Differential Flow Induced Chemical Instability on a Rotating Disk

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Conditions of differential flow induced chemical instability are obtained for a heterogeneous reaction on a rotating disk. Since the surface of a rotating disk is equiaccessible to diffusional transport, this is a unique arrangement where a homogeneous state does indeed exist in the presence of flow, and the symmetry breaking can be observed in an unequivocal way. Explicit instability limits are established for an autocatalytic two-component system near a saddle-node bifurcation point, where the instability occurs on a long scale along the streamlines.

The newest and least investigated mechanism of pattern formation in chemically reactive systems is the effect of differential flow induced chemical instability (DIFICI) suggested by Rovinsky and Menzinger [1]. The mechanism is based on a combination of autocatalytic action with a kind of a chromatographic effect. A standard system suitable for formation of Turing patterns includes a slowly diffusing "activator" and a rapidly diffusing "inhibitor" [2] (see also [3,4]). The symmetry breaking occurs when the inhibitor diffusing away from active locations suppresses chemical activity in their neighborhood. In the DIFICI mechanism, differential advection rather than diffusion causes a similar effect. The essential advantage is that a difference in advection rates of *any* sign may cause symmetry breaking, so that one is not constrained by the requirement of a higher diffusive rate of the inhibitor characteristic to the classical Turing mechanism.

The analysis of symmetry breaking in flow-through systems is, however, hindered by the lack of a basic homogeneous state. The original analysis by Rovinsky and Menzinger [1] was based on studying linear stability of a homogeneous state of a flow-through one-dimensional system. One can observe, however, that sustaining a stationary nonequilibrium state on a certain manifold generally necessitates some flux supplying reactants from and removing products to the environment and, consequently, gradients of thermodynamic variables in the direction of this flux. Thus, no spatially homogeneous state can, strictly speaking, exist, unless the exchange with the environment is carried out along the direction normal to this manifold (e.g., to a catalyst surface).

Some model autocatalytic reaction schemes, including the Puschinator model used in Ref. [1], do formally possess a homogeneous state. The reason is that they silently assume the presence of some large storage supplying the reactants and absorbing the products that are present explicitly as the variables of the model equations. A more stringent approach to the analysis of DIFICI involving a general reacting system in a realistic flow-through reactor would be to start with a slightly inclined concentration profile, and look for spontaneous development of steeper inhomogeneities with a characteristic length short compared to the reactor length. Such a stability analysis of an *inhomogeneous* state is, of course, far more difficult, and has not been implemented so far.

The aim of this Letter is to establish DIFICI conditions for a realistic system where spatially homogeneous states do exist (before being broken) in spite of a prevalently advective transport. A system of this kind cannot be one dimensional, as the reaction zone must be homogeneously accessible to mass transport. The appropriate setup is provided by a catalytic reaction on a *rotating disk*. This is an almost unique flow system with an equiaccessible active surface [5] that has become, due to this exclusive property, a standard tool for study of reactions limited by mass transport rates, especially in electrochemistry. The DIFICI mechanism is possible in this system due to different adsorption rates and surface capacitances of different reactants.

We consider a catalytic reaction on the surface of a rotating disk. The reactants are advected by the oncoming flow, assumed to be laminar. The bulk concentrations c_j obey the convective diffusion equation

$$\frac{\partial c_j}{\partial t} + (\mathbf{v} \cdot \nabla)c_j = \mathrm{Pr}_j^{-1}\nabla^2 c_j. \tag{1}$$

The equation is written in a dimensionless form. The time t is scaled by the inverse rotation frequency ω; the coordinates, by the viscous length $\sqrt{\nu/\omega}$, where ν is the kinematic viscosity; the scale for velocity $\mathbf{v}$ is $\sqrt{\nu\omega}$, and the concentration scale is the concentration of one of the reactants in the oncoming flow C^*; $\mathrm{Pr}_j = \nu/D_j$ is the Prandtl number for the jth species; D_j is the diffusivity; ∇^2 is the Laplace operator.

The boundary conditions on the rotating disk (at $z = 0$) include effects of adsorption and surface reaction. It is essential for the DIFICI mechanism to account for

surface capacitance effects. Denoting *dimensional* surface concentrations as C_j and neglecting surface diffusion, we write the balance equations on the catalytic surface in the form

$$\frac{\omega}{\chi}\frac{\partial C_j}{\partial t} = Q_j + R_j(\mathbf{C}). \tag{2}$$

Here χ is a dimensionless capacitance factor that can have a meaning of active surface area per unit nominal geometric area of the disk; R_j is the production rate of the jth reactant in surface reactions (dependent, generally, on concentrations of all adsorbed species); and Q_j is the net adsorption rate. It is convenient to present all variables and functions as arrays, denoted by respective bold letters: $\mathbf{C}, \mathbf{c}, \mathbf{R}(\mathbf{C}), \mathbf{Q}$. Assuming adsorption equilibrium described by isotherms $C_j = C_j(\mathbf{c})$ yields a relation between surface concentrations and bulk concentrations near the surface, arranged in the array $\mathbf{c}$. The net adsorption rates can be expressed through the diffusional flux at the surface of the rotating disk:

$$Q_j = D_j C^* \sqrt{\frac{\omega}{\nu}}\left(\frac{\partial c_j}{\partial z}\right)_{z=0}. \tag{3}$$

Using this in Eq. (2) yields the boundary conditions at $z = 0$ in a dimensionless matrix form

$$\mathbf{W}\frac{\partial \mathbf{c}}{\partial t} = \mathbf{L}\frac{\partial \mathbf{c}}{\partial z} + \mathbf{f}(\mathbf{c}). \tag{4}$$

Here $\mathbf{f}(\mathbf{c}) = (C^*\sqrt{\omega\nu})^{-1}\mathbf{R}(\mathbf{C}(\mathbf{c}))$ is the array of dimensionless kinetic functions, $\mathbf{W}$ is a matrix with the elements $W_{kj} = (C^*\chi)^{-1}\sqrt{\omega/\nu}\,(\partial C_k/\partial c_j)_{z=0}$, and $\mathbf{L}$ is the diagonal matrix with the elements $L_{jj} = \mathrm{Pr}_j^{-1}$.

In an unbounded system, the components of the flow field $\{v_r, v_\phi, v_z\}$ in Eq. (1) are expressed in cylindrical coordinates $\{r, \phi, z\}$ as [5]

$$v_r = rF(z), \qquad v_\phi = rG(z),$$
$$v_z = H(z), \tag{5}$$

where the functions $F(z)$, $G(z)$, and $H(z)$ have been computed numerically. The stationary concentration field depends on z only [5], and the dimensionless flux at the surface can be expressed as

$$\left(\frac{\partial c_j}{\partial z}\right)_{z=0} = (c_j^\infty - c_j^0)\,\Big/\int_0^\infty \exp\left\{\mathrm{Pr}_j\int_0^\zeta H(\xi)\,d\xi\right\}d\zeta, \tag{6}$$

where c_j^∞ are reactant concentrations in the oncoming flow, and $c_j^0 = c_j^s(0)$ should be determined from the boundary conditions (4). The integral in Eq. (6) can be evaluated with a high level of precision (unless at $\mathrm{Pr} \ll 1$) using the first term of expansion of the velocity field at $z \ll 1$ [5], i.e., approximating $H(z) \sim -az^2$ where

$a \approx 0.51$. Then Eq. (4) is rewritten as

$$-q_0\left(\frac{a}{3\mathrm{Pr}_j^2}\right)^{1/3}(c_j^\infty - c_j^0) = f_j(\mathbf{c}^0), \tag{7}$$

where $q_0 = 1/\Gamma(\frac{4}{3}) \approx 1.12$, and $\Gamma(x)$ is the gamma function.

Equation (7) may have multiple solutions when one of the reactions is autocatalytic. The solutions are spatially homogeneous, since the stationary flux does not depend on transverse coordinates. This expresses the basic property of transport towards an unbounded rotating disk: Its surface is equiaccessible. Further on, we shall investigate a possibility of spontaneous breaking of spatial homogeneity due to the DIFICI mechanism.

In order to study stability of a stationary solution, we consider small perturbations $\tilde{c}_j = c_j - c_j^s$. The convective diffusion equations for perturbations are identical to Eq. (1). Since the convective diffusion equations for all species differ by values of the Prandtl number only, we shall temporarily suppress the species indices. We shall rewrite the general Equation (1) in the cylindrical coordinate system corotating with the disk. Using a common boundary layer approximation, we shall neglect transverse diffusion. The latter may become important only if spontaneous transverse inhomogeneities emerge on a length scale of the same order of magnitude as the thickness of the diffusional boundary layer $(\nu/\omega)^{1/2}\mathrm{Pr}^{-1/3}$. Using also the expressions for the velocity components (5) yields

$$\frac{\partial\tilde{c}}{\partial t} + rF(z)\frac{\partial\tilde{c}}{\partial r} + [G(z)-1]\frac{\partial\tilde{c}}{\partial\varphi} + H(z)\frac{\partial\tilde{c}}{\partial z} = \mathrm{Pr}^{-1}\frac{\partial^2\tilde{c}}{\partial z^2}. \tag{8}$$

We seek solutions in the form

$$\tilde{c} = e^{\lambda t + in\varphi}r^{i\mu}Z(z), \tag{9}$$

where bounded single-valued solutions correspond to real μ and integer n, and the function $Z(z)$ obeys

$$\mathrm{Pr}^{-1}Z''(z) - H(z)Z'(z)$$
$$- \{\lambda + i\mu F(z) + in[G(z) - 1]\}Z(z) = 0. \tag{10}$$

The radial dependence in Eq. (9) breaks down (yielding oscillations with an arbitrarily short period) in an *exponentially close* vicinity of the origin. This could be repaired by bringing back transverse diffusional terms—but then, unfortunately, the variables cannot be separated. We shall proceed keeping in mind that the solutions to be obtained are inapplicable exponentially close to the origin, and assuming that the influence of this minute region can be neglected.

Since we are interested in perturbations excited by surface reactions, it can be safely assumed that they rapidly decay outside the diffusional boundary layer,

being advected back towards the surface by the oncoming flow. Therefore, we can use in Eq. (10) the one-term expansions of the velocity components [5]

$$F(z) \sim az, \qquad G(z) \sim 1 + bz,$$
$$H(z) \sim -az^2, \qquad (11)$$

where $a \approx 0.51$ and $b \approx -0.62$. Moreover, we shall assume that, due to high surface capacitances, the characteristic time scale defining evolution of surface concentrations in Eq. (4) far exceeds unity. Then it is sufficient to consider quasistationary solutions to Eq. (8), and set $\lambda = 0$. Introducing the new variable $\zeta = (\frac{a}{3} \mathrm{Pr})^{1/3} z$, we rewrite Eq. (10) in the form

$$Z''(\zeta) + 3\zeta^2 Z'(\zeta) - 9i\beta\zeta Z(\zeta) = 0, \qquad (12)$$

where $\beta = \frac{1}{3}(\mu + bn/a)$. The solution of (12) satisfying the asymptotic condition $Z(\zeta) \rightarrow 0$ at $\zeta \rightarrow \infty$ is expressed through the Kummer function $U(1 + i\beta, \frac{4}{3}, \zeta^3)$:

$$Z(\zeta) = \frac{\Gamma(1 + i\beta)}{\Gamma(\frac{1}{3})} Z(0)\zeta e^{-\zeta^3} U(1 + i\beta, \tfrac{4}{3}, \zeta^3). \quad (13)$$

Further on, we shall need the derivative of this solution only at $\zeta = 0$. Returning to the original variable z and restoring the species indices we have

$$\frac{dZ_j(0)}{dz} = -\left(\frac{a \, \mathrm{Pr}_j}{3}\right)^{1/3} q(\beta) Z_j(0), \qquad (14)$$

where

$$q(\beta) = \frac{3\Gamma(\frac{2}{3})\Gamma(1 + i\beta)}{\Gamma(\frac{1}{3})\Gamma(\frac{2}{3} + i\beta)}. \qquad (15)$$

Linearizing the boundary condition at the rotating disk Eq. (4) and using the expression for the flux (14) leads to the eigenvalue problem

$$[\mathbf{A} - \lambda\mathbf{W} - \mathbf{l}q(\beta)]\mathbf{Z}(0) = 0, \qquad (16)$$

where $\mathbf{A}$ is a matrix with the elements $a_{ij} = \partial f_i / \partial c_j$ computed at the stationary values $\mathbf{c} = \mathbf{c}_s^0$, and $\mathbf{l}$ is a diagonal matrix with the elements $l_{jj} = (\frac{a}{3})^{1/3} \mathrm{Pr}_j^{-2/3}$.

To obtain explicit DIFICI conditions, we shall consider a two-component system, and assume a linear adsorption relationship (Henry isotherm) $C_j = \gamma_j c_j$. The number of parameters in both Eqs. (7) and (16) can be reduced then by additional rescaling. Denoting $l = l_2\gamma_1/l_1\gamma_2$, we rewrite the eigenvalue problem (16) in an explicit form

$$\lambda^2 + \lambda[-\mathrm{tr}(\mathbf{A}) + q(\beta)(1 + l)] + \det(\mathbf{A})$$
$$- q(\beta)(a_{22} + la_{11}) + lq^2(\beta) = 0. \qquad (17)$$

Denoting $\lambda = \lambda_r + i\lambda_i, q = q_r + iq_i$, and separating the real and imaginary parts of Eq. (17) yields two real

equations

$$\lambda_r^2 - \lambda_i^2 + \lambda_r T_1 - \lambda_i q_i(1 + l) + T_2 = 0,$$
$$2\lambda_r\lambda_i + \lambda_i T_1 + \lambda_r(1 + l)q_i + T_3 = 0, \qquad (18)$$

where

$$T_1 = -\mathrm{tr}(\mathbf{A}) + q_r(1 + l),$$
$$T_2 = \det(\mathbf{A}) - q_r(a_{22} + la_{11}) + l(q_r^2 - q_i^2),$$
$$T_3 = q_i(2lq_r - a_{22} - la_{11}). \qquad (19)$$

The stationary solution is stable if $\lambda_r < 0$ for all real β.

The easiest way to detect possible symmetry breaking is to consider the behavior of λ_r at β close to zero. This analysis is applicable to autocatalytic systems, and should be carried out in the vicinity of a bifurcation point where the stationary solution is marginally stable, and the linearized equation has a zero eigenvalue $\lambda(0) = 0$. The latter is true when the free term in Eq. (17) (that becomes real at $\beta = 0$) vanishes, i.e., $T_2(0) = 0$. The sum of the two eigenvalues must be negative, which requires $T_1(0) > 0$. Thus, we impose the conditions

$$T_1(0) = -(a_{11} + a_{22}) + q_r(0)(1 + l) > 0,$$
$$T_2(0) = lq_r^2(0) - q_r(0)[a_{22} + la_{11}]$$
$$+ a_{11}a_{22} - a_{12}a_{21} = 0. \qquad (20)$$

At $\beta \ll 1$, the real part of λ is quadratic in β. If $\lambda_r''(\beta) > 0$, symmetry breaking is imminent. Using Eq. (19) this condition is expressed, after some algebra, in a compact form

$$\eta^2 - \eta\theta(l + 1 + \psi\theta) > 0, \qquad (21)$$

where

$$\theta = T_1(0) > 0, \qquad \psi = \tfrac{1}{2}q_r''(0)[q_i'(0)]^{-2} \approx 0.71,$$
$$\eta = 2lq_r(0) - la_{11} - a_{22}. \qquad (22)$$

In a particular case $l = 1$, we have $\theta = \eta$, and the inequality (21) cannot be satisfied. Thus, symmetry breaking is impossible in this case as expected.

In terms of the parameters θ, η, the instability domain lies in the half plane $\theta > 0$, and consists of two disconnected parts:

$$\eta > g_1(\theta) = \frac{\theta}{2}\left[l + 1 + \psi\theta + \sqrt{(l + 1 + \psi\theta)^2 - 4l}\right],$$
$$\eta < g_2(\theta) = \frac{\theta}{2}\left[l + 1 + \psi\theta - \sqrt{(l + 1 + \psi\theta^2) - 4l}\right]. \qquad (23)$$

Note that the expression under the radical sign is always positive when $\theta > 0$.

The symmetry breaking conditions can be expressed through more physically meaningful diagonal elements

a_{11}, a_{22} by presenting the latter with the help of Eqs. (22) as

$$a_{11} = \frac{\theta - \eta}{l - 1} + q_r(0), \qquad a_{22} = \frac{\eta - l\theta}{l - 1} + lq_r(0).$$

Using Eq. (23), the boundaries of the instability domain $\eta = g_i(\theta)$ defined by Eq. (23) are presented in the coordinates a_{11}, a_{22} as parametrically defined curves

$$a_{11} = \frac{\theta - g_i(\theta)}{l - 1} + q_r(0),$$

$$a_{22} = \frac{g_i(\theta) - l\theta}{l - 1} + lq_r(0), \tag{24}$$

where $\theta > 0$. The product of off-diagonal elements of the matrix $\mathbf{A}$ is fixed by Eq. (20). The instability domain is bounded by the two curves (24) joined at the point $\theta = 0$, on the one side, and by the locus of a homogeneous Hopf bifurcation, presented by the straight line $\theta = 0$, i.e., $a_{22} + a_{11} = q_0(l + 1)$, on the other side. The instability domains at different values of l are shown in Fig. 1. The domain shrinks as l comes closer to 1. It is notable that, unlike the Turing instability, which is possible only when the reactant with a lower diffusivity is autocatalytic (i.e., at $l > 1$, $a_{11} > 0$, or $l < 1, a_{22} > 0$), the DIFICI may be observed at some $l \neq 1$ when either a_{11} or a_{22} is positive.

The DIFICI on an equiaccessible reaction surface described in this Letter has a much richer mathematical structure than the DIFICI in a one-dimensional setting as originally proposed by Rovinsky and Menzinger [1]. A stationary pattern that may result from a one-dimensional DIFICI should obey, with diffusion neglected, the system of equations

$$v_i \partial c_i / \partial x = f_i(\mathbf{c}), \tag{25}$$

where v_i are different but *constant* velocities. A stationary pattern in this system, either periodic or chaotic,
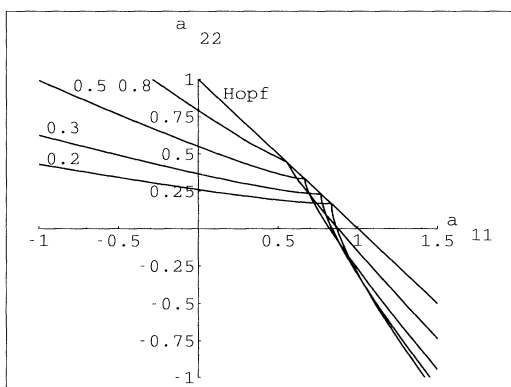

FIG. 1. DIFICI regions at different values of l. The symmetry breaking instability is observed between the straight line denoting the limit of homogeneous Hopf bifurcation and the curves marked by respective values of l. The diagonal elements a_{11}, a_{22} on both axes are rescaled by the factor $q_0(l + 1)$.

is evidently translated into a temporal pattern of a respective dynamical system, with x reinterpreted as time, and v_i as capacitance factors. Such a mapping upon a dynamical system is impossible in a realistic two- or three-dimensional setting where differential velocities are position dependent.

This Letter gives but a first glimpse at patterns on a catalytic surface due to differential advection by establishing a possibility of symmetry breaking at least in a long-scale mode. The long-scale analysis does not actually restrict us to conditions when *only* long-scale patterns are possible, since preferential excitation of long-scale modes occurs in the vicinity of a bifurcation point only. As parameters are shifted deeper into the instability region, the preferred wavelength would typically decrease. This may result either in the establishment of a (nearly) periodic pattern with a preferred wavelength, or in a turbulent pattern, in the case where excitations with different wavelengths are not damped by nonlinear interactions. Formation of short-scale small-amplitude patterns directly at a primary bifurcation point should be also possible, but apparently requires a more complex chemical system (with the number of reactants larger than two or with nonlinear adsorption isoterms) than that considered here.

The study of complex dynamics of large-amplitude patterns is beyond the scope of this Letter. Another problem for future study is competition between the DIFICI in the direction of flow and a common Turing instability in the transverse direction that was studied for one-dimensional flow by Dawson, Lawniczak, and Kapral [6]. Here one can obtain a full range of possibilities, starting from a pattern of purely advective origin, oriented across local streamlines (when these conditions are not met) and going to a pattern dominated by diffusion-induced instabilities, with an intermediate region where both destabilizing factors are active, and the dynamics is most complex.

The DIFICI effect must be present in a vide variety of practical reacting systems, where it is usually masked by inhomogeneities of other origin, e.g., due to inhomogeneities in mass transfer rates. It is important therefore that it be studied under controlled conditions. A rotating disk provides the most convenient experimental setup for studies of this kind.

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