

Two-dimensional Numerical Simulation Method for Convective Flow Structure Induced by Chemical Concentration Waves

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Keywords: Belousov-Zhabotinsky (BZ) reaction, elastic surface, Marangoni effect, Navier-Stokes equation.

Abstract: This paper presents a two-dimensional numerical simulation method for modeling a convective flow structure induced by chemical concentration waves of Belousov-Zhabotinsky (BZ) reaction in a two-dimensional rectangular domain of horizontal space and vertical depth. The method assumes a scenario in which an air-liquid interface of the BZ chemical solution has an elastic property and the Marangoni effect drives the surface motion of the interface. As a result of the surface motion, a convective flow is organized in the bulk of the chemical solution. The bulk flow of the chemical solution is described with the Navier-Stokes equations, and the chemical reaction is described with the Oregonator model. Thus, we couple the three systems of the bulk flow, the chemical reaction and the surface motion described with an elastic equation in the numerical simulation method. Results of several numerical simulations performed with the method show that a single chemical concentration wave propagates with a broad convective flow structure and a chemical concentration wave train propagates with a global flow structure. These flow structures are similar to those observed in real laboratory experiments.

1 INTRODUCTION

Pattern dynamics have been observed in a solution layer of the Belousov-Zhabotinsky (BZ) reaction system (Zaikin and Zhabotinsky, 1970). A reaction-diffusion model such as the Oregonator model describes the dynamics organizing the spatial patterns of chemical concentration distributions. The model represents an assembly of nonlinear chemical oscillators coupled with the diffusion of molecules (Field et al., 1972; Keener and Tyson, 1986; Jahnke et al., 1989). Thus, the target patterns and spiral waves of chemical pattern dynamics are understood within the framework of chemical reaction and molecular diffusion.

Pattern dynamics of flow will arise with propagating chemical waves. For example, oscillatory flow and flow waves appear in spiral chemical waves, and a strong flow velocity of convection appears in a single chemical wave with accelerating propagation. In contrast to the reaction-diffusion system, only a few studies for modeling and numerical simulation have examined the problem of self-organized flow structures in the BZ solution.

There are several evidences showing that a chem-

ical wave train or a single chemical wave induces a convective flow in a shallow layer of the chemical solution (Miike et al., 2010). There is a correlation between the two temporal changes of surface flow velocity and chemical concentration in the chemical wave train (Miike et al., 1988); a global surface flow structure having a circular or spiral shape travels with a chemical wave train (Matthiessen and Müller, 1995; Sakurai et al., 1997; Sakurai et al., 2003). Surface flow velocity at the center of a petri dish begins to change just after triggering a single chemical wave at an edge of the dish; the direction of the surface flow velocity changes from anti-parallel to parallel to the traveling direction of the chemical wave at the passage of the chemical wave (Miike et al., 1993).

There are two effects that induce flow in a chemical solution: the gravity effect induced by a density gradient and the Marangoni effect induced by a surface tension gradient. Matthiessen et al. (1996) proposed a model that takes account of both the gravity and Marangoni effects due to the concentration distributions of chemical species, and performed numerical simulation of organized flow structure. By quantitatively comparing the flow structure obtained

through their numerical simulation with that obtained in laboratory experiments, they concluded that the Marangoni effect due to a chemical concentration gradient is more dominant than the gravity effect in a single chemical wave (Matthiessen et al., 1996). Yoshikawa et al. (Yoshikawa et al., 1993) and Inomoto et al. (Inomoto et al., 2000) measured the dependence of surface tension on the concentrations of chemical species in the BZ solution; these experimental results support the results of Matthiessen et al. (1996).

More recently, Rossi et al. found chemical concentration waves segmented in the BZ reaction system (Rossi and Liveri, 2009), and performed its numerical simulation with the gravity and Marangoni effects (Rossi et al., 2012). They explored how the chemical concentration distributions and flow structure change with a thickness of the chemical solution layer and excitability of the chemical reaction. As results, they found that the segmented waves are caused in a thick chemical solution and with high excitability, and in that case the gravity effect is more effective than the Marangoni one in the segmented waves. Rongy et al. focused on the front of a chemical concentration wave propagating in a shallow layer of a chemical solution, and performed its numerical simulation with the solutal Marangoni effect under a variety of thickness of the solution layer without the gravity effect (Rongy and De Wit, 2007). They confirmed the dependence of a traveling speed on the thickness; the speed increases with the thickness of the solution. These results of numerical simulation were performed on the situation of propagating chemical reaction wave(s) in a thick solution layer more than 1 mm.

Nomura et al. (2004) assumed that the air-liquid interface of the chemical solution has an elastic property. Then, they proposed a one-dimensional model that consists of the Oregonator model and an elastic equation driven by the Marangoni effect. The one-dimensional model reproduced the global surface flow structure observed in a chemical wave train, and the surface flow velocity induced in far from a single chemical wave.

This paper presents a two-dimensional numerical simulation method for modeling convective flow structures induced by chemical concentration waves of BZ reaction in a two-dimensional rectangular domain of horizontal space and vertical depth. According to the result of Nomura et al. (2004), we assume that the air-liquid interface of the chemical solution is governed by the elastic equation; the bulk flow of the solution is governed by the Navier-Stokes equations. Although deformation of the interface was observed in previous laboratory experiments (Sakurai

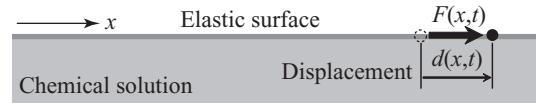


Figure 1: One-dimensional model for the air-liquid interface of a chemical solution. The model assumes that the surface has an elastic property. The surface tension gradient of the Marangoni effect induces a force $F(x,t)$ [see Eq. (5)], which induces surface displacement $d(x,t)$ of the elastic surface [see Eq. (3)].

et al., 2004), we do not consider the deformation in this paper. Thus, by coupling the three systems of the bulk flow, the chemical reaction and the surface motion, we carry out numerical simulation of the two dimensional system. Simulation results show that a broad convective flow structure is organized with a single chemical propagation wave and a global flow structure is organized with a chemical wave train.

2 MODELING AND NUMERICAL SIMULATION METHOD

2.1 Modeling Study

In the BZ reaction system, concentration distributions of chemical species u and v are governed by a set of reaction-diffusion equations with convection terms, as follows:

$$\begin{aligned} \frac{\partial u}{\partial t} &= D_u \nabla^2 u + R_u(u, v) - \mathbf{V} \cdot \nabla u, \\ \frac{\partial v}{\partial t} &= D_v \nabla^2 v + R_v(u, v) - \mathbf{V} \cdot \nabla v, \end{aligned} \quad (1)$$

in which t denotes time, D_u and D_v are the diffusion coefficients of $\nabla^2 u$ and $\nabla^2 v$, and $\mathbf{V} \cdot \nabla u$ and $\mathbf{V} \cdot \nabla v$ are convection terms. The functions $R_u(u, v)$ and $R_v(u, v)$ are the nonlinear chemical reaction terms, which are described by

$$\begin{aligned} R_u(u, v) &= \frac{1}{\varepsilon} \left[u(1-u) - fv \frac{u-q}{u+q} \right], \\ R_v(u, v) &= u - v, \end{aligned} \quad (2)$$

in the Oregonator model with positive constants of f and q and a positive small constant ε (Keener and Tyson, 1986; Jahnke et al., 1989).

According to the scenario proposed by (Nomura et al., 2004), we also assume that the air-liquid interface of the chemical solution has an elastic property, and the Marangoni effect induces horizontal surface displacement, as shown in Fig. 1. An elastic equation defined in space x and time t describes surface dis-

placement $d(x, t)$ induced by a force $F(x, t)$, as follows:

$$\frac{\partial^2 d}{\partial t^2} + a \frac{\partial d}{\partial t} = D_d \nabla^2 d + F(x, t), \quad (3)$$

in which a and D_d are constants. A temporal change of surface displacement d brings about the surface flow velocity of

$$V_s = \frac{\partial d}{\partial t}. \quad (4)$$

The function $F(x, t)$ represents the force induced by the surface tension gradient of the Marangoni effect. If we assume that the distribution of the chemical species $v(x, t)$ primarily induces the surface tension gradient (Matthiessen et al., 1996; Yoshikawa et al., 1993), the force $F(x, t)$ becomes

$$F(x, t) = b \frac{\partial v}{\partial x}, \quad (5)$$

with a coefficient b . Thus, the previous model proposed by Nomura et al. (Nomura et al., 2004) connects the Oregonator type reaction-diffusion model [Eqs. (1) and (2)] and the elastic equation [Eq. (3)] through the Marangoni effect of Eq. (5) and the convection terms.

The Navier-Stokes equations describe a flow field in the bulk of the BZ chemical solution. We consider a rectangular domain consisting of the horizontal space x and a vertical depth z . The Navier-Stokes equations defined in the two dimensional space (x, z) can be converted into two equations governing a stream function φ and a vorticity function ω , as shown in

$$\nabla^2 \varphi = -\omega, \quad \frac{\partial \omega}{\partial t} + \frac{\partial \varphi}{\partial z} \frac{\partial \omega}{\partial x} - \frac{\partial \varphi}{\partial x} \frac{\partial \omega}{\partial z} = \mu \nabla^2 \omega, \quad (6)$$

in which $\mathbf{V} = (V_x, V_z) = (\partial \varphi / \partial z, -\partial \varphi / \partial x)$ represents two-dimensional flow velocity and μ represents the kinematic viscosity of the chemical solution. We do not take account of the gravity effect due to the density distribution, as suggested by (Matthiessen et al., 1996).

In the bulk of the chemical solution, the Oregonator model of Eqs. (1) and (2) defined in the two-dimensional space (x, z) describes the chemical concentration distributions of $u(x, z, t)$ and $v(x, z, t)$.

The model proposed here couples the Navier-Stokes equations of Eq. (6) with the Oregonator model of Eqs. (1) and (2), through the one-dimensional elastic equation of Eq. (3). The elastic equation describes the displacement of the air-liquid interface of the chemical solution. Surface flow velocity or surface displacement induces a convective flow in the bulk of the chemical solution. Thus, we make use of the surface flow velocity V_s obtained by the elastic equation as the boundary condition of V_x in the Navier-Stokes equations.

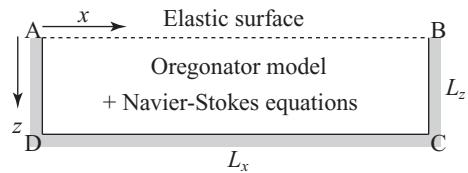


Figure 2: Rectangular domain utilized for modeling the two-dimensional flow field of a chemical solution. The Navier-Stokes equations describe a flow field in the bulk of the chemical solution [see Eq. (6)]; the Oregonator model with convection terms describes the chemical reaction in the domain [see Eq. (1)]. The elastic equation given in Eq. (3) governs the displacement of the air-liquid interface (A–B) of the domain. The right wall (B–C), the bottom (C–D), and the left wall (D–A) are rigid. See Eq. (7) for the boundary conditions. The rectangular domain consists of a horizontal axis x (space) and a vertical axis z (depth); L_x represents the width of the rectangular domain and L_z represents its depth.

2.2 NUMERICAL SIMULATION METHOD

We discretize the model equations of Eqs. (1), (3) and (6) with a finite difference method, in which spatial differences discretizing horizontal space and vertical depth are denoted by δx and δz and a temporal difference is denoted by δt .

On the one-dimensional elastic equation governing the air-liquid interface, we discretized the Laplacian operator ∇^2 in Eq. (3) with the three-point centered difference formula and the Crank-Nicolson scheme. Then, we solve a set of linear equations by the LDU decomposition method.

In the bulk of the chemical solution, we explicitly discretized the Laplacian operator ∇^2 in Eqs. (1) and (6) with the five-point centered difference formula. We discretized the convection terms of Eq. (1) with the two-point upwind scheme. We solved the set of linear equations obtained from $\nabla^2 \varphi = -\omega$ by the successive overrelaxation (SOR) method.

The initial conditions are $u = v = d = \varphi = \omega = 0$ over the one- or two-dimensional space. A single chemical wave can be generated by setting the distribution $u(x, z, t = 0)$ as $u = 1.0$ in a local area. A wave train, namely, a series of chemical waves is generated at a time interval λ .

The Dirichlet boundary condition governs both ends of the surface displacement ($d = 0$). The Neumann boundary condition governs the four sides of the two-dimensional rectangular domain of the two distributions u and v ($\partial u / \partial x = \partial u / \partial z = \partial v / \partial x = \partial v / \partial z = 0$).

On the Navier-Stokes equations, the stream function φ is zero along the four sides, and the vorticity function ω along the four sides: A–B, B–C, C–D and

D-A are governed by

$$\begin{aligned} \text{A-B: } & \omega(i\delta x, 0) = -2[V_s \delta z - \phi(i\delta x, \delta z)] / \delta z^2, \\ \text{B-C: } & \omega((I-1)\delta x, j\delta z) = -2\phi((I-2)\delta x, j\delta z) / \delta z^2, \\ \text{C-D: } & \omega(i\delta x, (J-1)\delta z) = -2\phi(i\delta x, (J-2)\delta z) / \delta z^2, \\ \text{D-A: } & \omega(0, j\delta z) = -2\phi(0, j\delta z) / \delta x^2, \end{aligned} \quad (7)$$

in which V_s represents the surface flow velocity of Eq. (4); the grid point $(i\delta x, j\delta z)$ represents the discrete position of (x, z) . Let $L_x \times L_z$ be the size of the two-dimensional space considered here as shown in Fig. 2. Then, in the boundary conditions of Eq. (7) $I = [L_x/\delta x]$ and $J = [L_z/\delta z]$ represent the total numbers of grid points in space x and depth z .

In the following numerical simulations, finite differences in space, depth and time were fixed at $\delta x = \delta z = 1/5$ and $\delta t = 1/10000$. The parameter settings were fixed at $D_u = 1.0, D_v = 0.6, q = 2.0 \times 10^{-3}, \varepsilon = 0.01$, and $\mu = 6.7$ (Jahnke et al., 1989).

3 NUMERICAL SIMULATION RESULTS

A previous model (Matthiessen et al., 1996; Diewald et al., 1996) connects the Oregonator model of Eqs. (1) and (2) with the Navier-Stokes equations given in Eq. (6) through the Marangoni effect due to a chemical concentration gradient of v along the air-liquid interface. The model takes account of the Marangoni effect as the boundary condition of the surface flow velocity V_x along the air-liquid interface, as follows:

$$\frac{\partial V_x}{\partial z} = M_a \frac{\partial v}{\partial x}, \quad (8)$$

in which M_a is a constant. The boundary conditions on ω for the side walls and bottom of the two-dimensional domain, and those on u, v and ϕ for the four sides of the domain are the same as those of the proposed model. The initial conditions of u, v, ϕ and ω are the same as those of the proposed model. The previous model does not take account of the gravity effect. The discretization methods utilized in the previous model are the same as those in the proposed model.

In order to compare the proposed model with the previous model mentioned above, we carried out two-dimensional numerical experiments on a single chemical wave. Figure 3(a) shows the result of the proposed model; the single chemical wave triggered at the left end travels in the horizontal position approximately $x = 220$ towards the right end. The surface flow velocity anti-parallel to the traveling direction

of the chemical wave induces a flow structure with a counter-clockwise direction in the bulk; this flow structure has some spatial extent in front of the chemical wave. Figure 3(b) shows the result of the previous model (Matthiessen et al., 1996; Diewald et al., 1996). While the single chemical wave is traveling in a similar horizontal position ($x = 220$), a flow structure exists in the vicinity of the chemical wave. There is no spatial extent of the flow structure in front of the chemical wave.

Results of previous laboratory experiments show that some spatial extent of a flow structure exists in front of the single chemical wave. Therefore, we suggest that the proposed model is able to reproduce a more plausible flow structure than the previous model for a single chemical wave.

We carried out additional numerical experiments on a wave train in a two-dimensional domain, in which chemical waves triggered at the left end traveled in the two-dimensional domain towards the right end. Figure 4(a) shows the result of the proposed model. A particular chemical wave organizes a pair of small convection rolls having clockwise and counter-clockwise directions.

Around the middle of the horizontal position in the two-dimensional domain, particular pairs of the convection rolls are almost symmetrical and most of them have similar strength of convection. Compared with these pairs traveling in the middle, those on the left side of the domain lack symmetry and have different strengths. The asymmetrical convection rolls with different strengths induces a global flow structure. In comparison with the results of the proposed model, the result of the previous model do not show such the global flow structure, as shown in Fig. 4(b). Uniform pairs of convection rolls travel maintaining almost uniform strength and symmetry.

In these two-dimensional numerical experiments, the absolute flow velocity obtained by the proposed model was small compared with that obtained using the previous model. Two-dimensional numerical experiments with the proposed model broke down for large values of b and D_d , and we therefore had to choose sufficiently small values of b and D_d to obtain results. In spite of such small values, the proposed model successfully presented the global flow structure. The model is a plausible candidate for simulating the two-dimensional flow structures self-organized in the systems of a single chemical wave and of a chemical wave train.

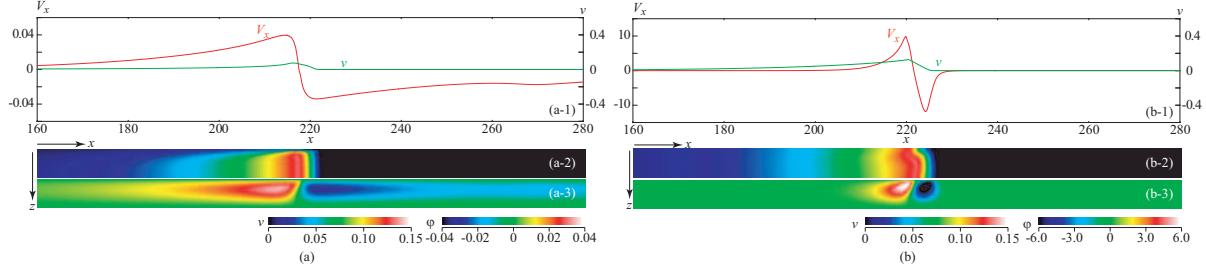


Figure 3: Result of a two-dimensional numerical experiment on a single chemical wave with (a) the proposed model and (b) the previous model (Matthiessen et al., 1996; Diewald et al., 1996). Figures (a-1) and (b-1) show one-dimensional spatial distributions of the concentration v and the flow velocity V_x along the air-liquid interface of the two-dimensional domain in the range of $160 \leq x < 280$. Figures (a-2) and (b-2) show two-dimensional spatial distributions of v , and Figs. (a-3) and (b-3) show distributions of the stream function φ , in the ranges of $160 \leq x < 280$ and $0 \leq z < 5$. The spatial size of the two-dimensional domain was $(L_x \times L_z) = (400 \times 5)$. All the distributions were obtained at $t = 10$. The single chemical wave was triggered at the left-top position at $t = 0$. The parameter settings of Eqs. (2), (3), (6) and (1) were $D_d = 10^3$, $a = 0.5$, $b = 100$ and $f = 2.5$; see Section 2.2 for the other parameter settings.

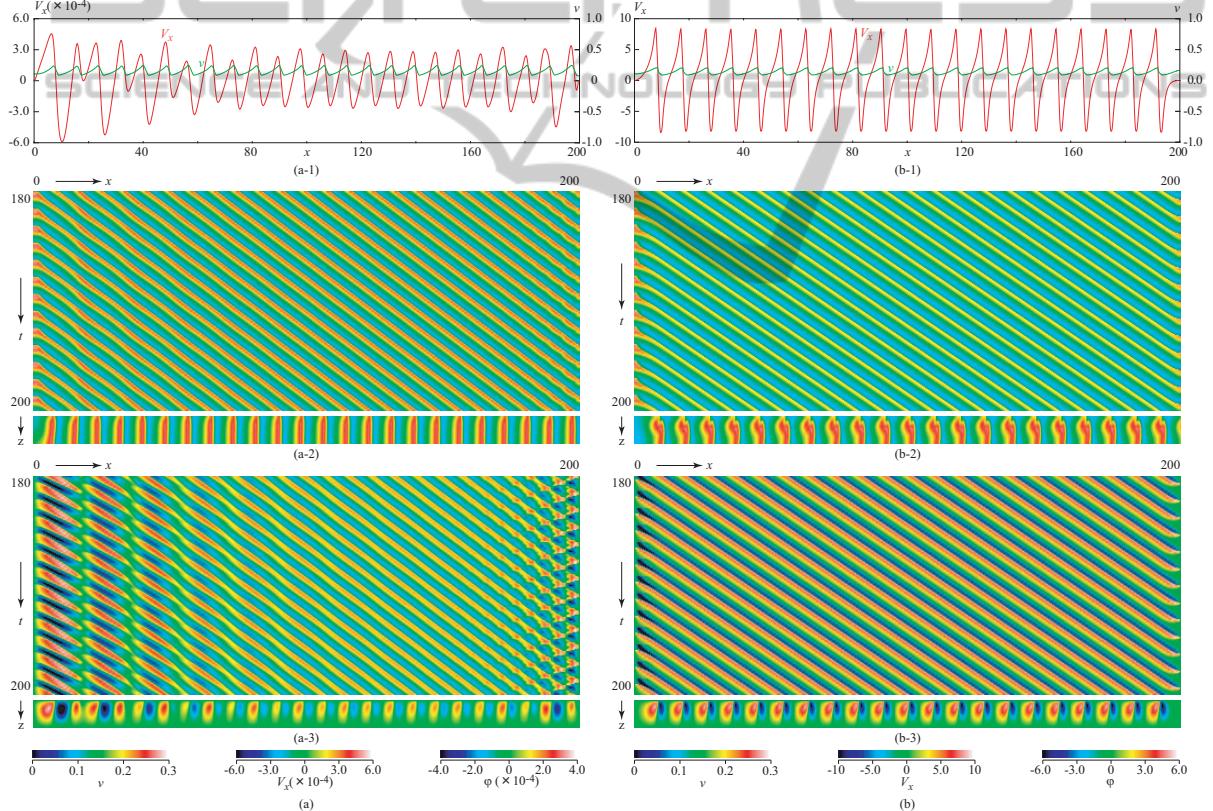


Figure 4: Result of a two-dimensional numerical experiment on a chemical wave train with (a) the proposed model and (b) the previous model (Matthiessen et al., 1996; Diewald et al., 1996). Figures (a-1) and (b-1) show one-dimensional spatial distributions of the concentration v and the flow velocity V_x along the air-liquid interface of the two-dimensional domain at $t = 200$. Figures (a-2) and (b-2) show spatiotemporal plots of v with their two-dimensional spatial distributions at $t = 200$. Figures (a-3) and (b-3) show spatiotemporal plots of V_x with their two-dimensional spatial distributions of the stream function φ at $t = 200$. Chemical waves were triggered at the time intervals of $\lambda = 1.55$ at the left-top position of the two-dimensional domain. The spatial size of the two-dimensional domain was $(L_x \times L_z) = (200 \times 5)$. The parameter settings of Eqs. (2), (3) and (5) were $f = 1.0$, $D_d = 100$, $a = 1.0$ and $b = 0.1$; see Section 2.2 for the other parameter settings.

4 CONCLUSIONS

This paper presented a numerical simulation method for explaining convective flow structures induced by a single chemical wave and a chemical wave train in a chemical solution layer of the BZ reaction. According to the previous result by Nomura et al. (Nomura et al., 2004), the model assumes a scenario in which the surface of the chemical solution has an elastic property. The concentration gradient of a chemical species along the surface induces a surface tension gradient, and brings about displacement of the elastic surface through the Marangoni effect. In addition, the surface displacement causes a bulk flow of the chemical solution, which can be described with the Navier-Stokes equations. Thus, the numerical simulation method proposed here couples an Oregonator type reaction-diffusion model with the Navier-Stokes equations via the elastic equation.

We carried out numerical experiments with the proposed model on a single chemical wave and a chemical wave train. The results of these experiments show that the proposed model reproduces the flow structures observed in laboratory experiments. That is, a flow structure induced by a single chemical wave has some spatial extent in front of the chemical wave; a flow structure induced by a chemical wave train has a global flow structure due to asymmetric convection rolls. A previous model did not predict such the flow structures in our numerical experiments. These results suggest that the assumption of the elastic property helps us to understand flow structures observed in the solution layer of the BZ reaction.

REFERENCES

- Diewald, M., Matthiessen, K., Müller, S. C., and Brand, H. R. (1996). Oscillatory hydrodynamic flow due to concentration dependence of surface tension. *Physical Review Letters*, 77:4466–4469.
- Field, R. J., Koros, E., and Noyes, R. M. (1972). Oscillations in chemical systems. II. Thorough analysis of temporal oscillation in the bromate-cerium-malonic acid system. *Journal of American Chemical Society*, 94:8649–8664.
- Inomoto, O., Abe, K., Amemiya, T., Yamaguchi, T., and Kai, S. (2000). Bromomalonic-acid-induced transition from trigger wave to big wave in the Belousov-Zhabotinsky reaction. *Physical Review E*, 61:5326–5329.
- Jahnke, W., Skaggs, W. E., and Winfree, A. T. (1989). Chemical vortex dynamics in the Belousov-Zhabotinskii reaction and in the two-variable oregonator model. *Journal of Physical Chemistry*, 93:740–749.
- Keener, J. P. and Tyson, J. J. (1986). Spiral waves in the Belousov-Zhabotinskii reaction. *Physica D*, 21:307–324.
- Matthiessen, K. and Müller, S. C. (1995). Global flow waves in chemically induced convection. *Physical Review E*, 52:492–495.
- Matthiessen, K., Wilke, H., and Müller, S. C. (1996). Influence of surface tension changes on hydrodynamic flow induced by traveling chemical waves. *Physical Review E*, 53:6056–6060.
- Miike, H., Miura, K., Nomura, A., and Sakurai, T. (2010). Flow waves of hierarchical pattern formation induced by chemical waves: The birth, growth and death of hydrodynamic structures. *Physica D*, 239:808–818.
- Miike, H., Müller, S. C., and Hess, B. (1988). Oscillatory deformation of chemical waves induced by surface flow. *Physical Review Letters*, 61:2109–2112.
- Miike, H., Yamamoto, H., Kai, S., and Müller, S. C. (1993). Accelerating chemical waves accompanied by traveling hydrodynamic motion and surface deformation. *Physical Review E*, 48:R1627–R1630.
- Nomura, A., Sakurai, T., Miike, H., and Hano, M. (2004). Model for the Belousov-Zhabotinsky reaction and surface flow structure induced by chemical concentration gradients. In *Proceedings of 2004 International Symposium on Nonlinear Theory and its Applications*, pages 363–366, Fukuoka, Japan.
- Rongy, L. and De Wit, A. (2007). Marangoni flow around chemical fronts traveling in thin solution layers: influence of the liquid depth. *Journal of Engineering Mathematics*, 59(2):221–227.
- Rossi, F., Budroni, M. A., Marchettini, N., and Carballido-Landeira, J. (2012). Segmented waves in a reaction-diffusion-convection system. *Chaos*, 22(3):037109 (11 pages).
- Rossi, F. and Liveri, M. L. T. (2009). Chemical self-organization in self-assembling biomimetic systems. *Ecological Modelling*, 220:1857–1864.
- Sakurai, T., Inomoto, O., Miike, H., and Kai, S. (2004). Structure of surface deformation waves induced in spiral pattern in the Belousov-Zhabotinsky reaction. *Journal of the Physical Society of Japan*, 73:485–490.
- Sakurai, T., Miike, H., Okada, K., and Müller, S. C. (2003). Spiral flow wave in a reaction-diffusion-convection system. *Journal of the Physical Society of Japan*, 72:2177–2180.
- Sakurai, T., Miike, H., Yokoyama, E., and Müller, S. C. (1997). Initiation front and annihilation center of convection waves developing in spiral structures of Belousov-Zhabotinsky reaction. *Journal of the Physical Society of Japan*, 66:518–521.
- Yoshikawa, K., Kusumi, T., Ukitu, M., and Nakata, S. (1993). Generation of periodic force with oscillating chemical reaction. *Chemical Physics Letters*, 211:211–213.
- Zaikin, A. N. and Zhabotinsky, A. M. (1970). Concentration wave propagation in two-dimensional liquid-phase self-oscillating system. *Nature*, 225:535–537.