

# Role of Nonideality of Diffusion Processes in the Formation of Dissipative Structures

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**Abstract**—It is shown that inhomogeneity of diffusion fluxes, which modifies Fick's law in chemical systems, where mono- and bimolecular reactions proceed through two intermediate components, may lead to the formation of spatial structures. Their analytic description is given on the basis of an exact solution to a set of nonlinear evolution equations. The conditions of existence are derived for time-dependent dissipative structures (limiting cycle) in the presence of nonideality of diffusion processes in the systems being considered.

Much attention has been given to describing the appearance of dissipative structures and nonequilibrium phase transitions in chemical reaction-diffusion systems since the nonlinear dynamics of such systems has to deal with fundamental problems [1, 2]. It should be noted that the character of nonlinearity of evolution equations that describe dissipative structures in the system being considered is of importance here since it determines the possibility of the appearance of oscillation regimes in chemical systems [3]. In [1, 4–6], it was shown that a limiting cycle cannot arise in a two-component system featuring two intermediate substances in reactions governed by mono- and bimolecular mechanisms. In the present study, it is shown that the presence of inhomogeneous diffusion fluxes in such systems may provide conditions for the appearance of a limiting cycle.

Limiting cycles occur in known models such as the brusselator and the Lotka–Volterra model [1, 6]. Also, they were observed experimentally in the Belousov–Zhabotinsky reaction [7, 8]. We note that the brusselator represents a system governed by a trimolecular reaction mechanism, where chemical processes are described by equations involving a cubic nonlinearity, which ensures the appearance of an oscillation regime, the character of diffusion (its ideality versus nonideality) being insignificant.

In [1, 6], it was indicated that, in models where reactions are governed by a mono- or a bimolecular mechanism, the condition necessary for the appearance of a limiting cycle is not realized in the case of ideal diffusion. In the present study, we consider nonideal diffu-

sion processes in models featuring mono- and bimolecular reaction mechanisms, and this changes the situation substantially. Nonideality and inhomogeneity of diffusion processes occurring in chemical reactions are described by the kinetic equation for the concentration of reactants with allowance for higher order derivatives of the concentration [9, 10]. Terms involving derivatives of order higher than 2 play the main role in creating the condition for the appearance of a limiting cycle.

It can be stated that a nonideal chemical system is more favorable for the appearance of instabilities than an ideal one. The effect of nonideality was analyzed in [1, 6] for the case of nonideality of the “regular solution” model—that is, the expression for the chemical potential was modified. In the present study, we consider a different-type nonideality in a chemical system; we refer to it by convention as the diffusion-type nonideality and take it into account, following [6]. In either case, one modifies Fick's law and, hence, diffusion equations. However, the equations obtained in the present study have a different structure and a different order.

We choose the model where the chemical system being considered is a mixture of an initial substance  $A$ , intermediate substances  $X_1$  and  $X_2$ , and a final reaction product  $B$ . We assume that the system is open to the inflow of substances from the ambient medium that are capable of transforming into  $X_1$  and  $X_2$ . We also assume that the system being considered is in a state of mechanical (but not thermodynamic) equilibrium in the absence of applied fields and that processes occurring in it are isothermal and isobaric. The concentrations of

the substances  $X_1$  and  $X_2$  are dependent on time and coordinates  $\mathbf{r}$ , while the concentrations of the substances  $A$  and  $B$  are taken to be constant.

The nonideality of diffusion can be taken into account by modifying Fick's law [6, 9, 10]. In order to do this, we represent the free energy as the sum of two parts; of these, one,  $f_{0i}[X_i(\mathbf{r})]$  ( $i = 1, 2$ ), corresponds to the free energy of a homogeneous liquid, while the other is a free energy that is proportional to the square of the concentration gradient  $\nabla X_i$ :  $f_i[X_i(\mathbf{r})] = f_{0i}[X_i(\mathbf{r})] + H[\nabla X_i(\mathbf{r})]^2/2$ , where the coefficient  $H > 0$  characterizes the inhomogeneity of diffusion fluxes. In the following, we refer to this coefficient as the inhomogeneity parameter and assume it to be constant. The ensuing consideration will be performed for the one-dimensional case. Assuming that the inhomogeneity parameter takes nearly the same value for the substances  $X_1$  and  $X_2$ , we represent the densities of the corresponding diffusion fluxes  $j_i$  in the form of a modified Fick equation,

$$j_i = -D_i \frac{\partial}{\partial x} \left( X_i - H \frac{\partial^2}{\partial x^2} X_i \right). \quad (1)$$

With allowance for Eq. (1), the balance equations for the concentration in the one-dimensional case,

$$\left( \frac{\partial X_i}{\partial t} \right)_{\text{diff}} = -\frac{\partial j_i}{\partial x}, \text{ assume the form}$$

$$\begin{cases} \frac{\partial X_1}{\partial t} = D_1 L_D [X_1] + F_1(X_1, X_2) \\ \frac{\partial X_2}{\partial t} = D_2 L_D [X_2] + F_2(X_1, X_2), \end{cases} \quad (2)$$

where  $D_i$  are the diffusion coefficients for an ideal chemical system that are constant at a constant temperature and the explicit expression for the differential operator involved is  $L_D = \frac{\partial^2}{\partial x^2} - H \frac{\partial^4}{\partial x^4}$ . Within the model being considered, the functions  $F_{1,2}(X_1, X_2)$  can be represented in the form [6]

$$\begin{aligned} F_1(X_1, X_2) &= a_0 \pm a_1 X_1 + a_2 X_2 - a_3 X_1^2 \\ &\quad \pm a_4 X_1 X_2 + a_5 X_2^2, \\ F_2(X_1, X_2) &= b_0 \pm b_1 X_2 + b_2 X_1 - b_3 X_2^2 \\ &\quad \pm b_4 X_1 X_2 + b_5 X_1^2, \end{aligned} \quad (3)$$

where  $a_j$  and  $b_j$  ( $j = 1, \dots, 5$ ) are positive constants corresponding to the reaction rates and the concentrations of the initial and final substances in the reaction being studied. The signs in (3) were chosen with allowance

for the possible types of processes involved in mono- and bimolecular reactions [5, 6].

It should be noted that one-component analogs of the set of Eqs. (2) for the case of an operator that is similar to  $L_D$  are used in the literature to describe self-organization of dislocation ensembles in solids (see, for example, [11]).

Suppose that stationary uniform states  $X_1^{(s)}$  and  $X_2^{(s)}$  defined as solutions to the set of equations  $F_1(X_1^{(s)}, X_2^{(s)}) = 0$  and  $F_2(X_1^{(s)}, X_2^{(s)}) = 0$  are known. We further linearize the set of Eqs. (2) in the vicinity of these states by introducing the vector  $\mathbf{Z} = (Z_1, Z_2)$ , where  $Z_j = X_j - X_j^{(s)}$  ( $j = 1, 2$ ). We then have

$$\frac{\partial \mathbf{Z}}{\partial t} = \hat{L}[\mathbf{Z}], \quad (4)$$

where the matrix of this set of equations has the form

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

We can readily obtain a solution to the set of Eqs. (4) in the form  $\mathbf{Z} = \mathbf{h}\psi(x)\exp(\omega t)$ , where  $\psi(x)$  are eigenfunctions of the operator  $L_D$ ;  $\mathbf{h}$  is a constant eigenvector of the matrix

$$\hat{L}(\lambda) = \begin{pmatrix} L_{11} + D_1 \lambda & L_{12} \\ L_{21} & L_{22} + D_2 \lambda \end{pmatrix}, \quad (5)$$

$\lambda$  being the eigenvalues of the operator  $L_D$ ; and  $\omega$  stands for the eigenvalues of the matrix in (5).

Applying standard boundary conditions that correspond to the vanishing of the function  $\psi(x)$  and its derivative at the boundaries of the system at  $x = \pm l$ ,  $\psi(l) = \psi(-l) = \psi'(l) = \psi'(-l) = 0$ , we find the eigenfunctions and eigenvalues of the operator  $L_D$ . Taking into account the symmetry of the system with respect to the coordinate origin, we break down the eigenfunctions into two components,  $\psi(x) = \psi_s(x) + \psi_a(x)$ , where  $\psi_s(x)$  and  $\psi_a(x)$  are symmetric and antisymmetric, respectively. These eigenfunctions describe spatial distributions of two types.

(i) Quasiperiodic structures:

$$\begin{aligned} \psi_s(x) &= C_s \left( \cos \mu_s x - \frac{\cos \mu_s l}{\cosh \nu_s l} \cosh \nu_s x \right), \\ \psi_a(x) &= C_a \left( \sin \mu_a x - \frac{\sin \mu_a l}{\sinh \nu_a l} \sinh \nu_a x \right). \end{aligned} \quad (6)$$

Here,  $C_{s,a}$  are normalization factors, while  $\mu_{s,a} = \sqrt{1/H + \eta_{s,a}^2/l^2}$  and  $\nu_{s,a} = \eta_{s,a}/l$ , where the quantities  $\eta_s$  are the real-valued roots of the equation

$$\eta_s \coth \eta_s = -\sqrt{l^2/H + \eta_s^2} \tan \sqrt{l^2/H + \eta_s^2}, \quad (7)$$

and the quantities  $\eta_a$  are the real-valued roots of the equation

$$\eta_a \coth \eta_a = \sqrt{l^2/H + \eta_a^2} \cot \sqrt{l^2/H + \eta_a^2}. \quad (8)$$

For quasiperiodic structures, the eigenvalues of the operator  $L_D$  are negative:

$$\lambda_{s,a}^{(q)} = -\frac{\eta_{s,a}^2}{l^2} \left( 1 + H \frac{\eta_{s,a}^2}{l^2} \right). \quad (9)$$

(ii) Aperiodic structures:

$$\Psi_s(x) = C_s \left( \cosh q_{1s}x - \frac{\cosh q_{1s}l}{\cosh q_{2s}l} \cosh q_{2s}x \right), \quad (10)$$

$$\Psi_a(x) = C_a \left( \cosh q_{1a}x - \frac{\sinh q_{1a}l}{\sinh q_{2a}l} \sinh q_{2a}x \right).$$

Here,  $q_{2s,a} = \zeta_{s,a}/l$  and  $q_{1s,a} = \sqrt{1/H - \zeta_{s,a}^2/l^2}$ , where the quantities  $\zeta_s$  are the real-valued roots of the equation

$$\zeta_s \tanh \zeta_s = \sqrt{l^2/H - \zeta_s^2} \tanh \sqrt{l^2/H - \zeta_s^2}, \quad (11)$$

and the quantities  $\zeta_a$  are the real-valued roots of the equation

$$\zeta_a \coth \zeta_a = \sqrt{l^2/H - \zeta_a^2} \coth \sqrt{l^2/H - \zeta_a^2}. \quad (12)$$

Concurrently, the real-valued roots of Eqs. (11) and (12) must satisfy the condition  $-l/H < \zeta_{s,a} < l/H$ ; under this condition, the eigenvalues of the operator  $L_D$  for aperiodic structures (10) are positive:

$$\lambda_{s,a}^{(n)} = \frac{\zeta_{s,a}^2}{l^2} \left( 1 - H \frac{\zeta_{s,a}^2}{l^2} \right). \quad (13)$$

For ideal diffusion processes (corresponding to  $H = 0$ ), aperiodic structures (10) do not arise, while the quasiperiodic structures reduce to single-component periodic structures. Thus, the formation of the above inhomogeneous spatial structures is due exclusively to the inhomogeneity of diffusion fluxes in a chemical reaction.

For time-dependent dissipative structures to be formed in a chemical system, the diagonal elements of the matrix in (5) must have opposite signs ( $\hat{L}_{11}\hat{L}_{22} < 0$ ). In a system featuring ideal diffusion ( $H = 0$ ) (see [6]), the operator  $L_D$  reduces to the operator  $\partial^2/\partial x^2$ , which has only negative eigenvalues,  $\lambda = -k_n^2$ , where  $k_n$  takes

discrete values whose explicit form is determined by  $l$  and by the type of boundary conditions. In this case, the diagonal matrix elements for an ideal two-component system featuring the mono- and bimolecular reaction mechanisms satisfy the inequalities  $\hat{L}_{11} = -|L_{11}| - D_1 k_n^2 < 0$  and  $\hat{L}_{22} = -|L_{22}| - D_2 k_n^2 < 0$ , whence it follows that  $\hat{L}_{11}\hat{L}_{22} > 0$ , and this proves the impossibility of the formation of dissipative structures in the case of ideal diffusion in the chemical system being considered.

The situation changes radically if nonideal diffusion processes are present in a chemical system (that is,  $H \neq 0$ ). In this case, aperiodic structures (10), for which the eigenvalues given by Eq. (13) are positive, are compatible with the condition  $\hat{L}_{11}\hat{L}_{22} < 0$ , since we now have  $\hat{L}_{11} = -|L_{11}| + D_1 \lambda_{s,a}^{(n)}$  and  $\hat{L}_{22} = -|L_{22}| + D_2 \lambda_{s,a}^{(n)}$ . The condition under which a limiting cycle arises may be realized in two cases:

(i)  $\hat{L}_{11} > 0$  and  $\hat{L}_{22} < 0$  if the possible values of the eigenvalues in (13) satisfy the inequalities  $\frac{|L_{11}|}{D_1} <$

$$\lambda_{s,a}^{(n)} < \frac{|L_{22}|}{D_2};$$

(ii)  $\hat{L}_{11} < 0$  and  $\hat{L}_{22} > 0$ , whence it follows that  $\frac{|L_{22}|}{D_2} < \lambda_{s,a}^{(n)} < \frac{|L_{11}|}{D_1}$ .

Thus, the condition necessary for the existence of dissipative structures, including a limiting cycle, can be satisfied in a two-component system featuring mono- and bimolecular reaction mechanisms.

In the present study, it has only been proven that the necessary condition for the existence of dissipative structures in the class of chemical systems governed by mono- and bimolecular reaction mechanisms can in principle be realized owing to inhomogeneity of diffusion processes. In order to formulate a sufficient condition in this class of chemical systems, it is necessary to solve the respective full nonlinear problem, but this can be done only by means of numerical or approximate methods.

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