A Reactive System with Diffusive Transport Displaying Two Different Symmetry-Breaking Dissipative Structures

Ariel Fernández
Department of Chemical Physics, The Weizmann Institute of Science, 76100 Rehovot, Israel

Oktay Sinanoğlu
Department of Chemistry, Yale University, New Haven, Connecticut 06511, USA

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An open reactive system is modelled by coupling the chemical kinetics to diffuse transport. This system operates far from the regime of linear irreversible thermodynamics. The kinetics correspond to a certain region in the parameter space of the Oregonator for which two symmetry-breakdowns occur:

a) A periodic orbit contained in an unstable manifold of the phase space. This solution is invariant under time-translations generated by a period.

b) A spatial stationary dissipative structure. This solution is invariant under a subgroup of the space symmetry group.

The initial time periodicity of the system is followed by a spatial pattern.

The restriction to the center manifold in the phase space allows to reduce an infinite-dimensional problem for the bifurcation of a semiflow to a finite dimensional system of ordinary differential equations. The ranges in the control concentrations for this dynamics is found in accord with the experimental values. We also demonstrate that if the vessel is stirred after the Turing pattern has emerged, the freezed wave is destroyed and the time-periodic behavior is achieved again.

Key words: Bifurcation under a symmetry group, Center Manifold Theorem, Dissipative structure.

1. Introduction

Temporal oscillations in the bromate-malonic-cerium B-Z-Z (Belousov-Zaikin-Zhabotinsky [1, 2]) reaction were first reported by Belousov [1]. Spatial organization for the same reaction under different experimental conditions was reported by Busse [3] imposing an initial gradient in the redox indicator (Ferroin).

A more striking experiment featuring initially temporal oscillations and then a spatial organization on which we shall concentrate in this paper, was discussed by Glansdorff and Prigogine [4].

The system is treated as open since the species Ce(III), BrO_3^-, malonic acid and H^+ are in large excess with respect to the concentration of the control chemicals Br^-, Ce(IV), $HBrO_2$ and their concentrations are regarded as parameters of the system.

Reprint requests to Dr. A. Fernández, Department of Chemical Physics, The Weizmann Institute of Science, 76100 Rehovot, Israel.

The experimental conditions reported by Glansdorff and Prigogine are:

$$\begin{aligned} &[\mathrm{Ce(III)}] \cong 8 \times 10^{-3}\ \mathrm{M},\\ &[BrO_3^-] \cong 3.5 \times 10^{-1}\ \mathrm{M},\\ &[\text{Malonic acid}] = 1.2\ \mathrm{M},\\ &[H^+] \cong 1.5\ \mathrm{M}. \end{aligned} \tag{1}$$

The temporal oscillations for the pair Ce(III)/Ce(IV) 30 minutes after mixing of the reactants are detected with the redox indicator.

Gradually, a spatial structure in horizontal layers with alternate excess of Ce(III) and Ce(IV) is observed and at the same time, the temporal oscillations cease. The investigation of this system leads to the study of the singular points of a vector field $\dot{\boldsymbol{Y}}$ on a linear functional space (the concentration space depending on a spatial coordinate). This vector field $\dot{\boldsymbol{Y}}$ couples Fick's diffusive transport to the local kinetic effects (see Field, Koros and Noyes [5, 6]). The problem is first reduced to a finite dimensional one by use of the center manifold theory whose foundations were put forward by Marsden (see for

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example [7]). This theory can be applied to the analysis of Turing instabilities [8] using infinite-dimensional bifurcation techniques [9]. The reader is referred to our paper [10] for the specialization of this theory to the analysis of the dissipative structures arising in open systems driven far from equilibrium (the hard and soft mode instabilities were studied without considering any coupling between organizations by Auchmuty [10]).

After the problem is reduced to Poincare's normal form [11] we derive the following interpretation for the dynamics discussed in [4]:

Let the symmetry group of the system be: $G \times \mathbb{R}$ where G is the spatial symmetry group and $\mathbb{R}$ represents time translations. This symmetry is broken simultaneously in two ways when the homogeneous steady state becomes unstable. A solution emerges which is invariant under $G \times A$ where A represents time translations of the form: $t \to t + na$, n an integer, a a fixed period.

Another solution emerges which is invariant under $B \times \mathbb{R}$ where B is a proper subgroup of G.

If our system were kept well-stirred ($G = B =$ identity) the $G \times A$-invariant solution is an attractive one.

If diffuse transport is included, then the $B \times \mathbb{R}$-invariant solution is attractive and the $G \times A$-invariant one is unstable since the whole manifold containing is becomes unstable.

It will be demonstrated that the fluctuations *initially* grow towards the limit cycle and afterwards they amplify towards the stable dissipative spatial structure.

The parameter space for the system will be denoted by the set of vectors (f, s, w, q). The relationship between the parameters f and w in the Field-Koros-Noyes model in correspondence with the different features of the dynamics will be explored. The region in the parameter space of interest to us is obtained by setting the small parameter $q = 0$ [11].

We shall now derive the fundamentals of the center manifold theory as applied by these authors to open systems operating far from the linear irreversible thermodynamics regime. (The reader is referred to [12] for further details.)

2. The Model

The model of Field, Koros and Noyes [5, 6] representing the basic features of the kinetics for the B-Z-Z system has been coupled with diffusive transport of the chemical species in the model of Tyson and Fife [13] where target pattern organizations are investigated.

The situation analyzed by Tyson and Fife presents no competition of different attractors in the phase space.

We shall consider the local effects described by the kinetic equations

$$\begin{aligned} \dot{X}_1 &= dX_1/dt = s(X_2 - X_1X_2 + X_1), \\ \dot{X}_2 &= dX_2/dt = s^{-1}(fX_3 - X_2 - X_1X_2), \\ \dot{X}_3 &= dX_3/dt = w(X_1 - X_3). \end{aligned} \tag{2}$$

In abbreviated notation, the kinetic equations coupled with diffusion have the form

$$\dot{\boldsymbol{X}} = F(\boldsymbol{X}) + D\boldsymbol{I}\,\partial^2/\partial r^2\,\boldsymbol{X} \tag{3}$$

(r is the spatial coordinate).

Clearly $\dot{\boldsymbol{X}}$ depends smoothly on w. We shall prove first that this model is capable of featuring simultaneously two different ways of losing the symmetry for w smaller than a certain critical value but that only one is detected: the one corresponding to an attractive symmetry-breaking solution displaying horizontal layers each of uniform concentration.

The value of the Fick coefficient D will be evaluated for this system in Section 3. $\boldsymbol{I}$ is the identity 3×3 matrix.

X_1, X_2, X_3 are proportional to the molar concentrations of the control species $HBrO_2$, Br^-, and Ce(IV) respectively (details can be found in [6]).

s and w are defined in Sect. 5, their orders of magnitude are: $s \sim 10^2$, $10^{-3} < w < 1$. The factor f is a stoichiometric factor that arises from the reduction of Ce(IV) reacting with species in large excess (like bromomalonic acid) to provide Br^-. The range $f > 1$ for the system given by (2) will be explored in detail.

For a fixed concentration of H^+, the external parameter $[BrO_3^-]$ can be regarded as the bifurcation parameter. The threshold values are given in Section 5.

2′. Attractive Structures in the Phase Space

The steady state of the kinetic equations (2) is

$$\boldsymbol{X}_0 = (X_{01}, X_{02}, X_{03}) = \left(\frac{f+1}{f-1}, \frac{1}{2}(1+f), \frac{f+1}{f-1}\right). \tag{4}$$

After the change of variables $\boldsymbol{Y} = \boldsymbol{X} - \boldsymbol{X}_0$, problem (3) can be written as

$$\dot{\boldsymbol{Y}} = J(F)|_{\boldsymbol{X}_0}\, \boldsymbol{Y} + \boldsymbol{N}(\boldsymbol{Y}) + D\boldsymbol{I}\frac{\partial^2}{\partial r^2}\boldsymbol{Y}, \tag{5}$$

where $J(F)|_{\boldsymbol{X}_0}$ is the Jacobian matrix of F evaluated at the steady state $\boldsymbol{X}_0$:

$$J(F)|_{\boldsymbol{X}_0} = (\partial F_i/\partial X_j)|_{\boldsymbol{X}=\boldsymbol{X}_0} \tag{6}$$

and

$$\boldsymbol{N}(0) = \frac{\partial \boldsymbol{N}(0)}{\partial X_j} = 0; \quad j = 1, 2, 3. \tag{7}$$

We shall denote

$$L = J(F)|_{\boldsymbol{X}_0} + D\boldsymbol{I}\frac{\partial^2}{\partial r^2} \tag{8}$$

and

$$L_\lambda = J(F)|_{\boldsymbol{X}_0} - \lambda^2 D\boldsymbol{I} = J(F)|_{\boldsymbol{X}_0} - \frac{n^2\pi^2}{\beta^2} D\boldsymbol{I}; \quad n = 0, 1, 2, \ldots. \tag{9}$$

The number β is the length in cm of the vessel of the reaction.

L acts on the space

$$H^2([0, \beta]) \times H^2([0, \beta]) \times H^2([0, \beta]) = S,$$

where $H^2([0, \beta])$ is the second Sobolev space [4] of real functions defined on the real interval $[0, \beta]$. The vector field $\dot{\boldsymbol{Y}} = \dot{\boldsymbol{Y}}_w$ is parametrically smoothly dependent on the parameter w and the map from $S \times \mathbb{R}$ to S given by $(\boldsymbol{Y}, w) \to \dot{\boldsymbol{Y}}_w(\boldsymbol{Y})$ is also smooth.

$J(F)|_{\boldsymbol{X}_0}$ can be regarded as a perturbation of $D\boldsymbol{I}\,\partial^2/\partial r^2$. Therefore, since the operator $D\boldsymbol{I}\,\partial^2/\partial r^2$ generates a compact analytic semigroup (for details, seen Kato [4]), i.e. $\{e^{tD\boldsymbol{I}\partial^2/\partial r^2}\}_{t>0}$, so does L.

It follows that problem (5) defines a flow F_t

$$F_t\, \boldsymbol{Y}(r) = \boldsymbol{Y}(r, t). \tag{10}$$

It represents the evolution of the system, and

$$D_S F_t|_{\boldsymbol{Y}=0} = \mathrm{e}^{tL}, \tag{11}$$

where D_S is the derivative in the sense of Fréchet [4] of F_t in $(H^2([0, \beta]))^3$.

$E(\varrho)$ for any complex number ϱ in the spectrum of L will represent the eigenspace with respect to L associated with the eigenvalue ϱ.

$E(\sigma(\partial^2/\partial r^2) = -\alpha^2)$ represents the eigenspace of L spanned by $\{\boldsymbol{v}_j \cos \alpha r\}_{j=1,2,3}$, where the $\boldsymbol{v}_j$'s are independent eigenvalues of the matrix operator L_α.

At this point we can state the center manifold theorem for semiflows (see for example Marsden [7] and also Holmes and Marsden [9]).

If the following conditions

$$\text{a)}\ \dim_R E[\mathrm{Re}\,\sigma(L) = 0] < \infty, \tag{12}$$

$$\text{b)}\ \dim_R E[\mathrm{Re}\,\sigma(L) > 0] < \infty \tag{13}$$

are fulfilled for problems (5) (Eq. (7) holds).

If at $w = w_0$ the operator L presents a spectrum intersecting the imaginary axis, there exists a center manifold M contained in $S \times R$ with the following properties:

1) M contains $(0, I)$, where I is an open interval around the bifurcation critical point w_0.

2) M is tangent to $E[\mathrm{Re}(\sigma(L)) = 0] \times R$ at $(0, w_0)$. We shall denote this: $M = T_0 E[0]$. (In the original problem (3), M is tangent to $E(0) \times R$ at the steady state $\boldsymbol{X}_0$.)

3) *M is locally invariant:* If $(\boldsymbol{Y}(r), w) \in M$ there exists $T = T(\boldsymbol{Y}(r), w)$ such that $(F_t(\boldsymbol{Y}), w) \in M$ for $0 \leqq t < T(\boldsymbol{Y})$.

4) *M is locally attractive:* There exists an open neighborhood U of M such that if $(\boldsymbol{F}_t(\boldsymbol{Y}), w) \in U$, $t \geqq 0$, then

$$\lim_{t\to\infty} \inf_{(\boldsymbol{V}, w) \in M} \sup_{r \in [0, \beta]} \| (\boldsymbol{F}_t(\boldsymbol{Y}(r)), w) - (\boldsymbol{V}(r), w) \| = 0.$$

5) M is invariant under some subgroup of $G \times R$, and it is tangent to the vector field

$$\dot{\boldsymbol{Y}}\colon (\boldsymbol{Y}, w) \to (\dot{\boldsymbol{Y}}_w(\boldsymbol{Y}), 0).$$

The manifold $T_0 E[\mathrm{Re}\,\sigma(L) > 0]$ is the unstable manifold (see [9] for details) and it is *locally repellent* (the definition is the dual of 4). The crucial property of the center manifold is 4). *It is this property that leads us to identify the center manifold with a dissipative structure of the system.*

If the only eigenvalue of L with vanishing real part is zero and it is an eigenvalue of L_λ for $\lambda \neq 0$, then $M = T_0 E(0)$ is a spatial dissipation structure arising from Turing instability.

If they are two purely imaginary eigenvalues of L ($\pm iA$, A a real number) which are also eigenvalues of L_0, and the third eigenvalue of L_0 is a negative real number, then $M = T_0 E(\pm iA)$ corresponds to temporal oscillations around the steady state. We denote $M_v = T_0 E(\sigma(\partial^2/\partial r^2) = -v^2)$.

A limit cycle will bifurcate from the steady state if the two complex conjugated eigenvalues λ, $\bar{\lambda}$ of L_0

cross the imaginary axis in the direction $\mathrm{Re}\,\lambda < 0 \rightarrow \mathrm{Re}\,\lambda > 0$ while the third eigenvalue remains negative ($\boldsymbol{J}(F)|_{x_0}$ is smoothly dependent on the control parameters, s, and w), cf. [11]. This means that the limit cycle will be locally attractive in M_0 but the whole manifold M_0 is locally repellent because two eigenvalues of L_0 have a positive real part.

The limit cycle is then attractive when regarded as a piece of M_0 but locally repellent when seen immersed in the whole concentration space.

If the diffusion coefficient D were zero, we would be left only with M_0, in which case the system would exhibit periodic behavior. Note that the symmetry group has changed from $G \times \mathbb{R}$ to $\{I\} \times \mathbb{R}$ ($\mathbb{R} \equiv$ time translations).

3. Stationary Waves in the B-Z-Z Reaction

The Turning instability in the B-Z-Z reaction can be explained using kinetic equations that can be regarded as a prototype for the onset of spatial symmetry-breaking instabilities.

We consider an autocatalytic step which enhances the local fluactuations of the concentration of the control species $HBrO_2$. This process competes with diffusion, which tends to reestablish the homogeneous state.

The balance between these competing forces leads to the existence of a dissipative spatial structure.

This simplified model will only be used to estimate the transport coefficient D. The Turing instability proves to occur also using the detailed Field-Körös-Noyes kinetic model [5] as shown in the analysis of the present section. In an early paper, Busse [3] reports spatially periodic variations in the concentration of the redox indicator Ferroin in the B-Z-Z reaction. The theory of center manifolds can be applied in the study of the soft-mode instability for the frozen spatial periodic dissipative structure that emerges in this reaction. First we shall consider a crude model to show how this pattern emerges. The autocatalytic production of $HBrO_2$ follows the overall reaction [6]

$$2\,\mathrm{Ce(III)} + \mathrm{BrO_3^-} + \mathrm{HBrO_2} + 3\,\mathrm{H^+} \rightleftharpoons 2\,\mathrm{Ce(IV)} + \mathrm{H_2O} + 2\,\mathrm{HBrO_2}. \quad (14)$$

This reaction can be spilt into two steps (each corresponds to a one electron transfer):

$$\mathrm{BrO_3^-} + \mathrm{HBrO_2} + \mathrm{H^+} \rightleftharpoons 2\,\mathrm{BrO_2^\cdot} + \mathrm{H_2O}, \quad (15)$$

$$\mathrm{Ce(III)} + \mathrm{BrO_2^\cdot} + \mathrm{H^+} \rightleftharpoons \mathrm{Ce(IV)} + \mathrm{HBrO_2}.$$

The rate for the autocatalytic production of $HBrO_2$ is given by

$$\dot{X} = kX + D\frac{\partial^2 X}{\partial r^2}, \quad (16)$$

$k \sim 0.4\ \mathrm{sec}^{-1}$ (cf. [3]).

Consider in the first place boundary conditions at infinity (or an infinite system). For the slice tangent to the eigenspace of $\partial^2/\partial r^2$ corresponding to the eigenvalue $-\lambda^2$ we have

$$\dot{X}_\lambda = kX_\lambda - \lambda^2 DX_\lambda, \quad (17)$$

where

$$X_\lambda(t) = \mathrm{Re}\int_{-\infty}^{+\infty} e^{-i\lambda r} X(r, t)\,\mathrm{d}r \quad (18)$$

is the Fourier transform of $X(r, t)$ corresponding to the eigenmode $\mathrm{Re}\,e^{i\lambda r}$. If the center manifold corresponding to the frozen dissipative structure lies at $M_\lambda = T_0 E(\sigma(\partial^2/\partial r^2) = -\lambda^2)$, then λ obeys

$$k - \lambda^2 D = 0 \quad (19)$$

or $\lambda = \sqrt{k/D}$ and the wavelength of the stationary wave is

$$\Lambda = \frac{2\pi}{\lambda} = 2\pi\sqrt{\frac{D}{k}}. \quad (20)$$

It was experimentally proved [3] that under the conditions $[\mathrm{BrO_3^-}] \cong 7 \cdot 10^{-2}$ M, $[\mathrm{CH_2(COOH)_2}] \cong 0.3$ M, $[\mathrm{Ce(III)}] \cong 10^{-3}$ M, Λ is approximately 0.5 mm.

This gives $D \cong 2.56 \times 10^{-5}\ \mathrm{cm^2\,sec^{-1}}$.

For a finite system, Neumann (no flux) boundary conditions are applied

$$\frac{\partial X}{\partial r}(0) = \frac{\partial X}{\partial r}(\beta) = 0.$$

The eigenmodes are now

$$\left\{\cos\frac{n\pi}{\beta} r\right\}, \quad n = 0, 1, 2, \ldots.$$

At the slice

$$T_0 E\left(\sigma\left(\frac{\partial^2}{\partial r^2}\right) = -\frac{n^2\pi^2}{\beta^2}\right) = M_{n\pi/\beta} = \left\{\mathrm{Re}\,\frac{1}{\beta^{1/2}}\int_0^\beta \exp\{-in\pi r/\beta\} f(r, t)\,\mathrm{d}r\right\}, \quad (22)$$

$f(r, t)$ belongs to $H^2([0, \beta])$ for each $t \geqq 0$

the evolution of the system is described by the equations

$$\dot{X}_n = kX_n - \frac{n^2\pi^2}{\beta^2} DX_n, \tag{23}$$

$$X_n(t) = \mathrm{Re}\,\frac{1}{\beta^{1/2}} \int_0^{\beta} \exp\{-in\pi r/\beta\}\, X(r,t)\,\mathrm{d}r. \tag{24}$$

In this case, if a center manifold exists, twice the length (2β) of the vessel is an integer multiple of the wavelength of the stationary dissipative structure

$$\Lambda = \frac{2\pi}{\lambda} = \frac{2\pi}{n\pi/\beta} = \frac{2\beta}{n}, \tag{25}$$

where n satisfies the secular equation

$$k - n^2\pi^2 D/\beta^2 = 0. \tag{26}$$

n can be regarded as the integer such that the dissipative structure lies in $M_{n\pi/\beta}$.

The problem is now to see whether such a structure might emerge using the model of Field, Körös and Noyes [5] coupled with diffusion.

We shall consider the case $f = 2$; the results can easily be derived for $1 < f < \sqrt{2} + 1$ in an analogous way. w will be regarded as the bifurcation parameter for the occurrence of the Turing instability.

The rleationship between f and w for stationary waves to occur was, to the best of our knowledge, not explored before.

The development of a spatial dissipative structure for this reaction was first reported by Zhabotinskii [2].

Consider again the space $T_0E(\sigma(\partial^2/\partial r^2) = -\lambda^2)$. We denote $\mu = \lambda^2 D$.

The equation that gives the evolution of the system in that manifold reads

$$\mathrm{Re}\int e^{-i\lambda r}\frac{\mathrm{d}}{\mathrm{d}t}(\boldsymbol{X}(r,t))\,\mathrm{d}r = \begin{pmatrix} -(s/2+\mu) & -2s & 0 \\ -3/2s & -(4/s) & 2/s \\ w & 0 & -(w+\mu) \end{pmatrix} \boldsymbol{X}_\lambda(r,t), \qquad (\boldsymbol{X}_\lambda = \mathrm{Re}\int e^{-i\lambda r}\boldsymbol{X}(r,t)\,\mathrm{d}r) \tag{28}$$

or

$$\dot{\boldsymbol{X}}_\lambda = J(F)|_{x_0}\boldsymbol{X}_\lambda - \mu D\boldsymbol{I}\boldsymbol{X}_\lambda$$

in abbreviated notation.

Since the spectrum of L is equal to the union of the spectra of $L_{\sqrt{\mu/D}}$'s ($\sigma(L) = \bigcup \sigma(L_{\sqrt{\mu/D}})$), the manifold $T_0E(\sigma(L)) = 0$ reduces to $T_0E(\sigma(L_{\sqrt{\mu/D}}) = 0)$ for certain μ.

A non-trivial center manifold will exist only if $L_{\sqrt{\mu/D}}$ has a zero eigenvalue, that is if

$$\det L_{\sqrt{\mu/D}} = -\{\mu^3 + \mu^2(s/2 + 4/s + w) + \mu(4w/s + sw/2 + 2) + 2w\} - w + 3\mu = 0. \tag{29}$$

This equation in μ will only have a positive solution if w lies in the range

$$0 < w < 1/s. \tag{30}$$

Since s is of the order 10^2 [6], (29) will only be satisfied if the orders of magnitude for the parameters are as follows:

$$\mu \lesssim 10^{-2}; \quad \mu \lesssim 1/s,$$
$$w \lesssim 10^{-2}; \quad w < \mu. \tag{31}$$

We observe that the order of magnitude of w is within the experimental range 10^{-3} to 1.

Since from Busse's experiment we can take $\beta \cong 1$ cm, $D \cong 2.56 \times 10^{-5}$ cm^2 sec^{-1}, there should be $n \leqq 10$, since $\mu = n^2\pi^2 D/\beta^2 \lesssim 10^{-2}$.

It is $n = 9$ in the experiment discussed by Glansdorff and Prigogine ([4], page 262).

If $\mu_0(w)$ is the value of μ for wich (20) is satisfied, the fluctuations will not regress to the "homogeneous" manifold $T_0E(\sigma(\partial^2/\partial r^2)) = 0$ but they will be amplified until a dissipative spatial structure lying in $T_0E(\sigma(\partial^2/\partial r^2) = -\mu_0/D)$ is reached. This is because this manifold is locally attractive in the sense described in Section 2. The Turing instability exists for any f in the range $1 < f < 1 + \sqrt{2}$ provided w lies in the range $(0, 1/s)$ (cf. Section 4).

The initially periodic behavior under the conditions stated above is a consequence of the center manifold theorem stated above. As the small periodic solutions bifurcate in the manifold M_0, the real part of the eigenvalues of L_0 becomes positive and the whole manifold M_0 becomes repellent. The oscillatory behavior is thus abandoned and replaced by a Turing spatial organization whose existence is ensured by the fulfillment of (29).

4. Can a Limit Cycle Exist While the Turing Instability is Sustained?

In this section, we shall demonstrate that there exists for any $1 < f < +\sqrt{2}$ a value $w_c(f, s)$ such that

if $0 < w < w_c(f, s)$, limit cycle oscillations occur when diffusion is neglected.

Therefore, the possibility of having both a Turing instability and a limit cycle can be materialized if $1 < f < 1 + \sqrt{2}$, $0 < w < w_c(f, s)$ and $0 < w < 1/s$.

In the last section it was shown that the dissipative spatial structure lies in

$$T_0 E(\sigma(\partial^2/\partial r^2) = -\mu_0/D).$$

This implies that the union $\bigcup_{0 \leqq \mu < \mu_0} T_0 E(\sigma(\partial^2/\partial r^2) = -\mu/D)$ is the unstable manifold and that

$$\bigcup_{\mu > \mu_0} T_0 E(\sigma(\partial^2/\partial r^2) = -\mu/D)$$

is the stable manifold for problem (3). Considering this problem in M_0 is exactly equivalent to neglecting diffusion in problem (5). In this section we shall consider the secular equation for problem (3) in M_0:

$$\Theta^3 + P\Theta^2 + Q\Theta + R = 0. \tag{32}$$

For $f > 1$, we get

$$P = w + \frac{s}{2}(1+f) + \frac{1}{s}\frac{f+1}{f-1} + \frac{1}{s} - s > 0,$$

$$Q = \frac{f+1}{1-f} + f + (P - w)\, w > 0,$$

$$R = w(f+1) > 0. \tag{33}$$

A center manifold for this problem will only exist if two of the eigenvalues $\Theta_{a,b}$ have zero real part (the complex conjugated ones), and the remaining real eigenvalues is negative. Since P, Q, R are positive, this implies that the secular equation should be factorized as follows:

$$(\Theta + M)(\Theta^2 + N) = 0. \tag{34}$$

M and N are positive real functions of w. The center manifold will then be $M = T_0 E(\sigma(\partial^2/\partial r^2)) = \pm i\sqrt{N}$. This factorization is possible if $PQ = R$ for certain values of w. (Then, $M = P$, $N = Q$.) This last equation reads

$$\left(\frac{s}{2}(1+f) + \frac{1}{s}\frac{f+1}{f-1} + \frac{1}{s} - s\right) w^2$$

$$+ \left[\left(\frac{s}{2}(1+f) + \frac{1}{s}\frac{f+1}{f-1} + \frac{1}{s} - s\right)^2 - \frac{2f}{f-1}\right] w$$

$$+ \left(\frac{s}{2}(1+f) + \frac{1}{s}\frac{f+1}{f-1} + \frac{1}{s} - s\right) \cdot \Delta = 0, \tag{35}$$

where

$$\Delta = \frac{f+1}{1-f} + f = \frac{(f-1)^2 - 2}{f-1} \tag{36}$$

is the determinant of the 2×2 upper submatrix of L_0. We only consider here the case $f > 1$.

Equation (35) will only have a positive solution if

$$\text{a)} \quad \left(\frac{s}{2}(1+f) + \frac{1}{s}\frac{f+1}{f-1} + \frac{1}{s} - s\right)^2 - \frac{2f}{f-1} < 0 \tag{37}$$

or

$$\text{b)} \quad \Delta < 0. \tag{38}$$

The first inequality never holds:

Multiplying the l.h.s. of (37) by the positive quantity $4s^2(f-1)^2$, and after a little algebra we get the term

$$[s^2(f-1)^2 + 4f + 2s^2]^2 - 8s^2 f(f-1), \tag{39}$$

which is always positive.

Therefore (35) has a positive solution if and only if $\Delta < 0$. Using (36), this condition reads

$$1 < f < 1 + \sqrt{2}. \tag{40}$$

At this point we observe that the upper bound thus analytically obtained is in perfect agreement with that obtained from numerical analysis of the linear stability of the steady state by Field and Noyes (cf. [6]). Their upper bound is 2.4142. The center manifold will exist for $w = w_c$, where w_c is the positive solution of (35).

As a consequence of the Hopf bifurcation theorem [14], for $0 < w < w_c$ the center manifold $T_0 E(\pm i\sqrt{Q})$ will become a limit cycle contained in M_0.

This is so because for $0 < w < w_c$ the complex conjugated eigenvalues have a positive real part:

$$w = w_c \to \pm i\sqrt{Q}, \tag{41}$$

$$0 < w < w_c \to \lambda_1(w) \pm i\lambda_2(w), \quad \lambda_1, \lambda_2 > 0.$$

5. Critical Values for the Control Parameters

In our case $f = 2$, w_c has the value (cf. (35))

$$w_c = \frac{-\left(\frac{1}{4}s^2 + \frac{16}{s^2}\right) + \sqrt{\left(\frac{1}{4}s^2 + \frac{16}{s^2}\right)^2 + 4\left(\frac{1}{2}s + \frac{4}{s}\right)^2}}{s + 8/s} \tag{42}$$

Since $s \sim 10^2$, we can give the approximate formula

$$w_c \cong \frac{-\frac{1}{4}s^2 + \sqrt{\frac{s^4}{16} + s^2}}{s}. \quad (43)$$

s is the square root of the quotient k_1/k_2, where k_1 is the rate constant for (14) and k_2 is the rate constant for the step

$$Br^- + BrO_3^- + 2H^+ \rightarrow BrO_2H + BrOH, \quad (44)$$

$$k_1 = k_{01}[H^+], \quad k_2 = k_{02}[H^+]^2 \quad \text{(cf. [6])}. \quad (45)$$

Field, Körös and Noyes [5] estimated

$$k_{01} = 1 \times 10^4\ M^{-2}\ sec^{-1},$$

$$k_{02} = 2 \times 1 \quad M^{-3}\ sec^{-1}. \quad (46)$$

In our experimental conditions

$$[H^+] \cong 1.5\ M, \quad [BrO_3^-] \cong 3.5 \times 10^{-1}\ M$$

we have

$$s = \sqrt{\frac{10^4}{2.1 \times 1.5}} \cong 60, \quad (47)$$

$$w_c \cong 0.031. \quad (48)$$

The stochiometric value $f = 2$ lies in the range imposed by (40). We can see that there exists a value w_0 of w such that for $0 < w < w_0$, both (29) and (35) are fulfilled: it suffices to take $w_0 = \text{Min}(w_c, 1/s)$ under our experimental conditions

$$w_0 = 1/s \cong 0.017. \quad (49)$$

w for our experimental conditions can be calculated as (cf. [6])

$$w = k/\sqrt{k_{01}\, k_{02}\, [H^+]^3 [BrO_3^-]}, \quad (50)$$

where k is the rate constant for the process

$$2Ce(IV) + BrCH(COOH)_2 + 2H_2O \quad (51)$$
$$\rightarrow 2Ce(III) + Br^- + CO_2 + 2HCOOH + 3H^+,$$

$k \sim 1\ sec^{-1}$,

$$w \cong \frac{1}{\sqrt{2.1 \times 10^4 \times (1.5)^3 \times 3.5 \times 10^{-1}}} \cong 0.0107. \quad (52)$$

Clearly $0 < w < w_0$ for those concentrations of the external species H^+ and BrO_3^-. $[BrO_3^-]$ can be regarded as the control parameter:

$$[BrO_3^-]_{H.B.} = k^2/w_c^2(s)\, k_{01}\, k_{02}[H^+]^3$$

is the critical value for Hopf-bifurcation of the temporal symmetry-breaking instability;

$$[BrO_3^-]_{T.I.} = s^2\, k^2/k_{01}\, k_{02}[H^+]^3$$

is the critical value for the Turing instability.

6. Interpretation of the Results

From (50) combined with the restriction $0 < w < w_0(f, s)$ it is clear that for a fixed concentration of H^+, the concentration of BrO_3^- can be regarded as the control parameter to obtain a dynamics presenting an unstable limit cycle and a spatial dissipative structure.

We observe that in the system under consideration, $[BrO_3^-]$ is bigger than in the experiment considered by Field and Noyes [6], in which only limit cyle oscillations occur.

If w lies in the range $1/s < w < w_c$ then, since (29) does not have a positive solution while (35) is fulfilled, only limit cycle behavior occurs. This is the case of the Field and Noyes experiment where $w > 1/s$ ($0.1610 > 1/77.27$, cf. [6]).

Observe that the large amplitude oscillations studied by Murray and Hastings [15] do not correspond to the bifurcating small amplitude periodic solutions obtained for $0 \leqq w \leqq w_c$. This is so since under the conditions of Hopf for bifurcation [14] the amplitude of small periodic modes should be proportional to $\sqrt{w_c - w}$ while the periodic solutions of Murray and Hastings have nonzero amplitude at $w = w_c$.

The reader is referred to the work of Hsu and Kazarinov [12] for further details.

Figure 1 displays a cross section of the phase portrait. Each "slice" $M_{\sqrt{\mu/D}}$ should be actually three dimensional because it is the eigenspace of the operator $L_{\sqrt{\mu/D}}$. In the figure, they have been represented by planes.

These planes should actually be glued at the steady state $\boldsymbol{X}_0$; they have been drawn detached from each other to avoid confusion. But if we increase $[BrO_3^-]$, then we can make $0 < w < 1/s$ as in the case of our experiment ($w = 0.0107$, $1/s \cong 0.017$). Under these conditions, we obtain:

1. A limit cycle lying in the unstable manifold M_0. (The existence of this limit cycle is a consequence of the Hopf bifurcation theorem [11].)

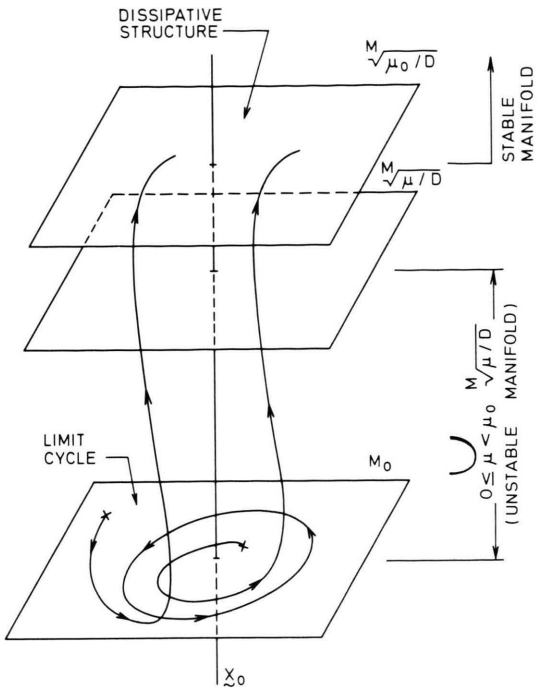

Fig. 1. Representation of the phase portrait for the non-stirred batch reactor. – The solid trajectories indicate the direction in which the fluctuations grow.

2. A center manifold lying in the manifold $M_{\sqrt{\mu_0/D}}$ where μ_0 is a positive solution of (29).

Initially the fluctuations will grow until the center manifold

$$M = T_0 E(\pm i\sqrt{Q(w_c, f)})$$

is reached. The limit cycle is an attractor only in M_0. As the diffusion becomes important, the whole manifold M_0 becomes unstable and the fluctuations will be amplified until the locally attractive manifold $M_{\sqrt{\mu_0(w,f)/D}}$ is reached, this manifold contains the spatial dissipative structure.

The situation can be depicted as follows:

$G \times A$-invariant manifold contained in M_0.

Attractive $B \times \mathbb{R}$-invariant manifold contained in $M_{\sqrt{\mu_0/D}}$.

7. Conclusion

We have considered a reaction-diffusion system which presents reflexion symmetry as well as time-translation symmetry when the homogeneous steady state is stable. For a certain range in the control parameters two different symmetry-breaking solutions simultaneously emerge. One of them breaks the reflexion symmetry if the wave number of the freezed wave is odd. It is this solution that will be observed in an experimental situation since it corresponds to the center manifold of the system.

If the vessel is stirred, the spatial organization is replaced by a temporal organization which in turn becomes the center manifold. By stirring the vessel, we destroy the spatial dissipative structure. This is equivalent to the virtual process of restricting the system to the manifold M_0 where the limit cycle is embedded, thus the temporal oscillations are reactivated.

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