

NONLINEAR CONCENTRATION WAVES IN AN IMPERFECT REACTING DIFFUSION SYSTEM

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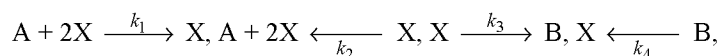
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A nonlinear differential equation describing the evolution of the intermediate reagent concentration is derived for the generalized Schlögl model of a chemical reaction in an imperfect system. It is demonstrated that concentration waves corresponding to a periodic analytic solution of the evolutionary equation arise in the imperfect system. Conditions of existence of periodic and solitary waves are formulated depending on the concentration of the initial component and the imperfection parameters of the examined system.

It is well known that imperfection of systems and inhomogeneity of the diffusion processes during chemical reactions lead to the occurrence of terms with higher-order derivatives of the concentration together with nonlinear nonpower-law terms in the kinetic equation for reagent concentrations [1–4]. In the last few years, modeling of physical and chemical processes based on nonlinear differential equations has become widespread for various applications (for example, see [5]). Under certain conditions, simpler equations describe the formation of spatially modulated structures [6]. As a rule, even in the case of rather simple nonlinear equations, a description of self-organization processes is qualitative in character, because it is rather difficult to obtain exact analytical solutions.

In the present work, an exact analytical solution of the evolutionary equation describing a periodic structure is obtained. The nonlinear evolutionary equation is retrieved by means of generalization of the Schlögl model of a chemical reaction [7].

As is well known, the chemical system in this model is a mixture of substances A , B , and X ; moreover, it is open for substances entering from the environment that can be transformed into the substance X inside of the reacting volume. The processes proceeding in this system are isothermal and isobaric. It is also assumed that the system is in mechanical (but not thermodynamic) equilibrium and is not influenced by external fields. The reaction is considered in which the initial substance A is transformed into the end product B through the intermediate substance X that catalyzes its own production. The scheme of the reaction is



where k_1, k_2, k_3 , and k_4 are positive reaction rate constants.

The substance concentration depends on time t and spatial coordinates $X = X(t, \mathbf{r})$, where \mathbf{r} is the radius-vector. The rate of changing the concentration of the reagent X can be written as

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

where $\left(\frac{\partial X}{\partial t}\right)_{\text{diff}}$ describes the concentration changes caused by the diffusion processes, and $\left(\frac{\partial X}{\partial t}\right)_{\text{chem}}$ describes the concentration changes caused by the chemical kinetics whose expression is well-known [2]:

$$\left(\frac{\partial X}{\partial t}\right)_{\text{chem}} = k_1AX^2 - k_2X^3 - k_3X + k_4B, \quad (2)$$

A , B , and X are concentrations of the corresponding reagents with $A \geq 0$, $B \geq 0$, and $X \geq 0$, and the concentrations of substances A and B are considered constant.

It is assumed that the system is a regular solution in which all molecules are packed in the same way and occupy the same volumes. Then the excess thermodynamic potential is written in the form [2]

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

where n is the number of moles in the system, n_i is the number of moles of molecules of the i th species, and the coefficients w_{ij} are determined by the formula $w_{ij} = (2\varepsilon_{ij} - \varepsilon_{ii} - \varepsilon_{jj})\theta$ in which ε_{ij} is the energy of interaction between molecules of the i th and j th species, and the numerical factor θ is determined by the liquid state model. The coefficients $w_{ij} > 0$ characterize the system imperfection caused by the interaction of molecules in the solution. In the examined case, the intermediate component X and components A and B form a regular solution, and only interaction between X and other components is considered imperfect; therefore, $w = w_{12}/RT$ is taken for binary solutions, where R is the universal gas constant and T is the temperature of the solution. This parameter can be called the imperfection parameter. It is well known [2] that a linear dependence of the diffusion coefficient of the substance X on its concentration

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

is observed for $X \ll 1$, where D is the diffusion coefficient of the perfect system taken to be constant (at a constant temperature), which is confirmed by the available experimental data. In stoichiometric coefficients entering into the concentration changes caused by chemical kinetics, the imperfection can be neglected.

The diffusion imperfection is often taken into account in the modified Fick law [1, 4]. The modification is based on the division of free energy into two components, with the first component $f_0[X(\mathbf{r})]$ describing the free energy of the homogeneous liquid, and the second component considering the inhomogeneity of phases by introducing the term proportional to the squared concentration gradient ∇X : $f[X(\mathbf{r})] = f_0[X(\mathbf{r})] + K[\nabla X(\mathbf{r})]^2/2$, where the coefficient $K > 0$ characterizes the inhomogeneity of the diffusion flux and is further referred to as the inhomogeneity parameter considered constant. If we consider that the substance enters inside of the reacting system, we also can take into account the contribution to the diffusion flux proportional to the concentration of the substance X . According to the modified Fick law, the diffusion flux density j in the one-dimensional case is written as follows:

$$j = sX - D(X) \frac{\partial}{\partial x} \left(X - K \frac{\partial^2}{\partial x^2} X \right), \quad (4)$$

where s is the proportionality constant. Since the balance equation for the concentration in the one-dimensional case has the form $\left(\frac{\partial X}{\partial t}\right)_{\text{diff}} = -\frac{\partial j}{\partial x}$, from Eq. (4) with allowance for Eq. (3) we obtain the equation

$$\begin{aligned} \left(\frac{\partial X}{\partial t}\right)_{\text{diff}} = & -s\frac{\partial X}{\partial x} + D\frac{\partial^2 X}{\partial x^2} - DK\frac{\partial^4 X}{\partial x^4} - 2Dw\left\{\left(\frac{\partial X}{\partial x}\right)^2 + X\frac{\partial^2 X}{\partial x^2}\right\} \\ & + 2DKw\left\{\frac{\partial X}{\partial x}\frac{\partial^3 X}{\partial x^3} + X\frac{\partial^4 X}{\partial x^4}\right\}. \end{aligned} \quad (5)$$

Equation (5) has phenomenological character; it was derived in [4] for $w = 0$ and $s = 0$. The deviation from the perfect internal properties of the system in Eq. (5) is taken into account by introducing special nonlinear terms, and the inhomogeneity of diffusion fluxes is taken into account by introducing terms comprising the fourth-order gradients. Both effects are considered small below, and the last to two nonlinear terms of Eq. (5) of higher order of smallness are neglected.

Having substituted Eqs. (2) and (5) into Eq. (1) with allowance for the above assumptions, we obtain the evolutionary equation for the examined model describing changes in the concentration of the reagent X :

$$\frac{\partial X}{\partial t} = -s\frac{\partial X}{\partial x} + D\frac{\partial^2 X}{\partial x^2} - DK\frac{\partial^4 X}{\partial x^4} - 2Dw\left\{\left(\frac{\partial X}{\partial x}\right)^2 + X\frac{\partial^2 X}{\partial x^2}\right\} + B' - k_3X + A'X^2 - k_2X^3, \quad (6)$$

where $Ak_1 = A'$, $Bk_4 = B'$, and primes are omitted below. For $w = 0$ and $s = 0$, Eq. (6) coincides to within the signs of the coefficients with the generalized Swift–Hohenberg equation [8, 9] used for modeling of the self-organization processes in dislocation ensembles.

Stationary homogeneous solutions $X^{(s)}$ of Eq. (6) and conditions of their stability were studied in detail in [2, 6].

To describe the processes of forming the periodic structures in the examined system, we have found an exact analytical solution of Eq. (6) expressed through the elliptic function:

$$X(x, t) = a \operatorname{dn}^2(k(x - st), q) + b, \quad (7)$$

where the parameters of the solution are fully determined by the coefficients of Eq. (6). Solution (7) describes the nonlinear stationary concentration wave with the parameters

$$a = \frac{2(5Dw + g)k^2}{k_2}, \quad (8)$$

$$b = \frac{4Dk^2(2 - q^2)\{15Kk_2 - 4w(5Dw + g)\} + (5Dw + g) - 3Dk_2}{k_2(3Dw + g)}, \quad (9)$$

$$k^4 = \frac{2(3k_2k_3 - A^2)(5Kk_2 - wg) + D\{2Aw(5Aw + 2k_2) - k_2(3k_2 + 34k_3w^2)\}}{16D(1 - q^2 + q^4)\{45K^2k_2^2 - 8w[g(3Kk_2 - 4Dw^2) + Dw(27Kk_2 - 20Dw^2)]\}}, \quad (10)$$

where we have used the designation $g = \sqrt{5D(5Dw - 6Kk_2)}$. The modulus of the elliptic function q is determined from the equation

$$8DKak^4q^4 + 2Dak^2q^2\{1 - 2w(a + b) + 4Kk^2\} + k_2(a + b)^3 - A(a + b)^2 + k_3(a + b) - B = 0, \quad (11)$$

in which Eqs. (8)–(10) have been substituted. As a result, Eq. (11) represents the irrational equation for q . Numerical analysis of Eq. (11) demonstrates that it has real roots for the modulus of the elliptic function $0 \leq q \leq 1$ given that the concentration of the initial component is in the interval $A_{\min} \leq A \leq A_{\max}$. These limiting concentration values A_{\min} and A_{\max} depend on the remaining parameters of Eq. (6), but it is most interesting to study the influence of the diffusion

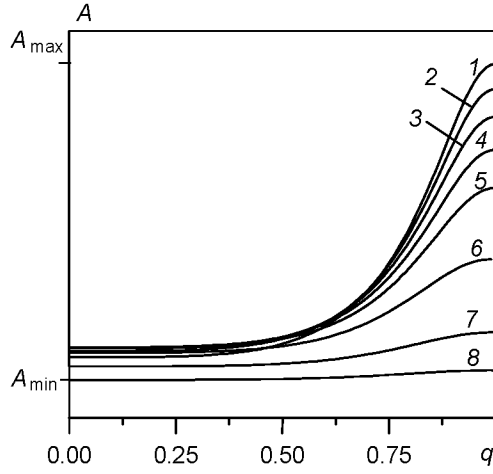


Fig. 1

Fig. 1. Dependence of A , in $\text{m}^3/(\text{s}\cdot\text{kg})$, on the modulus q for the system parameters $k_2 = 0.21 \text{ mb}/(\text{s}\cdot\text{kg}^2)$, $k_3 = 1.25 \text{ l/s}$, $w = 0.6 \text{ m}^3/\text{kg}$, $B = 0.5 \text{ kg/s}\cdot\text{m}^3$, $D = 2 \text{ m}^2/\text{s}$, and $K = 0$ (curve 1), 1.5 (curve 2), 2 (curve 3), 2.3 (curve 4), 2.5 (curve 5), 2.7 (curve 6), 2.8 (curve 7), and 2.83 m^2 (curve 8).

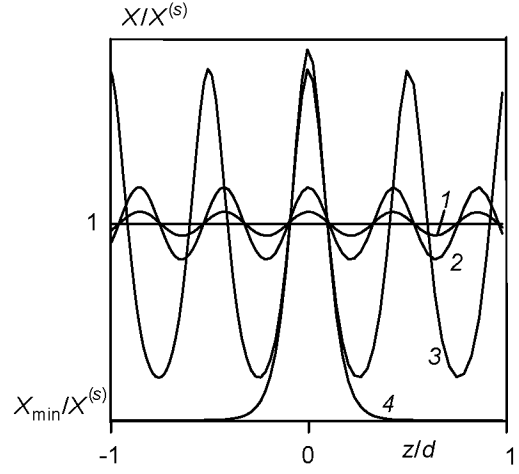


Fig. 2

Fig. 2. Dependence of the concentration ratio $X/X^{(s)}$ on z/d , where $z = x - st$, for the system parameters the same as in Fig. 1 and $K = 2 \text{ m}^2$ and for the concentration of the initial component $A = 0.9241$ (curve 1), 0.9254 (curve 2), and $0.9478 \text{ m}^3/(\text{s}\cdot\text{kg})$ (curve 3). Here curve 4 is for $A_{\text{max}} \approx 0.9539 \text{ m}^3/(\text{s}\cdot\text{kg})$. The straight line shows $X^{(s)}$ for $A = A_{\text{min}}$.

inhomogeneity parameter K . Figure 1 shows the dependence $A(q)$ obtained by numerical solution of Eq. (11). (Numerical values of the system parameters were chosen to make presentation more vivid, and concentrations $Ak_1 \rightarrow A$ and $Bk_4 \rightarrow B$.) The interval of allowable values of concentration of the initial component A is sharply narrowed with increasing K when the remaining parameters of Eq. (6) remain unchanged. The restriction $K \leq 5Dw^2/6k_2$ is also imposed on values of the diffusion inhomogeneity parameter for which concentration wave (7) exists.

An interesting peculiarity of the solution of Eq. (7) is that it exists at $K = 0$ and does not exist at $w = 0$. Therefore, for the propagation of nonlinear concentration waves (7), the deviation from the perfect solution is more significant than the deviation from the perfect diffusion. Figure 2 shows typical plots of solution (7) for the characteristic system size $-l \leq x \leq l$ (in the moving reference system with the boundary $d = l - st$). The wave profile remains unchanged with time in the reference system moving with the velocity s .

For $A = A_{\text{min}}$, $q = 0$ from Eq. (11); then from Eq. (7) we obtain the stationary homogeneous solution $X = X^{(s)} = a(A_{\text{min}}) + b(A_{\text{min}})$. With increasing A , perturbations of concentration X from this value arise in the form of waves (7); their amplitude and period increase.

For $A = A_{\text{max}}$, $q = 1$ from Eq. (11); then from Eq. (7) we obtain the solution in the form of a solitary stationary wave (curve 4 in Fig. 2):

$$X(x, t) = \frac{a_m}{\cosh^2 k_m (x - st)} + b_m, \quad (12)$$

where the parameters $a_m = a(A_{\text{max}})$, $b_m = b(A_{\text{max}})$, and $k_m = k(A_{\text{max}})$ are determined by Eqs. (8)–(10) for $A = A_{\text{max}}$ and $q = 1$. From Eq. (11) it follows that solution (12) exists only for $B(A_{\text{max}}) = b_m(k_2 b_m^2 - A_{\text{max}} b_m + k_3)$. The concentration maximum

$X_{\max} = a_m + b_m$ is observed in the center of the system; the concentration rapidly decreases to $X_{\min} = b_m$ with increasing distance from the system center.

It should be noted that for $D = 0$ and $s = 0$ (diffusion fluxes can be neglected completely in the case of very good mixing of components during the reaction), Eq. (6) also has an exact analytical solution. The derivation of this solution and analysis of its stability can be found, for example, in [2]. However, this solution is nonperiodic. This means that the diffusion processes, therewith imperfect, are the main mechanism of forming periodic structures (to which concentration waves belong) during monomolecular chemical reactions.

In conclusion, it should be noted that in this work, the exact periodic analytic solution of the nonlinear equation with higher-order derivatives describing nonlinear concentration waves has been obtained for the simple model of the chemical reaction. It is obvious that nonlinear equation (6) can also have solutions of other types. Though we have not found concrete realizations for the examined model of the chemical reaction, it is considered rather important from the theoretical point of view, since we have revealed the main mechanisms of forming the concentration waves. We have also elucidated the role of the imperfect diffusion processes.

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