Transition to Chaos via Collapse of Two-Torus in the Belousov-Zhabotinsky Reaction

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The transition of the dynamics of the Belousov-Zhabotinsky reaction from large peak oscillations to two-torus and chaos as a function of the flow rate is described.

Key words: Reaction kinetics – Oscillation – Two-torus – Chaos – Collapse of torus.

Different types of chaotic attractors in reaction kinetics have been reported. Prominent among them are attractors in continuous flow experiments of the Belousov-Zhabotinsky (BZ) reaction which combine the features of two complex limit cycles [1]. Argoul et al. reported a transition from quasi-periodicity to chaos starting with small peak oscillations, but the two regimes were observed in two different experiments [2]. If the transition from order to chaos occurred in the same experiment at different flow rates it was found to take place via period doubling [1, 3] or via intermittent bursts [4]. Among the universal routes to chaos predicted in chaos theory, however, these is a third one, namely, the route via Hopf bifurcation of a limit cycle to a two-torus [5]. We present experimental evidence for such a transition in the BZ reaction starting from large peak oscillations.

The BZ reaction was performed in a continuous flow stirred tank reactor as described in [6]. Two dual piston pumps were used for substrate input. The reactor volume was 30.5 ml, a temperature of $T = 25.0 \pm 0.05$ °C was maintained during the whole experiment and the solution was constantly stirred at 2000 rpm. The initial concentrations inside the reactor were 0.1 M sodium bromate, 0.3 M malonic acid, 0.6 M sulfuric acid, and 0.00025 M $Ce_2(SO_4)_3$. The potential E of a bromide selective electrode was recorded versus a silver/silver chloride reference system. Data were stored by means of a PDP 11 laboratory computer and analyzed using standard methods of dynamics.

Starting at a flow rate of 2.190 ml/min the reaction displayed a stable large amplitude oscillation. We investigated the dynamics of the reaction as function of increasing flow rate. The oscillation shows a single-peak sequence of relaxation type in the time series, an amplitude of about 10 mV and a frequency of 0.027 s^{-1}. The attractor reconstruction using the delay time method yields a complete limit cycle. The shape depends on the delay time chosen, but there are characteristic corners indicating deviations from a sinusoidal circle. Figure 1a shows a detail of the frequency analysis of this regime, and we find one sharp peak for the fundamental frequency f_1. In the complete spectrum there are more lines which turn out to be harmonics nf_1 of the fundamental frequency ($n = 2, 3, 4, \ldots$). In a cross-section of this cycle successive intersections with a two-dimensional plane gather round two points in the E_n/E_{n+1}-plane.

Increasing the flow rate we find a change in the dynamics. At 2.242 ml/min there is a slight but significant feature detectable in the time series. Blocks of some eleven peaks are separated by a small maximum (and minimum, respectively). The exact number of peaks in each block may vary from ten to twelve, but after that the reaction is back to its initial state. No further information can be gained from the attractor reconstruction or the Poincaré cross-section, because for a large number of points unavoidable noise in the signal covers the small effect. Only a broader limit cycle-like structure and two broad islands, respectively, can be detected. Strong evidence that we do not observe enhanced stochastic fluctuations close to a bifurcation point is delivered by the Fourier transform spectrum. A second frequency f_2 appears at 0.0074 s^{-1} (see Figure 1a). Now there are two peaks for the two incommensurable frequencies as well as the harmonics $2f_2$ and $3f_2$ and linear combinations $f_1 + nf_2$ ($n = -2, -1, 1, 2$) and $2f_2 + nf_2$ ($n = -2, -1$).

Further increase of the flow rate reveals that the two frequency regime is stable only in a narrow range of the parameter. At 2.258 ml/min the dynamics has changed drastically. The time series shows an aperiodic sequence of peaks, whereby sets of large amplitude single-peaks are irregularly interrupted by either two-peak or three-peak oscillations. The number of single-peaks in one set varies from six to about forty, but sets with more than twenty single-peaks appear less frequent. We never observed less than six single-peaks between two multi-peak oscillations. In contrast to the first periodic regime, in this regime there is a significant shift of the mean amplitude of single-peaks. In the Fourier spectrum (Fig. 1c) all sharp peaks are vanished with only a broad noisy band being left indicating chaos in the corresponding dynamics. Figure 2 shows the reconstruction of the chaotic attractor at this parameter set. We identify a darker region of large single-peaks and the irregular excursions to two-peak and three-peak oscillations (upper left corner). The complex Poincaré cross-section allows the distinction of three substructures. There are three diffuse islands formed by two-peak and three-peak oscillations, respectively. The first six or seven single-peaks following a multi-peak yield a narrow path that connects the diffuse islands of the multi-peak and the third substructure formed by intersections with additional single-peaks, another island. The point distribution in the last case is more dense than in the previous ones. This structure is clearly reminiscent of the cross-section of the first two regimes.

At still higher flow rates a chaotic state consisting of mixed mode oscillations only, and finally periodic mixed-mode states were observed.

Our interpretation for the transition from order to chaos uses established predictions from chaos theory [5]. The first regime was a stable limit cycle, the second regime, consisting of two independent fundamental frequencies, is a motion on a two-torus and the third regime reveals a chaotic attractor. We conclude that the limit cycle has lost its stability via a secondary Hopf bifurcation to give rise to a two-torus. Although the torus is stable in a finite range of parameters, it also loses stability and makes way for chaos in the reaction. Two mechanisms for this transition are possible. In the theory of Ruelle and Takens (see [5]) the quasiperiodic regime

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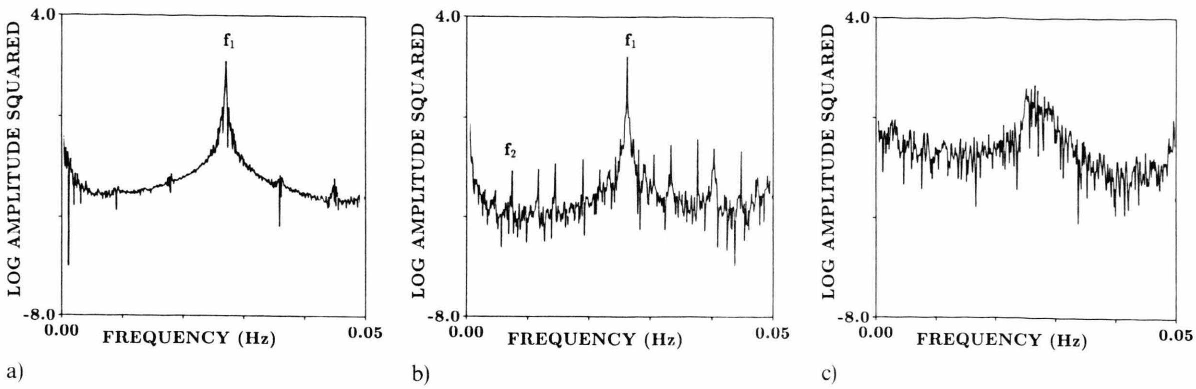

Fig. 1. Fourier transform spectra of the time series obtained from a bromide electrode at different rates. a) 2.190 ml/min, b) 2.242 ml/min, and c) 2.258 ml/min.

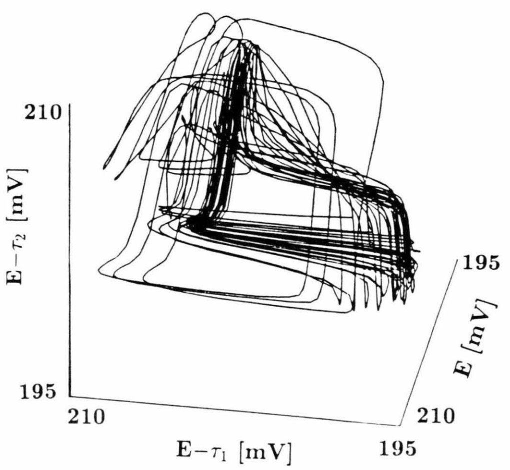

Fig. 2. Attractor reconstruction from the chaotic regime in Fig. 1c using two delay times τ of the bromide signal, $\tau_1 = 10$ s and $\tau_2 = 50$ s.

undergoes a (Hopf) bifurcation to a structurally unstable three-torus. In the Curry-Yorke model a transition from two-torus to chaos is found as well, but in this case the destabilized torus collapses. Due to experimental resolution and noise in the signal we were not able to resolve locked states on the torus preceding the transition to chaos [7]. We note that in the segments of the chaotic flow where the time series consists of single-peaks the cross-section shows a broad island of the former torus that slowly shifts until the trajectory leaves this region to do an excursion and come back again. This suggests instability of the torus and creation of a new regime which includes the former torus as a substructure. Neither the well-known transition to chaos on a winkled torus [8] nor doubling of the torus is observed [7]. The phenomenology of the transition and the cross-section suggests that the transition is due to collapse of the torus as the result of a collision with another (presumably also toroidal, see [9]) structure.

The creation of a torus from a limit cycle has been observed numerically in a model of the BZ reaction [10]. Barkley et al. assume that the torus loses stability as the result of a collision with an unstable torus. These results, however, were gained at the transition from the small (not large) limit cycle to the mixed-mode oscillation; also, the mixed state between toroidal and mixed mode oscillations was insufficiently characterized. It is an open question whether the experimentally observed chaotic attractor can in principle be embedded in three dimensions.

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