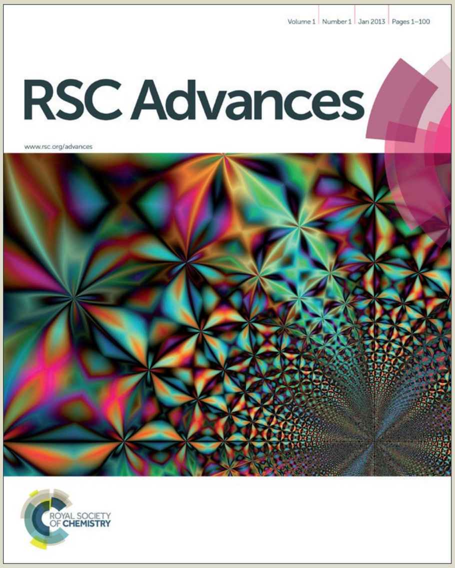
RSC Advances



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

RSC Advances

PAPER

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Oregonator Generalization as a Minimal Model of Quorum Sensing in Belousov-Zhabotinsky Reaction with Catalyst Confinement in Large Populations of Particles

E. Szabo[a]†

We consider the case of the Belousov-Zhabotinsky (BZ) oscillating reaction with metal catalyst confined in a discrete phase of cation-exchange resin particles, and we show that modelling of the sudden transitions from steady state to fully synchronized oscillations, previously described only in terms of quorum sensing, does not necessarily require particulate fine-graining of the models. As a minimal representation of the phenomenon we propose a generalized version of the Oregonator with only one additional parameter φ – the total volume fraction of the catalytic phase in the system. We show that the kinetic consequences of the catalyst confinement can be interpreted through φ acting as the second variable stoichiometric factor in the Oregonator mechanism, at the same time decreasing the order of autocatalysis, but also weakening the negative feedback. Based on the proposed model, analysis of the so-called quorum sensing is provided in terms of the classic notions of Hopf bifurcation. The model reproduces correctly that 1) oscillations of the system are only exhibited above a certain critical threshold of φ, and 2) as φ is decreased, so are the amplitudes of oscillations, while 3) the periods of oscillations remain almost the same. The model thus appears to be a reasonable minimal representation of the loci of full synchronization in the BZ reaction with catalyst confinement, and so it might have the potential of being a convenient starting point for further refinements representing more complicated transitions in this system.

1. Introduction

Progress in understanding of the internal dynamics of oscillating chemical systems also stimulated much interest in how they behave in external interaction. Since the pioneering report of synchronization between two Belousov-Zhabotinsky (BZ) oscillators by Marek and Stuchl,[1] investigations of chemical oscillations in reactors coupled by mass transfer found many followers,[2-16] whether using reactors with common walls with perforations, apertures, canal ports, or active transport between reactors using pumps. Additionally, coupling between oscillating reactions was also achieved without direct mass transfer, using bridged electrodes,[17] reactors mutually controlling each other's feed flow,[18,19] or common cooling circuits.[20] These efforts yielded a variety of phenomena, including rhythm splitting,[1,3] phase-difference locking,[2,8-10,14-17] oscillator death[4,8,17,19,20] and rhythmogenesis,[5,19,20] entrained responses to pulsed forcing,[6,7,11,16] presynchronization,[14] quasiperiodicity, bursting and chaos,[10-13,15,17] or coupled chaotic states.[12,13] Moreover, the investigations were also extended to three[21-26] or more interacting reactors,[27-32] offering further new insights into how these systems react to external stimuli in terms of their propagation,[21,22,27-30] or even their encoding and decoding.[31,32] Several approaches exist in studying collective dynamics of even larger numbers of oscillators. A remarkable body of experimental evidence has been collected for arrays of globally coupled electrodes,[33] exhibiting chaotic synchronization,[34-38] Kuramoto phase synchronization,[39-43] noise coherence,[44-46] amplitude death,[47] resonant clusters,[48] desynchronization,[49] effects of nonisochronicity,[50,51] and even genuine chimera symmetry breaking.[52] In another line of work, observations of BZ reaction droplets dispersed in oil[53] were extended by the use of microfluidics, affording continuous droplet chains[54] and droplet stacks,[55] which can synchronize into in-phase and anti-phase oscillations, Turing patterns, or phase clusters.

1.1. Large Populations of BZ Oscillators by Catalyst Confinement

A very straightforward method for preparing large populations of BZ oscillators was developed based on the possibility of confining the metal catalyst into particles of cation-exchange resin. Such catalyst-doped particles were immediately noted as very interesting for their ability to exhibit characteristic oscillations individually,[56] as well as in bulk.[57,58] While some authors focused on refining the mechanism of their oscillations, in particular the dependence of the natural frequencies on the radii of the resin beads,[59-61] majority directed their attention to how the increased numbers of

---

[a] *Department of Earth and Planetary Sciences, Harvard University, 100 Edwin H. Land Blvd, Cambridge, MA 02142, USA. E-mail: szabo@fas.harvard.edu*

† Current address: Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, Mlynská dolina, 84215 Bratislava, Slovakia. E-mail: erik.szabo@fns.uniba.sk

Electronic Supplementary Information (ESI) available: Detailed commentary to equations 1-5 and 11-12. See DOI: 10.1039/x0xx00000x these oscillators gave rise to synchronized activity, from small groups[62-66] to larger and larger monolayers.[67-69] More recently, unstirred setups were also used for observations of phase clusters and chimera-like patterns arising from specific coupling of the oscillators through selective illumination,[70,71] and even for observations of stochastic synchronization effects of noise.[72,73]

There is, however, only a few studies of these oscillators in stirred systems,[74-77] perhaps due to the obstacles that the stirring poses to proper imaging. Information extracted from such measurements is, in principle, limited to be only statistical, and not able to specify directly individual histories for each oscillator, even though recently, indirect evidence has been used to support existence of phase clusters in these systems,[77] despite this limitation. Still, the most prominent experimental observation in this line of work seems to be the fact that some critical density of catalytic particles is required to make the system oscillate in bulk.

1.2. Understanding the BZ Catalyst Particles' Quorum Sensing

In reminiscence of similar behavior in populations of bacteria or yeast,[78-81] the fact that there is a threshold in the total amount of oscillators required to observe bulk oscillations in the system was coined as quorum sensing.[75] Accordingly, the mechanistic explanation of the phenomenon was also formulated based on models heavily focused on representing each oscillator individually and examining the global dynamics of their synchronization through detailed statistics of their more local interactions.

Such fine-graining is certainly justified in situations where the examined phenomena are local in their character. Detailed consideration of phase information from individual oscillators is indispensable in studying any state of the system preceding full synchronization, e.g. transitions occurring gradually, through formation of clusters, or in studying chimera symmetry breaking etc. But one has to wonder whether there might be a more efficient approach for cases when the given collective behavior has a prominent component, which could be modelled as globally uniform, and whether the so-called quorum sensing might be such a case.

This follows the convenient approach to investigating coupled oscillators – starting with a first-order description of the dynamics that is globally uniform, e.g. based on the mean-field approximation, and only then adding the finer details, which are more localized, in further refinements. With populations of BZ oscillators, too, it should be of interest to distinguish these different orders in the dynamics of the system. Of course, there will be features, which can only be understood through fine-grained approaches, with full resolution in phase information. But perhaps we might have a better chance in understanding these more localized phenomena, if we first formulate an approximate framework for describing those aspects that arise globally. These could be consequences of the bulk chemical effects arising without regard to phase information, e.g. as a manifestations of catalyst confinement in modified overall stoichiometry of the system.

For sure, the so-called quorum sensing in populations of BZ oscillators certainly does seem to have a globally uniform aspect to it – based on the total content of catalyst-confining particles, the system can behave as a globally uniform oscillator, or it can be globally in a steady state. Although the existing experimental data[74-77] is not sufficient to map out a complete phase diagram and assert definite conclusions about how abundant are the mixed states of transitions between these extreme cases, it is without doubt that in many experiments the transition is sudden.[74-76] This makes it seem quite likely that even in modelling of these sudden transitions we might find an approximate first-order representation, where the local details of the transition are equally reduced. Perhaps, on this level, the corresponding threshold of the catalytic particles might not even need to be treated differently from the fact that some threshold concentrations of molecules are required with respect to any other reagent in the solution, e.g. malonic acid, or bromate.

How the concentrations of BZ reagents determine whether oscillations are exhibited or not is traditionally understood in terms of Hopf bifurcation, based on the global mass action of the species, without any need for fine-graining of the models by describing individually every single molecule involved. This is, obviously, in dramatic contrast to current interpretations of how the presence of oscillations in BZ reaction is determined, if the catalyst is confined into a discrete population of catalytic resin beads. The purpose of this paper is to analyze some models of such catalyst confinement in BZ oscillators, and attempt to clarify whether the particulate character of the catalytic phase plays a critical role in correct representation of its global behavior, or conversely, whether the so-called quorum sensing might be represented, to some extent, without the fine-graining, and understood in much simpler terms of Hopf bifurcation, as well.

2. Fine-Grained Modelling Bead By Bead

Despite the complex chemistry of BZ reaction, for many purposes the vital essence of its oscillations may be captured, with good agreement, by the classic Oregonator model[82] consisting of five reaction steps:

$$\begin{gathered}
A + Y \xrightarrow{k_1} X + P \\
X + Y \xrightarrow{k_2} 2P \\
A + X \xrightarrow{k_3} 2X + 2Z \\
2X \xrightarrow{k_4} A + P \\
B + Z \xrightarrow{k_5} 0.5fY
\end{gathered} \tag{1}$$

Mass balance of the intermediates leads to 3 differential equations describing the dynamics through concentrations of $HBrO_2$, Br^- and Ce^{IV}, denoted as X, Y and Z, respectively:

$$\frac{\mathrm{d}X}{\mathrm{d}t} = k_1AY - k_2XY + k_3AX - 2k_4X^2$$
$$\frac{\mathrm{d}Y}{\mathrm{d}t} = -k_1AY - k_2XY + 0.5fk_5BZ \qquad (2)$$
$$\frac{\mathrm{d}Z}{\mathrm{d}t} = 2k_3AX - k_5BZ$$

Of course, in the case of confining the catalyst into particles of cation-exchange resin, any of the steps, where species Z is involved, is also confined exclusively to this phase. As already pointed out, various levels of detail are possible in approaching a mathematical representation of such confinement. For example, in the line of one possible approach, Showalter et al.[74-77] chose to model the situation by considering each catalytic particle individually. Inside each particle, the chemical compositions were considered as homogeneous, represented by triplets of concentrations X_i, Y_i and Z_i. An extra pair of concentrations X_s and Y_s represented the composition of the surrounding solution. Therefore, for a system of N particles this approach yielded simulations based on 3N+2 differential equations.

While Showalter et al. chose to employ the ZBKE model[83] of BZ reaction for their calculations, the overall rationale of their approach may be implemented with any model. Adopting the outlined representation with the more traditional option, the Oregonator, the corresponding 3N+2 differential equations are:

$$\frac{\mathrm{d}X_i}{\mathrm{d}t} = k_1AY_i - k_2X_iY_i + k_3AX_i - 2k_4X_i^2 + \frac{k_{ex}S_i}{V_i}(X_s - X_i)$$
$$\frac{\mathrm{d}Y_i}{\mathrm{d}t} = -k_1AY_i - k_2XY_i + 0.5fk_5BZ_i + \frac{k_{ex}S_i}{V_i}(Y_s - Y_i)$$
$$\frac{\mathrm{d}Z_i}{\mathrm{d}t} = 2k_3AX_i - k_5BZ_i \qquad (3)$$
$$\frac{\mathrm{d}X_s}{\mathrm{d}t} = k_1AY_s - k_2X_sY_s - 2k_4X_s^2 - \frac{k_{ex}}{V_s}\sum_i S_i(X_s - X_i)$$
$$\frac{\mathrm{d}Y_s}{\mathrm{d}t} = -k_1AY_s - k_2X_sY_s - \frac{k_{ex}}{V_s}\sum_i S_i(Y_s - Y_i)$$

where S_i and V_i denote the individual surface area and volume of the i-th particle, V_s denotes the total volume of the solution, and k_{ex} is the mass transfer coefficient giving a characteristic of the mass exchange between the catalytic particles and the solution in the form of an intensive quantity, expressing the number of moles of an intermediate crossing the interface per unit of time per unit of interface area and per unit of concentration difference that causes the transport (specifically, k_{ex} is assumed to be identical for all species, X, Y and Z; for further details of how the above system of equations was derived and how k_{ex} should be understood, refer to more elaborate treatment available in Supplementary Information, Sections S2-S4).

3. Simplification to Single Catalytic Phase

In search for a representation that would distinguish the global (bulk) dynamics of the system from the more fine-grained (phase-dependent) features, model 3 can be greatly simplified by considering the case when the catalyst-carrying particles are monodisperse. In the regard of size, this was, in fact, already assumed by Showalter et al., even though their simulations still retained individual character of each particle in assumptions of random variations in their initial states, as well as in the stoichiometric factors f describing the organic subset of the reaction, which were chosen for each particle individually. However, if we consider all particles identical in every regard, including those that Showalter et al. varied, the whole population may be represented, at any time, by just one triplet of "unison" variables X_b, Y_b and Z_b. Denoting the radius of all particles as r, and their total volume as $\sum V_i = V_{b,tot}$, we arrive (as shown in Supplementary Information, Section S5) to the following description of the system:

$$\frac{\mathrm{d}X_b}{\mathrm{d}t} = k_1AY_b - k_2X_bY_b + k_3AX_b - 2k_4X_b^2 + \frac{3k_{ex}}{r}(X_s - X_b)$$
$$\frac{\mathrm{d}Y_b}{\mathrm{d}t} = -k_1AY_b - k_2XY_b + 0.5fk_5BZ_b + \frac{3k_{ex}}{r}(Y_s - Y_b)$$
$$\frac{\mathrm{d}Z_b}{\mathrm{d}t} = 2k_3AX_b - k_5BZ_b \qquad (4)$$
$$\frac{\mathrm{d}X_s}{\mathrm{d}t} = k_1AY_s - k_2X_sY_s - 2k_4X_s^2 - \frac{3k_{ex}V_{b,tot}}{rV_s}(X_s - X_b)$$
$$\frac{\mathrm{d}Y_s}{\mathrm{d}t} = -k_1AY_s - k_2X_sY_s - \frac{3k_{ex}V_{b,tot}}{rV_s}(Y_s - Y_b)$$

Having replaced 3N+2 variables by just five, the size of the problem is now independent from the number of catalyst-carrying particles, even though their combined (collective) effect still remains present – as "bulk" variables X_b, Y_b and Z_b.

4. The Simplest Model of Confined-Catalyst BZ

If the catalyst particles are small enough, the model may be reduced one step further, by assuming that X and Y are exchanged between the particles and the solution very fast (in the system 4, e.g., $r \to 0$ yields $3k_{ex}/r \to \infty$). Under these circumstances, only Z remains distributed inhomogeneously, as it is captured inside the catalytic particles. On the other hand, due to the fast mass transport, the concentrations of X and Y must become the same throughout the system, inside or out of the particles (for discussion showing that this assumption is, in fact, not any less realistic than assumptions already implied by other authors in all existing models of this particular system, see Supplementary Information, Section S6). Denoting the volume fraction of the system corresponding to the catalyst-carrying phase as $V_b/(V_b+V_s) = \varphi$, and emphasizing the confinement of Z (and all its reactions) exclusively to this fraction by denoting it as Z_φ, the system 4 is ultimately reformulated into just three equations (for detailed procedure of how this was derived see Supplementary Information, Section S6):

$$\frac{\mathrm{d}X}{\mathrm{d}t} = k_1AY - k_2XY + \varphi k_3AX - 2k_4X^2$$
$$\frac{\mathrm{d}Y}{\mathrm{d}t} = -k_1AY - k_2XY + 0.5\varphi f k_5BZ_\varphi \qquad (5)$$
$$\frac{\mathrm{d}Z_\varphi}{\mathrm{d}t} = 2k_3AX - k_5BZ_\varphi$$

Obviously, this representation of the BZ reaction with catalyst confined into a discrete fraction of the system is, just a generalized version of the original Oregonator, with only one additional parameter φ, which represents the total volume fraction of the catalyst-confining phase. In fact, the system of equations 5 corresponds to dynamical equations that could be derived directly from a modified version of the Oregonator, if the φ is not considered only as the volume fraction that the catalytic particles occupy in the system, but also as an additional variable stoichiometric factor, that modifies the production and consumption of X and Y in reactions involving the catalyst:

$$A + Y \overset{k_1}{\rightarrow} X + P$$
$$X + Y \overset{k_2}{\rightarrow} 2P$$
$$A + X \overset{k_3}{\rightarrow} (1+\varphi)X + 2Z \qquad (6)$$
$$2X \overset{k_4}{\rightarrow} A + P$$
$$B + Z \overset{k_5}{\rightarrow} 0.5\varphi fY$$

It is interesting to note that based on the modified mechanism 6, the overall kinetic effect of the catalyst confinement may be interpreted as simultaneous modification of the two steps that lie at the heart of Oregonator's nonlinearity. Decreasing the population of catalyst particles puts more emphasis (by giving more space) to the reactions that are catalyst-independent, and therefore it formally decreases the order of autocatalysis from 2 to 1+φ, but at the same also weakens the negative feedback loop, replacing f with φf.

5. Analysis of the Proposed Model

In the form given by the system of equations 5, the effect of the catalyst confinement on the reaction may be understood by analyzing these equations in the same way as originally undertaken with the Oregonator.[82,84,85] Firstly, after scaling to dimensionless form and with the steady-state assumption applied to Y, we arrive to a reduced system of two ODEs:

$$\varepsilon\frac{\mathrm{d}x}{\mathrm{d}\tau} = x(\varphi - x) + f\varphi z\frac{q-x}{q+x} \qquad (7)$$
$$\frac{\mathrm{d}z}{\mathrm{d}\tau} = x - z$$

Looking at the corresponding nullclines, in the specific case of φ = 1 the diagram will be just that of the original Oregonator. However, as the value of φ is decreased, the parabolic portion of the x-nullcline becomes, according to 7, $z \approx x(\varphi - x)/f\varphi$. Interestingly, this change is, at the same time significant and subtle, as illustrated by the nullcline diagrams for various values of φ, depicted in Figure 1.

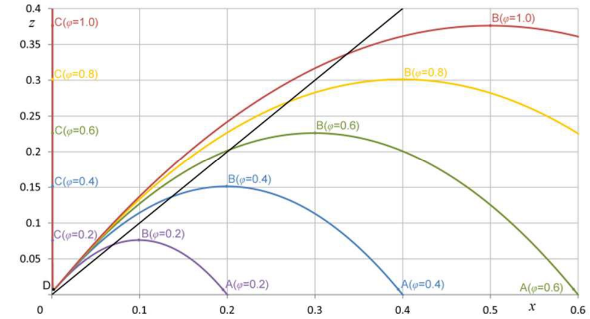


Figure 1. Nullcline diagram and positions of boundary points A-D of the ODE system 7 for values of *f*=2/3, *q*=8×10^{-4} and *φ*=1.0 (red), 0.8 (yellow), 0.6 (green), 0.4 (blue) and 0.2 (violet).

Even though the new parameter φ affects the absolute position of the steady state (and the magnitude of the limit cycle, for that matter), the relative geometry of the nullclines, on the other hand, remains qualitatively the same. For example, if f and q are such that the z-nullcline intersects the x-nullcline parabola at its vertex for φ = 1, the same will be true (approximately) for all other φ. Varying the stoichiometric factor f leads to the same type of bifurcation behavior as in the original Oregonator, and the bounds on the values of f allowing oscillations remain the same for all values of φ. Nevertheless, φ does affect the stability of the steady state as a function of ε, since the Jacobian of the system is given as:

$$\mathcal{J} = \begin{pmatrix} \dfrac{\varphi - 2x}{\varepsilon} - \dfrac{2\varphi f q z}{\varepsilon(q+x)^2} & 1 \\ \dfrac{\varphi f}{\varepsilon}\dfrac{q-x}{q+x} & -1 \end{pmatrix} \qquad (8)$$

The effect of φ on the locus of points in the ε-f plane where the trace of this Jacobian vanishes is demonstrated in Figure 2.

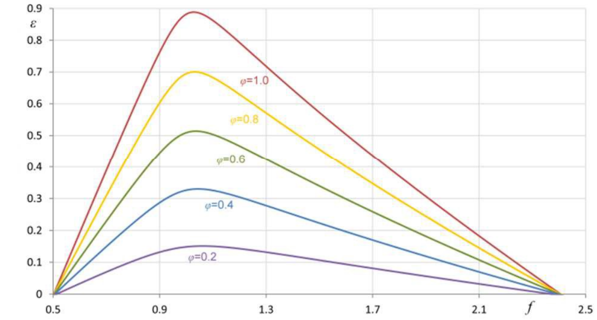


Figure 2. Locus of Hopf bifurcation points in the *f*-*ε* plane, delimiting the oscillatory region of the ODE system 7, for values of *f*=2/3, *q*=8×10^{-4} and φ=1.0 (red), 0.8 (yellow), 0.6 (green), 0.4 (blue) and 0.2 (violet).

6. Explaining the Effect of the Catalytic Phase Content

As can be seen in Figure 2, as well as proven mathematically, the values of ε corresponding to Hopf bifurcation points change almost proportionally with φ. The maxima of ε allowing oscillations are still at f=1, but their values drop by the factor of φ, and the area of the oscillatory region of the system shrinks accordingly. As a consequence, at any fixed value of ε (as given by the ratio of concentrations of bromate and organic substrate) oscillations may only appear if φ exceeds a certain threshold value corresponding to a critical content of catalytic particles, and below this threshold the system will evolve towards a stable steady state. Obviously, this reproduces the essence of observations that led to denoting the phenomenon as quorum sensing, only now in much simpler terms of the classic notions of Hopf bifurcation.

For further support of this model being a suitable minimal representation of the global dynamics of the catalyst-confined modification of BZ reaction, and the corresponding quorum sensing, we can also investigate how the parameter φ enters the expressions for approximate coordinates of the boundary points of the limit cycle of oscillations (in Figure 1 as A-D). This is summarized in Table 1, and a few examples of oscillations just around the critical value of φ are shown in Figure 3.

Table 1. The values of *x*, *y*, *z* for the extreme points of the limit cycle (denoted A-D, referring to Figure 1), expressed in terms of *f*, *q* and *φ*.

	x	y	z
A	$\varphi-(1+\sqrt{2})^2q$	$(1+\sqrt{2})^2q$	$(1+\sqrt{2})^2q/f$
B	$\varphi/2$	$\varphi/2$	$\varphi/4f$
C	$q+8q^2/\varphi$	$\varphi^2/8q$	$\varphi/4f$
D	$(1+\sqrt{2})q$	$(1+\sqrt{2}/2)\varphi$	$(1+\sqrt{2})^2q/f$

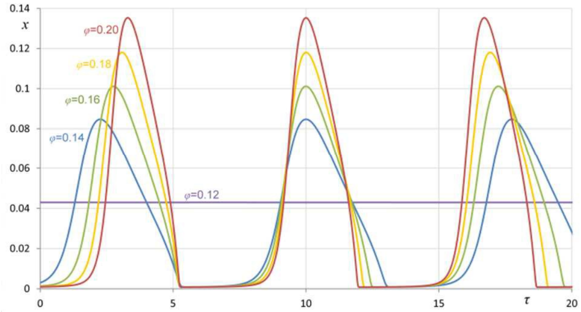


Figure 3. Limit cycle oscillations (red to blue) and the steady state (violet) in the values of *x*, as obtained by integration of the ODE system 7 for values of *f*=2/3, *q*=8×10^{-4}, *ε*=4×10^{-2}, and *φ*=0.20 (red), 0.18 (yellow), 0.16 (green), 0.14 (blue) and 0.12 (violet).

As clearly demonstrated by the coordinates in Table 1, as well as by the examples of oscillations in Figure 3, decreasing the value of φ also decreases the amplitudes of oscillations. Conversely, the period of oscillation seems to be affected by the value of φ to a much lesser extent. In fact, if we approximate the period by the time spent on the limit cycle between points A and B (referring to Figure 1), the period may be estimated as:

$$T_{AB}=\int_{x_A}^{x_B}\frac{\varphi-2x}{x(x+\varphi(f-1))}\,dx$$

$$T_{AB}=\left[\frac{lnx-(2f-1)ln(x+\varphi(f-1))}{f-1}\right]_{x_A}^{x_B} \tag{9}$$

If approximate values of $x_A\approx\varphi$ and $x_B\approx\varphi/2$ are used to evaluate this expression, it turns out that the parameter φ does not appear in the period of oscillation, and so the period of oscillation is approximately the same for all values of φ, being only a function of f in unchanged form as reported for the original Oregonator by Tyson.[84,85] These predictions about the amplitudes of oscillations and their periods offer further agreement of the proposed model with experimental data reporting the so-called quorum sensing among catalyst-carrying particles in BZ reaction.

7. How the Model Approaches Synchronization

Finally, it is worth noting that the proposed model of the confined-catalyst BZ oscillations also allows for a very straightforward expression of synchronization in the case when the system contains two initially distinct populations of catalyst-carrying particles. If their contents in the system are φ_1 and φ_2, and initially each of them is in a different state, i.e. with different initial values of Z, denoted as Z_1 and Z_2, the proposed model describes the system by a set of four equations:

$$\begin{aligned}\frac{dX}{dt}&=k_1AY-k_2XY+(\varphi_1+\varphi_2)k_3AX-2k_4X^2\\ \frac{dY}{dt}&=-k_1AY-k_2XY+0.5fk_5B(\varphi_1Z_1+\varphi_2Z_2)\\ \frac{dZ_1}{dt}&=2k_3AX-k_5BZ_1\\ \frac{dZ_2}{dt}&=2k_3AX-k_5BZ_2\end{aligned} \tag{10}$$

After scaling and application of steady-state approximation for Y, analogously as above, we find:

$$\begin{aligned}\varepsilon\frac{dx}{d\tau}&=x(\varphi_1+\varphi_2-x)+f(\varphi_1z_1+\varphi_2z_2)\frac{q-x}{q+x}\\ \frac{dz_1}{d\tau}&=x-z_1\\ \frac{dz_2}{d\tau}&=x-z_2\end{aligned} \tag{11}$$

This system of equations becomes particularly graphic with a more suitable change of variables. If instead of z_1 and z_2 we reformulate the equations in terms of just one of them, e.g. in terms of $z=z_2$, and their difference, $\zeta=z_1-z_2$, and instead of the two the contents of individual populations, φ_1 and φ_2, we pick just one of them, e.g. $\varphi=\varphi_1$, and instead of the other we reformulate in terms of their sum $\varphi_{tot}=\varphi_1+\varphi_2$, we obtain:

$$\varepsilon\frac{\mathrm{d}x}{\mathrm{d}\tau} = x(\varphi_{tot} - x) + f\varphi_{tot}z\frac{q-x}{q+x} + f\varphi\zeta\frac{q-x}{q+x}$$

$$\frac{\mathrm{d}z}{\mathrm{d}\tau} = x - z \qquad (12)$$

$$\frac{\mathrm{d}\zeta}{\mathrm{d}\tau} = -\zeta$$

In this system of three equations, the first two are analogous to the system 7, but there is one more equation that describes the difference between the two populations of catalytic particles. According to this last equation, this difference between the values of z in the two catalytic phases must decay exponentially to $\zeta \to 0$, until the system is governed again by only the first two equations, identical to system 7, but with the content of catalytic phase given by φ_{tot}.

Certainly, the situation can be more complicated in the case of more than two populations. However, the system of equations 12 demonstrates that under the assumptions given in developing the proposed model (corresponding to very strong coupling due to very fast mass transfer between the catalytic phase and the solution), two populations of catalyst-carrying particles will always synchronize, and the synchronized state will be approached exponentially. Whether this synchronized state will be oscillatory or a steady state is determined only by the total catalyst phase content φ_{tot}. This is illustrated in Figure 4, showing two populations of catalyst particles that would not be capable of producing oscillations on their own, but after synchronization their combined effect does yield oscillatory behaviour.

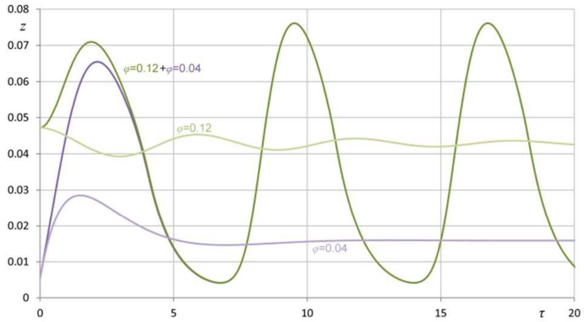


Figure 4. Two populations of catalyst-carrying particles, each evolving to a steady state when on its own (pale lines), but synchronized into oscillations when present together (dark lines), as obtained by integration of the ODE system 7 and 11 for values of f=2/3, q=8×10^{-4}, ε=4×10^{-2}, x[0]=0.047 (for all) and φ=0.12, z[0]=0.047 (green) and φ=0.04, z[0]=0.0053 (violet).

Conclusions

In conclusion, the proposed model seems to capture the essential features of the sudden transitions of the BZ reaction with particle-confined catalyst between its globally steady state and globally synchronized oscillations. These were previously interpreted only by the notion of quorum sensing and by deriving the global behavior from carefully analyzing how the individual particles interact locally. Certainly, the proposed model is not aimed to interpret all aspects of the dynamics of this system, e.g. it cannot provide any local details of the intermediate states involved in the transitions. These will be observed only with more elaborate models that consider each catalytic particle individually. However, predictions of the model are in agreement with how the fully synchronized states are observed experimentally. This suggests that the sudden transitions from non-oscillatory regime to uniform limit cycle oscillations at a specific threshold of the catalytic particle content may be understood in terms of the classic notions of Hopf bifurcation.

As a consequence, it seems that the sudden quorum sensing of catalyst-carrying particles in BZ reaction is, in essence, not too different from other transitions of the system, as observed when any other reagent crosses the threshold required for oscillations. Underlying the quorum sensing of the catalyst-confining particles, the system seems to have important features that are of global nature, contributing to its dynamics through the global mass balance of chemicals modifying the overall stoichiometry, rather than through phase details of individual interactions. Fine-graining of models to the level of individual particles for the purpose of representing this global behavior thus appears superfluous, and the proposed simple model seems to be a reasonable macroscopic limit for representation of the global aspect in the collective dynamics of BZ reaction with catalyst confinement in large populations of catalytic particles, including the phenomenon of their sudden quorum sensing. As such, we believe that it might provide a convenient approximate first-order representation of the system, suitable for adding further details of more localized features, i.e. phase information refinements.

Acknowledgements

The author wishes to thank to Juan Pérez-Mercader for mentoring and support, to Alberto P. Muñuzuri for critical reading of the manuscript and committed discussions about alternative interpretations of collective phenomena observed in BZ reaction with catalyst confinement, to J.-S. Gagnon for his many valuable advices on improving the clarity of the manuscript, and to all other members of Pérez-Mercader's team, for countless inspiring and motivating exchanges.

Notes and references

1 M. Marek, I. Stuchl, *Biophys. Chem.*, 1975, **3**, 241.
2 H. Fujii, Y. Sawada, *J. Chem. Phys.*, 1978, **69**, 3830.
3 K. Nakajima, Y. Sawada, *J. Chem. Phys.*, 1980, **72**, 2231.
4 K. Bar-Eli, S. Reuveni, *J. Phys. Chem.*, 1985, **89**, 1329.
5 M. Boukalouch, J. Elezgaray, A. Arneodo, J. Boissonade, P. De Kepper, *J. Phys. Chem.*, 1987, **91**, 5843.
6 M. Dolník, E. Padušáková, M. Marek, *J. Phys. Chem.*, 1987, **91**, 4407.
7 M. Dolník, M. Marek, *J. Phys. Chem.*, 1988, **92**, 2452.
8 M. F. Crowley, I. R. Epstein, *J. Phys. Chem.*, 1989, **93**, 2496.
9 M. Yoshimoto, K. Yoshikawa, Y. Mori, I. Hanazaki, *Chem. Phys. Lett.*, 1992, **189**, 18.
10 S. I. Doumbouya, A. F. Muenster, C. J. Doona, F. W. Schneider, *J. Phys. Chem.*, 1993, **97**, 1025.

11 J. Kosek, M. Marek, *J. Phys. Chem.*, 1993, **97**, 120.
12 M. J. B. Hauser, F. W. Schneider, *J. Chem. Phys.*, 1994, **100**, 1058.
13 K.-P. Zeyer, A. F. Münster, M. J. B. Hauser, F. W. Schneider, *Chem. Phys.*, 1994, **101**, 5126.
14 J. Miyazaki, S. Kinoshita, *Phys. Rev. E*, 2006, **74**, 056209.
15 A. Lekebusch, F. W. Schneider, *J. Phys. Chem. B*, 1997, **101**, 9838.
16 O. Pešek, L. Schreiberová, I. Schreiber, *Phys. Chem. Chem. Phys.*, 2011, **13**, 9849.
17 M. F. Crowley, R. J. Field, *J. Phys. Chem.*, 1986, **90**, 1907.
18 J. Weiner, R. Holz, *J. Phys. Chem.*, 1992, **96**, 8915.
19 R. Holz, F. W. Schneider, *J. Phys. Chem.*, 1993, **97**, 12239.
20 K.-P. Zeyer, M. Mangold, E. D. Gilles, *J. Phys. Chem. A*, 2001, **105**, 7216.
21 V. Votrubová, P. Hasal, L. Schreiberová, M. Marek, *J. Phys. Chem. A*, 1998, **102**, 1318.
22 V. Nevoral, V. Votrubová, P. Hasal, L. Schreiberová, M. Marek, *J. Phys. Chem. A*, 1997, **101**, 4954.
23 M. Yoshimoto, K. Yoshikawa, Y. Mori, *Phys. Rev. E*, 1993, **47**, 864.
24 K. Yoshikawa, K. Fukunaga, H. Kawakami, *Chem. Phys. Lett.*, 1990, **174**, 203.
25 N. Schinor, F. W. Schneider, *Biophys. Chem.*, 2000, **85**, 199.
26 P. Marmillot, M. Kaufman, J.-F. Hervagault, *J. Chem. Phys.*, 1991, **95**, 1206.
27 I. Stuchl, M. Marek, *J. Chem. Phys.*, 1982, **77**, 2956.
28 W. Hohmann, N. Schinor, M. Kraus, F. W. Schneider, *J. Phys. Chem. A*, 1999, **103**, 5742.
29 W. Hohmann, M. Kraus, F. W. Schneider, *J. Phys. Chem. A*, 1997, **101**, 7364.
30 J. P. Laplante, T. Erneux, *Physica A*, 1992, **188**, 89.
31 G. Dechert, K.-P. Zeyer, D. Lebender, F. W. Schneider, *J. Phys. Chem.*, 1996, **100**, 19043.
32 J.-P. Laplante, M. Pemberton, A. Hjelmfelt, J. Ross, *J. Phys. Chem.*, 1995, **99**, 10063.
33 I. Z. Kiss, W. Wang, J. L Hudson, *J. Phys. Chem. B*, 1999, **103**, 11433.
34 W. Wang, I. Z. Kiss, J. L Hudson, *Chaos*, 2000, **10**, 248.
35 W. Wang, I. Z. Kiss, J. L. Hudson, *Phys. Rev. Lett.*, 2001, **86**, 4954.
36 I. Z. Kiss, Y. Zhai, J. L. Hudson, *Phys. Rev. Lett.*, 2002, **88**, 238301.
37 I. Z. Kiss, Y. Zhai, J. L. Hudson, *Phys. Rev. Lett.*, 2005, **94**, 248301.
38 I. Z. Kiss, Q. Lv, J. L. Hudson, *Phys. Rev. E*, 2005, **71**, 035201.
39 I. Z. Kiss, J. L. Hudson, *Phys. Chem. Chem. Phys.*, 2002, **4**, 2638.
40 I. Z. Kiss, W. Wang, J. L. Hudson, *Chaos*, 2002, **12**, 252.
41 I. Z. Kiss, Y. Zhai, J. L. Hudson, *Science*, 2002, **296**, 1676.
42 I. Z. Kiss, Y. Zhai, J. L. Hudson, *Ind. Eng. Chem. Res.*, 2002, **41**, 6363.
43 Y. Zhai, I. Z. Kiss, J. L. Hudson, *Ind. Eng. Chem. Res.*, 2004, **43**, 315.
44 I. Z. Kiss, J. L. Hudson, G. J. Escalera Santos, P. Parmananda, *Phys. Rev. E*, 2003, **67**, 035201.
45 I. Z. Kiss, Y. Zhai, J. L. Hudson, C. Zhou, J. Kurths, *Chaos*, 2003, **13**, 267-278.
46 I. Z. Kiss, J. L. Hudson, J. Escalona, P. Parmananda, *Phys. Rev. E*, 2004, **70**, 026210.
47 Y. Zhai, I. Z. Kiss, J. L. Hudson, *Phys. Rev. E*, 2004, **69**, 026208.
48 I. Z. Kiss, Y. Zhai, J. L. Hudson, *Phys. Rev. E*, 2008, **77**, 046204.
49 Y. Zhai, I. Z. Kiss, H. Kori, J. L. Hudson, *Physica D*, 2010, **239**, 848.
50 M. Wickramasinghe, M. Mrugacz, I. Z. Kiss, *Phys. Chem. Chem. Phys.*, 2011, **13**, 15483.
51 M. Wickramasinghe, I. Z. Kiss, *Phys. Rev. E*, 2013, **88**, 062911.
52 M. Wickramasinghe, I. Z. Kiss, *PLoS ONE*, 2013, **8**, e80586.
53 O. Steinbock, S. C. Müller, *J. Phys. Chem. A*, 1998, **102**, 6485.
54 M. Toiya, V. K. Vanag, I. R. Epstein, *Angew. Chem.*, 2008, **120**, 7867.
55 M. Toiya, M.; H. O. González-Ochoa, V. K. Vanag, S. Fraden, I. R. Epstein, *J. Phys. Chem. Lett.*, 2010, **1**, 1241.
56 J. Maselko, K. Showalter, *Nature*, 1989, **399**, 609.
57 J. Maselko, J. S. Reckley, K. Showalter, *J. Phys. Chem.*, 1989, **93**, 2774.
58 J. Maselko, K. Showalter, *Physica D*, 1991, **49**, 21.
59 K. Yoshikawa, R. Aihara, K. Agladze, *J. Phys. Chem. A*, 1998, **102**, 7649.
60 R. Aihara, K. Yoshikawa, *J. Phys. Chem. A*, 2001, **105**, 8445.
61 D. S. Huh, M. S. Kim, S. J. Choe, *Bull. Korean Chem. Soc.*, 2001, **22**, 867.
62 N. Nishiyama, K. Eto, *J. Chem. Phys.*, 1994, **100**, 6977.
63 K. Miyakawa, T. Okabe, M. Mizoguchi, F. Sakamoto, *J. Chem. Phys.*, 1995, **103**, 9621.
64 N. Nishiyama, *Physica D*, 1995, **80**, 181.
65 N. Nishiyama, T. Matsuyama, *J. Chem. Phys.*, 1997, **106**, 3427.
66 D. Guo, Y. Li, B. Zheng, *J. Phys. Chem. A*, 2013, **117**, 6402.
67 R. Toth, A. F. Taylor, *J. Chem. Phys.*, 2006, **125**, 224708.
68 M. R. Tinsley, A. F. Taylor, Z. Huang, K. Showalter, *Phys. Chem. Chem. Phys.*, 2011, **13**, 17802.
69 M. R. Tinsley, A. F. Taylor, Z. Huang, K. Showalter, *Phys. Rev. Lett.*, 2009, **102**, 158301.
70 A. F. Taylor, P. Kapetanopoulos, B. J. Whitaker, *Phys. Rev. Lett.*, 2008, **100**, 214101.
71 M. R. Tinsley, S. Nkomo, K. Showalter, *Nature Phys.*, 2012, **8**, 662.
72 H. Fukuda, H. Nagano, S. Kai, *J. Phys. Soc. Jpn.*, 2003, **72**, 487.
73 H. Fukuda, H. Morimura, S. Kai, *Physica D*, 2005, **205**, 80.
74 R. Toth, A. F. Taylor, M. R. Tinsley, *J. Phys. Chem. B*, 2006, **110**, 10170.
75 A. F. Taylor, M. R. Tinsley, F. Wang, Z. Huang, K. Showalter, *Science*, 2009, **323**, 614.
76 M. R. Tinsley, A. F. Taylor, Z. Huang, F. Wang, K. Showalter, *Physica D*, 2010, **239**, 785.
77 A. F. Taylor, M. R. Tinsley, F. Wang, K. Showalter, *Angew. Chem. Int. Ed.*, 2011, **50**, 10161.
78 S. De Monte, F. d'Ovidio, S. Danø, P. G. Sørensen, *Proc. Natl. Acad. Sci. USA*, 2007, **104**, 18377.
79 C. M. Waters, B. L. Bassler, *Annu. Rev. Cell Dev. Biol.*, 2005, **21**, 319.
80 J. Jordi Garcia-Ojalvo, M. B. Elowitz, S. H. Strogatz, *Proc. Natl. Acad. Sci. USA*, 2004, **101**, 10955.
81 J. D. Dockery, J. P. Keener, *Bull. Math. Biol.*, 2001, **63**, 95.
82 R. J. Field, E. Körös, R. M. Noyes, *J. Am. Chem. Soc.*, 1972, **94**, 8649.
83 A. M. Zhabotinsky, F.; Buchholtz, A. B. Kiyatkin, I. R. Epstein, *J. Phys. Chem.*, 1993, **97**, 7578.
84 J. J. Tyson, *J. Chem. Phys.*, 1977, **66**, 905.
85 J. J. Tyson, *Ann. N. Y. Acad. Sci.*, 1979, **316**, 279.

TABLE OF CONTENTS

Oregonator demonstrates that quorum sensing in populations of Belousov-Zhabotinsky oscillators comes from modification of stoichiometry by catalyst confinement.