LIVING SYSTEMS
RESEARCH

Hydrodynamical Control of the Decoupling of Reaction, Diffusion and Convection in a Complex Chemical Reaction System

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Living Systems Research
at the "Reaction, Diffusion, and Molecular Communication" Workshop IGDK 1754
May, 25th 2020, *online*

COMPLEX SYSTEMS SOCIETY

Belousov Zhabotinsky Reaction
[Bjela'usov-Shabotinski]


nach ca. 30 Sekunden

Liquid reaction system containing *sulfuric acid, malonic acid, sodium bromate, sodium bromide and ferroin*.

Boris P. Belousov (1893-1970)

Anatol M. Zhabotinsky (1938-2008)

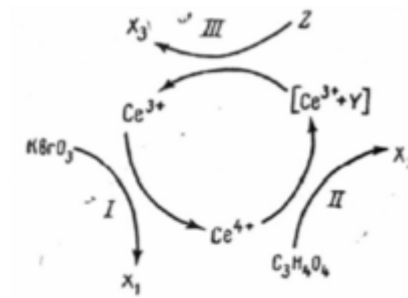
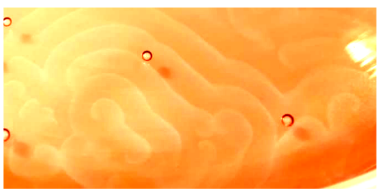
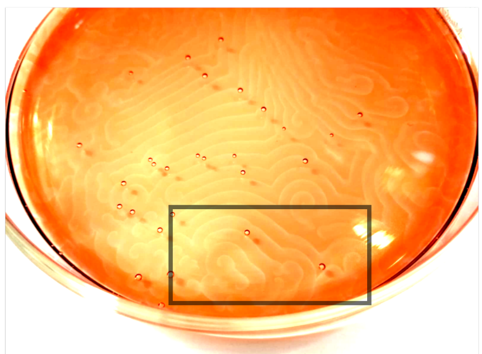


Bild 3. Vereinfachtes Reaktionsschema

X_1; X_2; X_3; Y; Z – unbekannte chemische Verbindungen, Z – möglicherweise $KBrO_3$ oder ein reduziertes Zwischenprodukt des $KBrO_3$

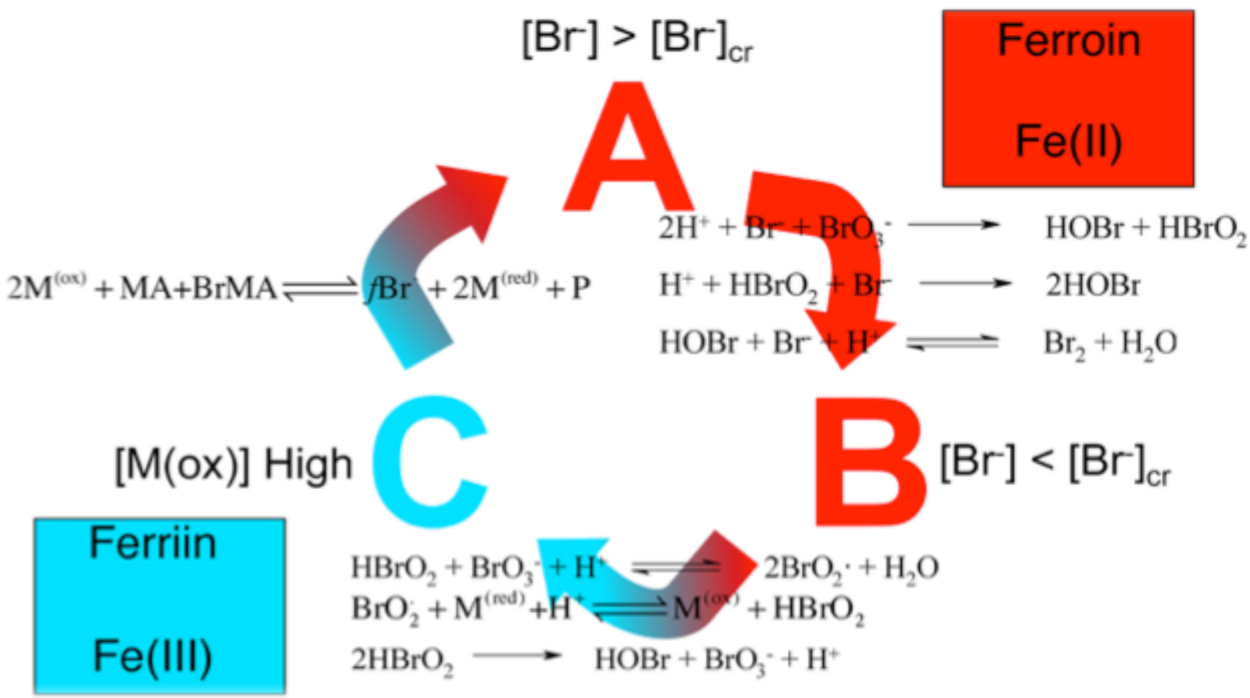
Cyclic (periodic) bromination of an organic species in acidic environment with the help of a catalyst

Belousov Zhabotinsky Reaction

Oscillation Mechanism

oscillations originate from the alternation of inhibitory and excitatory steps.

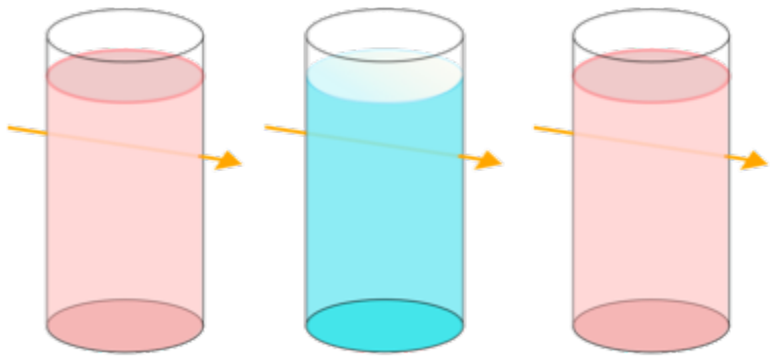
Activators: *$HBrO_2$, BrO_2-R*…
Inhibitors: *Br^-, Br_2* …



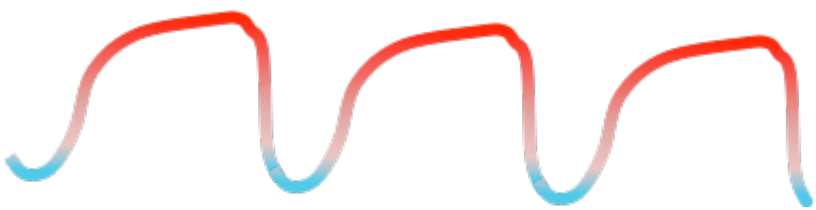
Belousov Zhabotinsky Reaction

Measurements

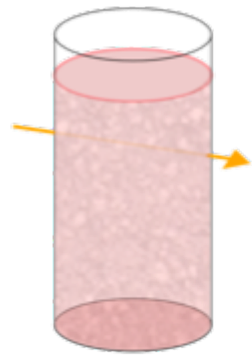
Absorbance photometric absorbance measurement at 700 nm (red)



periodic color change - *chemical kinetics is the main effect*



Aperiodic (chaotic) phase -
diffusion and convection is governing



Belousov Zhabotinsky Reaction

Molecular communication between synthetic compartments

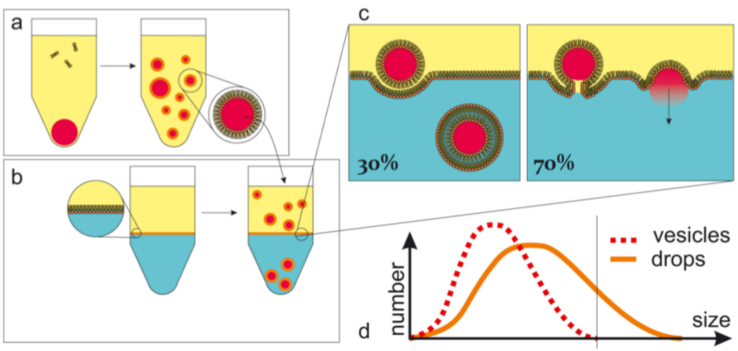


Fig. 5. a) Preparation of a water-in-oil macroemulsion with mineral oil, surfactants (POPC) and the I-solution. b) Preparation of an oil over O-solution system with surfactants at the interface. In a second step the macroemulsion droplets are inserted in this system and sink down due to the density difference between the I- and O-solution. c) As they wander through the interface they get a second layer of surfactants such that they now have a bilayer of phospholipids, i.e. they are vesicles now, if the conditions are good (only in about 30 % of all cases) - otherwise they merge with the interface and the I-solution is released into the O-solution (which is happening in about 70 % of all cases). d) This leads to a size distribution of the vesicles which does not allow vesicles greater then a critical size, even though the macroemulsion droplets generated in the first step were greater.

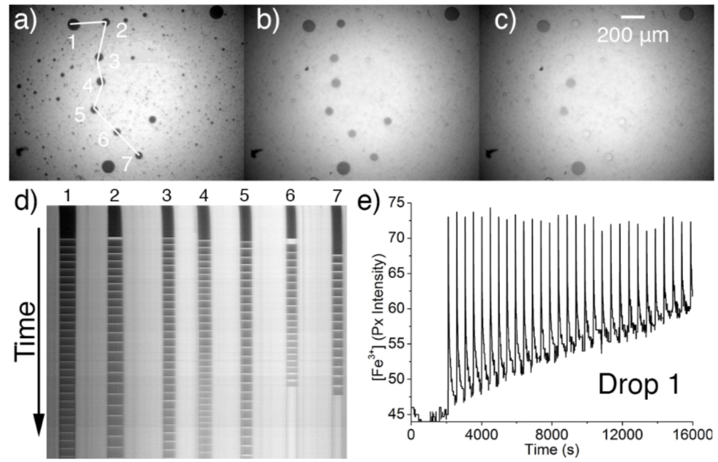
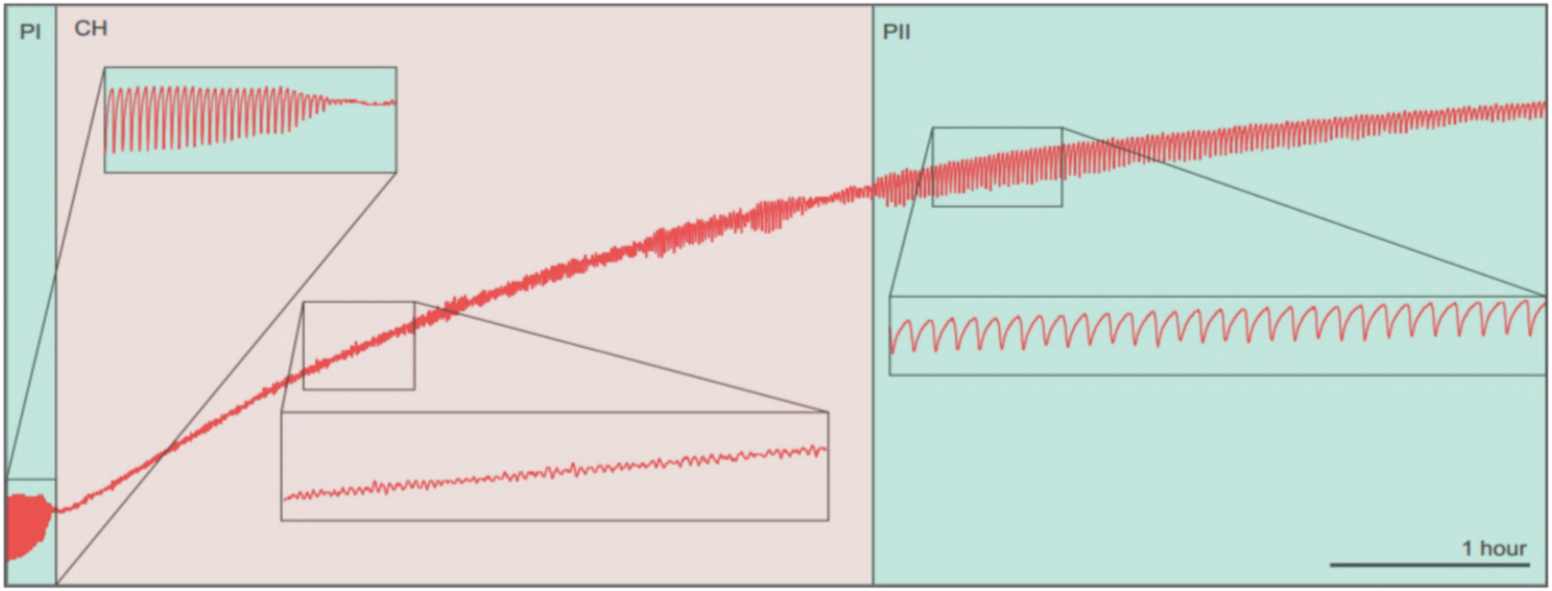


Fig. 6. a)–c) Dispersion in mineral oil of BZ aqueous droplets surrounded by lipids. Dark color and bright color indicate the reduced and the oxidized form of the catalyst, respectively. Snapshots are taken about 5000 s apart. d) ST plot built along the white line in panel a) showing the oscillations of the droplets 1–7, total time ∼ 16000 s. e) Time series reporting the oscillatory dynamics of droplet 1 extracted from the ST plot in panel d). Initial concentrations of the BZ reagents in the water phase are [MA] = 100 mM, [H_2SO_4] = 80 mM, [$NaBrO_3$] = 300 mM and ferroin = 3 mM. The concentration of the lipid in the oil is [POPC] = 3 mM.

Pasquale Stano, Florian Wodlei, Paolo Carrera, Sandra Ristori, Nadia Marchettini and Federico Rossi
Approaches to molecular communication between synthetic compartemts based on encapsulated chemical oscillators
Advances in Artificial Life and Evolutionary Computation, Communications in Computer and Information, 445, 2014
https://doi.org/10.1007/978-3-319-12745-3

Belousov Zhabotinsky Reaction

Long Time Behaviour under Non-stirring Conditions



Photospectrometric recording of the transmittance at λ = 700 nm

Belousov Zhabotinsky Reaction

The Chaotic Transient

ELSEVIER
Chemical Physics Letters 263 (1996) 429–434

Evidence of a chaotic transient in a closed unstirred cerium catalyzed Belousov–Zhabotinsky system

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period-1 (P1)-> quasiperiodicity (QP1) -> chaos (QT) = Ruelle-Takens-Newhouse scenario

chaos (QT) -> quasiperiodicity (QP2) -> period-1 (P2) =***inverse*** Ruelle-Takens-Newhouse scen.

ELSEVIER
Chemical Physics Letters 293 (1998) 145–151

Inverse Ruelle–Takens–Newhouse scenario in a closed unstirred cerium-catalysed Belousov–Zhabotinsky system

Mauro Rustici [a,*], Mario Branca [a], Antonio Brunetti [b], Carlo Caravati [a], Nadia Marchettini [c]

Belousov Zhabotinsky Reaction

Reaction Consumption and the Decouplingof Reaction, Diffusion and Convection

The kinetic functions $k_i(c_j, \bar{\lambda})$ are derived from the modified *Oregonator* model (see Appendix) and have the form

$$k_1(c_j,\bar{\lambda}) = \frac{dc_1}{d\tau} = \frac{1}{\varepsilon_1}\left(\frac{(qc_3 - c_1)}{(qc_3 + c_1)} fbc_2 + c_1(c_3 - c_1)\right) \quad (6)$$

$$k_2(c_j,\bar{\lambda}) = \frac{dc_2}{d\tau} = c_3c_1 - bc_2 \quad (7)$$

$$k_3(c_j,\bar{\lambda}) = \frac{dc_3}{d\tau} = -\frac{qc_3}{qc_3 + c_1} fbc_2 - c_1(c_1 - c_3) \quad (8)$$

where $j = 1,2,3$, c_1 is the concentration of bromous acid, c_2 is the concentration of the oxidized form of the catalyst, c_3 is the concentration of bromate and $\bar{\lambda} = \varepsilon_1, q, f, b$ is the set of kinetic parameters. Preliminary calculations showed that considering

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Role of the reagents consumption in the chaotic dynamics of the Belousov–Zhabotinsky oscillator in closed unstirred reactors

Nadia Marchettini,[a] Marcello Antonio Budroni,*[a] Federico Rossi,[b] Marco Masia,[c] Maria Liria Turco Liveri[d] and Mauro Rustici[c]

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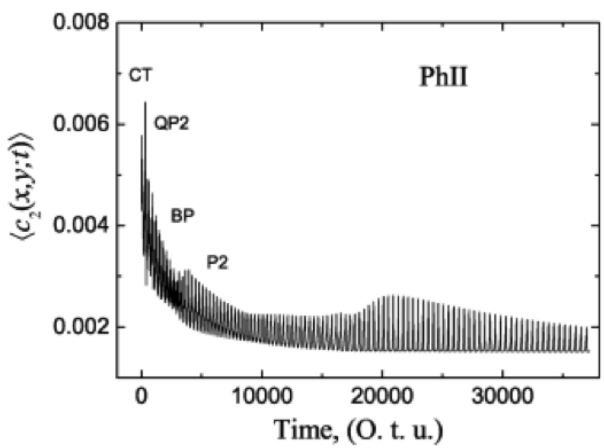
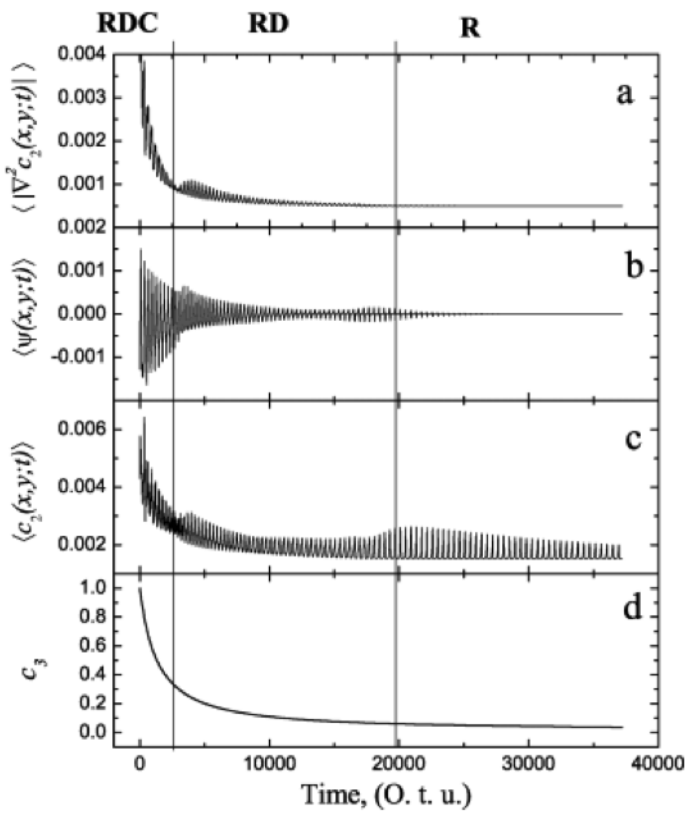


Fig. 2 Evolution of the catalyst ($\langle c_2(x,y;t)\rangle$) in the region PhII.

$$\frac{\partial c_i(x,y;t)}{\partial t} + D_\nu\left(u\frac{\partial c_i(x,y;t)}{\partial x} + v\frac{\partial c_i(x,y;t)}{\partial y}\right)$$
$$- D_i\nabla^2 c_i(x,y;t) = k_i(c_j,\bar{\lambda})\ i,j = 1,2,3$$

Belousov Zhabotinsky Reaction

Reaction Consumption and the Decoupling of Reaction, Diffusion and Convection

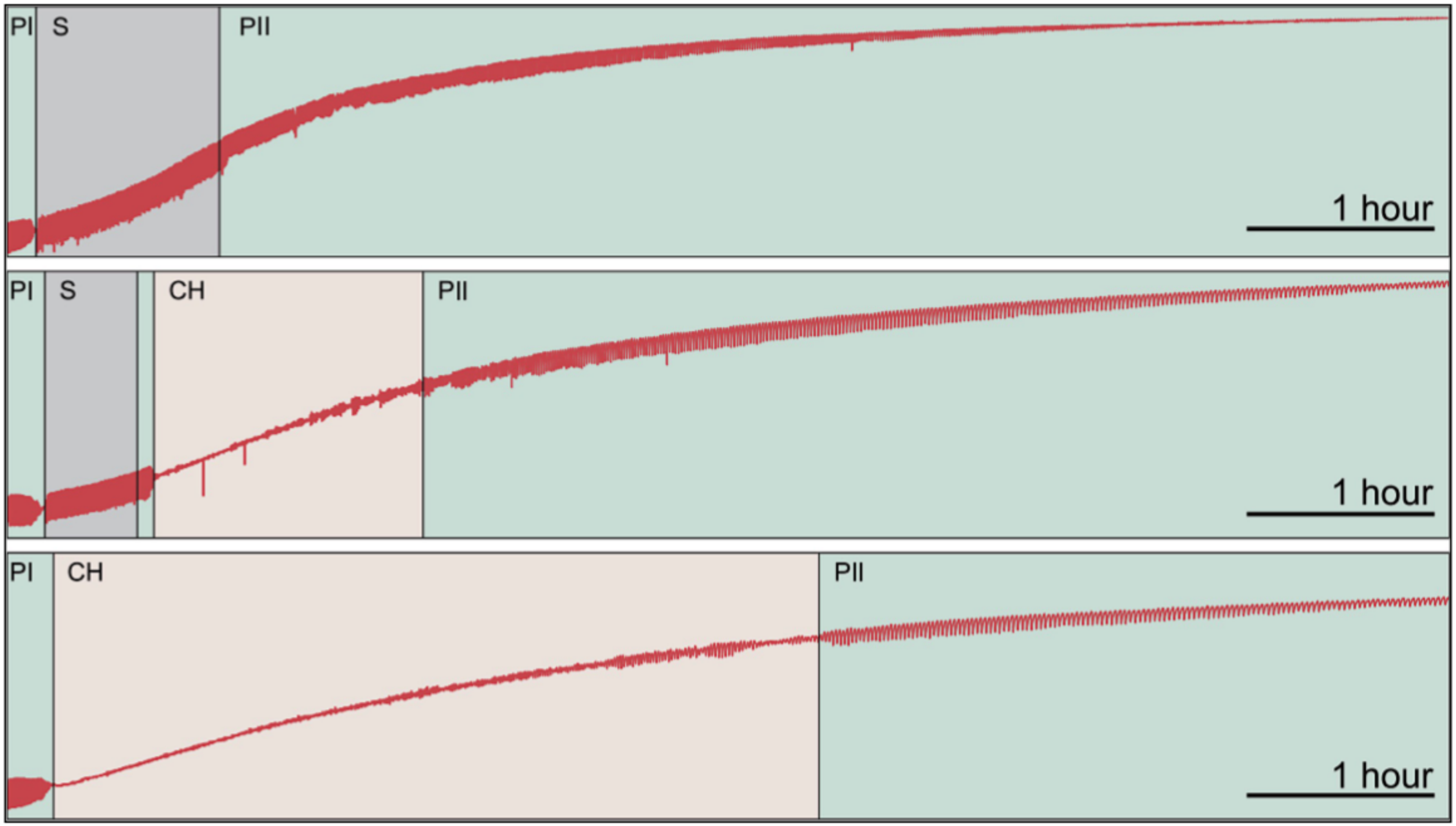


c_2 is the concentration of the oxidized form of the catalyst (e.g. Ferroin)

c_3 is the concentration of bromate (BrO_3^-)

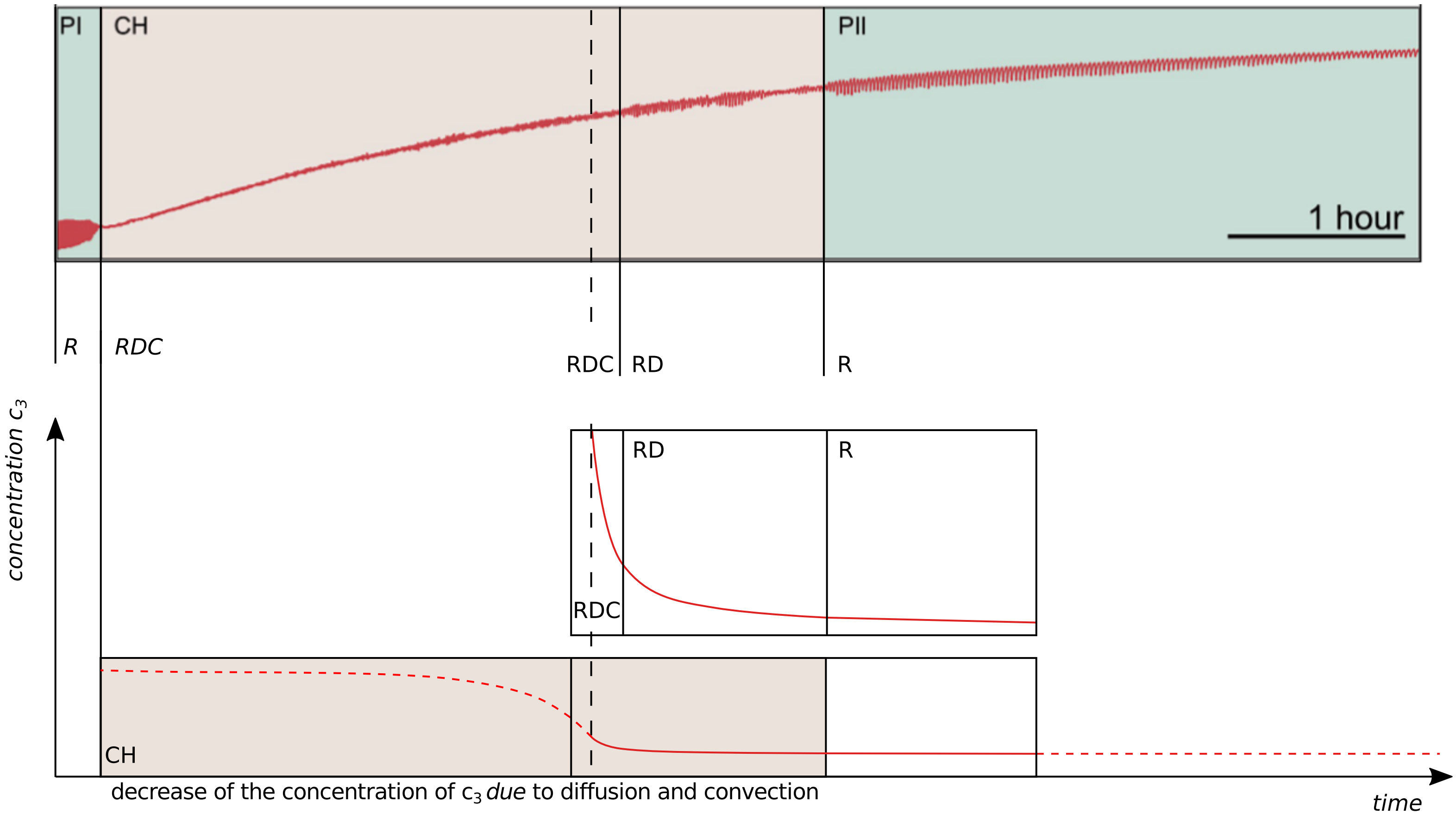
Belousov Zhabotinsky Reaction

Hydrodynamic Control of the Chaotic Transient



Belousov Zhabotinsky Reaction

Hydrodynamic Control of the Chaotic Transient



Belousov Zhabotinsky Reaction

Hydrodynamic Control of the Chaotic Transient

Assumptions

During the chaotic phase the concentration of c_3 goes down due to convection and diffusion

Stirring the system inhibits diffusion and convection

AND "moves" the system in direction of pure reactions

Belousov Zhabotinsky Reaction

Hydrodynamic Control of the Chaotic Transient

Open Questions and Future Tasks

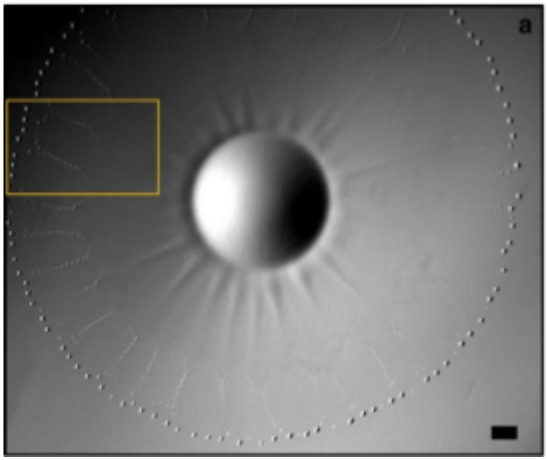
Determine if the shrinkage of the chaotic phase is *significantly* reduced by the stirring phase

Determine if the complete disappearance of the chaotic phase is consistent and not only an *artefact* of the decay of a T^3 torus into a stable T^2 torus (i.e. quasiperiodicty of period-2)

Theoretical modelization of the Reaction Diffusion Convection system to compare with the results of Marchettini et al.

Our Research

Living Systems Research



Self-Organiozation of a Dichloromethane Doplet on a Liquid Phase

Research on Complex Systems

Experiment

Self-Organizing Chemical Systems

Self-Organizing Biological Systems
Ants

Theory

Analytical (*periodic*) solutions to ordinary differential equations (Lienard Type, etc.)

Conditions for dynamical systems to become chaotic (by means of Lyapunov exponent, dimensional analysis of the attractor, etc)

Understanding the Transition to Chaos of complex systems by simulation of systems of different degrees of freedom

Our Group

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Theory and Experiment (Chemical Complexity and Self-Organization, Social Insects)

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Theory and Simulations (Study of numerical solutions of dynamical systems of different degrees of freedom)