Collision-Stable Waves in Excitable Reaction-Diffusion Systems

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We discuss the interaction of stable pulse solutions modeling reduction waves in the Belousov-Zhabotinsky reaction in a spatially one-dimensional reaction-diffusion system. We find that in the range of parameters close to a subcritical Hopf bifurcation the counterpropagating pulses do not annihilate in a collision but emerge after the collision with a size and shape unchanged compared to those well before the collision. Under similar conditions these pulse solutions are reflected at zero-flux surfaces ("echo waves").

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The discovery of solitons in integrable equations in Hamiltonian or purely dispersive systems [1] has initiated extensive research, cf. [2,3]. The question whether solitonlike behavior (we consider the definition of the soliton used in applied science, i.e., as a solitary wave which asymptotically maintains its shape and velocity after a collision with other solitary waves, cf. [4]) can also be observed in strongly dissipative systems was posed a long time ago and answered partially positively [5,6].

Structurally stable pulselike solutions in one and two spatial dimensions were observed in the quintic complex Ginzburg-Landau equation describing the envelope of wave amplitudes in the neighborhood of a subcritical Hopf bifurcation by Thual and Fauve [7,8], and the connection with the nonlinear Schrödinger equation limit possessing a soliton solution was also discussed. The interaction of such localized pulselike solutions was also studied numerically by Brand and Deissler [9,10]. They have shown that the counterpropagating pulses in this situation can either mutually annihilate or they can interact so that they emerge after the collision with a size and shape unchanged compared to those well before the collision.

Most experimental studies with excitable pulse waves in chemical systems were performed with the Belousov-Zhabotinsky (BZ) reaction [11]. Two basic types of excitable waves may develop in the BZ reaction mixture depending on reaction conditions—reduction and oxidation waves [12]. In recent experiments with the reduction ferroin-catalyzed waves in the BZ reaction the range of concentrations where stationary propagation of reduction waves occurs was determined [13]. It was also observed that the reduction and oxidation pulse waves do not always annihilate in the course of collision, but form target patterns generating new pulse waves [14].

Recently it was also shown that the behavior of the amplitudes of oscillations close to the Hopf bifurcation point in the BZ reaction can be described by means of the Stuart-Landau equation with the values of the parameters evaluated experimentally for the three most important components including $HBrO_2$, Br^-, and the redox catalyst [15].

In this Letter we shall use the current version of the kinetic model of the BZ reaction proposed by Zhabotinsky *et al.* [16], which describes well spatial profiles and propagation of both oxidation and reduction waves [14,16]. We shall present examples of simulations where the solitary reduction waves not only annihilate each other in the head-on collision and decay as is most often observed in excitable reaction-diffusion systems [17,18], but also are reconstructed after the collision (solitonlike behavior) and are reflected on zero-flux surfaces (echo waves).

The reaction-diffusion system with Fickian diffusion in one spatial dimension can be described in the form

$$\frac{\partial c_j}{\partial t} = d_j \frac{\partial^2 c_j}{\partial \zeta^2} + s_j\,, \tag{1}$$

supplemented by a set of appropriate boundary and initial conditions, where the symbols d_j, c_j, and s_j denote diffusion coefficient, concentration, and overall net source kinetic term of the jth component, respectively, ζ is the spatial coordinate, and t is time.

The simplified reaction scheme and mathematical model considered in this Letter are based on a recently improved Oregonator-class model [16] of the BZ reaction valid for both cerium and ferroin catalyst. The concentrations X, Y, U, and Z of the four species $HBrO_2$, Br^-, $HBrO_2{}^+$, and $Fe(phen)_3{}^{3+}$ are the components of the reaction rates, and the source terms s_j for these species are given by the relations

$$\begin{aligned} s_X &= -k_2 h_0 XY + k_3 h_0 AY - 2k_4 X^2 - k_5 h_0 AX \\ &\quad + k_{-5} U^2 + k_6 UW - k_{-6} XZ\,, \\ s_Y &= -k_2 h_0 XY - k_3 h_0 AY + q k_8 R + k_9 B\,, \\ s_U &= 2(k_5 h_0 AX - k_{-5} U^2) - k_6 UW + k_{-6} XZ\,, \\ s_Z &= k_6 UW - k_{-6} XZ - k_7 BZ + k_{-7} h_0 RW\,. \end{aligned} \tag{2}$$

The concentration of the reduced form of the catalyst, $W = [Fe(phen)_3{}^{2+}]$, is computed from the relation $Z + W = C$, where C is the total catalyst concentration. Con-

TABLE I. Model parameter values.

Parameter	Value	Parameter	Value
k_2 ($M^{-2} s^{-1}$)	2×10^6	k_6 ($M^{-1} s^{-1}$)	1×10^8
k_3 ($M^{-2} s^{-1}$)	12.0	k_{-6} ($M^{-1} s^{-1}$)	3.0
k'_4 ($M^{-2} s^{-1}$)	3×10^3	k_8/k_{-7} (M^2)	1×10^{-5}
k_5 ($M^{-2} s^{-1}$)	150	$k_7 k_8/k_{-7}$ ($M s^{-1}$)	1×10^{-5}
k_{-5} ($M^{-1} s^{-1}$)	4.2×10^6	k_9 (s^{-1})	6×10^{-6}
d_{HBrO_2} (10^{-5} cm^2 s^{-1})	2.0	$d_{HBrO_2{}^+}$ (10^{-5} cm^2 s^{-1})	1.6
d_{Br^-} (10^{-5} cm^2 s^{-1})	2.084	$d_{Fe(phen)_3{}^{3+}}$ (10^{-5} cm^2 s^{-1})	0.603
q	0.467	$h_0 = 0.004 + 0.96[H^+] + 0.314[H^+]^2$	
$A_0 = [NaBrO_3]_0$ (M)	0.358	$k_4 = k'_4(1 + 0.87 h_0)$	
C (M)	0.005	$K_{HBrO_3} = 0.2 + 7.0 h_0$	
$[H^+]$ (M)	0.35	$A = A_0[H^+]/(K_{HBrO_3} + [H^+])$	

centration of the brommalonic radical $R = [BrMA\cdot]$ is expressed from the quasi-steady-state approximation

$$R(Z,W) = k_7 BZ/(k_{-7} h_0 W + k_8). \tag{3}$$

The symbols A and B denote the concentrations of $HBrO_3$ and brommalonic acid, respectively, h_0 is the Hammet acidity function, and q is the stoichiometric parameter. The values of reaction rate coefficients k_i, stoichiometric parameter q, diffusion coefficients d_i, initial reactant concentrations, and several empirical relations are summarized in Table I.

Let us discuss first the situation around homogeneous solutions, where the diffusion terms in (1) are neglected. A typical situation in the parameter space close to the subcritical Hopf bifurcation is represented in Fig. 1(a), where the unstable limit cycle (ULC) is nested between the stable focus (SF) and the stable limit cycle (SLC). The depicted minimal and maximal values show the amplitude of oscillations on the branch of periodic solutions.

The projection of the concentration phase space into the Z-X plane is shown in Figs. 1(b) and 1(c) for $B = 0.05$ M. A perturbation of the SF which will bring the trajectory outside the basin of attraction bounded by the unstable limit cycle will cause the system to oscillate with large amplitude oscillations. A spatially distributed reaction-diffusion system (1) stimulated at one point from the homogeneous spatially uniform SF state by a superthreshold perturbation responds by generation of a pulse wave with the wave back-damped into the original steady state.

In most experimentally observed situations [14] the head-on collision of two reduction waves causes their annihilation similarly as in the case of oxidation waves [19]. Such a situation is depicted in Fig. 2. The chosen value of the parameter $B = 0.05$ M is located inside the region of coexistence of stable steady state and stable limit cycle. We can observe two stationary propagating stable pulses and their annihilation in the course of collision. In contrast to the situation in the homogeneous case [cf. Figs. 1(b) and 1(c)] where the oscillating solution is asymptotically stable, diffusion drives the refractory tail of the propagating pulse to stable focus, and thus no oscillations in the variable Z are observed.

The "solitonlike behavior" in the course of collision of two asymptotically stable reduction waves was found in the parameter region close to the subcritical Hopf bifurcation ($B = 0.0504$ M) and is depicted in Fig. 3. The waves nearly disappear for a short time after the

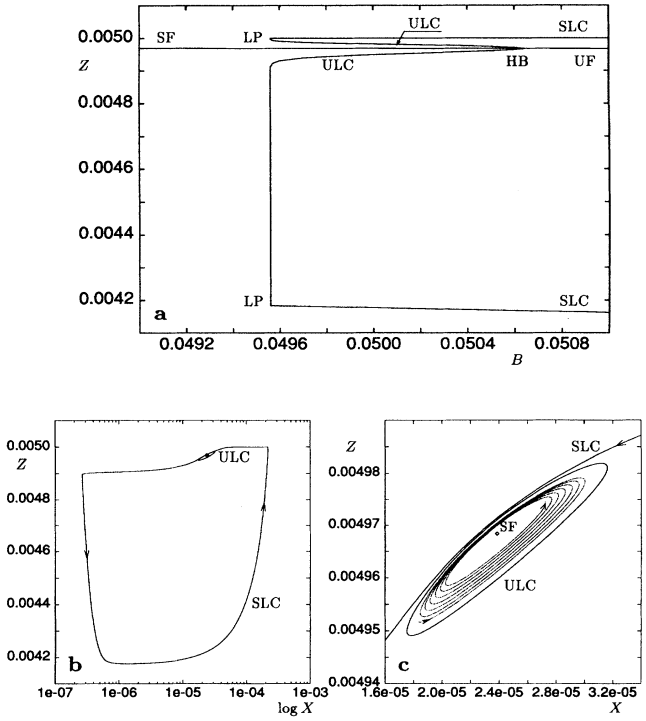

FIG. 1. (a) Dependence of the value of Z (catalyst concentration) on the parameter B, homogeneous solutions of (1) with source terms (2) close to the subcritical Hopf bifurcation. SF—stable focus, UF—unstable focus, HB—Hopf bifurcation point, SLC—stable limit cycle, ULC—unstable limit cycle, and LP—limit point on the branch of periodic solutions. Projection of the concentration phase space into (b) Z–log X and (c) Z-X plane (detail) for $B = 0.05$ M. Part of the trajectory inside the attractive basin of the stable focus (SF) is shown in (c).

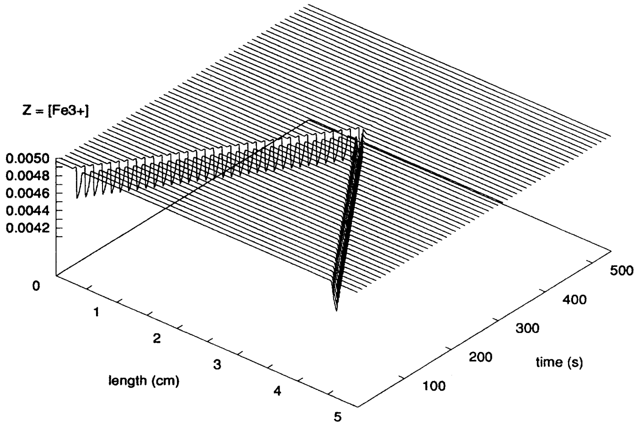

FIG. 2. Stationary propagating reduction waves annihilating each other after the head-on collision, $B = 0.05$ M.

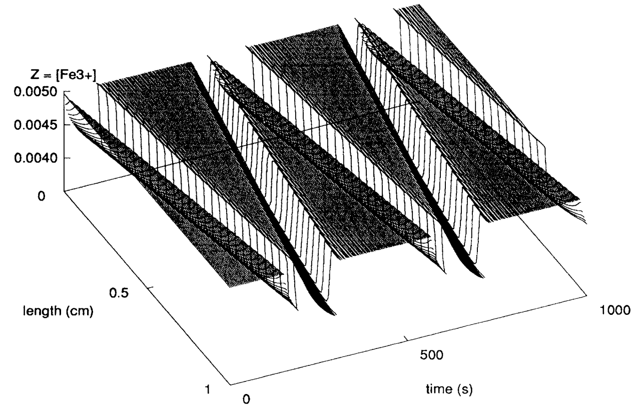

FIG. 4. Echo waves reflected on impermeable (zero-flux) surface, $B = 0.05$ M.

collision (spatial profiles become nearly homogeneous at $t = 135$ s), and then they are regenerated and continue propagation in the original direction. The collision of two rear sides of the counterpropagating reduction waves causes local superthreshold excitation to occur, and the concentration trajectory of the system (1) at the point of collision continues in the motion along the spatiotemporal limit cycle rather than decaying into stable focus. Newly generated pulses of excitation start to propagate in both directions and apparently reconstruct the original pulse waves.

The reflection of pulse waves on the zero-flux boundary for $B = 0.05$ M is depicted in Fig. 4. Multiple reflections of these echo waves cause perpetual propagation of the pulsed wave on the studied domain. Excitable waves reflected on zero-flux boundaries (echo waves) were studied earlier in the SH kinetics model for practically the same situation in the phase plane [20]. Also Petrov, Scott, and Showalter [21] observed wave stopping and reflection on zero-flux surfaces in the cubic autocatalysis model, but in a situation with three coexisting steady-state solutions (one of them stable), and explained the stopping of the wave by the effect of reactant depletion at the wave front and the reversal of the direction of wave propagation by the reactant influx into the rear of the wave. The mechanism of the wave reflection in Fig. 4 is different from that proposed in [21]. It is similar to the mechanism of solitonlike behavior discussed above. The reflection of the echo wave is generated here by the intrinsic transient caused by the collision of the rear of the wave with the impermeable zero-flux boundary.

The interaction of the solitonlike and the echo behavior observed when, for the same values of parameters, the system was initially perturbed at three different positions is shown in Fig. 5. Complex spatiotemporal patterns develop in this case. Let us note that for $B = 0.05$ M the stationary propagating pulses annihilate in the course of the head-on collision (cf. Fig. 2), but nonstabilized pulses with a large amplitude can be reexcited (cf. Fig. 5).

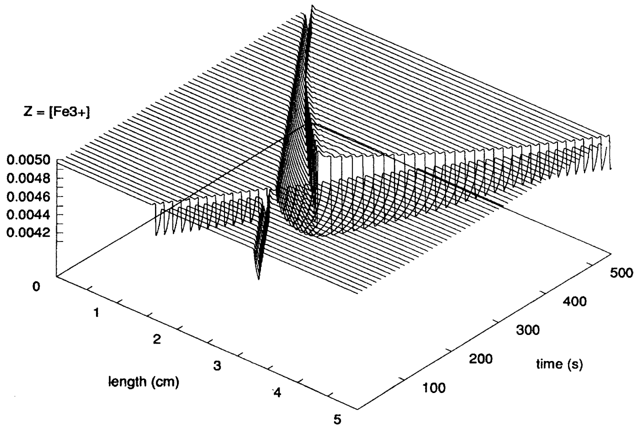

FIG. 3. Collision-stable stationary propagating reduction waves. Solitonlike behavior in the parameter range, where both oscillations and stable steady state coexist, $B = 0.0504$ M.

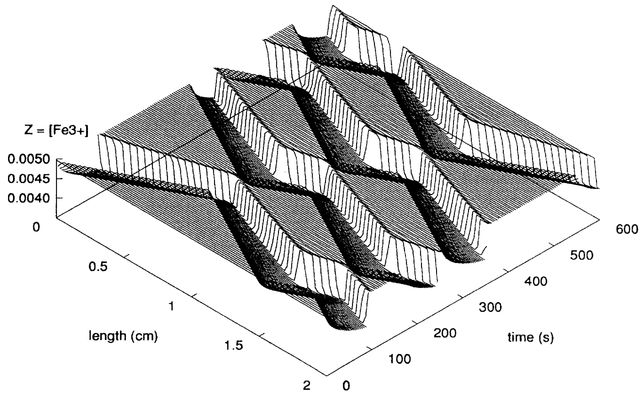

FIG. 5. Interaction of solitonlike and echo waves leads to complex spatiotemporal pattern. Initial pattern was perturbed from uniform profile at three different locations, $B = 0.05$ M.

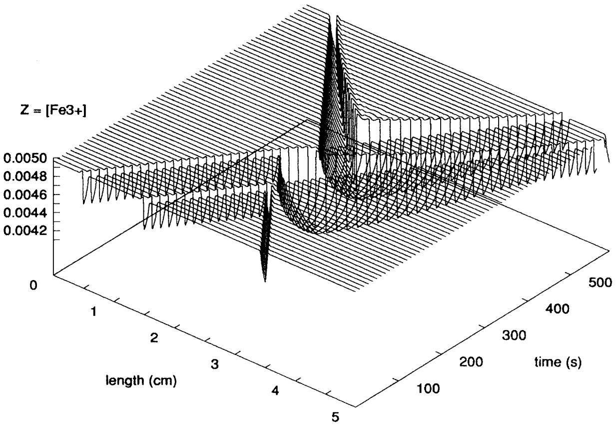

FIG. 6. Solitonlike interaction of two- and single-pulse counterpropagating reduction waves, $B = 0.0504$ M.

The "solitonlike" collision of two pulses propagating from the left with a single pulse propagating from the right is shown in Fig. 6. The pulse waves reappear after interpenetration and continue propagation in the original directions. This together with Fig. 3 confirms that the waves are not simply reflected in the course of collision. A similar observation was made by Brand and Deissler in the simulations of the interaction of counterpropagating one- and two-particle states in the coupled envelope equations [9].

Several experiments with waves in chemical systems recently reported observations which could be interpreted on the basis of the above described behavior [22–24].

In the examples of the solitonlike and echo phenomena discussed in this Letter we did not need to invoke an assumption of the heterogeneity of the reaction medium. However, the proper neighborhood of subcritical Hopf bifurcation seems to be the only necessary condition for the observed reexcitation after collision. Similarly as in the above discussed examples of collision-stable waves in the Ginzburg-Landau (envelope) equations [7–10] it seems necessary that the model has to also possess proper dynamic properties which create the reexcitation in the course of the collision. The process of reexcitation of reduction waves in the course of collision can also be connected with the nonmonotonicity of the spatial profile at the back of the wave. The attempts to model collision-stable behavior in the case of oxidation waves failed until now because of the long and monotonic refractory tail of these waves.

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