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Chemical Oscillations and Spatial Structures in Polymerisation Reactions

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Abstract

This article discusses the possibility of coupling a polymerization reaction to an oscillatory kinetic model, complemented by diffusion which can lead to spatial structure. We used three well–known mathematical models of oscillators: a variant of the Rossler multivibrator, a model proposed by Edelstein, and the Oregon Oscillator. One or some of the terms in the equations of these models come from a polymerization reaction, while the other terms of these equations will come from collateral processes. So, almost any reaction could become oscillatory and/or with dissipative structure, adding the adequate collateral processes. The propagation stages are considered as invariants and initiation reactions of order $\alpha = 0$, 1, or 2, and termination reactions of order $\beta = 1$ or 2 are assumed. Except in the case $\alpha = 1$, $\beta = 2$, all six remaining reactions combinations (α, β) can be coupled to least one, and often to several of the models. The effects of destabilization a stable homogeneous steady state by the presence of diffusion is also discussed, which is always be possible.

Introduction

Theoretical and experimental studies of oscillating reactions have been studied at many laboratories and the interest of this type of phenomena has increased rapidly which led to the discovery of oscillations in biochemical and chemical systems [1]. Interestingly, in the early studies, thermodynamicists and applied mathematicians worked out models for such reactions and discussed the feasibility of oscillations in homogeneous chemical systems. Later a general criterion was available for the type of chemical reactions that could present undamped oscillations [1].

When the first discoveries in oscillatory chemical reactions [2] and spatial structures were found in chemical systems [3] (e.g., concentration waves), mathematical expressions to fit experimental results were looked for.

Adequate models for the chemical oscillations [4] are provided by non-linear ordinary differential equations when they are considered as precursors of the formal kinetic development. Partial differential equations [5] could explain the appearance of spatial rearrangements when they are applied to the reaction kinetics considering spatial diffusion. There are some kinetic reaction mechanisms, which are in general very complex that can be fit to mathematical models to predict the apparition of oscillations and/or spatial arrangements [6]. Recently, it has been suggested [7] that the mathematical equations of these models could be divided in two groups. Some of these equations will consider the main reactions (object to study), and the rest of them will take in account collateral processes. So, almost any reaction could become oscillatory and/or with dissipative structure by adding the adequate collateral processes. In this paper, examples of the application of this idea to polymerisation reactions, is shown.
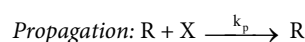
General Theory

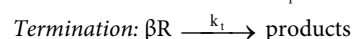### Polymerisation processes and rate equations [7]

Three steps are considered in the polymerisation reactions:

Initiation: $\qquad \alpha X \xrightarrow{\ k_i\ } R$
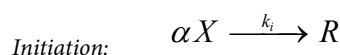
where reaction rate is of the form $R_i \sim X^\alpha$, and α can take the values 0, 1 or 2

Propagation: $R + X \xrightarrow{\ k_p\ } R$

reaction rate is of the form $R_p \sim RX$

Termination: $\beta R \xrightarrow{\ k_t\ }$ products

In this case reaction rate is of the form $R_t \sim R^\beta$ and β can take the values 1 or 2.

By assuming the steady state for the propagators R, that is $R_i = R_t = R_t$, it is obtained that $R \sim X^{\alpha/\beta}$; then the expression for the polymerisation rate $\dot{X}_{pol}$ becomes:

$$\dot{X}_{pol} = -\alpha \cdot k_i \cdot X^\alpha - k_g \cdot X^{\frac{\alpha}{\beta}+1} \tag{1}$$

where k_g includes the constants k_p and k_t.

The term X represents monomer concentration, and the propagation stages are considered as invariants and the different mechanisms of the polymerisations will be denoted using the symbols $[\alpha,]$ [7,8], where the initiation reaction (α) can be of zero, first, 1, or second order and the termination reaction (β) can be of of first or second order.

Analysis without diffusion

Ordinary differential equations system [4,9] in two variables, X and Y, will be considered

$$\dot{X} = M(X, Y)$$
$$\dot{Y} = N(X, Y) \tag{2}$$

where the variable Y represents the concentration of a specie that appears in a collateral process. The steady states denoted by $SS_{(i)}$, fulfill the equalities $\dot{X} = 0$, $\dot{Y} = 0$, and the X and Y concentrations can be calculated by solving $M(X_0, Y_0) = 0$, $N(X_0, Y_0) = 0$ equations. A linearized variational system [10,11] is obtained when considering the perturbations defined as:

$$x(t) = X - X_0$$
$$y(t) = Y - Y_0 \qquad (3)$$

the system is of the form

$$\dot{x} = cx + gy$$
$$\dot{y} = ax + by \qquad (4)$$

where the coefficients

$$c = \left(\frac{\partial M}{\partial x}\right)_0, \; g = \left(\frac{\partial M}{\partial y}\right)_0, \; a = \left(\frac{\partial N}{\partial x}\right)_0, \; b = \left(\frac{\partial N}{\partial y}\right)_0$$

are the elements of the characteristic no–diffusive matrix

$$M_0 = \begin{pmatrix} c & g \\ a & b \end{pmatrix}$$

This matrix trace is

$$T_0 = b + c \qquad (5)$$

and its determinant is

$$Det_0 = bc - a \qquad (6)$$

In the neighbourhood of the steady state (SS) the solutions of (3) are in the form

$$x = Ae^{\omega t}$$
$$y = Be^{\omega t} \qquad (7)$$

where, ω are the roots of the equation:

$$\omega^2 - T_0 \cdot \omega + Det_0 = 0 \qquad (8)$$

The steady state is unstable if, at least, one of these roots has a positive real part. It occurs when $Det_0 < 0$. However, this condition causes the SS to be a "saddle point", which normally involves explosions, and so, it is discarded as realistic chemical model.

A root with a positive real part can be obtained if $T_0 > 0$.

If $T_0 = 0$ and the discriminant is:

$$\Delta_0 = T_0^2 - 4Det_0 \qquad (9)$$

if $Det_0 < 0$ then $\Delta_0 > 0$, the steady state is a node; if $Det_0 > 0$ then $\Delta_0 < 0$, i the steady state s a focus.

In all the equations systems that will be examined, the condition $Det_0 > 0$ will be fulfilled, and the transitions from $T_0 < 0$ to $T_0 = 0$ and to $T_0 > 0$ will be possible, that is, from a stable focus ($T_0 \le 0$, $\Delta_0 \approx - 4Det_0 < 0$) to node ($T_0 = 0$, $\Delta_0 = - 4Det_0 < 0$) and to unstable focus ($T_0 \ge 0$, $\Delta_0 \approx - 4Det_0 < 0$). Hopf [12] proved that this bifurcation leads to the apparition of a limit cycle around the unstable focus, with sustained oscillations of the system. In this paper, the Hopf bifurcations existence in all the studied cases is verified.

Including the diffusion process

If diffusion effects along one dimension (r) are considered, the equations (2) take the form [13,10]

$$\frac{\partial X}{\partial t} = M(X, Y) + D_x \frac{\partial^2 X}{\partial r^2}$$
$$\frac{\partial Y}{\partial t} = N(X, Y) + D_y \frac{\partial^2 Y}{\partial r^2} \qquad (10)$$

where D_x and D_y are diffusion coefficients, respectively. In this context, the steady states are named homogeneous steady state (HSS). Their stability can also be studied by linearization, and when suitable perturbations for the desired boundary conditions are defined. In this paper, the Neuman´s conditions [10] (of no–flow in the system boundary) are used:

$$x(t,r) = Ae^{\omega t} \cos nr = X - X_0$$
$$y(t,r) = Be^{\omega t} \cos nr = Y - Y_0 \qquad (11)$$

where n is the wave number, which under the conditions x(0, L) = ± A and y(0, L) = ±B, must satisfy,

$$n = \frac{m\pi}{L}$$

where L is the length of the system and m = 0, 1, 2, 3, ...(an integer)

The secular matrix of the linearized system takes the form

$$M_n = \begin{pmatrix} c - D_x n^2 & g \\ a & b - D_y n^2 \end{pmatrix} \qquad (12)$$

whose trace is

$$T_n = T_0 - (D_x + D_y) \cdot n^2 \qquad (13)$$

and the determinant is

$$Det_n = Det_0 - n^2 \cdot (bD_x + cD_y) + D_x \cdot D_y \cdot n^4 \qquad (14)$$

Now, trace and determinant depend on the wave number, n. The roots of the secular equation

$$\omega^2 - T_n \cdot \omega + Det_n = 0 \qquad (15)$$

will be also dependent on the wave number. As in the no diffusive case, if one of those roots has a positive real part, the homogeneous steady state will be unstable. That can be so because of the conditions $Det_n < 0$, or $T_n > 0$. The condition $T_n > 0$ is impossible to be fulfilled, unless in the no diffusive case $T_0 > 0$, that is, the homogeneous steady state was already unstable in diffusion absence. So, it is impossible a homogeneous stable steady state, which fulfilled $T_0 < 0$, $Det_0 > 0$, to be destabilized by diffusion. Besides, in the case $T_0 > 0$, if ω had a positive real part because of being $T_n > 0$, that positive real part would be $\omega_{Re+} = T_n/2$ if $\Delta n = T_n^2 - 4Det_n < 0$, or $\omega_{Re+} = [(T_n + \Delta n^{1/2})/2]$ if $\Delta n \ge 0$; in one or the other case, the higher positive value of this real part will be reached when n = 0. That means that in the case of where are several solutions (for some n values), when it is allowed by the limit conditions, the homogeneous solution (n = 0), will be amplified faster and predominates above the no homogeneous ones, and the presence of spatial structures is not probable.

The condition $Det_n < 0$ has not been considered yet. If $p = n^2$, it can be expressed as a second grade polynomial:

$$Det_n = Det_0 - p \cdot (bD_x + cD_y) + D_x D_y p^2 < 0 \qquad (16)$$

and it is possible that it could be fulfilled in some interval $p_1 < p < p_2$ (although $T_0 > 0$ and $Det_0 > 0$, case in which it can be said that the homogeneous steady state can be destabilized by diffusion. Independently of $p_2 > p_1 > 0$, and $p_1 p_2 = Det_0/D_x \cdot D_y$, it is necessary $Det_0 > 0$ to be firstly fulfilled. Moreover, as $p_1 + p_2 = [(b \cdot D_x + c \cdot D_y)/D_x \cdot D_y] > 0$, it is necessary that $bD_x + cD_y > 0$. Finally, the condition for that interval

to exist is that the discriminant must be positive,

$$\Delta_{(16)} = (b \cdot D_x + c \cdot D_y)^2 - 4D_x \cdot D_y \cdot Det_0 > 0 \qquad (17)$$

If all of those conditions are fulfilled, as $T_n < T_0 < 0$, $Det_n < 0 < Det_0$, the inequality $\sqrt{\Delta_n} > \sqrt{\Delta_0}$ will be also fulfilled, and so, $T_n + \sqrt{\Delta_n} > T_0 + \sqrt{\Delta_0}$ could be accepted. The positive real part of ω will be higher for some n $\neq 0$, than for n = 0, and if that is so, the no homogeneous perturbation increases more quickly than the homogeneous one (if both of them coexist and compete).
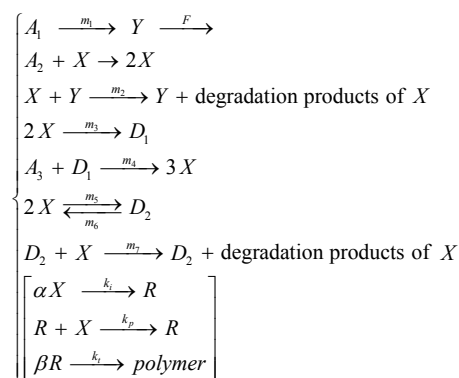
If the homogeneous steady state is unstabilized for any wave number, n, an initial fluctuation having a Fourier component with that n, will force the system to go out from the homogeneous steady state and a new spatial arrangement produced by fluctuations [14] will be obtained.

Now, the three mathematical models will be analysed.

Models

Rossler modified model [7,15,16]

1A. without diffusion:

$$\begin{cases} A_1 \xrightarrow{m_1} Y \xrightarrow{F} \\ A_2 + X \rightarrow 2X \\ X + Y \xrightarrow{m_2} Y + \text{degradation products of } X \\ 2X \xrightarrow{m_3} D_1 \\ A_3 + D_1 \xrightarrow{m_4} 3X \\ 2X \underset{m_6}{\overset{m_5}{\rightleftarrows}} D_2 \\ D_2 + X \xrightarrow{m_7} D_2 + \text{degradation products of } X \\ \begin{bmatrix} \alpha X \xrightarrow{k_i} R \\ R + X \xrightarrow{k_p} R \\ \beta R \xrightarrow{k_t} polymer \end{bmatrix} \end{cases}$$

The kinetic equations:

$$\begin{cases} \dot{X} = A_1 - m_1 X + A_2 X - m_2 XY - 2m_3 X^2 + 3m_1 A_3 D_1 - 2m_5 X^2 + 2m_6 X^2 - m_7 D^2 X - \alpha k_i X^\alpha - k_p RX \\ \dot{Y} = m_1 X - FY \\ \dot{D_1} = m_3 X^2 - m_4 A_3 D_1 \\ \dot{D_2} = m_5 X^2 - m_6 D_2 \\ \dot{R} = k_i X^\alpha - \beta k_t R^\beta \end{cases}$$

When $\dot{D_1} = 0$, $\dot{D_2} = 0$, $\dot{R_0} = 0$, they are reduced to two equations:

$$\begin{cases} \dot{X} = A_1 + (A_2 - m_1)X - m_2 XY + m_3 X^2 - \dfrac{m_7 m_5}{m_6} X^3 - \alpha k_i X^\alpha - k_p \left(\dfrac{k_i}{\beta k_t}\right)^{1/\beta} X^{(\alpha/\beta)+1} \\ \dot{Y} = m_1 X - FY \end{cases}$$

and the following equations are obtained:

$$\begin{aligned} \dot{X} &= -k_1 XY + k_2 X^2 - k_3 X^3 + k_4 X + k_5 \\ \dot{Y} &= k_6 X - k_7 Y \end{aligned} \qquad (18)$$

where the values of $k_1, k_2, k_3, k_4, k_5, k_6$ and k_7 are defined as follows:

Considering the polymerizations types {0, 1} and {0, 2}:

$$A_1 = k_5; \ A_2 = m_1 - k_g = k_4 \left(con \ k_g = \ k_p \left(\dfrac{k_i}{\beta k_t}\right)^{1/\beta}, \ \beta = 1, \ \beta = 2 \right),$$

$$m_2 = k_1, \ m_3 = k_2, \ \dfrac{m_7 m_5}{\quad} = \quad_3, \ k_6 = m_1, \ k_7 = -F$$

for the polymerization type {1, 1}:

$$A_1 = k_5; \ A_2 = -m_1 - k_i = k_4, \ m_2 = k_1, \ m_3 - \dfrac{k_i k_p}{\beta k_t} = k_2, \ \dfrac{m_7 m_5}{m_6} = k_3, \ m_1 = k_6, \ F = k_7$$

for polymerization type {2, 1}:

$$A_1 = k_5; \ A_2 - m_1 = k_4, \ m_2 = k_1, \ m_3 - 2k_i = k_2, \ \dfrac{m_7 m_5}{m_6} + k_p \left(\dfrac{k_i}{2k_t}\right)^{1/2} = k_3, \ m_1 = k_6, \ F = k_7$$

when the polymerization type {2, 2} is considered:

$$A_1 = k_5; \ A_2 - m_1 = k_4, \ m_2 = k_1, \ m_3 - 2k_i - k_p \left(\dfrac{k_i}{2k_t}\right) = k_2, \ \dfrac{m_7 m_5}{m_6} = k_3, \ m_1 = k_6, \ F = k_7$$

A. A concrete case [7] will be considered. With the following values of the constants: $k_1 = 1$, $k_2 = 0.9$, $k_3 = 1$, $k_4 = 0.2$, $k_5 = 0.01$, $k_6 = 1.5\varepsilon$ and $k_7 = \varepsilon$. The system becomes :

$$\begin{aligned} \dot{X} &= -XY + 0.9X^2 - X^3 + 0.2X + 0.01 \\ \dot{Y} &= \varepsilon(1.5X - Y) \end{aligned} \qquad (19)$$

This system has an only one homogeneous steady state ($X_0 = 0.271$, $Y_0 = 0.4065$) and its secular matrix is

$$M_0 = \begin{pmatrix} c = 0.061 & g = -0.7305 \\ a = 1.5\varepsilon & b = -\varepsilon \end{pmatrix}$$

with $T_0 = 0.061 - \varepsilon$, will be positive if $\varepsilon < 0.061$, and $Det_0 = 0.3455\varepsilon > 0$. So, (19) admits Hopf bifurcation and a limit cycle around the unstable steady state for $\varepsilon < 0.061$.

1B. Considering that there is a diffusion process, (18) becomes:

$$\begin{aligned} \dfrac{\partial X}{\partial t} &= -k_1 XY + k_2 X_2 - k_3 X_3 + k_4 X + k_5 + D_x \dfrac{\partial^2 X}{\partial r^2} \\ \dfrac{\partial Y}{\partial t} &= k_6 X - k_7 Y + D_y \dfrac{\partial^2 Y}{\partial r^2} \end{aligned} \qquad (20)$$

and using the constants values of Section 1A

$$\begin{aligned} \dfrac{\partial X}{\partial t} &= -XY + 0.9X_2 - X_3 + 0.2X + 0.01 + D_x \dfrac{\partial^2 X}{\partial r^2} \\ \dfrac{\partial Y}{\partial t} &= \varepsilon \cdot (1.5X - Y) + D_y \dfrac{\partial^2 Y}{\partial r^2} \end{aligned} \qquad (21)$$
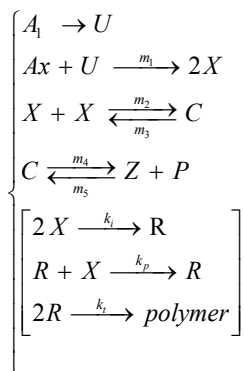
The secular matrix is

$$M_n = \begin{pmatrix} 0.061 - D_x n^2 & -0.271 \\ 1.5\varepsilon & -\varepsilon - D_y n^2 \end{pmatrix}$$

whose trace is $T_n = 0.061 - \varepsilon - (D_x + D_y)n^2$, and the determinant, $Det_n = 0.3455\varepsilon - n^2 \cdot (0.061 \cdot D_y - \varepsilon \cdot D_x) + D_x D_y n^4$. The condition $Det_0 > 0$ is fulfilled; the $bD_x + cD_y > 0$ implies that $0.061D_y > \varepsilon \cdot D_x$, and (17) requires $(0.061D_y - \varepsilon D_x)^2 > 4D_x \cdot Dy \cdot 0.3455\varepsilon$. For $\varepsilon = 1$ (value in which $T_0 < 0$), $D_x = 1$, $D_y = 600$ (adequate units), this condition is also fulfilled. p = 0.025 could be a possible value of p that makes $Det_n < 0$; for that p value, the real part of T_0 is $(0.021/2)$, and its higher than the real part of T_0, $-(T_0/2) < 0$ (since $\Delta_0 \approx -0.5 < 0$, the homogeneous steady state was an stable state).

Edelstein model [7,17,18]

2A. This model is based in an enzymatic mechanism [18-20] whose substrate is monomer X. That makes possible to be applied in biochemical polymerisations

$$\begin{cases} A_1 \ \rightarrow U \\ Ax + U \ \xrightarrow{\ m_1\ } 2X \\ X + X \ \underset{m_3}{\overset{m_2}{\rightleftarrows}} C \\ C \ \underset{m_5}{\overset{m_4}{\rightleftarrows}} Z + P \\ \begin{bmatrix} 2\,X \xrightarrow{\ k_i\ } R \\ R + X \xrightarrow{\ k_p\ } R \\ 2R \xrightarrow{\ k_t\ } polymer \end{bmatrix} \end{cases}$$

The kinetic equations are:

$$\begin{cases} \dot{X} = m_1 XU - 2m_2 XY + m_3 C + m_4 C - k_p R X \\ \dot{U} = A_2 - m_2 XU \\ \dot{Z} = -m_2 ZX + m_3 C + m_4 C - m_5 ZY \\ \dot{C} = m_2 ZX - m_3 C - m_4 C + m_5 Zp \\ \dot{R} = k_i X^2 - 2k_t R^2 \end{cases}$$

Which are reduced to two variables if $\dot{Z} = 0$, $\dot{R} = 0$, $\dot{C} = 0$. Observe that $\dot{Z} + \dot{C} = 0$, then Z + C = B = constant, resulting in the following equations:

$$\begin{cases} \dot{X} = m_1 XU - \left(2k_i + k_p \cdot \sqrt{a^2 + k_i / 2k_t}\right)X^2 - \left[B(m_3 + m_4)(m_1 X + m_3)/(m_2 X + m_5 p + m_3 + m_4)\right] \\ \dot{Y} = A_1 - m_1 XU \end{cases}$$

with the definitions

$$A_1 = A_2/\mu, m_2/\mu = k_i, 2k_i + k_p\sqrt{k_i/2k_t} = k_2, B(m_3+m_4)m_2 = k_3, B(m_3+m_4)m_3 = k_4, m_3 B = k_5, A_2 = k_8, m_1 = k_9$$

it is obtained:

$$\dot{X} = k_1 XY - k_2 X^2 - \frac{k_3 X + k_4}{k_5 X + k_6} + k_7$$

$$\dot{Y} = k_8 - k_9 XY \tag{30}$$

This model applies only to the polymerization type {2,2}.

Considering the following values [7] for the constants (in adequate units): $k_1 = 1/\mu$, $k_2 = 1/\mu$, $k_3 = 60/\mu$, $k_4 = 60/\mu$, $k_5 = 1$, $k_6 = 2.2$, $k_7 = 30/\mu$, $k_8 = 16.858$ and $k_9 = 1$, the equations system becomes:

$$\dot{X} = \frac{1}{\mu}(XY - X^2 - \frac{60(X+1)}{X+2.2} + 30)$$

$$\dot{Y} = 16.858 - XY \tag{31}$$

which has a steady state in $X_0 = 2$, $Y_0 = 8.429$. The secular matrix is

$$M_n = \begin{pmatrix} c = \dfrac{0.3474}{\mu} & g = \dfrac{2}{\mu} \\[2mm] a = -8.429 & b = -2 \end{pmatrix}$$

and the trace, $T_0 = (0.3474/\mu) - 2$, if $T_0 = 0.1737$, then $T_0 > 0$. Moreover, $Det_0 = (16.1633/T_0) > 0$. So, if $\mu < 0.1737$, a limit cycle around the unstable steady state exits.

2B. If the diffusion is considered, (30) can be written as

$$\frac{\partial X}{\partial t} = k_1 XY - k_2 X^2 - \frac{k_3 X + k_4}{k_5 X + k_6} + k_7 + D_x \frac{\partial^2 X}{\partial r^2}$$

$$\frac{\partial Y}{\partial t} = k_8 - k_9 XY + D_y \frac{\partial^2 Y}{\partial r^2} \tag{32}$$

and with the values for the parameters previously used:

$$\frac{\partial X}{\partial t} = \frac{1}{\mu}(XY - X^2 - \frac{60(X+1)}{X+2,2} + 30) + D_x \frac{\partial^2 X}{\partial r^2}$$

$$\frac{\partial Y}{\partial t} = 16,858 - XY + D_y \frac{\partial^2 Y}{\partial r^2} \tag{33}$$

The secular matrix is

$$M_n = \begin{pmatrix} \dfrac{0.3474}{\mu} - D_x n^2 & \dfrac{2}{\mu} \\[2mm] -8.429 & -2 - D_y n^2 \end{pmatrix}$$

whose trace is

$$T_n = \frac{0.3474}{\mu} - 2 - (D_x + D_y)n^2$$

and the determinant

$$Det_n = \frac{16.1633}{\mu} - n^2\left(\frac{0.3474}{\mu}D_y - 2D_x\right) + D_x D_y n^4$$

$Det_0 > 0$ is fulfilled. In order to fulfill the conditions
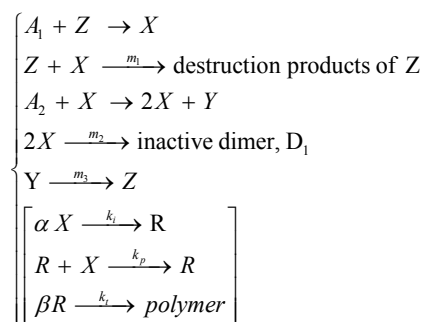
$$\frac{0.3474}{\mu}D_y > 2D_x$$

and

$$\left(\frac{0.3474}{\mu}D_y - 2D_x\right)^2 > 4D_y D_x \frac{16.1633}{\mu}$$

the values $\mu = 1$ (that leads to $T_0 < 0$), $D_x = 1$, $D_y = 600$, are used. So, the conditions for $Det_n < 0$ are fulfilled if $p = 0.2$, value that provides a real part of ω (0.0181/2), higher than the real part of ω_0 (without diffusion), $(\omega_0/2) < 0$, since $\Delta_0 < 0$. The homogeneous steady state was a stable focus and it could be destabilized by diffusion.

Oregon oscillator [7,21], Stiffly coupled oregonator [22]

5A. It was conceived first by Field and Noyes [21] as a model developed from the well-known Belousov–Zhabotinsky oscillating reaction [2]. Those authors explained it in three variables, but it is possible to reduce it to two variables assuming that the third one is always maintained in steady state (stiff coupling) [23], without losing its main important characteristics.

$$\begin{cases} A_1 + Z \ \rightarrow X \\ Z + X \ \xrightarrow{\ m_1\ } \text{destruction products of } Z \\ A_2 + X \ \rightarrow 2X + Y \\ 2X \ \xrightarrow{\ m_2\ } \text{inactive dimer, } D_1 \\ Y \ \xrightarrow{\ m_3\ } Z \\ \begin{bmatrix} \alpha\,X \xrightarrow{\ k_i\ } R \\ R + X \xrightarrow{\ k_p\ } R \\ \beta R \xrightarrow{\ k_t\ } polymer \end{bmatrix} \end{cases}$$

The kinetic equations are:

$$\begin{cases} \dot{X} = A_1 Z - 2m_1 ZX + A_2 X - 2m_2 X^2 - \alpha k_i X^\alpha - k_p RX \\ \dot{Y} = A_2 X - m_3 Y \\ \dot{Z} = - A_1 Z - m_3 Y \\ \dot{R} = k_i X^\alpha - \beta k_t R^\beta \end{cases}$$

Which are reduced to two variables if $\dot{Z} = 0$ (*stiff coupling*), $\dot{R} = 0$;

$$\begin{cases} \dot{X} = \dfrac{(A_1 - m_1 X) m_3 Y}{A_1 + m_1 X} + A_2 X - 2m_2 X^2 - \alpha k_i X^\alpha - k_p \left(\dfrac{k_i}{\beta k_t} \right)^{1/\beta} X^{(\alpha/\beta)+1} \\ \dot{Y} = A_2 X - m_3 Y \end{cases}$$

Considering polymerizations type {0, 1} and {0,2} and with the definitions:

$A_1 = k_1, m_1 = k_2, A_1/m_3 = k_3, m_1/m_3 = k_4, k_6 = 2m_2 +, k_5 = A_2 - k_p (k_i/\beta k_t)^{1/\beta}, k_7 = A_2, k_8 = m_3$

The kinetic equations take the form:

$$\dot{X} = \frac{Y(k_1 - k_2 X)}{k_3 + k_4 X} + k_5 X - k_6 X^2 \tag{34}$$

$$\dot{Y} = k_7 X - k_8 Y$$

Polymerization type {1, 1} with the definitions:

$A_1 = k_1, m_1 = k_2, A_1/m_3 = k_3, m_1/m_3 = k_4, k_5 = A_2 - k_i, k_6 = 2m_2 + k_p (k_i/k_t), k_7 = A_2, k_8 = m_3$

results in (34).

$A_1 = k_1, m_1 = k_2, A_2/m_3 = k_3, m_1/m_3 = k_4, k_5 = A_2, k_6 = 2m_2 + 2k_i + k_p (k_i/2k_t)^{1/2}, k_7 = A_2, k_8 = m_3$

Polymerization {2, 2} and the definitions:

give as a result equations (34).

3A. Assuming the following values for the parameters [7] $k_1 = 1$, $k_2 = 1$, $k_3 = 1$, $k_4 = 1$, $k_5 = 1$ and $k_6 = 8.375 \cdot 10^{-6}$ (proposed value by Field y Noyes considering the bromine chemistry [24], in order to explain the Belousov–Zhabotinsky reaction); $k_7 = \varepsilon$ and $k_8 = \varepsilon$, the system (34) becomes:

$$\dot{X} = \frac{Y(1 - X)}{1 + X} + X - 8.375 \cdot 10^{-6} X^2 \tag{35}$$

$$\dot{Y} = \varepsilon (X - Y)$$

There is a steady state in $X_0 = Y_0 = 488.68$. The secular matrix is

$$M_0 = \begin{pmatrix} c = 0.9877 & g = -0.9959 \\ a = \varepsilon & b = -\varepsilon \end{pmatrix}$$

and the trace is $T_0 = 0.9877 - \varepsilon$. $Det_0 = 8.176 \cdot 10^{-3} \varepsilon > 0$. If $\varepsilon < 0.9877$, the steady state will be unstable and a limit cycle around it will be arise.

3B. Introducing the diffusion process, (34) can be written as

$$\frac{\partial X}{\partial t} = \frac{Y(k_1 - k_2 X)}{k_3 + k_4 X} + k_5 X - k_6 X^2 + D_x \frac{\partial^2 X}{\partial r^2}$$

$$\frac{\partial Y}{\partial t} = k_7 X - k_8 Y + D_y \frac{\partial^2 Y}{\partial r^2} \tag{36}$$

Using the same constants that in 3B, the system is

$$\frac{\partial X}{\partial t} = \frac{Y(k_1 - X)}{1 + X} + X - 8.375 \cdot 10^{-6} X^2 + D_x \frac{\partial^2 X}{\partial r^2}$$

$$\frac{\partial Y}{\partial t} = k_7 X - k_8 Y + D_y \frac{\partial^2 Y}{\partial r^2} \tag{37}$$

with the following secular matrix

$$M_n = \begin{pmatrix} 0.9877 - D_x n^2 & -0.9959 \\ \varepsilon & -\varepsilon - D_y \cdot n^2 \end{pmatrix}$$

whose trace is,

$$T_n = 0.9877 - \varepsilon - (D_x + D_y) \cdot n^2$$

and the determinant,

$$Det_n = 8,176 \cdot 10^{-3} \varepsilon - n^2 (0.9877 D_y - \varepsilon D_x) + D_x D_y n^4$$

When $Det_0 > 0$, the conditions $0.9877 \cdot D_y > \varepsilon \cdot D_x$, and (17) if $\varepsilon = 1$ (that means $T_0 < 0$), $D_x = 1$, $D_y = 2$, can be fulfilled; for example, the value $p = 0.2$ satisfies the conditions for $Det_n < 0$. For that value, the real part of ω_n is $0.2837/2$, higher than the part corresponding to $n = 0$, that would be $T_0/2 < 0$ (since $\Delta_0 < 0$). The homogeneous steady state is a stable focus.

Conclusion

Except for the polymerisation {1, 2}, the rest of the polymerisations types considered in this paper can fit, at least, to one and frequently to some of the three mentioned oscillators. Supercritical bifurcation defbpf, with limit cycle apparition in absence of diffusion, is possible in all the considered models. Moreover, in all cases, it is possible to get an unstable homogeneous steady state of diffusion, and a homogeneous steady state (stable in diffusion presence) can be destabilized by diffusion. By the moment, it is difficult to predict the scientific [25-30] or technological applications that could have the theoretical development made in this paper.

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