Formation of New Types of Inhomogeneous Spatial Structures in the Chemical Reaction in Imperfect Systems

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ABSTRACT: Taking the system imperfection and the inhomogeneity of the diffusion processes into account derives the extension of a simple chemical reaction model proposed by Schlogl. The Fick equation modification makes the breakdown of the ideality of diffusion. It leads to high-order spatial derivatives of a concentration in an evolution equation. The system imperfection is also taken into account by the excess Gibbs function of a regular solution. It leads to modification of the chemical potential as well as to the dependence of a diffusion coefficient on a reagent concentration. The formation of the spatial inhomogeneous structures being stable during the chemical reaction under definite conditions is due to the breakdown of an ideal system. Certain spatial inhomogeneous structures can exist only in the imperfection system and do not appear in an ideal system. Three new types of spatial inhomogeneous structures appear: periodic, quasi-periodic, and nonperiodic structures. The functions characterizing concentration contain two terms. Note that in the ideal systems, the quasi-periodic and nonperiodic structures cannot exist. This means that such a new spatial structure formation is due to the system imperfection. The parameters characterizing the system imperfection represent the coefficients at nonlinear terms and a high-order spatial derivative in the evolution equation. This permits consideration of a system deviation from the ideal as a significantly nonlinear phenomenon. The conditions of spatial structure stability are determined mainly by parameters that describe the system imperfection.   © 2004 Wiley Periodicals, Inc. Int J Quantum Chem 100: 426–434, 2004

1. Introduction

The chemical reaction description by using nonlinear equations has been carried out for a long time. Investigation of the chemical system properties described by complicated nonlinear differential equations containing a high-order spatial derivative and different types of nonlinear terms [1] are very interesting. The considering of such equations for the different applications is activated in recent years [2, 3].

The extension of a simple chemical reaction model proposed by Schlogl [4] is derived by taking the system imperfection and inhomogeneity of diffusion processes into account. The meaning of the Fick equation modification [5–7] makes the breaking of the ideality of diffusion. It leads to the appearance of high-order spatial derivatives of a concentration in an evolution equation.

The system imperfection also is taken into account by excess Gibbs function of regular solution [8, 9]

$$G = \frac{1}{n} \sum_{i \leq j} w_{ij} n_i n_j,$$

where n is the total mole number, and n_i is the mole number of i-type molecules. The values of w_{ij} are determined by $w_{ij} = (2\varepsilon_{ij} - \varepsilon_{ii} - \varepsilon_{jj})\theta$, where ε_{ij} is an energy of interaction between the molecules of i- and j-types, θ is a constant depending on a liquid state model. The w_{ij} characterizes the system imperfection. In the case of the binary solution it is more convenient to use the positive parameter $w = w_{12}/RT$, where T is temperature and R is the universal gas constant.

Parameter w is the imperfection parameter. Taking w into account leads to modification of the chemical potential and also to the diffusion coefficient dependence on a reagent concentration [10] in the system considered.

The formation of the spatial inhomogeneous structures being stable during the chemical reaction under definite conditions is due to the breakdown of an ideal system. Certain spatial inhomogeneous structures can exist only in the imperfection system and do not appear in the ideal system.

The parameters characterizing the system imperfection represent the coefficients at nonlinear terms and a high-order spatial derivative in the evolution equation. This fact permits consideration of system deviation from ideality as a significantly nonlinear phenomenon. The conditions of spatial structure stability are determined by namely parameters describing the system imperfection. The derivation of these conditions is held based on the linearization of the evolution equation. The same phenomena were considered while analyzing the scattering of excitations in non-linear media with a spatial dispersion [11, 12].

2. Evolution Equation

Using the Schlogl model [4], we consider the chemical system consisting of substances A, B, and X mixed. It is supposed that the system is isothermal and isobar. The substance A transmutes in the substance B by means of the substance X. The scheme of this reaction can be illustrated as follows:

$$A + 2X \underset{k_2}{\overset{k_1}{\rightleftarrows}} 3X$$

$$X \underset{k_4}{\overset{k_3}{\rightleftarrows}} B$$
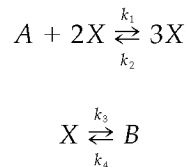
where k_1, k_2, k_3, k_4 are constants of reaction rates. All the reaction constants are positive.

Let us consider the concentration of the substance X depends on time t and spatial coordinates: $X = X(t, r)$, where r is the radius-vector. The speed of concentration X changing has the form

$$\frac{\partial X}{\partial t} = \left(\frac{\partial X}{\partial t}\right)_{diff} + \left(\frac{\partial X}{\partial t}\right)_{chem}, \qquad (1)$$

where $(\partial X/\partial t)_{diff}$ is the concentration changing due to diffusion processes and $(\partial X/\partial t)_{chem}$ is the concentration changing due to chemical kinetics only. The last term of Eq. (1) is studied well and has the form [9]:

$$\left(\frac{\partial X}{\partial t}\right)_{chem} = k_1 A X^2 - k_2 X^3 - k_3 X + k_4 B, \qquad (2)$$

where A, B, and X are the concentrations of the corresponding substances. The concentrations A and B are constant and positive. As shown in this report [10], taking the inhomogeneity of the diffusion processes into account leads to the linear dependence of the diffusion coefficient on the concentration X in the form

$$D(X) = D \cdot (1 - 2wX), \qquad (3)$$

where D is a diffusion coefficient in an ideal system representing the constant (at constant temperature), and w is determined earlier as the imperfection parameter. The modified Fick equation takes the form [5]

$$j = -D(X) \cdot \nabla(X - K\nabla^2 X), \qquad (4)$$

where j is diffusion flux density, $D(X)$ is determined by Eq. (3), K is a positive constant characterizing inhomogeneity of the diffusion flux, and ∇ is nabla. The calculation of

$$\left(\frac{\partial X}{\partial t}\right)_{diff} = -\operatorname{div} j$$

leads to the equation

$$\left(\frac{\partial X}{\partial t}\right)_{diff} = D\nabla^2 X - DK\nabla^4 X - 2Dw[(\nabla X)^2$$
$$+ X\nabla^2 X] + 2DKw[\nabla X\nabla^3 X + X\nabla^4 X]. \quad (5)$$

Substituting Eqs. (2) and (5) into Eq. (1) and neglecting by terms with DKw in Eq. (5) we derive the evolution equation in the form

$$\frac{\partial X}{\partial t} = D\nabla^2 X - DK\nabla^4 X - 2Dw[(\nabla X)^2 + X\nabla^2 X]$$
$$+ k_4 B - k_3 X + k_1 A X^2 - k_2 X^3. \quad (6)$$

With $w = 0$ in Eq. (6), we obtain the equation proposed by Cahn and Hilliard [6]; Equation (6) is known as the Swift–Hohenberg modified equation [13, 14]. We suppose that the system considered is one-dimensional and finite. Then, in Eq. (6), instead ∇X it is possible to write X'_x meaning the partial derivative over coordinate x:

$$\frac{\partial X}{\partial t} = D(X''_{xx} - KX^{(4)}_{4x}) - 2Dw[(X'_x)^2 + XX''_{xx}]$$
$$+ k_4 B - k_3 X + k_1 A X^2 - k_2 X^3. \quad (7)$$

3. Spatial Inhomogeneous Structure Classification

Let us analyze the spatial inhomogeneous structures that appear in the reaction-diffusion system under consideration, based on nonlinear Eq. (7). The kinetic approach uses the linear stability principle. We will consider asymptotic solutions of Eq. (7) and their stability. For this class of solutions, it is known how to investigate stability without finding the general solution of Eq. (7). For this class of solutions, the overall nonlinear problem can lead to the corresponding local linear one. According to Lyapunov's theorem [9], it is possible to analyze the stability of nonlinear problem solutions on the basis of analyzing the stability of the solution for the corresponding linear problem.

The stationary homogeneous states for Eq. (7) have been well studied [9, 15, 16]. Let us linearize Eq. (7) near the stationary homogeneous state $X^{(s)}$, with $Z = X - X^{(s)}$. As a result, we obtain

$$\frac{\partial Z}{\partial t} = -\omega_0 Z + D \cdot L_D[Z], \qquad (8)$$

where $\omega_0 = 3k_2 X^{(s)^2} - 2k_1 A X^{(s)} + k_3$ is the damping velocity of homogeneous state $X^{(s)}$, L_D is the linear differential operator taking the form

$$L_D = (1 - 2wX^{(s)})\frac{\partial^2}{\partial x^2} - K\frac{\partial^4}{\partial x^4}.$$

The solution of Eq. (8) can be written as $Z(x, t) = \psi(x)\exp(-\omega t)$, where $\psi(x)$ and λ are the eigenfunction and eigenvalue of the operator L_D respectively, $\omega = \omega_0 - D\lambda$.

Spatial inhomogeneous structure is determined by the eigenfunctions of the operator L_D. To find all such eigenfunctions it is necessary to solute the Sturm-Liouville problem $L_D[\psi(x)] = \lambda\psi(x)$ with standard boundary conditions at the boundaries of the system considered $-l \leq x \leq l$: $\psi(l) = \psi(-l) = \psi'(l) = \psi'(-l) = 0$.

The fact that the system under consideration is symmetrical relatively the point $x = 0$ allows us to search the eigenfunction in the form

$$\psi(x) = \psi_s(x) + \psi_a(x), \qquad (9)$$

where $\psi_s(x)$ is a symmetric state and $\psi_a(x)$ is an antisymmetric state.

The characteristic equation of the differential equation $L_D[\psi(x)] = \lambda\psi(x)$ has the form

$$Kq^4 - (1 - 2wX^{(s)})q^2 + \lambda = 0. \qquad (10)$$

The solutions of the characteristic equation (10) determine the certain spatial inhomogeneous structures appeared in the system considered.

3.1. PERIODIC STRUCTURES

The first type of spatial inhomogeneous structure described is called the periodic structures. These structures can exist under conditions $X^{(s)} > 1/2w$ and $0 < \lambda < \lambda_m$, where $\lambda_m = [1 - 2wX^{(s)}]^2/4K$. The characteristic equation (10) has four imaginary solutions, $q_j = \pm i\kappa_{1,2}$ ($j = 1, 2, 3, 4$), under these conditions. The solution of the Sturm–Liouville problem has the form (9) where the symmetric and antisymmetric states can be written as

$$\psi_s(x) = C_s\left(\cos \kappa_{1s}x - \frac{\cos \kappa_{1s}l}{\cos \kappa_{2s}l}\cos \kappa_{2s}x\right),$$

$$\psi_a(x) = C_a\left(\sin \kappa_{1a}x - \frac{\sin \kappa_{1a}l}{\sin \kappa_{2a}l}\sin \kappa_{2a}x\right), \quad (11)$$

where $C_{s,a}$ are constants, $\kappa_{1a,s} = \sqrt{\kappa_c^2 - \xi_{a,s}^2/l^2}$, $\kappa_{2a,s} = \xi_{a,s}/l$, $\kappa_c^2 = (2wX^{(s)} - 1)/K > 0$. The values ξ_s are the real solutions of the equation

$$\xi_s\tan \xi_s = \sqrt{\xi_c^2 - \xi_s^2}\tan \sqrt{\xi_c^2 - \xi_s^2}, \quad (12)$$

where $\xi_c = \kappa_c l$. The values ξ_a are the real solutions of the equation

$$\xi_a\cot \xi_a = \sqrt{\xi_c^2 - \xi_a^2}\cot \sqrt{\xi_c^2 - \xi_a^2}. \quad (13)$$

The real solutions of Eqs. (12) and (13) exist under conditions $-\xi_c < \xi_{s,a} < \xi_c$. The eigenvalues of the problem considered are found by Eq. (10) meaning the solutions of Eqs. (12) and (13):

$$\lambda_{s,a} = K\frac{\xi_{s,a}^2}{l^2}\left(\kappa_c^2 - \frac{\xi_{s,a}^2}{l^2}\right). \quad (14)$$

Note that the periodic structures appear in the ideal systems (at $w = 0$ and $K = 0$), but they have a simpler configuration [9].

3.2. QUASI-PERIODIC STRUCTURES

The second type of spatial inhomogeneous structures described is called as the quasi-periodic structures. Such the structures can exist under condition $\lambda < 0$, while the characteristic equation (10) has two imaginary solutions, $q_{1,2} = \pm i\mu$ and two real ones

$q_{3,4} = \pm \nu$. The solution of the Sturm–Liouville problem has the form (9), where the symmetric and antisymmetric states can be written as

$$\psi_s(x) = C_s\left(\cos \mu_s x - \frac{\cos \mu_s l}{\cosh \nu_s l}\cosh \nu_s x\right),$$

$$\psi_a(x) = C_a\left(\sin \mu_a x - \frac{\sin \mu_a l}{\sinh \nu_a l}\sinh \nu_a x\right), \quad (15)$$

where $\mu_{s,a} = \sqrt{\kappa_c^2 + \eta_{s,a}^2/l^2}$, $\nu_{s,a} = \eta_{s,a}/l$. The values η_s are the real solutions of the equation

$$\eta_s\tanh \eta_s = -\sqrt{\xi_c^2 + \eta_s^2}\tan \sqrt{\xi_c^2 + \eta_s^2}. \quad (16)$$

The values η_a are the real solutions of the equation

$$\eta_a\coth \eta_a = \sqrt{\xi_c^2 + \eta_a^2}\cot \sqrt{\xi_c^2 + \eta_a^2}. \quad (17)$$

The eigenvalues of the problem considered are found from Eq. (10), meaning the solutions of Eqs. (16) and (17):

$$\lambda_{s,a} = -K\frac{\eta_{s,a}^2}{l^2}\left(\kappa_c^2 + \frac{\eta_{s,a}^2}{l^2}\right). \quad (18)$$

Note that for $X^{(s)} < 1/2w$, the values κ_c^2 and ξ_c^2 become negative. Hence in this case the condition of existence of the real solutions of Eqs. (16) and (17) appears in the form

$$-|\xi_c| < \eta_{s,a} < |\xi_c|.$$

3.3. NONPERIODIC STRUCTURES

The third type of spatial inhomogeneous structures described is called as the nonperiodic structures. Such the structures can exist under conditions $X^{(s)} < 1/2w$ and $0 < \lambda < \lambda_m$ while the characteristic equation (10) has four real solutions. The solution of the Sturm–Liouville problem has the form (9), where the symmetric and antisymmetric states can be written as

$$\psi_s(x) = C_s\left(\cosh q_{1s}x - \frac{\cosh q_{1s}l}{\cosh q_{2s}l}\cosh q_{2s}x\right),$$

$$\psi_a(x) = C_a\left(\sinh q_{1a}x - \frac{\sinh q_{1a}l}{\sinh q_{2a}l}\sinh q_{2a}x\right), \quad (19)$$

where $C_{s,a}$ are the constants, $q_{2s,a} = \zeta_{s,a}/l$, $q_{1s,a} = \sqrt{q_c^2 - \zeta_{s,a}^2/l^2}$, $q_c^2 = (1 - 2wX^{(s)})/K > 0$.

The values ζ_s are the real solutions of the equation

$$\zeta_s \tanh \zeta_s = \sqrt{\zeta_c^2 - \zeta_s^2} \tanh \sqrt{\zeta_c^2 - \zeta_s^2} \qquad (20)$$

where $\zeta_c = q_c l$. Values ζ_a are the real solutions of the equation

$$\zeta_a \coth \zeta_a = \sqrt{\zeta_c^2 - \zeta_a^2} \coth \sqrt{\zeta_c^2 - \zeta_a^2}. \qquad (21)$$

Real solutions for Eqs. (20) and (21) exist under conditions $-\zeta_c < \zeta_{s,a} < \zeta_c$. The eigenvalues of the problem considered are found from Eq. (10) meaning the solutions of Eqs. (20) and (21):

$$\lambda_{s,a} = K \frac{\zeta_{s,a}^2}{l^2} \left(q_c^2 - \frac{\zeta_{s,a}^2}{l^2} \right). \qquad (22)$$

Note that in the ideal systems (at $w = 0$ and $K = 0$), the quasi-periodic (15) and nonperiodic (19) structures cannot exist. This means that such a new spatial structure formation is due primarily to the system imperfection. Therefore, this result must be considered a significant nonlinear phenomenon.

4. Stability Conditions of Inhomogeneous Structures

The inhomogeneous spatial structures considered can be stable at determined values of initial component concentration A, imperfection parameter w and diffusion inhomogeneity K. The state $Z(x, t) = \psi(x)\exp(-\omega t)$ is stable under the condition $\omega = \omega_0 - D\lambda > 0$ where eigenvalues λ must be taken in the different spatial structures.

Analysis of the stability problem shows that implementation of $\omega_0 - D\lambda_{s,a} > 0$, where $\lambda_{s,a} > 0$ is determined by Eq. (14), is needed for the periodic structures (11). Meaning $\omega_0 > 0$ it leads to the condition

$$(Dw^2 - 3k_2K)(X^{(s)} - X_1)(X^{(s)} - X_2) \geq 0, \qquad (23)$$

where

$$X_{1,2}(A)$$

$$= \frac{Dw/2 - k_1K\{A \mp \sqrt{(A - A_1)(A - A_2)}\}}{Dw^2 - 3k_2K},$$

$$A_{1,2} = \frac{Dw \pm \sqrt{(Dw^2 - 3k_2K)(D - 4k_3K)}}{2k_1K}.$$

$$(24)$$

Condition (23) can be fulfilled in the two following cases, $X_1 < X_2$ and $A_1 < A_2$.

1. If the system parameters are bound by $w > \sqrt{3k_2K/D}$ and $D > 4k_3K$, it must be realized $X^{(s)} > X_2$.

2. If the system parameters are bound by $w < \sqrt{3k_2K/D}$ and $D < 4k_3K$, it must be realized $X_1 < X^{(s)} < X_2$.

The conditions formulated should be mentioned as restrictions on the initial component concentration A. In both cases, it is necessary to obtain $X_{1,2}$ of Eq. (24), for which $X_{1,2}(A) > 1/2w$ and $A > A_2$.

The analysis of stability of the nonperiodic structures [see Eq. (19)] leads to $\omega_0 - D\lambda_{s,a} > 0$, where $\lambda_{s,a} > 0$ is determined by Eq. (22). Meaning $\omega_0 > 0$ it leads to the additional restriction on the solutions of the equations (20) and (21) $-\zeta_1 < \zeta_{s,a} < \zeta_1$, where $\zeta_1^2 = (\zeta_c^2/2)\{1 - \sqrt{1 - (4\omega_0 l^4/DK\zeta_c^2)}\}$. Solutions $\zeta_{s,a}$ are real while obtaining Eq. (24), for which $X_{1,2}(A) < 1/2w$ and $A > A_2$.

The analysis of stability of the quasi-periodic structures [see Eq. (15)] leads to $\omega_0 - D\lambda_{s,a} > 0$. In this case, $\lambda_{s,a} < 0$ is determined by Eq. (18). For $\omega_0 > 0$ the quasi-periodic structures are always stable if $X^{(s)} > 1/2w$ and if $X^{(s)} < 1/2w$ structures (15) are stable while taking into account the condition $-|\xi_c| < \eta_{s,a} < |\xi_c|$ derived in section 3.2.

A more interesting situation for the stability analysis of quasi-periodic structures is realized at $\omega_0 < 0$. Under this condition it is necessary to consider two following cases.

1. If $X^{(s)} > 1/2w$ the stability condition takes the form $\eta_{s,a} < -\eta_1$ and $\eta_{s,a} > \eta_1$, where $\eta_1^2 = (\xi_c^2/2)\{\sqrt{1 + (4|\omega_0|l^4/DK\xi_c^4)} - 1\}$.

2. If $X^{(s)} < 1/2w$ for stability of quasi-periodic structures, it is enough to realize the condition $-|\xi_c| < \eta_{s,a} < |\xi_c|$ derived in section 3.2.

5. Nonlinear Concentration Waves in Imperfect System

Let us suppose now that the flux density of component X also depends linearly on their con-

centration. Hence, in the one-dimensional case, the flux density of the model considered has the form

$$j = \nu_X X - D(X) \cdot \frac{\partial}{\partial x}\left(X - K\frac{\partial^2}{\partial x^2}X\right), \quad (25)$$

where ν_X is the constant. The calculation of $(\partial X/\partial t)_{diff} = -\mathrm{div}\, j$ leads to equation

$$\frac{\partial X}{\partial t} = -\nu_X X'_x + D(X''_{xx} - KX^{(4)}_{4x}) - 2Dw[(X'_x)^2 + XX''_{xx}]$$

$$+ B' - k_3 X + A'X^2 - k_2 X^3, \quad (26)$$

where $Ak_1, = A'$, $Bk_4 = B'$, but apostrophes will be missed in the following. Equation (26) for $\nu_X = 0$ coincides with Eq. (7).

Here is found the exact solution of Eq. (26). It is termed by an elliptical function

$$X(x, t) = a\, \mathrm{dn}^2(k(x - \nu_x t), q) + b, \quad (27)$$

where the solution parameters are entirely determined by the coefficients of Eq. (26), and describes the process of forming periodical structures. Solution (27) is a concentration nonlinear steady wave. Its parameters are

$$a = \frac{2(5Dw + g)k^2}{k_2}, \quad (28)$$

$$b = \frac{4Dk^2(2 - q^2)[15Kk_2 - 4w(5Dw + g)] + (5Dw + g) - 3Dk_2}{k_2(3Dw + g)}, \quad (29)$$

$$k^4 = \frac{2(3k_2 k_3 - A^2)(5Kk_2 - wg) + D\{2Aw(5Aw + 2k_2) - k_2(3k_2 + 34k_3 w^2)\}}{16D(1 - q^2 + q^4)\{45K^2 k_2^2 - 8w[g(3Kk_2 - 4Dw^2) + Dw(27Kk_2 - 20Dw^2)]\}}, \quad (30)$$

where a notation is $g = \sqrt{5D(5Dw - 6Kk_2)}$; an elliptical function modulus q is determined by the following equation

$$8DKak^4q^4 + 2Dak^2q^2\{1 - 2w(a + b) + 4Kk^2\}$$

$$+ k_2(a + b)^3 - A(a + b)^2 + k_3(a + b) - B = 0, \quad (31)$$

in that it is necessary to substitute Eqs. (28)–(30). As a result, Eq. (31) is an irrational equation with respect to q. It is found by numerical analysis of Eq. (31) that it has real solutions in the interval of possible values of the elliptical function modulus $0 \le q \le 1$ under the condition that the concentration values of an initial component are limited in the interval $A_{min} \le A \le A_{max}$. These boundary concentration values A_{min} and A_{max} depend on other parameters of Eq. (26), but studying influence of the diffusion inhomogeneity parameter K is of greatest interest. The results of the numerical solution of Eq. (31) are shown on Figure 1, where the reverse dependencies $A(q)$ are illustrated for clarity. The interval of the concentration possible values of the initial component A converges sharply with increasing K at fixed other values of Eq. (26) parameters. Upon that $K \le 5Dw^2/6k_2$ is also the limiting of diffusion inhomogeneity parameter values for which the concentration wave (27) exists.

The interesting feature of the solution (27) is that it can exist at $K = 0$, but not at $w = 0$. So the deviation from resolution ideality is more important than the one from diffusion ideality for prop-
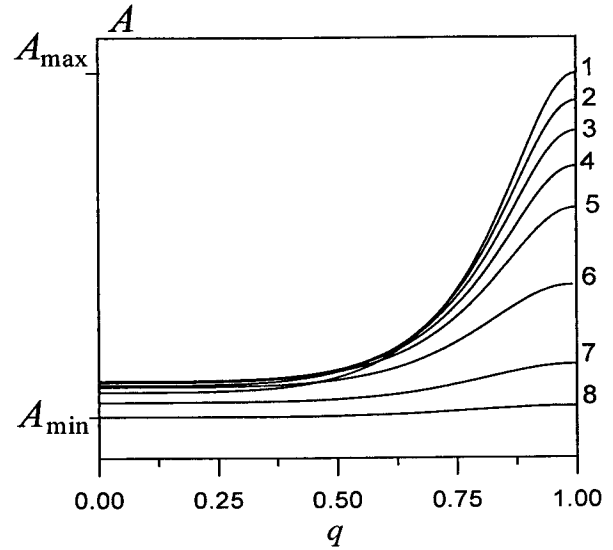

FIGURE 1. Concentration of the initial product A taken for the fixing values of the system parameters ($k_2 = 0, 21$; $k_3 = 1, 25$; $w = 0, 6$; $B = 0, 5$; $D = 2$) and for different values of the K: (1): 0; (2): 1, 5; (3): 2; (4): 2, 3; (5): 2, 5; (6): 2, 7; (7): 2, 8; (8): 2, 83.
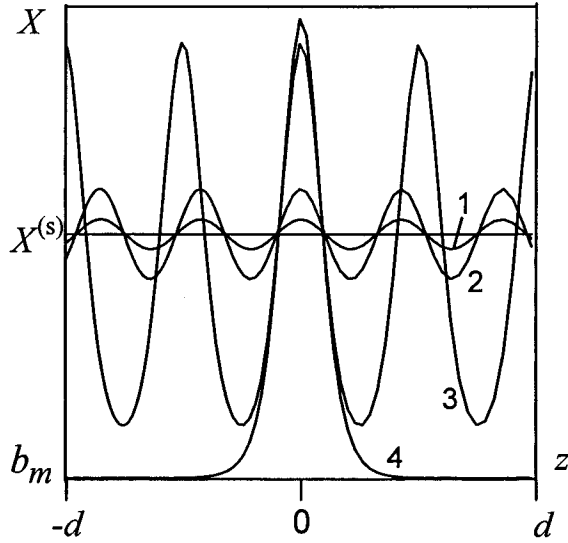
FIGURE 2. Concentration of the product X taken for the fixing values of the system parameters (the values of the system parameters are the same as for Fig. 1, but $K = 2$) and for different values of the concentration of the initial product A: (1): 0, 9241; (2): 0, 9254; (3): 0, 9478; (4): $A_{max} \approx 0$, 9539. The straight line corresponds to $X^{(s)}$ for $A = A_{min}$.

agating the nonlinear concentration waves (27). The typical plots of solution (27) are represented in Figure 2 at a specific system size $-l \le x \le l$ (in a moving frame with the bound $d = l - v_x t$). A wave profile does not change over time in the frame moving with the wave velocity equal to v_x.

Then the steady homogeneous solution $X = X^{(s)} = a(A_{min}) + b(A_{min})$ follows from Eq. (27) at $A = A_{min}$ and $q = 0$, as it results from Eq. (31). Beginning from this value, concentration distortions appear as waves for which an amplitude and a period increase with increasing A.

At $A = A_{max}$ from Eq. (31), following $q = 1$ and from Eq. (27), the solution as solitary wave of the stationary profile is obtained (the plot 4 of Fig. 2):

$$X(x, t) = \frac{a_m}{ch^2(k_m(x - v_x)t)} + b_m, \qquad (32)$$

where the parameters $a_m = a(A_{max})$, $b_m = b(A_{max})$, $k_m = k(A_{max})$ are determined by Eqs. (28–30), or at $A = A_{max}$ and $q = 1$, and from Eq. (31) follows that the solution (32) exists only at a certain value of $B(A_{max}) = b_m(k_2 b_m^2 - A_{max} b_m + k_3)$. The concentration maximum $X_{max} = a_m + b_m$ is placed in the

system center. The concentration rapidly falls up to the value $X_{min} = b_m$, moving away from this center.

It follows that at $D = 0$ and $v_x = 0$ (full neglecting diffusion fluxes is possible when good mixing occurs during the reaction), Eq. (26) also has the exact analytical solution that one can find to be derived, for instance, in [9]. However, this solution isn't periodical. It means that the basic mechanism of forming periodical structures such as the concentration waves for chemical reactions of a monomolecular type is diffusion processes, being no ideal.

6. Instabilities in Two-Component Imperfection System With Mono- and Bimolecular Mechanism of Reaction

It has been proved [9, 17] that in an ideal two-component reaction-diffusion system with mono- and bimolecular reaction mechanism the instabilities (accurately, the limiting cycles) cannot appear. We will show that taking the imperfection of diffusion processes in the same systems into account leads to the possibility of the existence of the dissipative structures corresponding to the limiting cycles.

Based on [9], let us consider the chemical system consisting of substances A, B, X_1, X_2 mixed. Substance A transmutes in the substance B by means of substances X_1, X_2. Such a two-component system is described by the two differential equations in the general form

$$\begin{cases} \dfrac{\partial X_1}{\partial t} = D_1 L_D[X_1] + F_1(X_1, X_2), \\ \dfrac{\partial X_2}{\partial t} = D_2 L_D[X_2] + F_2(X_1, X_2), \end{cases} \qquad (33)$$

where X_1, X_2 are the concentrations of two components, respectively. The general form of the functions $F_{1,2}(X_1, X_2)$ is written in the form [9]

$$F_1(X_1, X_2) = a_0 \pm a_1 X_1 + a_2 X_2$$
$$- a_3 X_1^2 \pm a_4 X_1 X_2 + a_5 X_2^2,$$

$$F_2(X_1, X_2) = b_0 \pm b_1 X_2 + b_2 X_1$$
$$- b_3 X_2^2 \pm b_4 X_1 X_2 + b_5 X_1^2, \qquad (34)$$

where a_j and b_j ($j = 1, \ldots, 5$) are positive. In Section 2 it was shown that in the one-dimension system, the linear differential operator

$$L_D = \frac{\partial^2}{\partial x^2} - K \frac{\partial^4}{\partial x^4},$$

where K is a positive constant characterizing inhomogeneity of the diffusion flux, must describe the imperfection of diffusion processes. We neglect the excess Gibbs function of the regular solution (see section 1). It is supposed that the system is isothermal and isobar and the concentrations A and B are constant.

We suppose that the stationary homogeneous states $X_1^{(s)}$ and $X_2^{(s)}$ have been found from the system of equations $F_1(X_1^{(s)}, X_2^{(s)}) = 0$, $F_2(X_1^{(s)}, X_2^{(s)}) = 0$. Let us linearize the system (33) near the stationary homogeneous states $X_1^{(s)}$, $X_2^{(s)}$ and put $\mathbf{Z} = (Z_1, Z_2)$ where $Z_j = X_j - X_j^{(s)}$ ($j = 1, 2$). We obtain the system in matrix form

$$\frac{\partial \mathbf{Z}}{\partial t} = \hat{L}[\mathbf{Z}], \qquad (35)$$

where the matrix

$$\hat{L} = \begin{pmatrix} L_{11} + D_1 L_D & L_{12} \\ L_{21} & L_{22} + D_2 L_D \end{pmatrix}, \qquad L_{ij} = \frac{\partial F_i}{\partial X_j}\bigg|_{X_j = X_j^{(s)}}.$$

The solution of the system (35) has the form $\mathbf{Z} = \mathbf{h}\psi_{s,a}(x)\exp(\omega t)$, where $\psi_{s,a}(x)$ is the eigenfunction of the operator L_D, $\mathbf{h}$ is the constant eigenvector of the matrix

$$\hat{L}(\lambda_{s,a}) = \begin{pmatrix} L_{11} + D_1\lambda_{s,a} & L_{12} \\ L_{21} & L_{22} + D_2\lambda_{s,a} \end{pmatrix}, \qquad (36)$$

$\lambda_{s,a}$ are the eigenvalues of the operator L_D, and ω are the eigenvalues of the matrix (36). The Sturm–Liouville problem for operator L_D has been solved in Section 3 for the case $w \neq 0$. Setting $w = 0$, we obtain that in this case the quasi-periodic structures (15) and nonperiodic structures (19) exist only.

The quasi-periodic structures (15) are determined by the negative eigenvalues

$$\lambda_{s,a}^{(q)} = -\frac{\eta_{s,a}^2}{l^2}\left(1 + K\frac{\eta_{s,a}^2}{l^2}\right), \qquad (37)$$

where $\eta_{s,a}$ are the real solutions of Eqs. (16) and (17), respectively.

The nonperiodic structures (19) are determined by the positive eigenvalues

$$\lambda_{s,a}^{(n)} = \frac{\zeta_{s,a}^2}{l^2}\left(1 - K\frac{\zeta_{s,a}^2}{l^2}\right), \qquad (38)$$

where $\zeta_{s,a}$ are the real solutions of Eqs. (20) and (21), respectively, and $-\zeta_c < \zeta_{s,a} < \zeta_c$, $\zeta_c = l/\sqrt{K}$. Note that the eigenvalues (37) and (38) depends on K and l only. It is different from the eigenvalues (18) and (22).

It is known that diagonal elements of the matrix (36) must have different signs ($\hat{L}_{11}\hat{L}_{22} < 0$) for the dissipative structures appearing in the system considered. Also it is known that $L_{11} < 0$ and $L_{22} < 0$ in the two-component system with mono- and bimolecular reaction mechanism [9, 17].

In the system with ideal diffusion ($K = 0$), the operator L_D becomes the ordinary Laplace operator having the negative eigenvalues $\lambda = -k^2$, where k has discrete values determined by l and the form of boundary conditions only. It is leads to $\hat{L}_{11} = -|L_{11}| - D_1 k^2 < 0$ and $\hat{L}_{22} = -|L_{22}| - D_2 k^2 < 0$. As a result we see $\hat{L}_{11}\hat{L}_{22} > 0$. It means that the limiting cycles cannot appear in the system considered with ideal diffusion [9, 17].

It is very interesting to note that in the system with imperfection diffusion processes ($K \neq 0$), the opposite situation could be realized. In this case, the nonperiodic structures (19) having positive eigenvalues (38) exist. This leads to $\hat{L}_{11} = -|L_{11}| + D_1\lambda_{s,a}^{(n)}$ and $\hat{L}_{22} = -|L_{22}| + D_2\lambda_{s,a}^{(n)}$. The situation of interest to us, $\hat{L}_{11}\hat{L}_{22} < 0$, can be realized in the two following cases:

1. $\hat{L}_{11} > 0$ and $\hat{L}_{22} < 0$, which can be from $(|L_{11}|/D_1) < \lambda_{s,a}^{(n)} < (|L_{22}|/D_2)$;
2. $\hat{L}_{11} < 0$ and $\hat{L}_{22} > 0$ which can be from $(|L_{22}|/D_2) < \lambda_{s,a}^{(n)} < (|L_{11}|/D_1)$.

It is proved that the structure instabilities corresponding to the limiting cycles can appear in a two-component system with imperfection of diffusion processes and with the mono- and bimolecular reaction mechanism.

7. Conclusions

It is necessary to note that in the framework of the simple chemical reaction model we describe

the new types of spatial inhomogeneous structures. Based on the nonlinear evolution equation, we prove that spatial inhomogeneous structure formation is due to the system imperfection only.

It should also be noted that we succeeded in obtaining the exact periodical solution of an analytical form describing nonlinear concentration waves of the nonlinear equation maintaining the high-order derivatives within a simple model of a chemical reaction. It is obvious that the considered nonlinear equation (26) can have other types of solutions as well. Although concrete realizations are not found for the chemical reaction model considered, it is seen to be important from a theoretical point of view, namely, the basic mechanisms of forming concentrations waves are revealed on the basis of it, and a role of the nonideal diffusion processes is demonstrated.

Based on the simple chemical model, we have proved the possibility of existence of the structure instabilities corresponding to the limiting cycles in a two-component system with imperfect diffusion processes and with a mono- and bimolecular reaction mechanism.

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