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LETTERS

On the Phase Dynamics in the BZ Reaction

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We have studied the phase dynamics in an oscillatory chemical system (Belousov−Zhabotinsky reaction). The phase distribution and isophase lines in the 2D phase space were reconstructed. The dynamics proved to be well described in terms of the Burgers equation. The phase dependence of the coefficients of the equation was taken into account to estimate the region of the applicability of the Burgers equation.

1. Introduction

The description in terms of a nonlinear phase diffusion equation[1] allows one to understand the basic features of the dynamics of oscillatory chemical systems. Particularly, this approach was recently applied to the Belousov−Zhabotinsky (BZ) reaction to study phase waves and dephasing waves[2,3] and a phase rotor.[4−6]

Conventionally, the nonlinear phase diffusion equation[1]

$$\frac{\partial \phi}{\partial t} = \omega_0 + D\nabla^2\phi + A|\nabla\phi|^2 \qquad (1)$$

describes the instantaneous frequency of oscillations $\partial\phi/\partial t$ as a sum of three terms: the frequency of bulk oscillations ω_0, a diffusion-like term proportional to the Laplacian of phase $\nabla^2\phi$, and a term proportional to the squared gradient of phase $|\nabla\phi|^2$. The equation equivalent to eq 1 is known in physics as the Burgers equation.

The coefficients D and A are usually assumed to be constants. Their values for the BZ reaction were recently reported in ref 3. Theoretically,[1] these coefficients are obtained by averaging some scalar phase-dependent functions $D(\phi)$ and $A(\phi)$ over the period of oscillations. These quantities are given by:

$$D(\phi) = \nabla_u\phi D \frac{d\mathbf{u}_0}{d\phi} \qquad (2)$$

$$A(\phi) = \nabla_u\phi D \frac{d^2\mathbf{u}_0}{d\phi^2}$$

where the vector $\mathbf{u}_0(\phi)$ is a point on the stable limit cycle in the phase space $\{\mathbf{u}\}$, $\nabla_u\phi$ is the gradient of phase in the phase space at $\mathbf{u} = \mathbf{u}_0$, D is the matrix of diffusion coefficients in the original reaction-diffusion equation. The details of the derivations and discussion of the meaning of the above formula can be found in ref 1. For our purpose it is important to note that in the case of equal diffusion coefficients, which holds approximately for many chemical systems, $D(\phi)$ becomes a constant. However, this is not the case for $A(\phi)$.

In this paper we present estimations of the dependence of A on the phase ϕ. $A(\phi)$ is determined in such a way that its substitution into eq 1 allows one to correctly reproduce a family of traveling waves obtained in the numerical simulations of the BZ reaction. The change of the shape of function $A(\phi)$ with the wavenumber k is studied. We also plot isophase lines and

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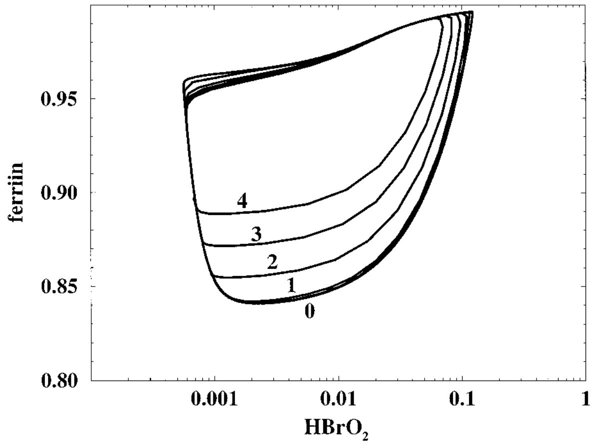

Figure 1. Dependence of the shape of the limit cycle on the wavenumber k. The curves marked as 0−4 correspond to $k = 0$, 20.8, 30.5, 40.8, and 54.2 rad/cm, respectively. $k = 54.2$ rad/cm is close to the maximum possible in the medium.

a distribution of the phase as a function of main parameters of the BZ reaction: bromous acid and ferriin.

2. Results

We used a two-variable model of the BZ reaction[7] with rate constants estimated in ref 8 to simulate an oscillatory chemical system

$$\frac{dx}{d\tau} = \frac{1}{\epsilon}\left[x(1-x) - \left(2q\alpha\frac{z}{1-z} + \beta\right)\frac{x-\mu}{x+\mu}\right] \qquad (3)$$

$$\frac{dz}{d\tau} = x - \alpha\frac{z}{1-z}$$

where

$$\mathrm{Fe(phen)}_3^{3+} = Cz, \quad \mathrm{HBrO}_2 = \frac{k_1A}{2k_4}x, \quad \epsilon = \frac{k_1A}{k_4C},$$

$$\alpha = \frac{k_4K_8B}{(k_1Ah_0)^2}, \quad \mu = \frac{2k_4k_7}{k_1k_5}, \quad t = \frac{k_4C}{(k_1A)^2h_0}\tau, \quad \beta = \frac{2k_4k_{13}B}{(k_1A)^2h_0},$$

$$C = [\mathrm{Fe(phen)}_3^{2+} + \mathrm{Fe(phen)}_3^{3+}], \quad A = [\mathrm{NaBrO_3}],$$

$$B = [\mathrm{CH_2(COOH)_2}], \quad h_0 = \text{acidity function},$$

$$q = 0.6 \text{ is a stoichiometric factor}$$

The rate constants k_i are:

$$k_1 = 17.8\ \mathrm{M^{-2}\,s^{-1}}, \quad k_4 = 3023\ \mathrm{M^{-1}\,s^{-1}},$$

$$k_5 = 1.78 \times 10^6\ \mathrm{M^{-2}\,s^{-1}}, \quad k_7 = 2.67\ \mathrm{M^{-2}\,s^{-1}},$$

$$K_8 = 3.56 \times 10^{-6}\ \mathrm{M\,s^{-1}}, \quad k_{13} = 1.78 \times 10^{-7}\ \mathrm{s^{-1}}$$

To study spatiotemporal effects, we added diffusion terms to eqs 3

$$\frac{dx}{d\tau} = F(x,z) + \nabla_\rho^2 x \qquad (4)$$

$$\frac{dz}{d\tau} = G(x,z) + \delta\nabla_\rho^2 z$$

$$\rho_i = r_i\left[\frac{k_1^2A^2h_0}{k_4CD_x}\right]^{0.5}$$

where $F(x,z)$ and $G(x,z)$ are the right-hand sides of eqs 3, ρ denotes scaled spatial coordinates, ∇_ρ^2 is the Laplacian operator with respect to the coordinates ρ, and $\delta = D_z/D_x$ is the ratio of the diffusion coefficients, assumed to be unity here.

The model has been verified experimentally to adequately simulate spatiotemporal phenomena in the real BZ reaction.[3,6,8−10] The numerical values of the model parameters used in this work were identical with those used in ref 3. This set of parameters when used with eqs 3 and 4 was experimentally tested to be suited for simulations of phase-wave and trigger-wave dynamics.[2,3,6]

To reconstruct phase distributions, we simulated periodic traveling waves of different wavenumbers k. For such waves the dynamics of any point of the medium can be presented by a closed loop (limit cycle) in the phase space. The limit cycles at different values of k are shown in Figure 1.

It is seen that there are only little deviations in the shape as long as k remains small (curves 0, 1). However, starting from curve 2, an increase of k results in a marked shrinking of the limit cycle (Figure 1).

The limit cycle corresponding to 0 k (i.e. to bulk oscillations) was calculated using eqs 3. It was calibrated in such a way that for any point on this limit cycle a unique phase in the range from 0 to 2π was assigned (see the description of the procedure in ref 3). To estimate the phase for points that do not lie on the limit cycle, the following assumption was used:[11] the phase at a point **P** in the phase space was assumed to be equal to the phase at a point $\mathbf{P}_c$ lying on the limit cycle, provided that $\mathbf{P} \rightarrow \mathbf{P}_c$ at $t \rightarrow \infty$ when the system evolves according to the diffusionless eqs 3. Such a definition provides a natural and unambiguous algorithm for calculating the phase.

The phase distribution calculated in this way is shown in Figure 2a. The isophase lines, i.e., lines connecting the points with equal phases, are presented in Figure 2b. Notice that there is a region where the isophase lines are condensed. The analysis shows that this region coincides with the location of unstable branch of the nullcline for the fast variable: $\{F(x,z) = 0\}$. Actually, near the nullclines a small deviation in the position of a point results in a large deviation when the point approaches the limit cycle; at the point of intersection of the nullclines (fixed point) the phase is not defined at all, and this is a so-called phaseless point.

The calculated distribution $\phi(x,z)$ allowed us to estimate the dependence of the coefficients of the Burgers equation (eq 1) using eq 2. For the case of equal diffusion coefficients, $D(\phi)$ becomes a constant as expected; $A(\phi)$ proved to have a complicated dependence on ϕ as presented in Figure 3a. $A(\phi)$ has a two distinct maxima near $\phi = 0$ and $\phi = 1.2$, corresponding to the rise and drop of bromous acid, and a large plateau for $1.5 < \phi < 5$ corresponding to the gradual decrease of ferriin.

In eq 2 it is assumed that the state points stay sufficiently close to the limit cycle. To avoid this constraint, which is necessary for traveling waves with a not too small k, we calculated the dependence $A(\phi)$ directly from eq 1. For this purpose we carried out computer simulations of a pulse circulating in a ring in a way similar to that used for calculation of the dispersion relation in ref 3. The calculated distributions of species $x(r,t)$ and $z(r,t)$ were used to reconstruct the phase distribution $\phi(r,t)$ at every point r and moment t as described above. Then, after estimating the appropriate derivatives and substituting the data to eq 2, it was possible to estimate $A(\phi)$.

It is seen that for $k < 30$ rad/cm the shape of $A(\phi)$ (Figure 3b) is similar to that estimated from analytical formula (Figure 3a). For larger k an additional negative spike near $\phi = 4.8$ rad occurs. The appearance of this spike is clearly seen in a plot of the dependence of $A(\phi,k)$ Figure 2c.

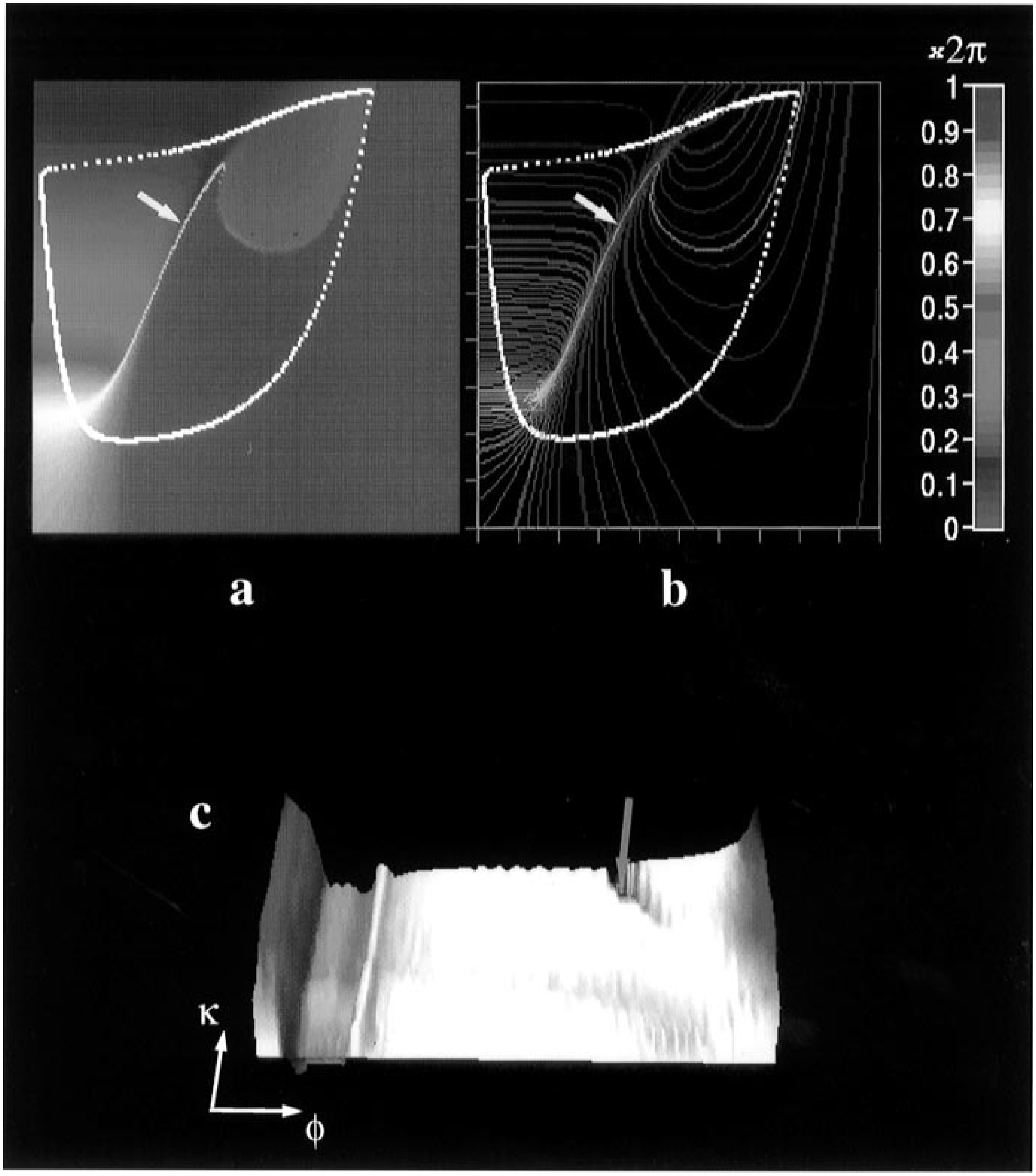

Figure 2. Phase distribution (a) and isophase lines (b) on the plane “bromous acid”−“ferriin”. Limit cycle is shown by white dots. Yellow arrows point to a place where isophase lines are condensed that corresponds to the unstable branch of the nullcline $\{F(x,z) = 0\}$. (c) The coefficient A in eq 1 as a function of ϕ and k. Note that A hardly depends on k for small k, but for large k an additional pit occurs (marked with a blue arrow). ϕ ranged from 0 to 2π rad; k ranged from 10 to 32 rad/cm.

3. Discussion

In this paper we presented evaluations of the distribution of the phase for a realistic model of a chemical system. We used this distribution to estimate the dependence of $A(\phi)$; surprisingly, it proved to be a rather complicated function (Figure 3). The particular shape of this function is important for short term behavior.

Little change of the shape of $A(\phi)$ with k for $k < 30$ rad/cm says indicates in this range the Burgers equation (eq 1) is a good model for the description of the dynamics for the both short and long term behavior.

It should be emphasized that the range $0 < k < 30$ rad/cm is a surprisingly wide range of wavenumbers, because, formally speaking, the theory of phase dynamics is applicable for small perturbations of the limit cycle that expected for $k \rightarrow 0$.

It should be noted that a critical value of $k \approx 30$ rad/cm was recently found to occur while analyzing the dispersion relation.[3] This was the point of inflation of the dispersion curve that is

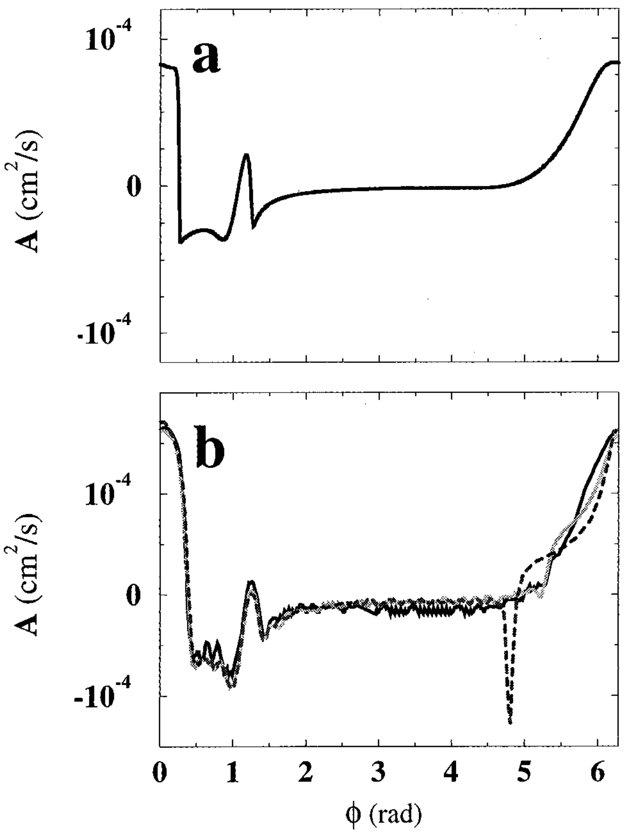

Figure 3. Dependence of the coefficient A in eq 1 on ϕ estimated theoretically (a) and from computations (b). The curves in (b) correspond to different values of k: a black line for $k = 12.6$, a gray line for $k = 20.8$ and a dashed line for $k = 30.5$. Note that for $k < 30$ the shape of $A(\phi)$ is similar to that estimated theoretically.

believed to separate phase-wave and trigger-wave branches of the dispersion relation. According to that paper, the dynamics in the system significantly changes while crossing the inflation point. Thus, the observed change of the shape of $A(\phi)$ for $k \approx 30$ rad/cm can be associated with a transition from the phase-wave to the trigger-wave dynamics.

In this paper we used the definitions of frequency ω and wavenumber k as in ref 3, i.e. as derivatives of the phase $\phi(x,t)$ on time and space. An obvious alternative definition of these quantitatives is $\omega = 2\pi/T$ and $k = 2\pi/\lambda$, where T and λ are the period and wavelength of a wave train. The later definition is frequently used in the literature on wave dynamics in the BZ reaction, but it requires "a wave train" to occur. The other definition involves several subtle points as well: there are regions where the phase distribution is steep, and there are points of undetermined phase. However, the definition is more universal; that is why it is used in this work.

A significant rise in the density of isophase lines near the slow branch of the nullcline $\{F(x,z) = 0\}$ (Figure 2b) provides an interesting method for an experimental analysis of oscillatory systems. Actually, if the regions where isophase lines are dense are plotted, it is possible to reconstruct partly the nullclines of the system, which seems to provide a unique experimental approach for a system for which there is no reliable model.

It should be noted that in ref 11 there was presented a distribution of isophase lines for the FitzHugh–Nagumo (FHN) model, which looks like that in Figure 2b. Similarity of the isophase lines geometry in the BZ reaction and in the FHN model, which is used in biology to simulate nerve and cardiac pulses, emphasizes that the dynamics studied is of universal nature.

This paper is devoted to the study of the dynamics of phase waves in the BZ reaction. Such waves have longer wavelengths in comparison with the well-studied trigger waves. However, it is not realistic for the typical scale of phase waves to be dozens of centimeters, but it can fall to less than 2 mm, as was experimentally demonstrated in a recent study.[6] In fact, by varying the composition of the reaction (i.e. increasing the concentration of sulfuric acid or of sodium bromate), the wavelength can be made even shorter.

Finally, we would like to emphasize that in the analysis presented above we did not rely on specific details of the BZ reaction. Thus, we believe that the methods based on the reconstruction of phase distribution can be applied to wide spectrum of nonlinear systems.

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