# A Reaction-Diffusion Model for a Chemo-Hydrodynamical Effect in a Belousov Zhabotinsky Oscillator

Mihnea R. Hristea, Jakob Klien and Florian Wodlei*

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Fachübergreifende Forschungscluster der Alpen-Adria-Universität Klagenfurt

ALPEN-ADRIA UNIVERSITÄT KLAGENFURT I WIEN GRAZ

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LIVING SYSTEMS **RESEARCH**, Roseggerstr. 27/2, A-9020 Klagenfurt, AUSTRIA, EU, www.ilsr.at, *florian.wodlei@ilsr.at

Cluster ***Self-Organizing Systems***, Universität Klagenfurt, A-9020 Klagenfurt, AUSTRIA, EU, https://selforganizing.wordpress.com/

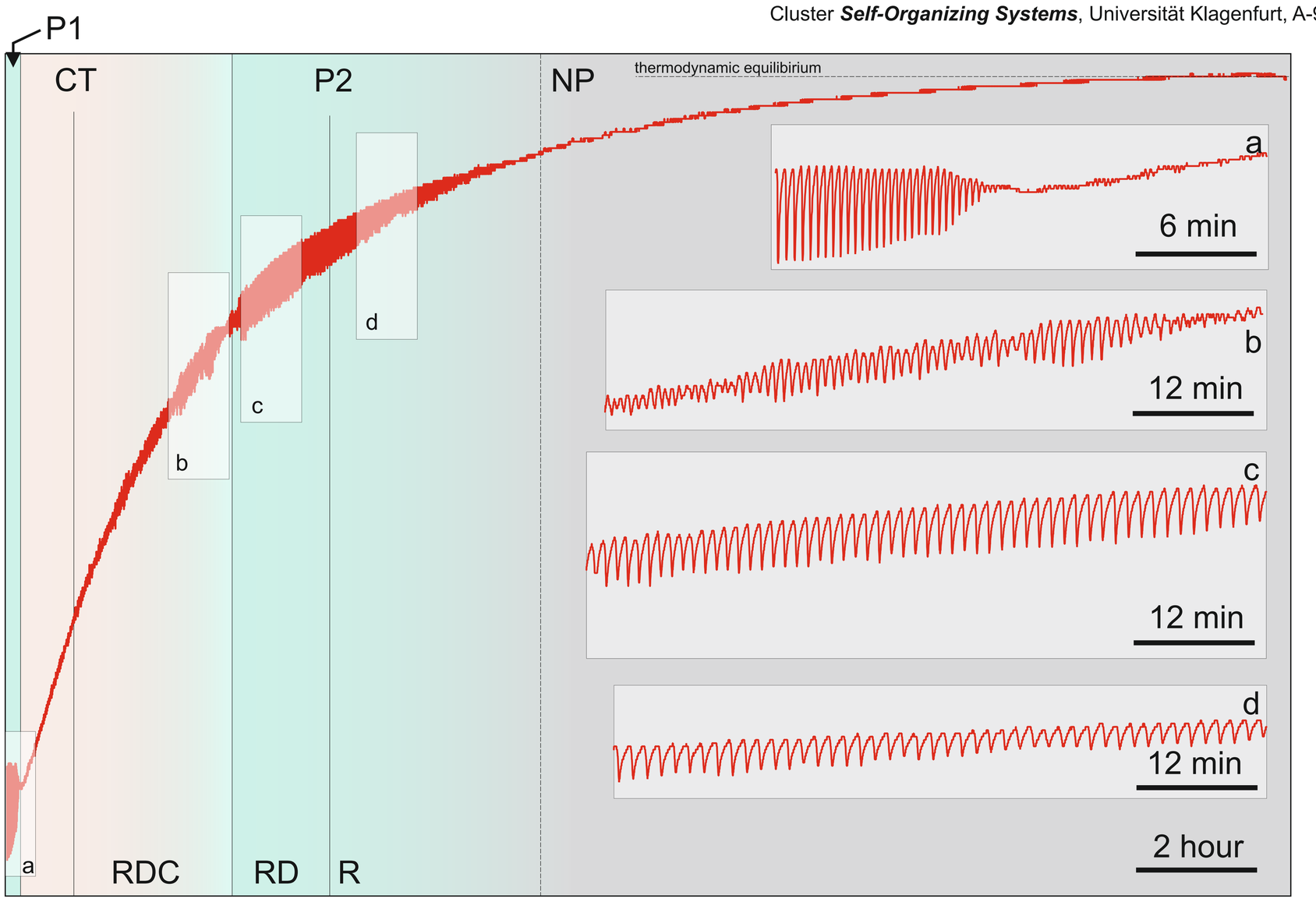


*Figure 1: Long-term evolution of an unstirred ferroin-catalyzed Belousov Zhabotinsky Reaction. Labels on top indicating the different stages: P1: first periodic phase; CT: chaotic transient; P2: second periodic phase; NP: non-periodic phase leading to the thermodynamic equilibrium. Labels on the bottom indicating the dominant effects at play (after Marchettini et al. [2]): RDC: Reaction + Diffusion + Convection; RD: Reaction + Diffusion; R: Reaction dominated regime. Insets are showing the magnification of the boxes in the different regimes. Total time around 22 hours.*

***ABSTRACT.*** The coupling between the nonlinear kinetics and the transport phenomena leads to a complex evolution of a closed unstirred Ferroin-catalyzed Belousov Zhabotinsky reaction. An initially periodic phase evolves into a chaotic one, which itself evolves back into another periodic phase that last until the reaction reaches thermodynamic equilibrium. We have discovered that a limited stirring phase can result in the disappearance of the chaotic transient, leading to a purely periodic evolution of the system. We describe this effect here in detail and show our first results in modeling this complex behavior.
After successfully implementing a modified FKN [1] reaction model developed by Marchettini et al. [2] that assumes reactants consumption we are following the original ideas of Turing [3] to take also diffusion into account. With this simplified reaction-diffusion model we are able to reproduce the periodic behavior of the system. Modifying this reaction-diffusion equation by adding an advective term to model the limited stirring of the system is the task of our ongoing research.

## Experimental Facts - The Effect of a Limited Stirring Phase

The effect of a limited stirring phase was investigated under different conditions (changing dimension and volume of the beaker, different stirring rates and times). In general we can distinguish three scenarios:

1) If the BZ reaction is not stirred it evolves from a periodic (PI) over an aperiodic (CH) to a second periodic phase (PII) (this behavior is also reported by Marchettini et al. [1])

2) If the BZ reaction is stirred for (at least) 30 minutes right after the first periodic phase (PI) the behavior changes. During stirring the oscillations become regular and after stopping they continue for some while. Then a chaotic phase (CH) as in case (1) starts which again after some time changes into a second periodic phase (PII)

3) If the BZ reaction is stirred for (at least) 60 minutes right after the first periodic phase (PI) the behavior changes again. During stirring the oscillations become regular and after stopping they remain regular and the periodic behavior continues. I.e. the chaotic phase ***disappears.***

## Materials and Methods

For the preparation of the Belousov Zhabotinsky reaction we used a solution of sodium bromate 0.5 M (concentration in the cuvette: 0.1 M), malonic acid 1.5 M (concentration in the cuvette: 0.38 M), sulfuric acid 3.06M concentration in the cuvette: 0.77 M), sodium bromide 0.18 M (concentration in the cuvette: 0.02 M) and ferroin 0.026 M (concentration in the cuvette: 0.4 mM (from the redox indicator, Reag. Ph. Eur., Eo in sulfuric acid 1 mol/l = +1.06 volt (Fluka) from Sigma Aldrich)).
For measuring the color change we used a self-made LED/LDR combination as photometric unit, which was connected to the multimeter VC820 with USB that enabled us to record the color oscillations with the computer.

## Qualitative Understanding of the Effect

As discussed in details by Marchettini et al. [1], the processes at play in a closed non-stirred BZ reaction system in addition to the chemical reactions are diffusion and convection .
The existence of a chaotic transient and the reappearance of a second periodic phase before reaching thermodynamical equilibrium can be understood in a temporal decoupling of this processes. While at the beginning the system is dominated by chemical reactions, diffusion and convection become more and more important while the system evolves into the chaotic regime.
As reagents get consumed this effect is inversed leading to a mainly chemical reaction dominated regime which again shows a high periodicity like in the first periodic phase.
In this sense the reagents consumption (mainly of the bromate) triggers the back-transition to peridicity.

Since in our case the system is stirred for a limited time right after the first periodic phase, we clearly influence the contribution of the different processes at play. Obviously by stirring the system, we suppress diffusion and natural convection while reagents consumption is still going on.
Our hypothesis is, that the shrinkage and further the dissapearance of the chaotic phase is simply due to the fact that by stirring the system the chemical reactions are more efficient and the reagents consumption is talking place faster. In this sense stirring the system longer is leading the system faster towards the second periodic regime.

## Mathematical Model - Chemical Reaction

The system is modeled in terms of the well known FKN model. There it is assumed that only intermediate species are changing. In other words reagents consumption is not take into account.
Marchettini et al. have adapted this model in such a way that the concentration of the reactants, which were assumed to be constant, i.e. malonic acid and bromate, are now also changing in time (see (1), $f_i$, $i$=1,2,3,Y).
In this sense the model by Marchettini et al. can be understood as a generalization of the FKN model, to which it reduces when reagents consumption is neglected.
Since now also convection and diffusion are at play they were also included in the model. The full description of the system is shown in (1), where the last equation is the Navier-Stokes equation in the Boussinesq approximation. As a first approach we solved the chemical kinetic part (i.e. $f_i$, $i$=1,2,3,Y) numerically.
The solutions for a particular set of initial conditions are shown in fig. 2. We observe a monotonous decrease of the bromate concentration which is accompanied by damped periodic oscillations of ferroin and bromous acid.

## Mathematical Model - Reaction Diffusion

As a next step we are now also taking diffusion into account by following the original ideas of Turing [3], i.e. by taking just one spatial dimension (i.e. «1-dimensional diffusion») and by linearization of the chemical reaction part. In a first approach we solved the simplified 2-variable « FKN-Turing» model, in which we were able to get periodic solutions for a certain set of parameter (see Fig. 3).

$$\begin{cases} \frac{\partial c_1}{\partial \tau} + \vec{u}_\tau \cdot \tilde{\nabla} c_1 = \Delta c_1 + \underbrace{\frac{1}{\varepsilon_1}\left[(q c_3 - c_1) y + c_1 (c_3 - c_1)\right]}_{f_1} \\ \frac{\partial c_2}{\partial \tau} + \vec{u}_\tau \cdot \tilde{\nabla} c_2 = \delta_2 \Delta c_2 + \underbrace{c_1 c_3 - b c_2}_{f_2} \\ \frac{\partial c_3}{\partial \tau} + \vec{u}_\tau \cdot \tilde{\nabla} c_3 = \delta_3 \Delta c_3 \underbrace{- (q y + c_1) c_3 + \frac{1}{2} c_1^2}_{f_3} \\ \frac{\partial y}{\partial \tau} + \vec{u}_\tau \cdot \tilde{\nabla} y = \delta_Y \Delta y + \underbrace{\frac{1}{\varepsilon_2}\left[ -(q c_3 + c_1) y + f b c_2 \right]}_{f_Y} \\ \frac{\partial \vec{\omega}}{\partial \tau} + \vec{u}_\tau (\tilde{\nabla} \vec{\omega}) = S_c \left[ \Delta \vec{\omega} + \frac{D}{\nu} (\vec{\omega} \tilde{\nabla}) \vec{u}_\tau - \mathrm{Ra}_i \vec{\psi}_i \right] \end{cases} \quad (1)$$

In solving the full 3-variable « Marchettini-Turing » model we are not getting oscillatory solutions (even without diffusion!). We have theoretically proven that in this case oscillations are not possible.

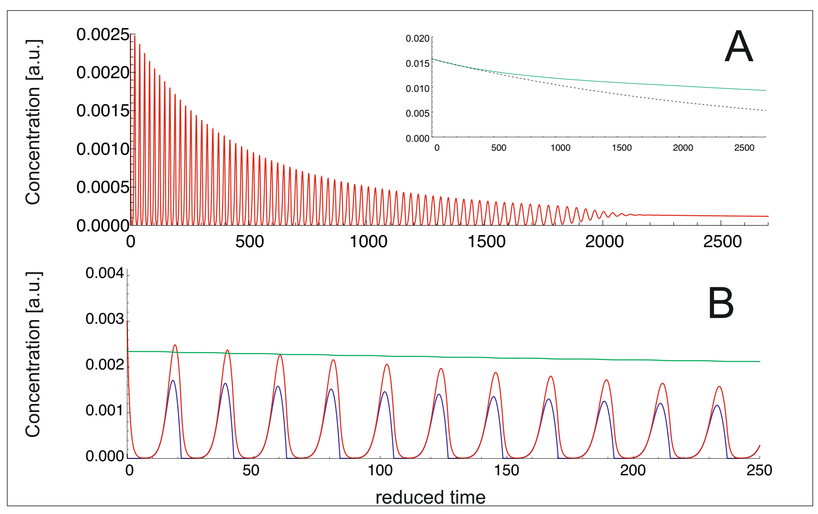


*Figure 2: Results of the numerical solution of the chemical part of the model. **A**: Concentration of Ferroin. Inset of A: Concentration of bromate (is decreasing slower then an exponential function (dashed blackline)). **B**: Concentration of bromate (green), ferroin (red) and bromous acid (blue) (different concentrations are not to scale).*

## Discussions and Outlook

The non-existence of a periodic solution in the full 3-variable « Marchettini-Turing » model seems to be caused by the linearization of the system (1). Nevertheless, by solving the problem numerically we are able to reproduce the oscillatory behavior (Fig. 2).
It seems that the local linearization of the kinetics of Marchettini et al. does not reflect the global behavior of the system and therefore we do not get anymore periodic solutions.

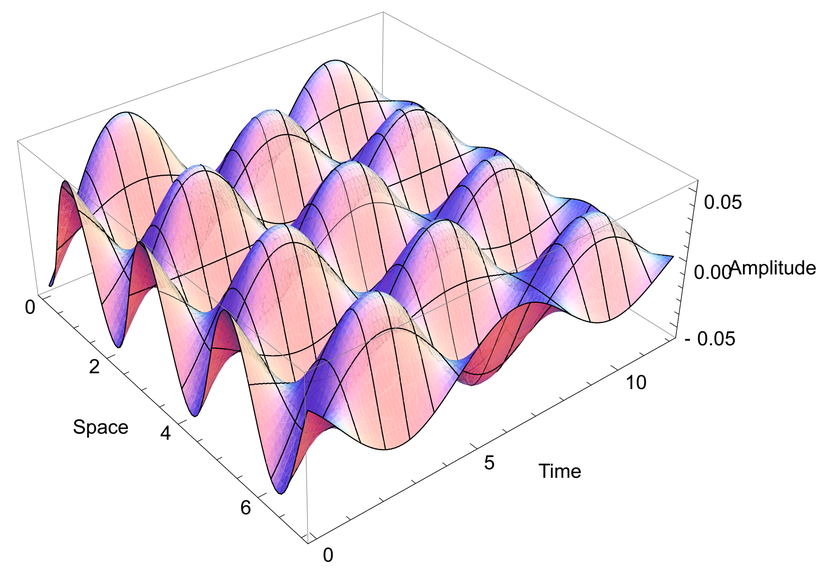


*Figure 3: Results of the simplified 2-variable FKN model. Space, time and amplitude for bromous acid in abritrary units.*

Turing, in contrast, could get oscillations even in a 3-dimensional model, but his model was constructed in purely mathematically way, i.e. with no underlying chemical kinetics.
The next step therefore will be to work with a more complete model by taking into account also nonlinear terms. In the end our overall aim still is to reproduce fully the experimental results shown in Fig. 1, as Marchettini et. al did, and incorporate a stirring term that could also explain the here described stirring effect.

***Literature***

[1] Field, Richard J.; Noyes, Richard M. J. Chem. Phys. 60: 1877–1884 (1974)
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[3] Rossi, F.; Budroni, M. A.; Marchettini, N.; Cutietta, L.; Rustici, M. & Liveri, M. L. T. Chemical Physics Letters, 480, 322-326 (2009)