Quasiperiodic to bursting oscillations transition in the model of the Belousov–Zhabotinsky reaction

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Complex dynamics of the BZ-oscillator: the transition from quasiperiodic to bursting regimes was simulated based on an eleven-stage reaction scheme; the transition was realized in two forms: (i) smooth deformation of the T^2-tore due to its interaction with an unstable stationary point; (ii) a sharp change over between the regimes.

Experimental studies of the auto-oscillation Belousov–Zhabotinsky (BZ) reaction have revealed a variety of dynamics: from simple quasisinusoidal oscillations to quasiperiodic, bursting, complex periodic and various chaotic ones.[1–4]

Some types of these regimes were reproduced with more or less success in various models[1,5,6] based on oversimplified schemes. However, studies of the finer effects (in particular transitions between regimes) were faced with some difficulties. Thus[6] quasiperiodic and mixed-mode oscillations were simulated and studied in detail, but the continuous transition between them was not seen. Recently[7,8] we showed that, based on the detailed eleven-stage scheme of Ruoff and Noyes, not only can all known types of BZ oscillations be modelled but the experimentally observable alternation order could also be reproduced:

SS – QS – QP – B – CP – B – QP – QS – SS,

where SS = stationary state; QS = quasisinusoidal oscillations of low amplitudes; QP = quasiperiodic regimes; B = bursting oscillations; CP = a complex succession of chaotic and periodic regimes. This allowed us to study the mechanisms of the BZ dynamic transformations in more detail. This paper concerns the transition from quasiperiodicity to bursting.

The reaction scheme under consideration[9] is as follows:

$$BrO_3^- + Br^- + 2H^+ \rightleftarrows HBrO_2 + HOBr \quad (1)$$

$$HBrO_2 + Br^- + H^+ \rightarrow 2HOBr \quad (2)$$

$$BrO_3^- + HBrO_2 + H^+ \rightleftarrows 2BrO_2^{\bullet} + H_2O \quad (3)$$

$$BrO_2^{\bullet} + M^{(n-1)+} + H^+ \rightleftarrows HBrO_2 + M^{n+} \quad (4)$$

$$2HBrO_2 \rightarrow BrO_3^- + HOBr + H^+ \quad (5)$$

$$HOBr + Br^- + H^+ \rightleftarrows Br_2 + H_2O \quad (6)$$

$$RH + Br_2 \rightarrow RBr + Br^- + H^+ \quad (7)$$

$$HOBr + R^{\bullet} \rightarrow ROH + Br^{\bullet} \quad (8)$$

$$RH + Br^{\bullet} \rightarrow Br^- + H^+ + R^{\bullet} \quad (9)$$

$$RH + M^{n+} \rightarrow M^{(n-1)+} + H^+ + R^{\bullet} \quad (10)$$

$$2R^{\bullet} + H_2O \rightarrow RH + ROH \quad (11)$$

where RH stands for malonic acid, and M^{n+} for metal ions.

As in refs. 7–9, modification of the closed system with permanent the initial concentrations of BrO_3^- and RH were calculated which allow one to obtain stationary regimes. Calculations were carried out by the m,k-method[10] with a relative precision of $\varepsilon_r = 10^{-5}$–10^{-6} and an integration step of 0.1–1 s. The constant k_8 was used as a variable parameter which determines the rate of Br^- formation. The other parameters used are as follows:[8]

$k_1 = 2.1$ dm^9 mol^{-3} s^{-1}; $k_{-1} = 1 \times 10^4$ dm^3 mol^{-1} s^{-1};

$k_2 = 3 \times 10^6$ dm^6 mol^{-2} s^{-1};

$k_3 = 42$ dm^6 mol^{-2} s^{-1}; $k_{-3} = 4.2 \times 10^7$ dm^3 mol^{-1} s^{-1};

$k_4 = 8 \times 10^4$ dm^6 mol^{-2} s^{-1}; $k_{-4} = 8.9 \times 10^3$ dm^3 mol^{-1} s^{-1};

$k_5 = 3 \times 10^3$ dm^3 mol^{-1} s^{-1};

$k_6 = 8 \times 10^9$ dm^6 mol^{-2} s^{-1}; $k_{-6} = 110$ s^{-1};

$k_7 = 4.6 \times 10^{-3}$ dm^3 mol^{-1} s^{-1};

$k_8 = 10^6 - 10^7$ dm^3 mol^{-1} s^{-1};

$k_9 = 10^6$ dm^3 mol^{-1} s^{-1};

$k_{10} = 0.2$ dm^3 mol^{-1} s^{-1};

$k_{11} = 3.2 \times 10^9$ dm^3 mol^{-1} s^{-1};

$[Br^-]_0 = 10^{-5}$ mol dm^{-3}; $[M^{n+}]_0 = 5 \times 10^{-4}$ mol dm^{-3};

constants: $[BrO_3^-] = 0.08$ mol dm^{-3}; $[RH] = 0.2$ mol dm^{-3}; $[H^+] = 1$ mol dm^{-3}.

There are two areas of each kind of oscillation's existence in the model, corresponding to the oxidized (with low k_8 values) and reduced (higher k_8 values) form of the catalyst. Accordingly, two areas of quasiperiodic oscillations (with toroidal attractor — T^2-tore[11] — in a phase space) and two forms of transition to bursting oscillations — 'mild' and 'rigid' are observed.

Figures 1 and 2 describe the first case. Quasiperiodic regimes, arising in the model as a result of secondary Hopf bifurcation, are considered to be two-frequency and look like high frequency oscillations modulated by a low frequency component on the kinetic curves. Moving from the bifurcation point (when k_8 increases) the amplitude of a second frequency grows which leads to an increase in the modulation depth (Figure 1). Thus, phase portraits demonstrate a decrease of the T^2-tore internal diameter. Simultaneously, the tore increases and approaches an unstable saddle focus stationary point (Figure 2). This evolution is caused by their interaction ('attraction' of phase trajectories by a stable manifold of the saddle focus and 'rejection' by a two-dimensional unstable one). The approach of the phase point to the stationary point is accompanied by a slowing down of its movement, and it begins to spend more and more time in the vicinity of the latter. Subsequently, sloping areas are observed on kinetic curves whose length rises as k_8 increases up to the appearance of pronounced bursting oscillations (Figure 3). This process coincides with the formation of an homoclinic structure[12] in the system, causing complex organization of phase space and chaotic character of bursting attractors (Figure 3*c*). The continuous character of the quasiperiodic regimes evolution described above is in good agreement with experimental observations.[4]

Thus, the left hand side of the diagram shows a smooth transition without abrupt changes of the attractor's structure. Similar T^2-tore evolution was observed previously in simpler model.[6] However, as the authors of ref. 6 noted, they could not monitor the transition to bursting oscillations due to calculation difficulties.

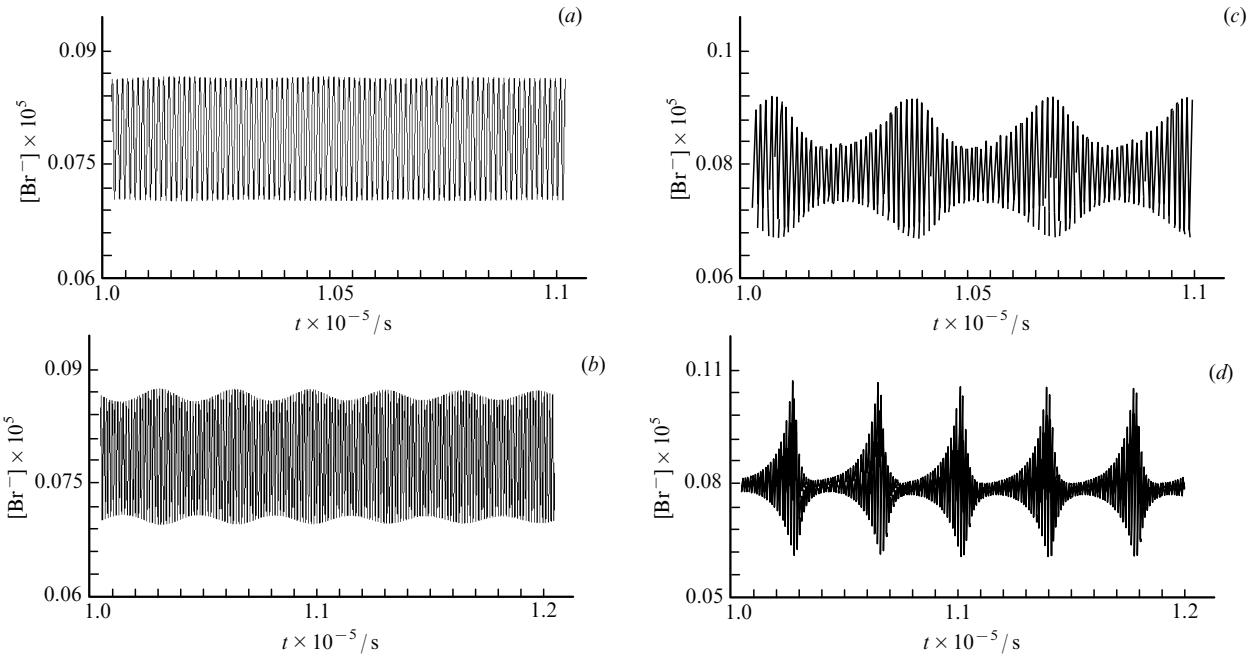

Figure 1 Kinetic curves of quasiperiodic oscillations. $k_8 \times 10^{-6}$ = 2.117 (*a*); 2.118 (*b*); 2.119 (*c*); 2.120 (*d*) dm^3 mol^{-1} s^{-1}.

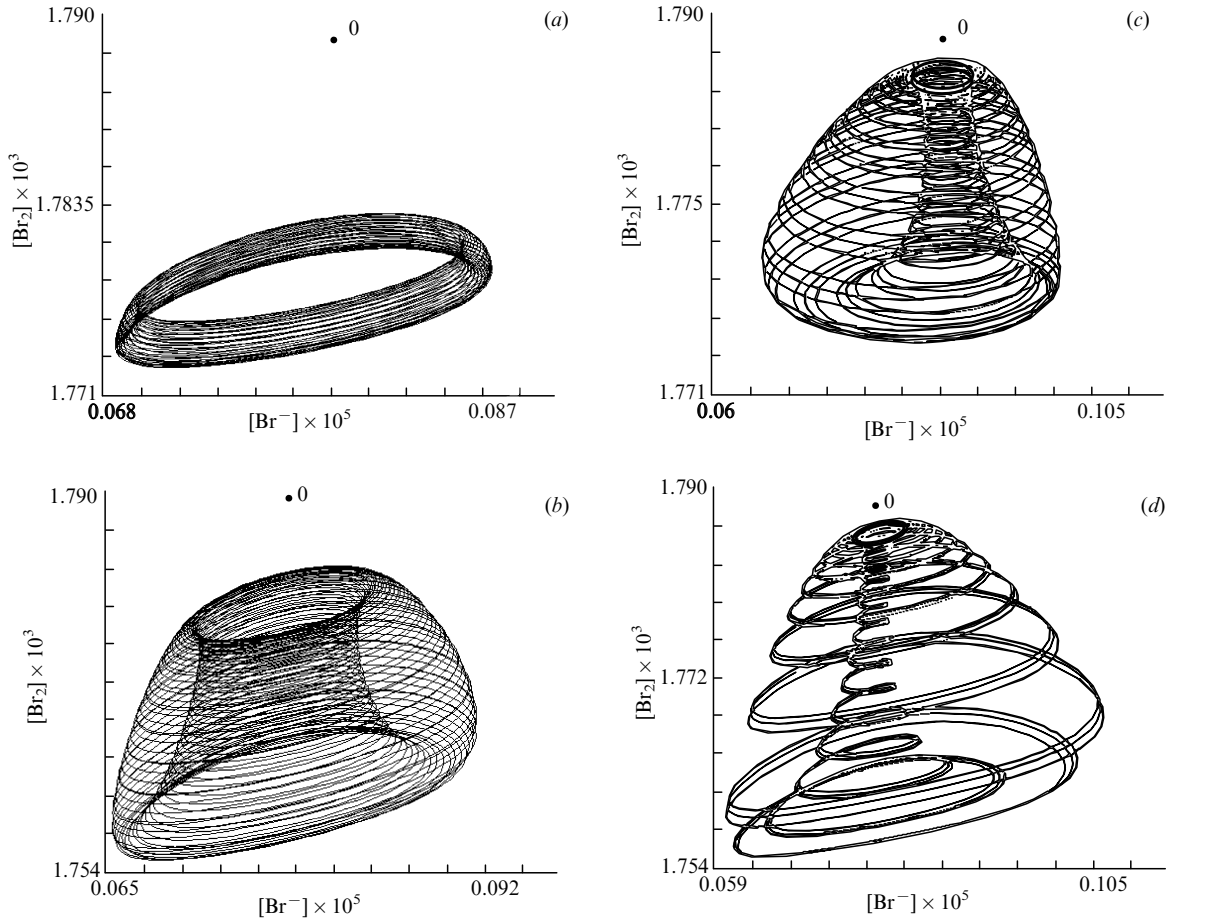

Figure 2 Tore transformation during 'mild' transition to bursting oscillations. $k_8 \times 10^{-6}$ = 2.117 (*a*); 2.118 (*b*); 2.119 (*c*); 2.120 (*d*) dm^3 mol^{-1} s^{-1}. 0 is an unstable stationary point (saddle focus).

In the right hand side of the diagram this transition is very sharp. The quasiperiodic and bursting regimes in Figure 4 were obtained with k_8 values differing by less than 10^{-8}%. Probably, these oscillating states coexist in a range of k_8 values, and when the parameter changes the sharp transition from one regime to another occurs. The existence area for quasiperiodic regimes was calculated to be much less (by 1–2 orders of magnitude) than that for bursting oscillations. Apparently, this is why the direct transition from bursting to stationary state, by passing quasiperiodicity, is often observed in experiments.[3,4]

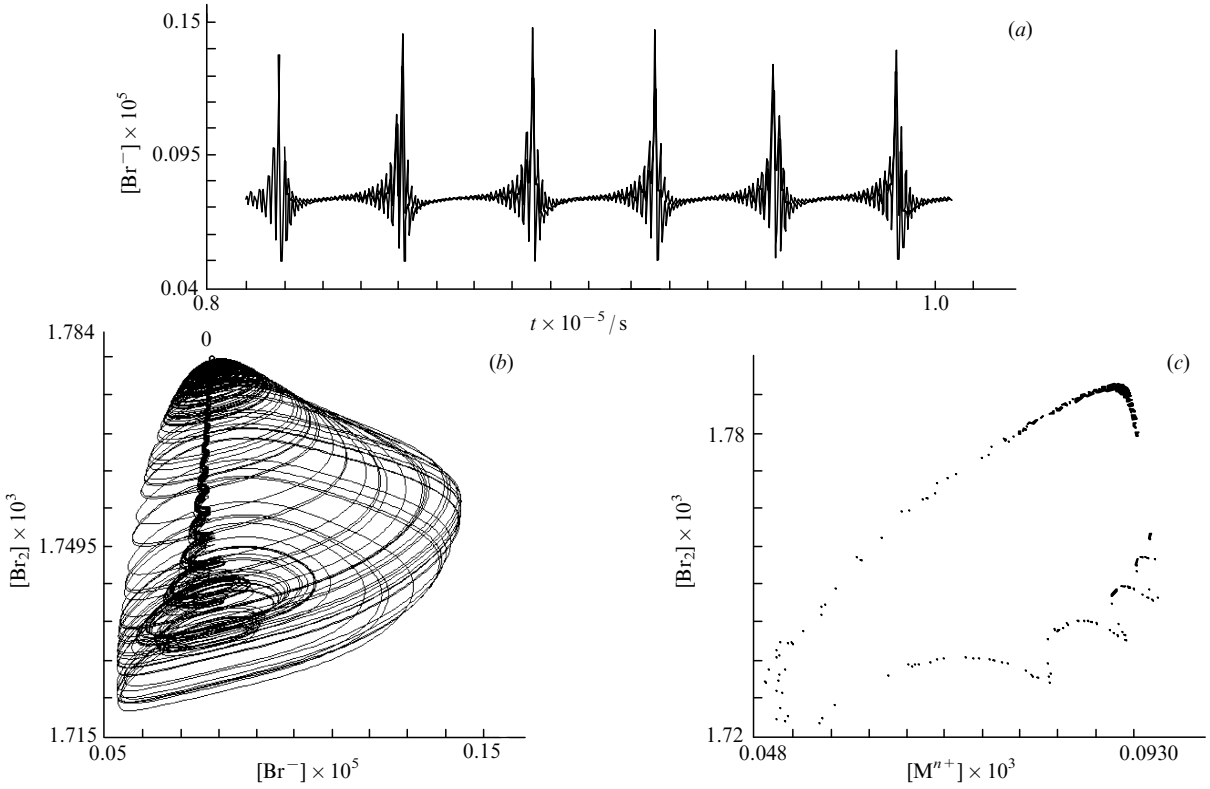

Figure 3 Kinetics (*a*), phase portrait (*b*), and Poincare section (*c*) of bursting oscillations. ($k_8 = 2.14 \times 10^6$ dm^3 mol^{-1} s^{-1} , 0 is unstable stationary point).

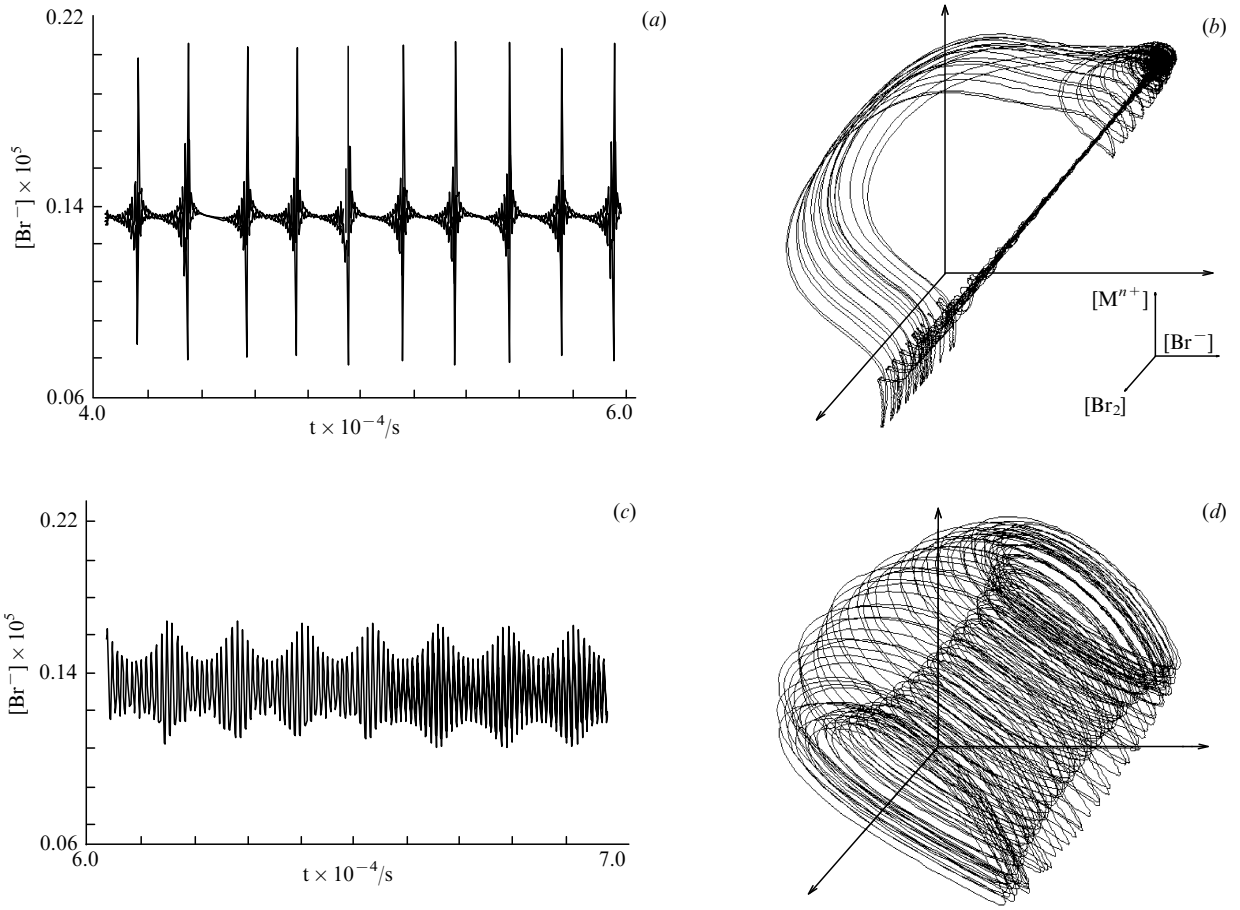

Figure 4 'Rigid' transition between bursting [(*a*), (*b*), $k_8 = 7.370306040 \times 10^6$ dm^3 mol^{-1} s^{-1}] and quasiperiodic [(*c*), (*d*), $k_8 = 7.370306041 \times 10^6$ dm^3 mol^{-1} s^{-1}] regimes. (*a*), (*c*) kinetic curves; (*b*), (*d*) phase portraits.

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