1991, **94**, 1134.

11 B. R. Johnson, S. K. Scott and B. W. Thomson, *Chaos*, 1997, **7**, 350.

12 P. V. Covebey and A. N. Chaudry, *J. Chem. Phys.*, 1992, **97**, 7448.

13 P. E. Strizhak and A. L. Kawczysky, *J. Phys. Chem.*, 1995, **99**(27), 10 830.

14 A. Wacker, S. Bose and E. Schöll, *Europhys. Lett.*, 1995, **31**, 257.

15 H. Nagashima, *J. Phys. Soc. Jpn.*, 1980, **49**, 681.

16 J. Wang, P. G. Sørensen and F. Hynne, *J. Phys. Chem.*, 1994, **98**(3), 725.

17 M. Rustici, M. Branca, A. Brunetti, C. Caravati and N. Marchettini, *Chem. Phys. Lett.*, **293**, 145.

18 M. Rustici, C. Caravati, E. Petretto, M. Branca and N. Marchettini, *J. Phys. Chem.*, 1999, **103**(33), 6564.

19 N. Marchettini and M. Rustici, *Chem. Phys. Lett.*, 2000, **317**(6), 647.

20 M. Rustici, R. Lombardo, M. Mangone, C. Sbriziolo, V. Zambrano and M. L. Turco Liveri, *Faraday Discuss.*, 2001, **120**, in the press.

21 M. Masia, V. Zambrano, N. Marchettini and M. Rustici, *Chem. Phys. Lett.*, 2001, **341**(3/4), 285.

22 J. P. Zbilut and C. L. Webber, Jr, *Phys. Lett. A*, 1992, **171**(3/4), 199.

23 C. L. Webber, Jr and J. P. Zbilut, *J. Appl. Physiol.*, 1994, **76**(2), 965.

24 C. L. Webber, Jr, M. A. Schmidt and J. M. Walsh, *J. Appl. Physiol.*, 1995, **78**(3), 814.

25 L. L. Trulla, A. Giuliani, J. P. Zbilut and C. L. Webber, Jr, *Phys. Lett. A*, 1996, **223**(4), 155.

26 J. P. Eckmann, S. O. Kamphorst and D. Ruelle, *Europhys. Lett.*, 1987, **4**(9), 973.

27 F. Takens, Detecting strange attractors in fluid turbulence, in *Dynamical Systems and Turbulence*, Springer, Berlin, 1981, 366–381.

28 J. S. Iwansky and E. Bradley, *Chaos*, 1998, **8**(4), 861.

29 http://homepages.luc.edu/~cwebber/

30 http://www.mpipks-dresden.mpg.de/~tisean/TISEAN/_2.1/index.html

31 R. Hegger, H. Kantz and T. Schreiber, *Chaos*, 1999, **9**(2), 413.

32 T. Schreiber and A. Schmitz, *Physica D*, 2000, **142**(3/4), 346.

33 D. Kaplan and L. Glass, in *Understanding Nonlinear Dynamics*, Springer, New York, 1995.

34 E. Ott, in *Chaos in Dynamical Systems*, Cambridge University Press, Cambridge, 1993.