Excitation fronts in a spatially modulated light-sensitive Belousov-Zhabotinsky system

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The evolution of excitation wave fronts in a spatially modulated light-sensitive Belousov-Zhabotinsky system is investigated experimentally and theoretically. The excitation wave propagates in a thin, quasi-two-dimensional reaction layer, which is illuminated through a periodical gray level mask. The light-induced differences in excitability and velocity give rise to a temporal and spatial modulation of the initially flat fronts. The experimental front evolution is described in the framework of a kinematical theory as developed earlier for nonuniformly curved systems.

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Excitation waves are dynamical structures observed in many biological, chemical, and physical systems [1,2]. Controlling the dynamics of these different excitable media is an important field of current research. The chemical laboratory model of excitation waves, as they appear in the Belousov-Zhabotinsky (BZ) reaction, have been investigated with homogeneous and inhomogeneous distributions of different control parameters in planar [3,4] and nonplanar geometries [5–7]. Thereby excitability in a planar system can be controlled by changing the organic substrate [8], by applying an electrical field [9] or by illumination, if the light-sensitive variant of the BZ reaction is used [10]. In this context, the light-sensitive ruthenium-catalyzed BZ system has been developed during the past decade to a powerful tool for the investigation of self-organization and its control in spatiotemporal structures in excitable media [11,12].

In a recent work [7] the authors investigated wave propagation on a periodically, nonuniformly curved surface $z=A\sin(bx)\sin(by)$, where A denotes the small surface amplitude and $b=2\pi/\lambda$ the wave vector with the wavelength λ of the surface undulation. The experimental results were compared with predictions from a kinematical theory [13–15] developed to describe the motion of a front on this surface. With the assumption of sufficiently small surface undulations exact solutions of the front shape were obtained.

One possible interpretation of the observed phenomena is the fact that the propagation velocity of a wave propagating on a nonuniformly curved surface becomes spatially nonuniform after projection on the z plane. This leads to the conclusion that similar phenomena can be also expected in other systems, e.g., in planar ones, in which velocity changes arise from sources other than surface curvature.

In this paper we report on investigations of the propagation of excitation waves in a planar system illuminated in a spatially modulated fashion and compare our theoretical results with the above mentioned kinematical approach that has proven to be applicable to curved surfaces [7].

To describe wave propagation in an excitable medium a set of reaction-diffusion equations is widely used [16], such as the two-component system

$$\frac{\partial u}{\partial t}=D_u\Delta u+F(u,v),$$
$$\frac{\partial v}{\partial t}=D_v\Delta v+\epsilon G(u,v), \tag{1}$$

where u and v are variables, which are usually called activator and inhibitor, respectively. The small parameter $\epsilon\ll 1$ determines two quite different time scales for u and v. D_u and D_v are the corresponding diffusion constants. The nonlinear functions $F(u,v)$ and $G(u,v)$ describe the local kinetics of this excitable system.

In order to simulate the dynamics of the light-sensitive system investigated in this work one can use either a modified Oregonator model as in Ref. [17] or the kinematical theory mentioned above [18]. The latter one is based on the eikonal equation [19]

$$V=V_0-DK, \tag{2}$$

which describes the linear relationship between the propagation velocity V in the normal direction of a curved excitation front and its local curvature K. V_0 is the velocity of a flat wave with $K=0$. The slope D is approximately equal to the diffusion constant D_u of the activator in Eq. (1).

For an analytical study of the evolution of an endless front, propagating in a two-dimensional planar system one can use the kinematical theory. In this theory, excitation wave is completely determined by specifying the line of its front. As shown in Ref. [15], the form and evolution of the wave front $K(\ell,t)$ obey the following integro-differential equation

$$\frac{\partial}{\partial \ell}\left[K\int_0^{\ell}KV d\xi\right]+\frac{\partial K}{\partial t}+\frac{\partial^2 V}{\partial \ell^2}+K^2V=0, \tag{3}$$

where ℓ denotes the arclength of the front.

In nonplanar systems K is called the geodetic curvature and the right hand side of Eq. (3) is equal to $-\Gamma V$, with Γ being the Gaussian curvature of the surface [20]. This modi-

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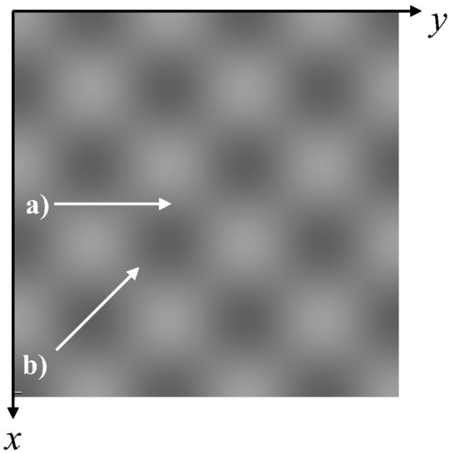

FIG. 1. The smoothed checkerboard gray level mask. The arrows indicate wave propagation in (a) horizontal and (b) diagonal directions across the periodically gray level mask.

fied Eq. (3) has been used in Ref. [7] to investigate the front propagation on a slightly modulated curved surface.

In our experiments we used a mask with gray level distribution as shown in Fig. 1. The light transmitted through such a mask has an intensity that can be described by

$$I = I_0 - C\cos(bx)\cos(by) \tag{4}$$

with a median gray value I_0, a small gray level amplitude C, and the wave vector $b = 2\pi/\lambda$. In this planar system λ denotes the wavelength of the gray level mask. The nonuniform illumination of the planar reaction layer results in corresponding variations of the propagation velocity V_0. High light intensity reduces the wave velocity, whereas an intensity lower than I_0 increases the propagation velocity. Expanding the eikonal equation (2) for a uniform medium, one obtains

$$V = V_0 + B\cos(bx)\cos(by) - DK \quad (B \ll V_0) \tag{5}$$

to describe the propagation of light-sensitive excitation waves. The amplitude of the velocity change is indicated by B. Note that excitation wave propagation in nonuniform medium composed of straight stripes was experimentally studied in Refs. [18,21].

The small modulation amplitude B induces only small deformations of the initially flat wave front. For theoretical analysis the linear approximation of the kinematical equation can be used if the front deformations are considered to be sufficiently small $(K \ll b \ll V_0/D)$. In this case one can neglect the nonlinear and higher order terms in the basic kinematical Eq. (3) to obtain the reduced equation

$$\frac{\partial K}{\partial t} + \frac{\partial^2 V}{\partial \ell^2} = 0. \tag{6}$$

For explaining the effects in arbitrary propagation directions we need a comoving coordinate system as shown in Fig. 2.

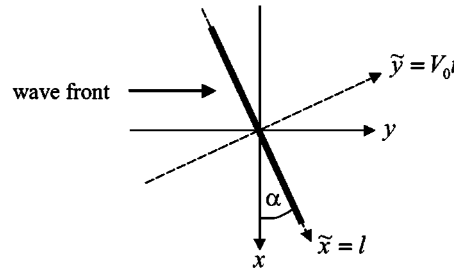

FIG. 2. Schematic figure of the coordinate transformation into the comoving coordinate system.

First we performed the coordinate rotation

$$x = \tilde{x}\cos\alpha - \tilde{y}\sin\alpha,$$

$$y = \tilde{x}\sin\alpha + \tilde{y}\cos\alpha,$$

with α being the angle between the front and the x axis. In this new coordinate system the x axis corresponds to the arclength ℓ of the front which propagates along the y axis at a velocity V_0. Now this coordinate system is moving together with the wave and the velocity of the front can be specified as

$$V(\ell,t) = V_0 + \frac{B}{2}[\cos(\kappa_1\ell - \omega_1 t) + \cos(\kappa_2\ell + \omega_2 t)] - DK, \tag{7}$$

where $\kappa_1 = \sqrt{2}b\cos\beta$, $\omega_1 = \sqrt{2}bV_0\sin\beta$, $\kappa_2 = \sqrt{2}b\sin\beta$, and $\omega_2 = \sqrt{2}bV_0\cos\beta$ with $\beta = \alpha + \pi/4$. Then we substitute Eq. (7) into Eq. (6). Using the Fourier transform technique the resulting equation can be solved analytically, yielding,

$$K(\ell,t) = \frac{B}{2}\left[\frac{\kappa_1^2}{\sqrt{D^2\kappa_1^4 + \omega_1^2}}\cos(\kappa_1\ell - \omega_1 t + \Theta_1) + \frac{\kappa_2^2}{\sqrt{D^2\kappa_2^4 + \omega_2^2}}\cos(\kappa_2\ell + \omega_2 t - \Theta_2)\right], \tag{8}$$

with $\tan\Theta_1 = \omega_1/(D\kappa_1^2)$ and $\tan\Theta_2 = \omega_2/(D\kappa_2^2)$.

The evolving shape of the wave front given by Eq. (8) in the comoving system corresponds to a superposition of two counterpropagating waves. The angle of the propagation direction is included in the coefficients κ_1, ω_1, κ_2, and ω_2. Therefore, the interaction strongly depends on this angle. We consider two particular cases.

First, the "horizontal case" ($\alpha = 0$ and therefore $\beta = \pi/4$) with wave propagation parallel to the y axis. For this value of the angle β the coefficients become $\kappa_1 = \kappa_2 = b$ and $\omega_1 = \omega_2 = bV_0$. Substituting these values into Eq. (8) we obtain

$$K(\ell,t)_{\mathrm{horiz}} = \frac{Bb}{\sqrt{D^2b^2 + V_0^2}}\cos(b\ell)\cos(bV_0 t - \Theta), \tag{9}$$

where $\Theta = V_0/(Db)$. Equation (9) can be interpreted as a "standing wave" in the comoving frame with a spatially and a temporally oscillating cosine function that causes deforma-

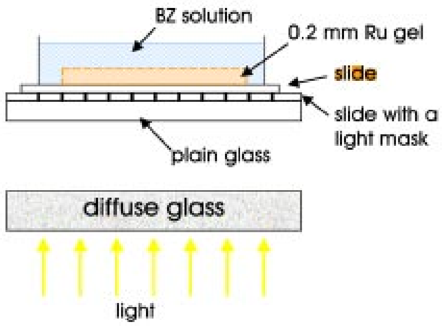

FIG. 3. Schematic drawing of the experimental setup. The 0.2-mm-thick ruthenium gel is placed on a transparency and then covered with the BZ solution. The light is homogenized with a diffuse glass and reaches the reaction system after transmission through the gray level mask.

tions of the initially flat front. The spatial period is the same as that of the gray level mask in Fig. 1.

Second, in the "diagonal case" (e.g., $\alpha=\pi/4$ and $\beta=\pi/2$) with diagonal wave propagation, the coefficients become $\kappa_1=0$, $\omega_1=\sqrt{2}bV_0$, $\kappa_2=\sqrt{2}b$, and $\omega_2=0$. Now Eq. (8) loses the time dependence and the solution can be written as

$$K(\ell)_{\mathrm{diag}}=\frac{B}{2D}\cos(\sqrt{2}b\ell). \tag{10}$$

Unlike the horizontal case, the spatial period of the wave front is now reduced by a factor $\sqrt{2}$ and its shape remains constant in time.

Now we turn to the experiments in which the modulated mask was applied to the light-sensitive BZ reaction. Ferroin, the normally used redox catalyst of BZ waves, is replaced by the *tris*(2,2′-bipyridine)ruthenium(II) complex $(Ru(bpy)_3^{2+})$ [10]. The reduced state of this catalyst promotes the autocatalytic production of $HBrO_2$, the crucial activator and propagator species. Illuminating the catalyst produces the photochemically excited state $(Ru^*(bpy)_3^{2+})$ which then catalyzes the production of the inhibitor species Br^- [22] and decreases the excitability and velocity of excitation waves [23]. By changing the applied illumination to the system it is possible to control the local excitability and thus the dynamics of the excitation waves [24].

The catalyst $(Ru(bpy)_3^{2+})$ (Ru) was immobilized in a silica gel matrix (Fluka) [25] in order to avoid hydrodynamic perturbations [26] and to increase the photosensitivity of the Ru-BZ system [27]. For decreasing the distance between the gel and the gray level mask, the gel with a thickness of 0.2 mm was placed on a transparency as shown in Fig. 3.

The stock solutions of 2.0*M* NaBr, 2.0*M* $NaBrO_3$, and 4.0*M* malonic acid (all from Riedel–de Haën) were prepared in distilled water. The catalyst $(Ru(bpy)_3^{2+})$ (21.4 m*M*, Johnson Matthey) was prepared in 25 m*M* H_2SO_4. No further treatment was applied to H_2SO_4 (5*M*, Roth). To make the reaction solution more homogeneous and to increase the volume of the chemical components we used two different solutions which were poured successively onto the gel (see Ref. [28]). Disregarding the bromination of malonic acid, the initial concentrations in the gel matrix were calculated as follows: 390 m*M* H_2SO_4, 173 m*M* malonic acid, 90 m*M* NaBr, 200 m*M* $NaBrO_3$, and 4.20 m*M* $(Ru(bpy)_3^{2+})$.

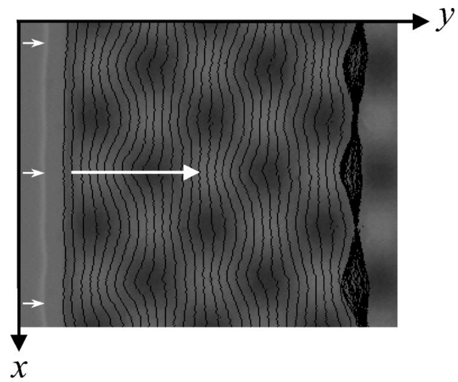

FIG. 4. Experimental data of an excitation wave, propagating in the horizontal direction, as indicated by the long white arrow, over a periodically illuminated area (4). The bright line in front of the three small arrows on the left hand side of the image corresponds to the initial, nearly flat front in the homogeneously illuminated region. The time interval between the 30 consecutive front shapes is $\Delta t=20.0$ s. The 6th to 30th front contours are superimposed at the last position to show the deformations and the resulting standing wave, as predicted in Eq. (9). Image area: 39.3×28.7 mm^2.

Placing a straight silver wire onto the gel in the reaction solution causes the appearance of flat excitation waves. To accelerate the initiation, the silver wire was protected against the light by inserting a black paper between the light mask and the transparency with the gel. The two-dimensional transmission of blue light through the system was detected with a monochrome charge-coupled-device camera (Hitachi KP-M1 CCIR, 758 pixel×576 pixel). Single frames were digitized online with a rate of 1.0 frame/s using an image-acquisition card (Data-Translation DT3155). The digital data were analyzed later on a personal computer.

The gray values for the mask as shown in Fig. 1 were calculated with a 8-bit resolution and printed on transparencies using a laser printer HP Laserjet 5P/5MP Postscript with 600 dpi. The ratio between the intensity of the incident light and the light transmitted through the printed transparency had to be optimized. If the gray value is too high, the contrast between the front and the mask is too low. Consequently it is difficult to detect the wave position. For this reason the minimum gray value was limited to 0.25% of the maximum gray value, and the average light intensity I_0 was set to 0.33 mW/cm^2 with an amplitude C of 0.22 mW/cm^2.

For the experiments with wave propagation in the diagonal direction we cut the transparency diagonally and placed the mask with the cut side parallel to the flat wave front. For the horizontal case the masks were used without alterations. The gray level masks used for the experiments had a wavelength λ of 10 mm.

The deformations of an initially flat excitation front propagating in the horizontal direction across the periodi-

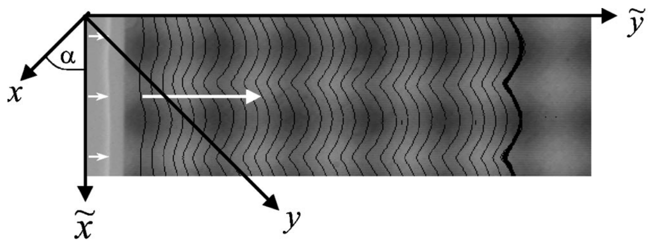

FIG. 5. Experimental data of an excitation wave, propagating in the diagonal direction, as indicated by the long white arrow, across a periodically illuminated area (4). The bright line in front of the three small arrows in the left hand side of the image corresponds to the initial, nearly flat front in the homogeneously illuminated region. The time between the 31 consecutive front lines is $\Delta t = 20.0$ s. The last 16 front positions are superimposed. As predicted in Eq. (10) there are no temporal changes in the front shape. Image area: 47.9×16.0 mm^2.

cally illuminated Ru-BZ system are shown in Fig. 4 in aseries of 30 consecutive snapshots of the front shape ($\Delta t = 20.0$ s). In the left part of the image one can see the initiated, nearly flat front in the homogeneously illuminated part. After propagating across the gray level mask for about 60 s the front shows significant deviations from its initially flat geometry. These deformations are superimposed for same y values at the last position resulting in the predicted ''standing wave'' of Eq. (9) with periodical knots in the front shape evolution.

Figure 5 shows 31 consecutive snapshots ($\Delta t = 20.0$ s) of the initially flat excitation front propagating in the diagonal direction through the modulated Ru-BZ system. The initiated, nearly flat wave front can be seen in the homogeneously illuminated left part of the image. After a short time the wave has reached the periodically illuminated gray level mask and is being deformed. Initially, these deformations are only slight but will increase for some time. The last 16 wave fronts, which have a constant front undulation, are superimposed at the last position.

The visible distinction of the front curves from sinusoidal shapes is due to the fact that the illumination is not slightly modulated and, therefore, the contribution of the nonlinear item in Eq. (3) is not negligible. On the other hand the main theoretical predictions (''standing wave'' in ''horizontal case'' and stationary periodical shape of the front in ''diagonal case'') are in perfect agreement with experimental results.

From the general solution, which is valid for front propagation in arbitrary directions we extracted two important special cases. Note that different results have been obtained in Ref. [7] for the front evolution on nonuniformly curved surfaces. However, the front dynamics that can be indicated as a standing wave as shown in Fig. 4 of this paper for the horizontal case has been found for the diagonal case in Ref. [7]. The time independent spatial deformation for wave propagation in the diagonal direction (Fig. 5) in this light modulated system shows interesting similarities to the horizontal case in Ref. [7]. The only differences are the temporal oscillations of those parts of the front shape that lag behind during the propagation across the curved surface. These were found in Ref. [7] but do not appear in this study, which is a result of the existence of κ_1^2 and κ_2^2 in Eq. (8) in the upper part of the fractions. They do not appear in the analytical result of Ref. [7]. In this case, it is not possible to set one part of the sum equal to 0 if $\kappa_1 = 0$ or $\kappa_2 = 0$.

The work reported in this paper shows that the dynamics of light-sensitive excitation waves propagating in a periodically modulated Ru-BZ system performs a complex spatiotemporal process. Depending on the angle between the front and the modulated medium we obtained two simple equations of wave evolution. For the front shape of waves propagating in a horizontal direction we get a spatial and temporal dependence [Eq. (9)], whereas front shapes of waves propagating in a diagonal direction are only spatially dependent [Eq. (10)]. The reasonable good agreement between the theoretical and experimental results supports the theoretical approach developed for periodically modulated systems elaborated in a recent work [7]. There we emphasized that this theoretical approach can be applied to a variety of systems, in which the velocity varies by changing the excitability. Here we have shown the first application of this theory to a periodically illuminated light-sensitive BZ system.

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