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Chaos in a Simulated Belousov–Zhabotinsky Reaction

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Proceeding from an eleven-step reaction scheme, complex dynamic behaviour has been simulated for a Belousov–Zhabotinsky oscillator, in particular a transition from steady state to quasiperiodic and bursting oscillations, and futher on to regular relaxation oscillation *via* a complicated sequence of alternating periodic and chaotic regimes.

A variety of complex dynamic modes in the Belousov–Zhabotinsky (BZ) reaction, that cannot be rationalized within the known models, requires further investigation with respect to the fine structure of the oscillating mechanism with still more complicated reaction schemes.[1,2] Free organic radicals $R^\cdot$ are important in this mechanism as direct precursors of Br^- in a reaction sequence.[3–5] Thus, it would be interesting to consider the reaction scheme proposed by Ruoff and Noyes,[6] including a step involving interaction of $R^\cdot$ with HOBr, reactions (1)–(11),

$$BrO_3^- + Br^- + 2H^+ \rightleftarrows HBrO_2 + HOBr \quad (1)$$
$$HBrO_2 + Br^- + H^+ \longrightarrow 2HOBr \quad (2)$$
$$BrO_3^- + HBrO_2 + H^+ \rightleftarrows 2BrO_2^\cdot + H_2O \quad (3)$$
$$BrO_2^\cdot + Me^{(n-1)+} + H^+ \rightleftarrows HBrO_2 + Me^{n+} \quad (4)$$
$$2HBrO_2 \longrightarrow BrO_3^\cdot + HOBr + H^+ \quad (5)$$
$$HOBr + Br^- + H^+ \rightleftarrows Br_2 + H_2O \quad (6)$$
$$RH + Br_2 \longrightarrow RBr + Br^- + H^+ \quad (7)$$
$$HOBr + R^\cdot \longrightarrow ROH + Br^\cdot \quad (8)$$
$$RH + Br^\cdot \longrightarrow Br^- + H^+ + R^\cdot \quad (9)$$
$$RH + Me^{n+} \longrightarrow Me^{(n-1)+} + H^+ + R^\cdot \quad (10)$$
$$2R^\cdot + H_2O \longrightarrow RH + ROH, \quad (11)$$

where RH corresponds to malonic acid and Me^{n+} stands for cerium(IV) ions.

Ibison and Scott[7] used the method of quasistationary concentrations to remove the fast steps involving $R^\cdot$ and $Br^\cdot$, and succeded in simulating mixed-mode, bursting and quasisinusoidal oscillations and chaos in the BZ reaction. Our independent studies[8] were based on a complete eleven-step scheme with vivid regards for the fast variables, and allowed us to simulate a more wide scale of complex periodic and aperiodic modes, including quasiperiodic oscillations and small-scale chaos.

Our research is concerned here with studies on large-scale chaos arising at lower concentrations of a catalyst $[Me^{n+,(n-1)+}] = 5 \times 10^{-4}$ M in this system. As with earlier studies,[8] we calculate a variant for the closed system, but one which maintains initial concentrations of BrO_3^- and RH at a steady level, allowing for stationary regimes. The system of differential equations, in accordance with reactions (1)–(11), was integrated by the $(m–k)$-method[9] at relative precision $\varepsilon_r = 10^{-5}$–10^{-6} (some chaotic regimes have been calculated at the $\varepsilon_r = 10^{-7}$ level) with the integration step 0.1–1 s. The constant k_8 was taken as a variable parameter that determined the rate of formation of Br^- from HOBr. The values of the remaining constraints were:

$k_1 = 2.1$ M^{-3} s^{-1}
$k_{-1} = 1 \times 10^4$ M^{-1} s^{-1}
$k_2 = 3 \times 10^6$ M^{-2} s^{-1}
$k_3 = 42$ M^{-2} s^{-1}
$k_{-3} = 4.2 \times 10^7$ M^{-1} s^{-1}
$k_4 = 8 \times 10^4$ M^{-2} s^{-1}
$k_{-4} = 8.9 \times 10^3$ M^{-1} s^{-1}
$k_5 = 3 \times 10^3$ M^{-1} s^{-1}
$k_6 = 8 \times 10^9$ M^{-2} s^{-1}
$k_{-6} = 110$ s^{-1}
$k_7 = 4.6 \times 10^{-3}$ M^{-1} s^{-1}
$k_8 = 10^6$–10^{-7} M^{-1} s^{-1}
$k_9 = 10^6$ M^{-1} s^{-1}
$k_{10} = 0.2$ M^{-1} s^{-1}
$k_{11} = 3.2 \times 10^9$ M^{-1} s^{-1}

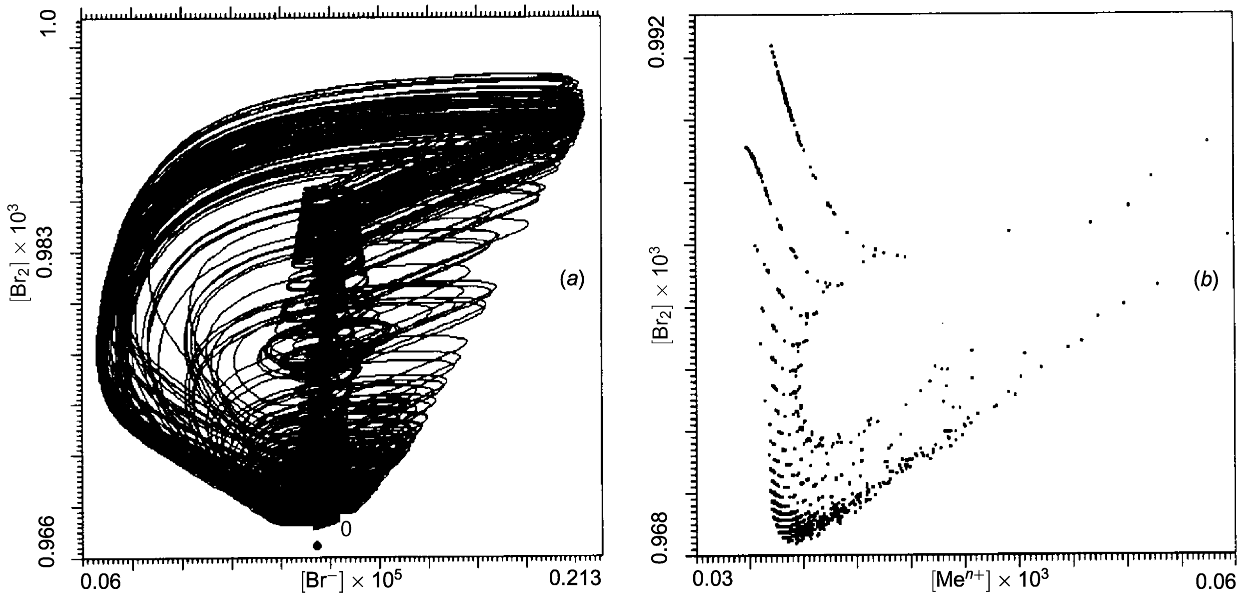


Fig. 1 The phase portrait (*a*) and the Poincare section (*b*) of the bursting ($k_8 = 7.370306 \times 10^6$ M^{-1} s^{-1}).

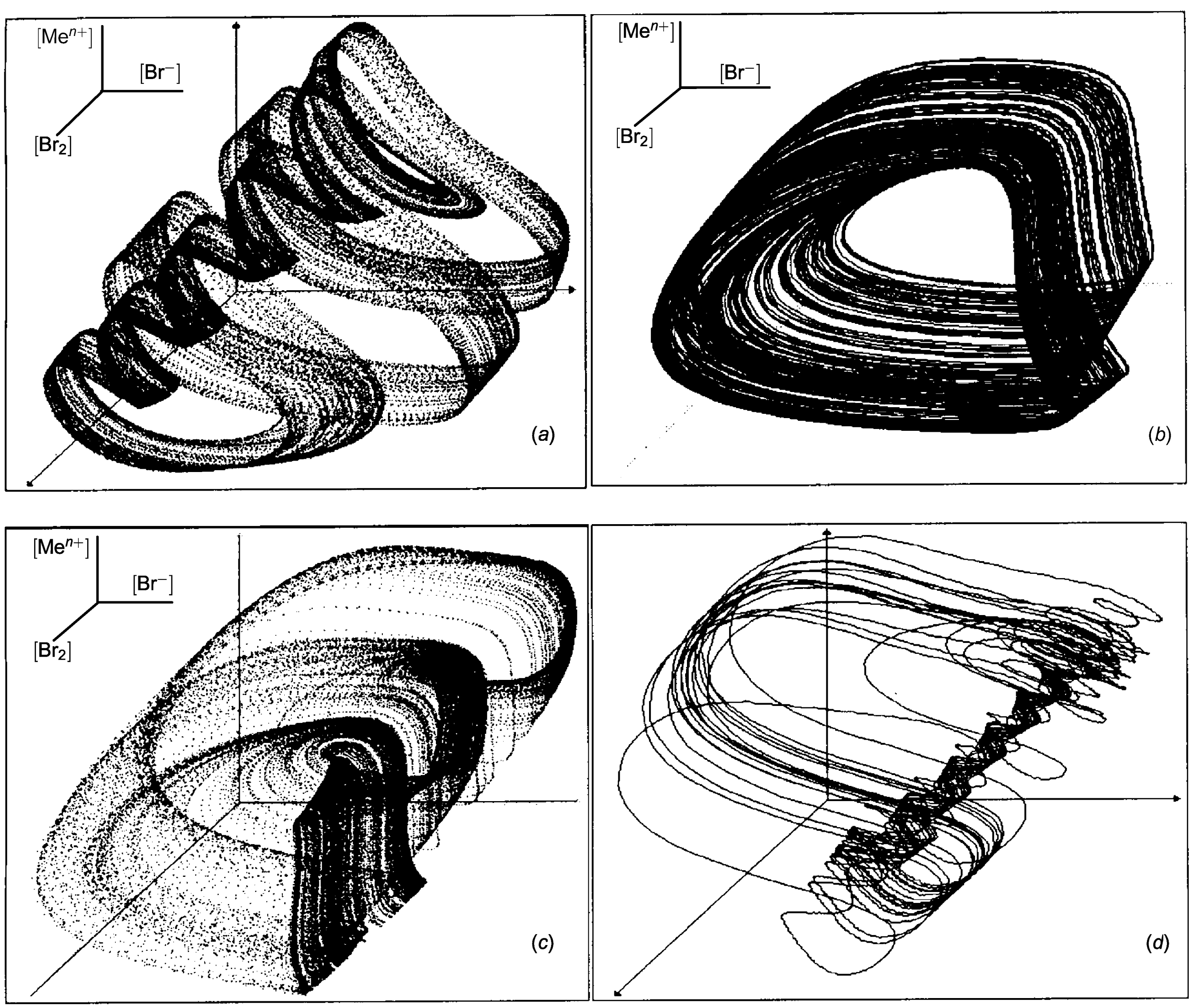


Fig. 2 The phase portraits of characteristic chaotic regimes. $10^{-6} \times k_8 = 2.40$ (*a*); 5.36 (*b*); 6.00 (*c*); 7.00 (*d*) M^{-1} s^{-1}.

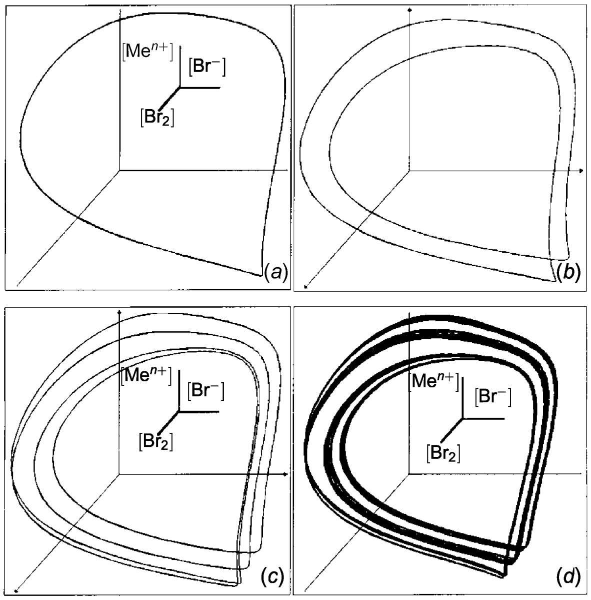


Fig. 3 The phase portraits of the regimes from periodic-doubling cascade $(L)^2$, $(L)^4$, $(L)^8$ (*a–c*) and the threshold chaotic state (*d*). $10^{-6} \times k_8 = 5.32$ (*a*); 5.33 (*b*); 5.33004 (*c*); 5.3301 (*d*) $M^{-1}\,s^{-1}$.

$[Br^-]_0 = 10^{-5}$ M, $[Me^{n+}]_0 = 5 \times 10^{-4}$ M; constants: $[BrO_3^-] = 0.08$ M, $[RH] = 0.2$ M, $[H^+] = 1$ M.

The values k_1–k_6, k_{10}, k_{11}, are chosen according to refs. 5, 10 and 11. Preliminary calculations with varying values of k_8 and k_9 have shown that for a similar type of effect on the system dynamics the sensitivity to k_9 is less then to k_8. Therefore, k_9 has been accepted as constant and equal to 10^6 $M^{-1}\,s^{-1}$. The value k_7 accepted here should be considered as an adjustable parameter which make it possible to reproduce correctly the region by reagent concentrations where oscillations exist.

The following diagram shows the regimes in the system, where SS is steady state; QS, quasisinusoidal oscillations; QP, quasiperiodic modes; B, bursting; L^nS^m, a complex periodic regime with n large-amplitude and m low-amplitude oscillations for a period; C, chaos.

As the analysis conducted has shown, the appearance of oscillations in the system is connected with the Hopf bifurcation, which converts the initial stable focus into an unstable one (saddle-focus). The regular quasisinusoidal oscillations arising turn further into quasiperiodic ones (T^2-tore) with two independent frequencies. At the origin of this mode the percentage modulation of the oscillations is low, then grows to some critical value. This may be observed at the phase portraits as a contraction of the interior of the tore. Subsequently, a rapid increase in the oscillation amplitude

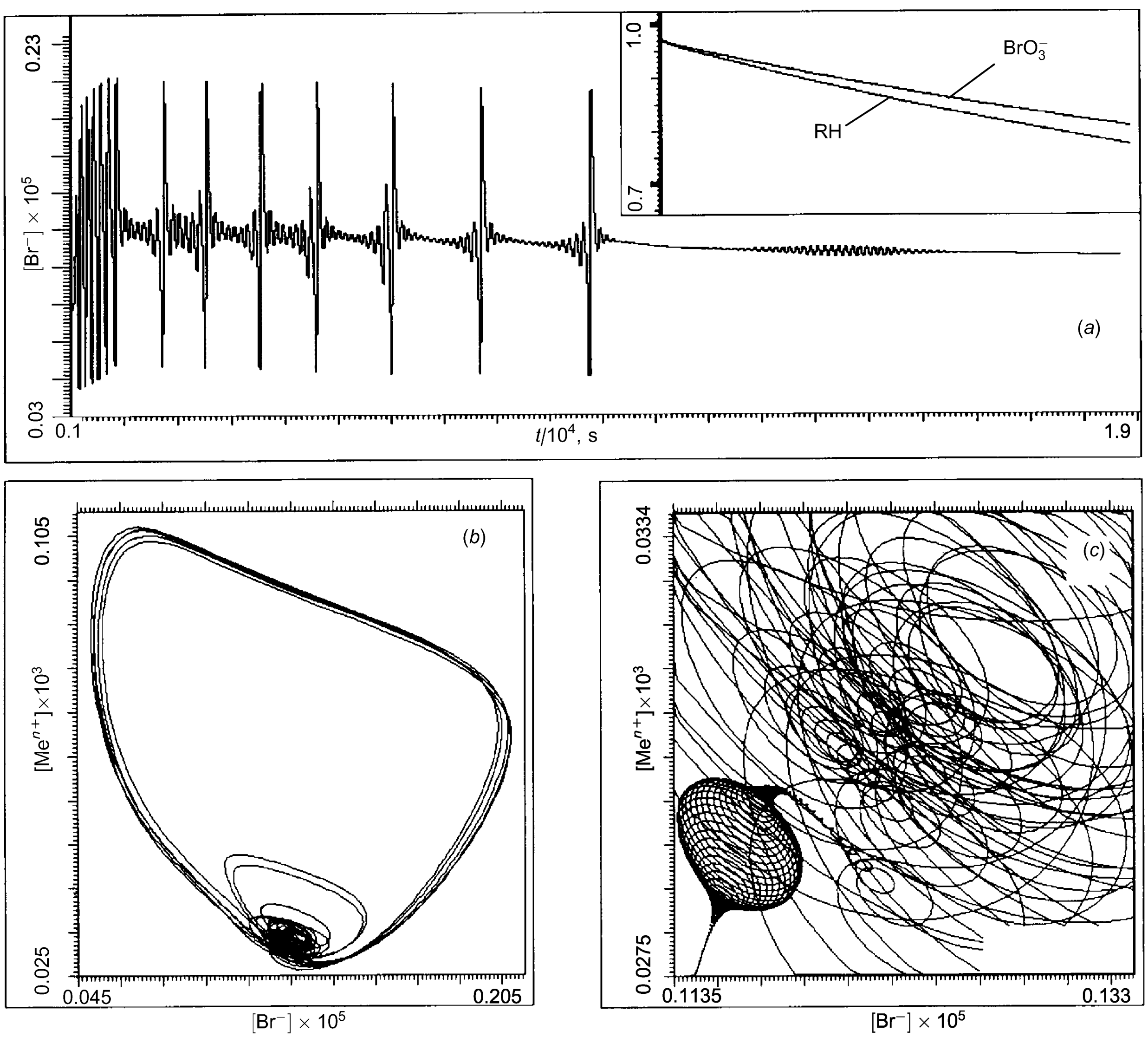
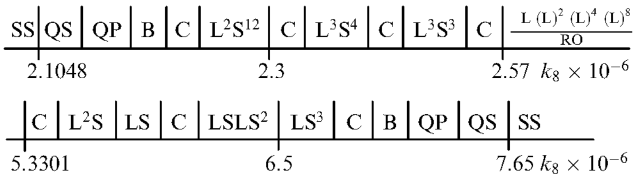


Fig. 4 Aperiodicity in the close system (batch reactor) at $k_8 = 6.15 \times 10^6$ $M^{-1}\,s^{-1}$, $[BrO_3^-]_0 = 0.08$ M, $[RH]_0 = 0.2$ M, $[Br^-]_0 = 1 \times 10^{-5}$ M, $[Me^{n+}]_0 = 5 \times 10^{-4}$ M, $[H^+] = 1$ M. (*a*) Kinetic curve (at the insertion the relative change of the reagent concentrations at the same time is shown), (*b*) the phase portrait of the system, (*c*) enlarged part of its central "spot".



occurs, resulting in bursting. The screw chaotic attractor responding to them (Fig. 1) is bound closely with the homoclinic trajectory (of separatrix type of the saddle-focus singular point). The existence of the latter stipulates the complex folded form of the given attractor (this form is seen clearly on the Poincare section).

The bursting oscillations are followed by a complicated sequence of alternating chaotic and complex periodic regimes with gradually increasing amplitude and reducing number of small-scale oscillations, which merge into regular monoperiodic relaxation oscillations. With further variations in k_8, the modes change in the opposite order, hence the symmetry appears in the diagram shown earlier. Fig. 2 shows phase portraits of the peculiar chaotic states in the left- and right-hand sections of the diagram.

The transition from the relaxation oscillations to chaos occurs *via* a Feigenbaum-like period-doubling cascade. Fig. 3 shows periodic $(L)^2$, $(L)^4$, $(L)^8$ and threshold chaotic states. Indications of similar transitions were observed for some different regimes too.

The pattern of chaotic dynamics, observed from our calculations, agrees with the experimental results reported by Arneodo *et al.*[12] The transition described from quasiperiodicity to chaos and a complex alternating periodic-chaotic sequence (from relaxation oscillations to bursting) are similar to the events obtained in their work.

The studies of Györgyi and Field,[13,14] which have subjected to criticism the simulated chaos results presented in earlier work, compel us to treat carefully the results of these calculations. The analysis conducted has shown that the chaotic regimes of the model under study are characterized by sufficiently wide regions of existence (judged by the parameter k_8), and their nature does not change qualitatively at higher precision levels of the calculations. We suppose that the adduced results are arguments for the existence of the purely "kinetic" chaos in the BZ-system, which is stipulated exclusively by the reaction mechanism peculiarities and the system of differential equations describing it. Additional confirmation is the chaos (Fig. 4) which appears in the calculation of the close variant (batch reactor) of the model where the homogeneity is manifested very clearly.

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