A DYNAMICAL MODEL FOR PERIODIC AND CHAOTIC OSCILLATIONS IN THE BELOUSOV–ZHABOTINSKY REACTION

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Received 16 June 1981

A simple dynamical model is presented which completely reproduces the experimentally obtained peculiar sequence of periodic and chaotic states in the Belousov–Zhabotinsky reaction.

The homogeneous Belousov–Zhabotinsky reaction is a remarkable example of chemical self-sustained oscillations [1]. In recent years experimental evidence has been obtained that these oscillations may be not only periodic, but also chaotic [2–5]. It is generally accepted now that this phenomenon may be explained in terms of the "strange attractor" concept. Furthermore, strange attractors have already been found in some kinetic models [6,7]. However, no explicit comparison of theoretical and experimental results is known to the author.

In this letter we propose a "strange attractor interpretation" of the recent accurate and detailed observations [4]. In these experiments a peculiar sequence of transitions between periodic and chaotic regimes was obtained when a single parameter g, the flow rate of the reagents (see figs. 1,2 below), was varied. We present a simple dynamical system with just the same sequence of regimes. In other words, a mathematical structure of chemical chaos is suggested.

Our model is the following system of ODE's:

$$\dot{x} = hx + y + 0.1z,$$

$$\dot{y} = -x, \qquad (1)$$

$$\epsilon\dot{z} = f(x,z) \equiv \tanh[100(1+4z - 16x)] - 4(z + x + x^3).$$

If $\epsilon \ll 1$, the flow is restricted to a 2-D S-shaped slow manifold $f(x,z) = 0$ with the only fixed point lying on one of its stable branches (say, branch A) [‡1]. This steady state (0, −0.025..., 0.25...) is stable for $h < 0.10...$ and is unstable for $h > 0.10...$. It should be mentioned that such a structure of the phase space was proposed in ref. [2] on the basis of the experimental data.

Let us fix $\epsilon = 0.1$ and vary h. The numerically obtained behavior of $z(t)$ is plotted in figs. 1, 2 where the corresponding experimentally observed regimes [4] are also presented. It is seen that model (1) accounts well for the experimental facts. The only exception is the regime in fig. 2b where a stochastic sequence of 4- and 5-peak pulses was observed in the experiments, and our model gives about 10% of 3-peak pulses additionally.

For a more detailed investigation of the nature of the transitions between chaotic and periodic states the method of the Poincaré map was used. Following the well-known Lorenz approach [10] we constructed a one-dimensional mapping connecting subsequent maxima z_i, $i = 1,2, ...,$ of the variable $z(t)$: $z_{i+1} = F(z_i)$ (figs. 1,2).

This mapping has three definite regions (see fig. 1a).

1. $z_i < z^0$. In this case part of the trajectory from one maximum to the next surrounds the fixed point and remains on branch A. The mapping is nearly linear: $z_{i+1} = F_1(z_i) \approx z_i \exp[\pi(h - 0.1)]$.

2. $z_i > z^0$. In this case the trajectory enters the other stable branch of the slow manifold ($z(t)$ reaches its deepest minimum at this moment) and then reenters the branch A. An explicit analytical expression for F_2 cannot be given.

[‡1] Systems of this type have been investigated in refs. [8,9].

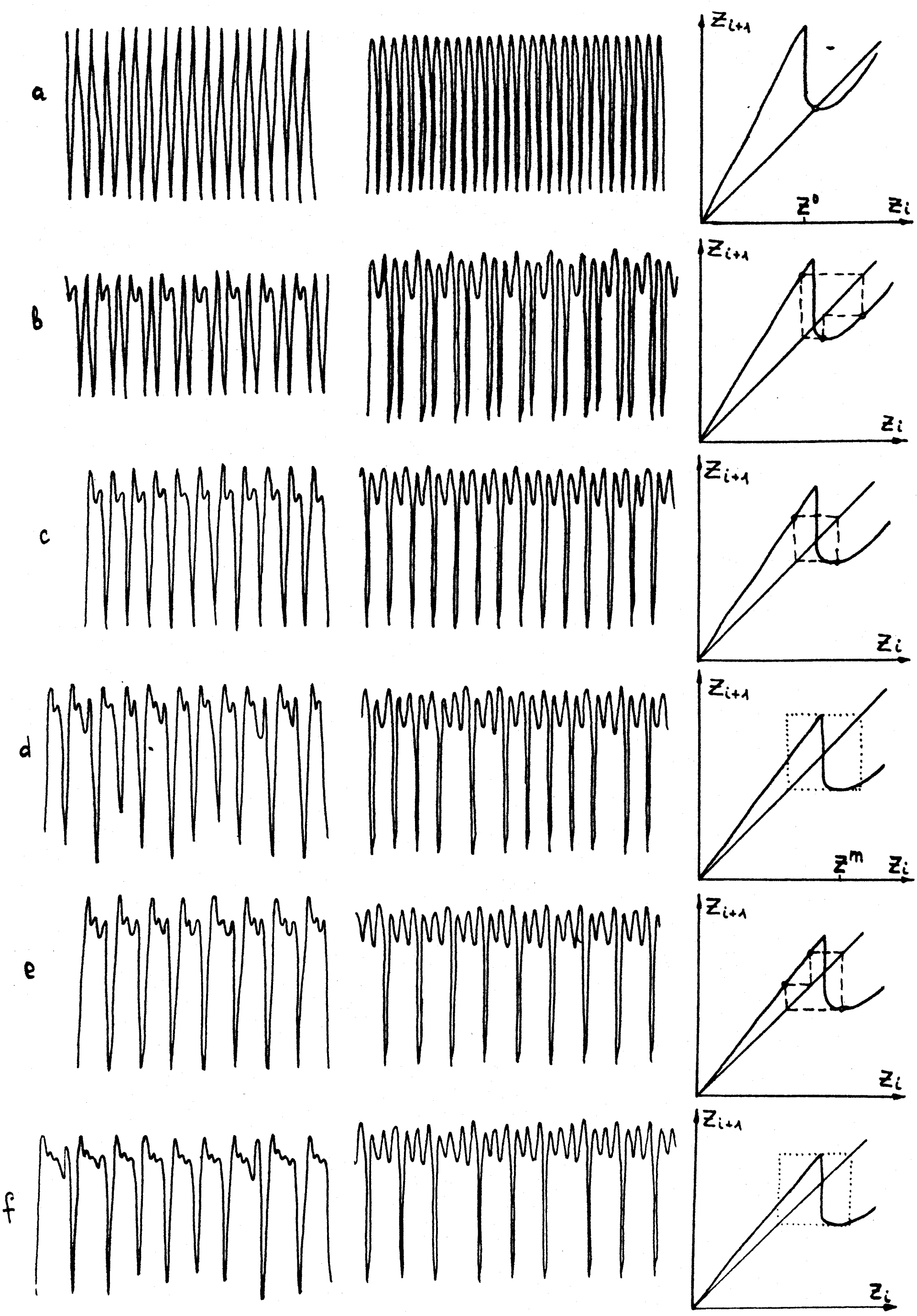

Fig. 1. Recordings from the experiments with the Belousov–Zhabotinsky reaction for different flow rates g (left column, redrawn from ref. [4]), $z(t)$ behavior (center) and the corresponding Poincaré maps (right column) in model (1) for different h. Stable periodic points on the maps are shown by circles, strange attractors are denoted by dotted squares: (a) one-peak periodic pulses (g = 2.91 mℓ/min, h = 0.3); (b) periodic sequence of one-peak and two-peak pulses (g = 3.76 mℓ/min, h = 0.25); (c) two-peak periodic pulses (g = 4.06 mℓ/min, h = 0.2); (d) chaotic mixture of two-peak and three-peak pulses (g = 4.31 mℓ/min, h = 0.188); (e) three-peak periodic pulses (g = 4.34 mℓ/min, h = 0.18); (f) chaotic mixture of three-peak and four-peak pulses (g = 4.51 mℓ/min, h = 0.1652).

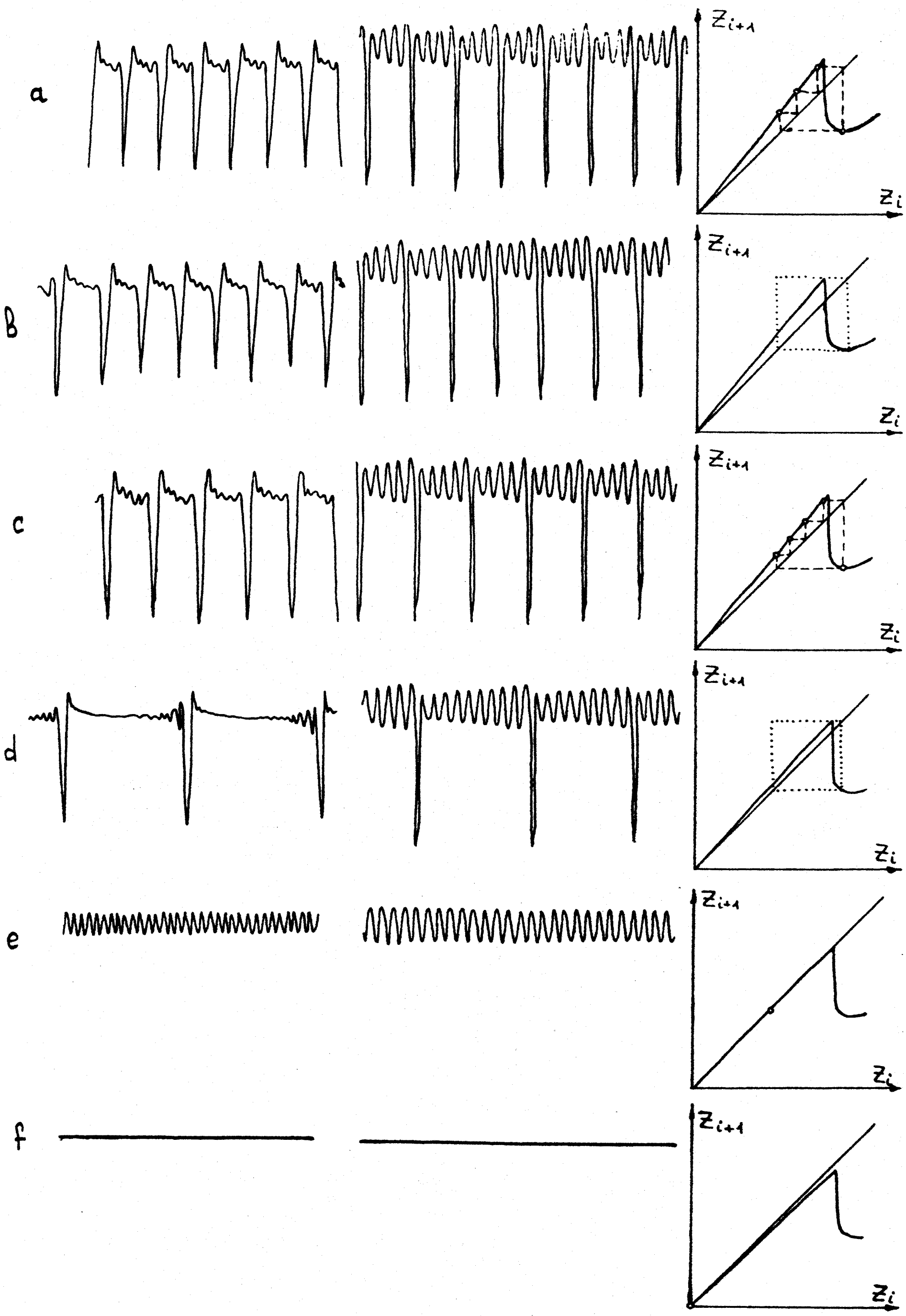

Fig. 2. The same as in fig. 1: (a) four-peak periodic pulses (g = 4.62 mℓ/min, h = 0.16); (b) chaotic mixture of four- and five-peak pulses (g = 4.76 mℓ/min, h = 0.1501); (c) periodic five-peak pulses (g = 5.37 mℓ/min, h = 0.148); (d) chaotic many-peak pulses (g = 5.37 mℓ/ min, h = 0.12); (e) no peaks; small stable limit cycle (g = 5.42 mℓ/min, h = 0.1004); (f) stable fixed point (g = 5.5 mℓ/min, h = 0.08).

3. $z_i \approx z^0$. In this intermediate case the trajectory follows the unstable branch of the slow manifold and $dF_3(z)/dz \approx \exp(\epsilon^{-1})$. Thus for $\epsilon \to 0$ the width of this region is negligible and F_3 may be considered as a discontinuous function. So one cannot apply here results of the theory of continuous mappings (see, for example, ref. [11]).

The mappings constructed provide a clear interpretation of the dynamical properties of model (1). Indeed, the $z(t)$ behavior has the form of a sequence of pulses from one deep minimum to another, i.e. from one iteration with $z_i > z^0$ to the next. Therefore, the number of peaks in a pulse equals the number of iterations with $z_i < z^0$ plus 1. With the decrease of h the slope of F_1 becomes closer to unity and the average number of peaks in a pulse increases.

Transitions between periodic and chaotic regimes are also readily described. Indeed, F_1 is a uniformly expanding mapping and F_2 has a single smooth minimum z^m (see fig. 1d), where contraction of trajectories occurs. Thus a cycle has to pass near z^m to be stable. If $F^n(z^m) \approx z^m$ with small n ($n \leqslant 5$ for the experiments), a stable cycle is observed (figs. 1a, b, c, e; 2a, c). But if z^m "fails to hit" its neighbourhood, instability prevails during wandering in the expanding region, and oscillations become chaotic (figs. 1d, f; 2b, d). It should be noted, that more complex periodic states were numerically observed (for example, a combination of two 3-peak pulses and two 4-peak pulses), which apparently cannot be experimentally distinguished from chaotic states due to inevitable fluctuations.

Finally, at $h \approx 0.1$ nonlinearity in F_1 plays a role and a stable limit cycle completely contained on the branch A appears (fig. 1e). For $h < 0.10...$ this cycle shrinks to the fixed point (fig. 1f).

In conclusion we would like to point out that the $z_{i+1} = F(z_i)$ mapping may be constructed directly from the experimental data (cf. ref. [3]). This construction is rather simple in the chaotic regime: one ergodic trajectory gives the whole picture. In the periodic regime one may try to use transient components of the process.

The author thanks A.M. Zhabotinsky for useful discussions.

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