Modeling a Chemo-Hydrodynamical Effect in a Closed Ferroin-catalyzed Belousov Zhabotinsky Oscillator

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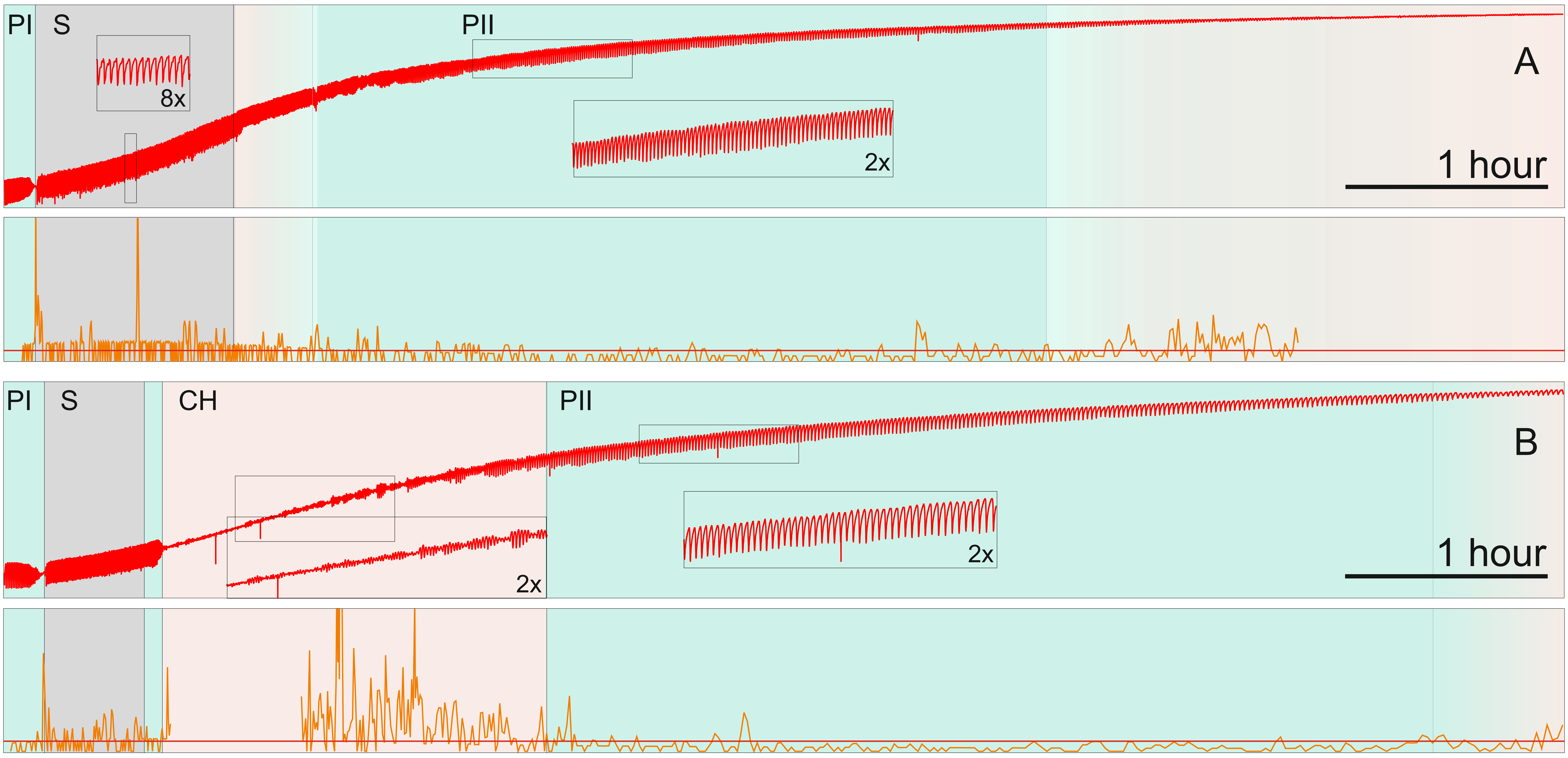

Figure 1: *Periodic color change (oscillations of the transmittance at 600 nm are shown). In general there exist four distinct regions (phases): the first periodic phase (PI), the stirring phase (S) and a short periodic phase right after (PS), the aperiodic (chaotic) phase (CH) and the second periodic phase (PII).* ***A:*** *stirring time 60 min at 30°C.* ***B:*** *stirring time 30 min at 30°C. Below every time series there is a plot of the relative variation of the period time as a function of time. This relative variation of the period time was used to analyse the periodicity of the signal i.e. to decide where the different phases start and end. Red line indicates a value of 4% relative variation of the period time, our threashold value deciding if the signal is periodic or not.*

Abstract. In a closed Ferroin-catalyzed Belousov Zhabotinsky reaction complex oscillations are generated by the coupling between the nonlinear kinetics and the transport phenomena. The long-term behaviour shows a chaotic transient between two periodic phases. We found that a limited stirring phase in the otherwise unstirred reaction can result in the disappearance of this chaotic transient. We describe here this effect in detail and model it by following the idea of reaction consumption by Marchettini et al. By combining the well known FKN model with the Navier-Stokes equation in the Boussinesq approximation it is possible to reproduce the characteristic longtime behaviour of the closed Belousov Zhabotinsky reaction. We give here the first results of our ongoing research on modifying the above mentioned model by incorporating a limited stirring phase.

Experimental Facts

In our experiments the effect of stirring on the BZ reaction has other effects too apart from the pure homogenization of the system:

1) If the BZ reaction is stirred with a 'high' rate, the color oscillations stops immediatly, but when the stirring is stopped, the oscillations restart.
2) If the BZ reaction is stirred with a 'low' rate, the color oscillations sustain and moreover the time period of the oscillations becomes regular (see fig. 1 grey areas)

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) (shown in fig.1.B)

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 (shown in fig.1.A).

Materials and Methods

For the preparation of the Belousov Zhabotinsky reaction we used a solution of sodium bromate (0.1 M), malonic acid (0.38 M) sulfuric acid (0.8 M), sodium bromide (0.018 M) and ferroin (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 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

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.

$$\begin{cases} \frac{\partial c_1}{\partial \tau} + \vec{u}_\tau \cdot \tilde{\nabla} c_1 = \Delta c_1 + \underbrace{\frac{1}{\varepsilon_1}\left[(qc_3 - c_1)y + c_1(c_3 - c_1)\right]}_{f_1} \\ \frac{\partial c_2}{\partial \tau} + \vec{u}_\tau \cdot \tilde{\nabla} c_2 = \delta_2 \Delta c_2 + \underbrace{c_1 c_3 - bc_2}_{f_2} \\ \frac{\partial c_3}{\partial \tau} + \vec{u}_\tau \cdot \tilde{\nabla} c_3 = \delta_3 \Delta c_3 \underbrace{- (qy + c_1)c_3 + \frac{1}{2}c_1^2}_{f_3} \\ \frac{\partial y}{\partial \tau} + \vec{u}_\tau \cdot \tilde{\nabla} y = \delta_Y \Delta y + \underbrace{\frac{1}{\varepsilon_2}\left[-(qc_3 + c_1)y + fbc_2\right]}_{f_Y} \\ \frac{\partial \vec{\omega}}{\partial \tau} + \vec{u}_\tau(\tilde{\nabla}\vec{\omega}) = S_c\left[\Delta\vec{\omega} + \frac{D}{\nu}(\vec{\omega}\tilde{\nabla})\vec{u}_\tau - \mathrm{Ra}_i \vec{\psi}_i\right] \end{cases} \quad (1)$$

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.

The overall aim is to solve the full set of equations, take also into account a limited stirring phase and verify our hypothesis.

Literature

[1] N. Marchettini, M.A. Budroni, F. Rossi, M. Masia, M.L. Turco Liveri, M. Rustici. *Phys. Chem. Chem. Phys. (2010) 12, 11062-11069*
[2] S. K. Scott: Chemical Chaos, *Claderon Press, Oxford, 1991*

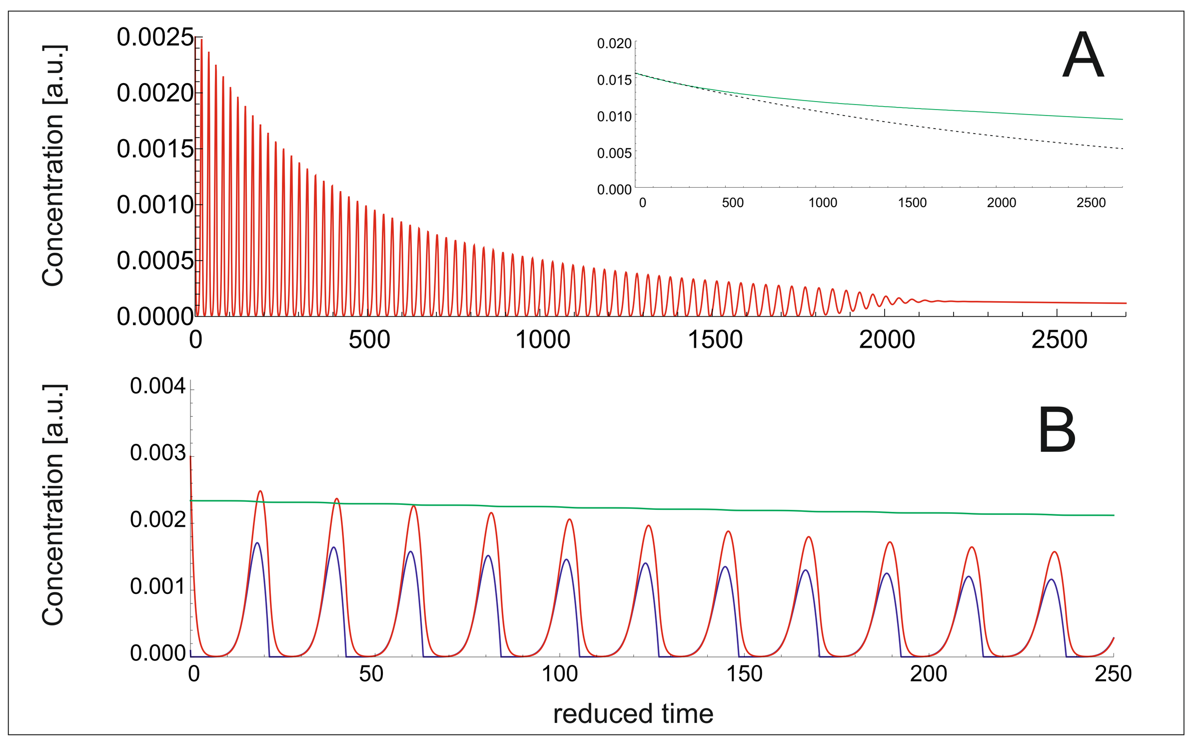

Figure 2: Results of the numerical solution of the chemical part of the model. ***A:*** *Concentration of Ferroin. Inset of A: Concentration of bromate (is decreasing slower then an exponential function (dashed blackline)).* ***B:*** *Concentration of bromate (green), ferroin (red) and bromo-malonic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