ALPEN-ADRIA UNIVERSITÄT KLAGENFURT | WIEN GRAZ
LIVING SYSTEMS RESEARCH

Florian Wodlei and Mihnea R Hristea

Hydrodynamic Control of Chaos in a Belousov Zhabotinsky Oscillator

Conference on Complex Systems 2018
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CCS2018
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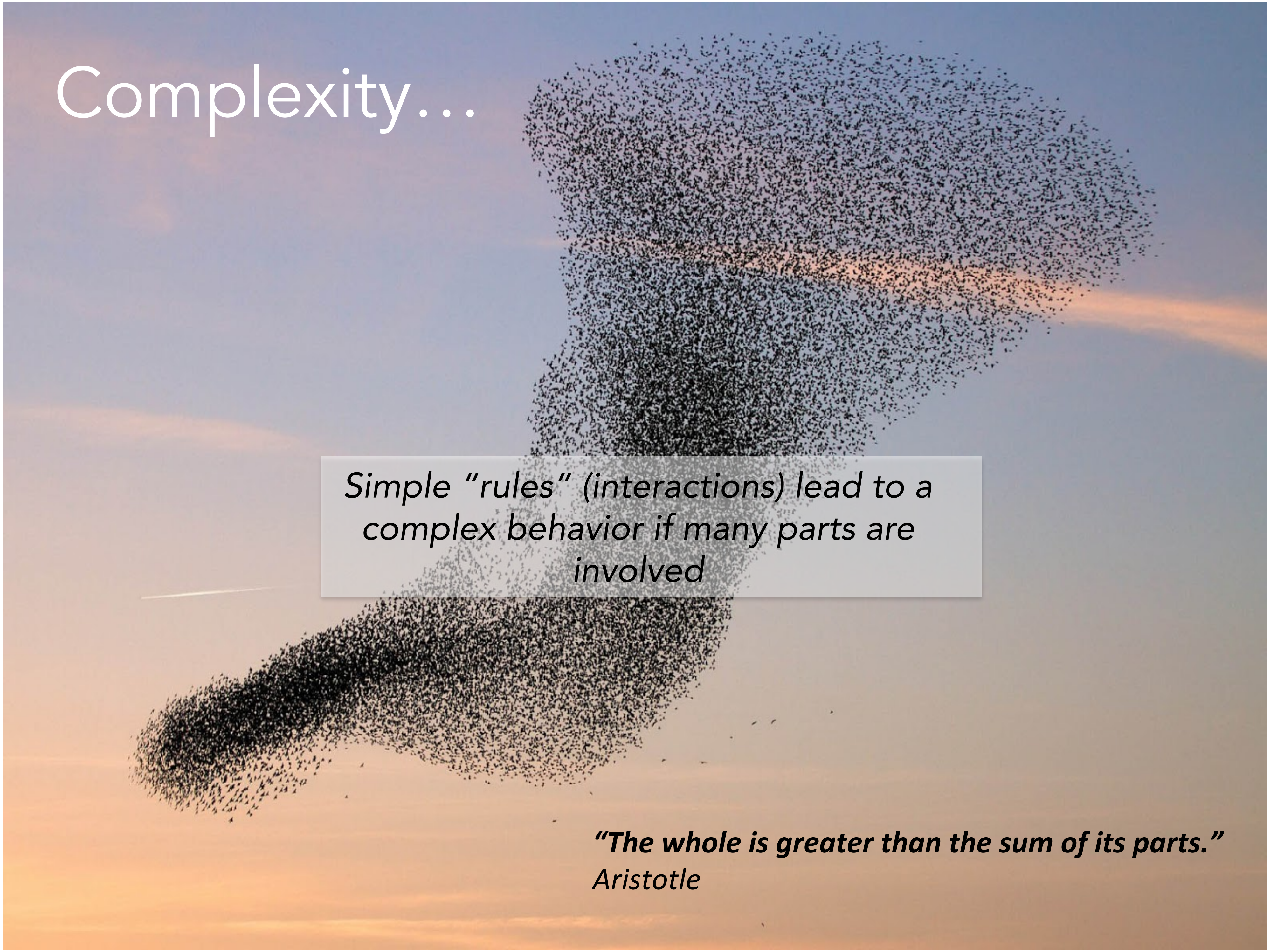

Complexity…
Simple "rules" (interactions) lead to a complex behavior if many parts are involved
"The whole is greater than the sum of its parts."
Aristotle

Chaos…

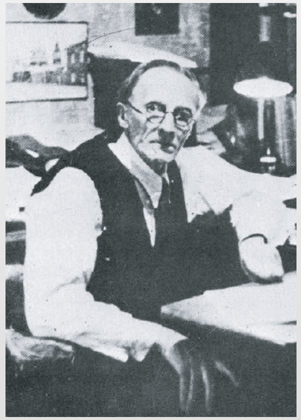
Something is chaotic if we cannot find an order

Deterministic Chaos: sensitivity to initial conditions

Greek ***χάος*** means "emptiness, vast void, chasm, abyss"

The Belousov Zhabotinsky Reaction

*[Bjela’***u***sov-Shabat***i***nski]*



Boris P. Belousov

Anatol M. Zhabotinsky

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

1. Неорганическая часть					
1	$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O$	$2.3\cdot10^{9}$	8	$BrO_3^- + HOBr + H^+ \rightarrow 2HBrO_2$	$7.5\cdot10^{-9}$
2	$Br_2 + H_2O \rightarrow HOBr + Br^- + H^+$	2.0	9	$BrO_3^- + HBrO_2 + H^+ \rightarrow Br_2O_4 + H_2O$	33.0
3	$Br^- + HBrO_2 + H^+ \rightarrow 2HOBr$	$2.0\cdot10^{6}$	10	$Br_2O_4 + H_2O \rightarrow BrO_3^- + HBrO_2 + H^+$	2200
4	$2HOBr \rightarrow Br^- + HBrO_2 + H^+$	$2.0\cdot10^{-5}$	11	$Br_2O_4 \rightarrow 2BrO_2^{\bullet}$	$7.4\cdot10^{4}$
5	$Br^- + HBrO_3^- + 2H^+ \rightarrow HOBr + HBrO_2$	2.0	12	$2BrO_2^{\bullet} \rightarrow Br_2O_4$	$1.4\cdot10^{9}$
6	$HOBr + HBrO_2 \rightarrow Br^- + HBrO_3^- + 2H^+$	3.3	13	$Ce^{3+} + 2BrO_2^{\bullet} + H^+ \rightarrow HBrO_2 + Ce^{4+}$	$5.2\cdot10^{4}$
7	$2HBrO_2 \rightarrow BrO_3^- + HOBr + H^+$	$3.0\cdot10^{3}$	14	$HBrO_2 + Ce^{4+} \rightarrow Ce^{3+} + 2BrO_2^{\bullet} + H^+$	$7.0\cdot10^{3}$
2. Реакции с участием органических веществ					
а) Реакции без участия и образования радикалов					
15	$MA \rightarrow ENOL$	$3.0\cdot10^{-3}$	20	$TTA + HOBr \rightarrow BrTTA + H_2O$	5.0
16	$ENOL \rightarrow MA$	200.0	21	$BrO_2MA + H_2O \rightarrow HBrO_2 + TTA$	1.0
17	$ENOL + Br_2 \rightarrow BrMA + Br^- + H^+$	$1.91\cdot10^{6}$	22	$BrO_2MA \rightarrow HOBr + MOA$	1.0
18	$MA + HOBr \rightarrow Br_2MA + H_2O$	8.2	23	$BrO_2TTA \rightarrow HBrO_2 + MOA$	1.0
19	$Br_2MA + H_2O \rightarrow MA + HOBr$	0.1	24	$BrTTA \rightarrow Br^- + MOA + H^+$	1.0
б) Реакции с образованием радикалов					
25	$Ce^{4+} + BrMA \rightarrow Ce^{3+} + BrMA^{\bullet} + H^+$	0.09	29	$Ce^{4+} + MOA + H_2O \rightarrow Ce^{3+} + OA + {}^{\bullet}COOH + H^+$	10.0
26	$Ce^{4+} + MA \rightarrow Ce^{3+} + MA^{\bullet} + H^+$	0.23	30	$HOBr + OA \rightarrow Br^{\bullet} + {}^{\bullet}COOH + CO_2 + H_2O$	140.0
27	$Ce^{4+} + TTA \rightarrow Ce^{3+} + TTA^{\bullet} + H^+$	0.66	31	$Ce^{4+} + OA \rightarrow Ce^{3+} + {}^{\bullet}COOH + H^+ + CO_2 + H^+$	10.0
28	$HOBr + MOA \rightarrow Br^{\bullet} + OA + {}^{\bullet}COOH$	140.0	32	$BrO_3^- + OA + H^+ \rightarrow BrO_2^{\bullet} + {}^{\bullet}COOH + CO_2 + H^+$	$1.6\cdot10^{-5}$
в) Реакции гибели радикалов					
33	$2Br^{\bullet} \rightarrow Br_2$	$1.0\cdot10^{8}$	44	$MA^{\bullet} + Br^{\bullet} \rightarrow BrMA$	$1.0\cdot10^{9}$
34	$Br^{\bullet} + BrMA^{\bullet} \rightarrow Br_2MA$	$1.0\cdot10^{9}$	45	$MA^{\bullet} + Ce^{3+} + H^+ \rightarrow MA + Ce^{4+}$	$1.7\cdot10^{4}$
35	$2BrMA^{\bullet} + H_2O \rightarrow BrMA + BrTTA$	$1.0\cdot10^{8}$	46	$MA^{\bullet} + BrO_2^{\bullet} \rightarrow BrO_2MA$	$5.0\cdot10^{9}$
36	$BrMA^{\bullet} + MA + H_2O \rightarrow MA + BrTTA$	$1.0\cdot10^{9}$	47	$2TTA^{\bullet} \rightarrow TTA + MOA$	$1.0\cdot10^{9}$
37	$BrMA^{\bullet} + TTA^{\bullet} + H_2O \rightarrow TTA + BrTTA$	$1.0\cdot10^{9}$	48	$TTA^{\bullet} + {}^{\bullet}COOH \rightarrow TTA + CO_2$	$2.0\cdot10^{9}$
38	$BrMA^{\bullet} + Ce^{4+} + H_2O \rightarrow Ce^{3+} + BrTTA + H^+$	$1.0\cdot10^{7}$	49	$TTA^{\bullet} + Br^{\bullet} \rightarrow BrTTA$	$1.0\cdot10^{9}$
39	$BrMA^{\bullet} + BrO_2^{\bullet} + H_2O \rightarrow HBrO_2 + BrTTA$	$5.0\cdot10^{9}$	50	$TTA^{\bullet} + Ce^{3+} + H^+ \rightarrow TTA + Ce^{4+}$	$1.7\cdot10^{4}$
40	$BrMA^{\bullet} + {}^{\bullet}COOH \rightarrow BrMA + CO_2$	$5.0\cdot10^{8}$	51	$TTA^{\bullet} + BrO_2^{\bullet} \rightarrow BrO_2TTA$	$5.0\cdot10^{9}$
41	$2MA^{\bullet} + H_2O \rightarrow MA + TTA$	$3.2\cdot10^{9}$	52	$2{}^{\bullet}COOH \rightarrow OA$	$1.2\cdot10^{9}$
42	$MA^{\bullet} + TTA^{\bullet} + H_2O \rightarrow 2TTA$	$1.0\cdot10^{9}$	53	${}^{\bullet}COOH + Ce^{4} \rightarrow Ce^{3+} + CO_2 + H^+$	$1.0\cdot10^{7}$
43	$MA^{\bullet} + {}^{\bullet}COOH \rightarrow MA + CO_2$	$2.0\cdot10^{9}$	54	${}^{\bullet}COOH + Br^{\bullet} \rightarrow Br^- + CO_2 + H^+$	$1.0\cdot10^{9}$
			55	${}^{\bullet}COOH + BrO_2^{\bullet} \rightarrow HBrO_2 + CO_2$	$5.0\cdot10^{9}$
г) Реакции продолжения цепи					
56	$MA^{\bullet} + Br_2 \rightarrow BrMA + Br^{\bullet}$	$1.5\cdot10^{8}$	69	$BrMA^{\bullet} + HOBr \rightarrow BrTTA + Br^{\bullet}$	$1.0\cdot10^{5}$
57	$MA^{\bullet} + HOBr \rightarrow TTA + Br^{\bullet}$	$1.0\cdot10^{7}$	70	$BrMA^{\bullet} + BrO_3^- + H^+ \rightarrow BrTTA + BrO_2^{\bullet}$	40.0
58	$MA^{\bullet} + BrO_3^- + H^+ \rightarrow TTA + BrO_2^{\bullet}$	40.0	71	${}^{\bullet}COOH + BrMA \rightarrow Br^- + MA^{\bullet} + CO_2 + H^+$	$1.0\cdot10^{7}$
59	$MA^{\bullet} + TTA \rightarrow MA + TTA$	$1.0\cdot10^{5}$	72	${}^{\bullet}COOH + Br_2 \rightarrow Br^- + Br^{\bullet} + CO_2 + H^+$	$1.5\cdot10^{8}$
60	$TTA^{\bullet} + MA \rightarrow MA^{\bullet} + TTA$	$1.0\cdot10^{5}$	73	${}^{\bullet}COOH + HOBr \rightarrow Br^{\bullet} + CO_2 + H_2O$	$2.0\cdot10^{7}$
61	$MA^{\bullet} + BrMA \rightarrow MA + BrMA^{\bullet}$	$1.0\cdot10^{5}$	74	${}^{\bullet}COOH + BrO_3^- + H^+ \rightarrow BrO_2^{\bullet} + CO_2 + H_2O$	$2.1\cdot10^{3}$
62	$BrMA^{\bullet} + MA \rightarrow BrMA + MA^{\bullet}$	$5.0\cdot10^{2}$	75	$Br^{\bullet} + MA \rightarrow Br^- + MA^{\bullet} + H^+$	$1.0\cdot10^{5}$
63	$TTA^{\bullet} + BrMA \rightarrow TTA + BrMA^{\bullet}$	$2.0\cdot10^{5}$	76	$Br^{\bullet} + TTA \rightarrow Br^- + TTA^{\bullet} + H^+$	$1.0\cdot10^{6}$
64	$BrMA^{\bullet} + TTA \rightarrow BrMA + TTA^{\bullet}$	$5.0\cdot10^{3}$	77	$Br^{\bullet} + BrMA \rightarrow Br^- + BrMA^{\bullet} + H^+$	$5.0\cdot10^{6}$
65	$TTA^{\bullet} + Br_2 \rightarrow BrTTA + Br^{\bullet}$	$1.0\cdot10^{8}$	78	$Br^{\bullet} + MOA + H_2O \rightarrow Br + OA + {}^{\bullet}COOH + H^+$	$2.0\cdot10^{3}$
66	$TTA^{\bullet} + HOBr \rightarrow MOA + Br^{\bullet} + H_2O$	$1.0\cdot10^{7}$	79	$Br^{\bullet} + OA \rightarrow Br^- + {}^{\bullet}COOH + CO_2 + H^+$	$2.0\cdot10^{3}$
67	$TTA^{\bullet} + BrO_3^- + H^+ \rightarrow MOA + BrO_2^{\bullet} + H_2O$	40.0	80	$BrO_2^{\bullet} + OA \rightarrow HBeO_2 + {}^{\bullet}COOH + CO_2$	$1.0\cdot10^{2}$
68	$BrMA^{\bullet} + Br_2 \rightarrow Br_2MA + Br^{\bullet}$	$1.0\cdot10^{6}$			

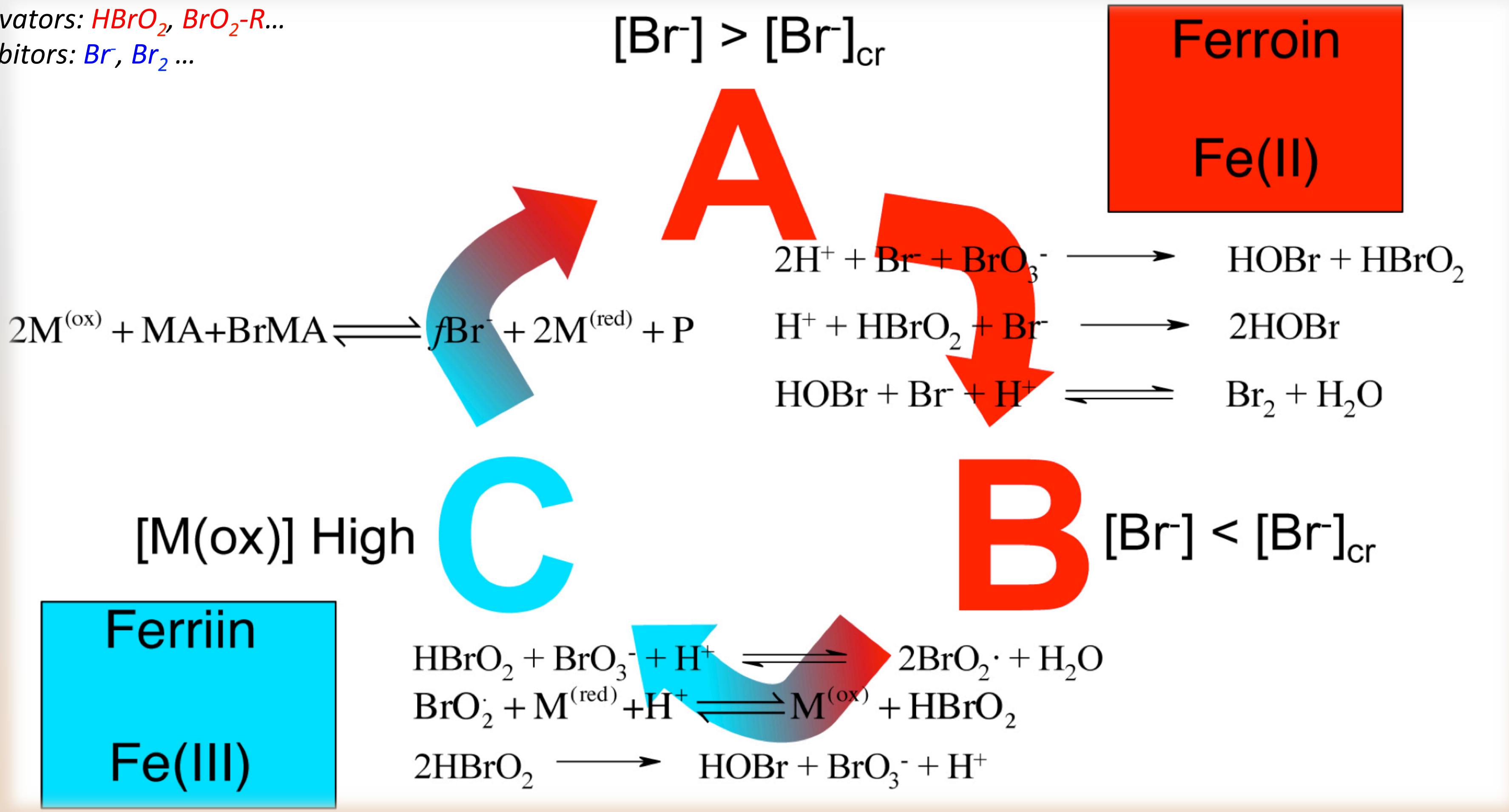
80-stage reaction mechanism of the Belousov-Zhabotinsky reaction from

Gyorgyi L., Turanyi T., Field R.J. **Mechanistic Details of the Oscillatory Belousov-Zhabotinskii Reaction** *J.Phys.Chem. - 1990. - V.94. - №.18. - P. 7162-7170.*

The Belousov Zhabotinsky Reaction

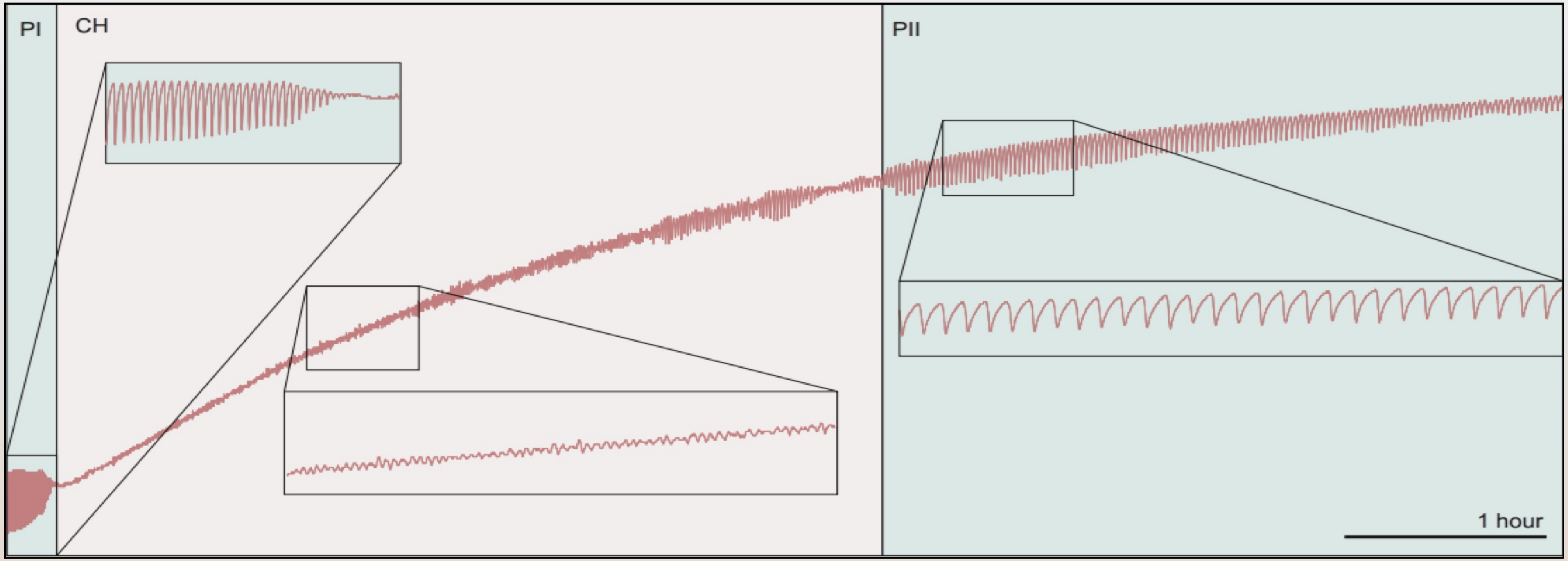
Oscillation Mechanism

oscillations originate from the alternation of inhibitory and excitatory steps.
Activators: $HBrO_2$, BrO_2-R…
Inhibitors: Br^-, Br_2 …



The Belousov Zhabotinsky Reaction

Long Time Behavior under non-stirring Conditions



Photospectrometric recording of the transmittance at λ = 600 nm

The Belousov Zhabotinsky Reaction

Deterministic Chaos in a Chemical System


IOP Publishing — European Journal of Physics

Eur. J. Phys. **35** (2014) 045005 (12pp) — doi:10.1088/0143-0807/35/4/045005

Butterfly effect in a chemical oscillator

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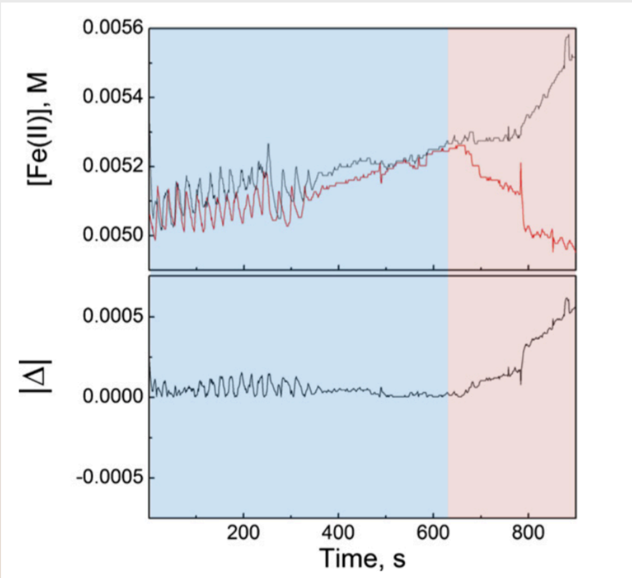
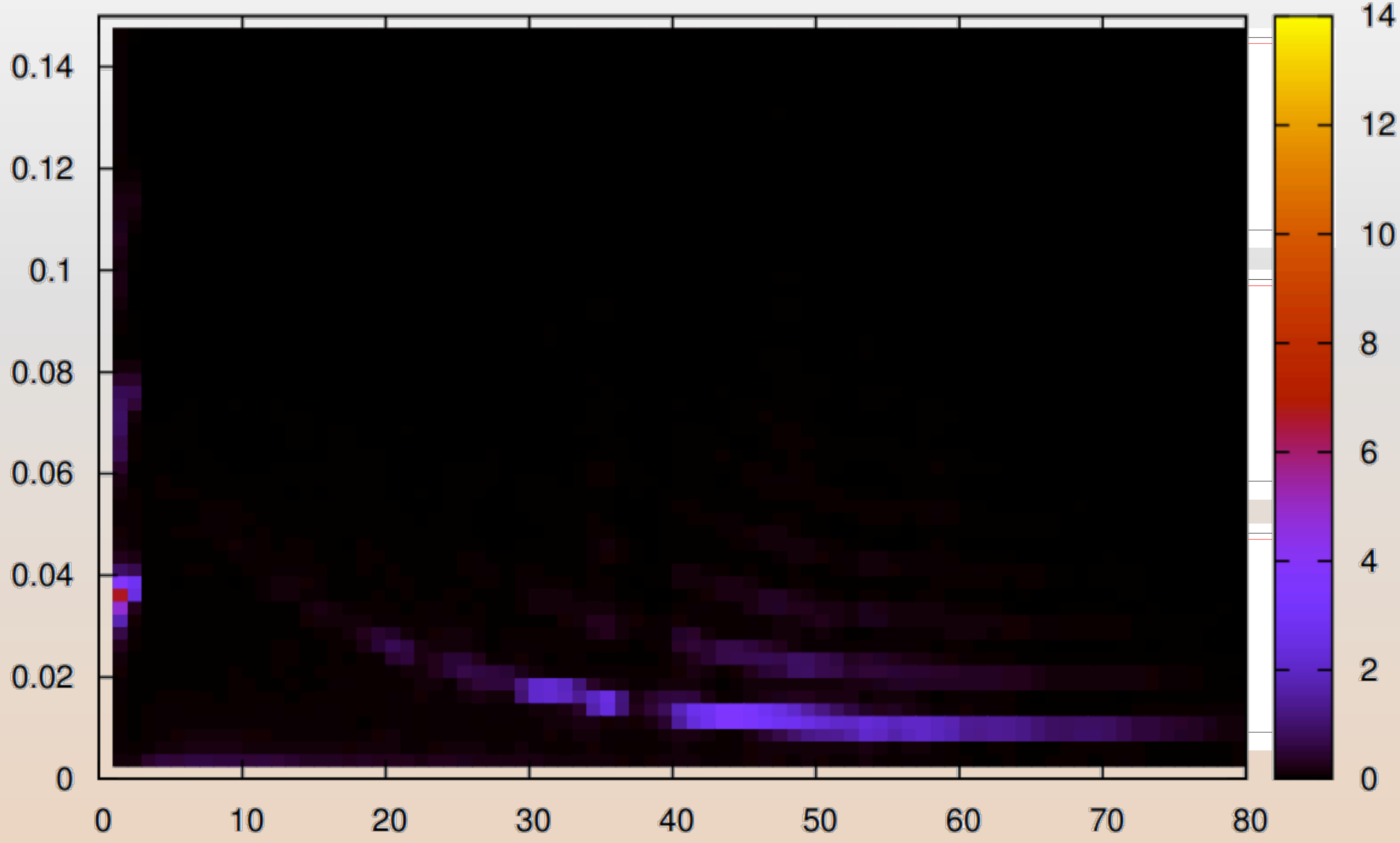


The Deviation of the transmittance signals of two "identic" solutions

The Belousov Zhabotinsky Reaction

Charactarisation of the Transient

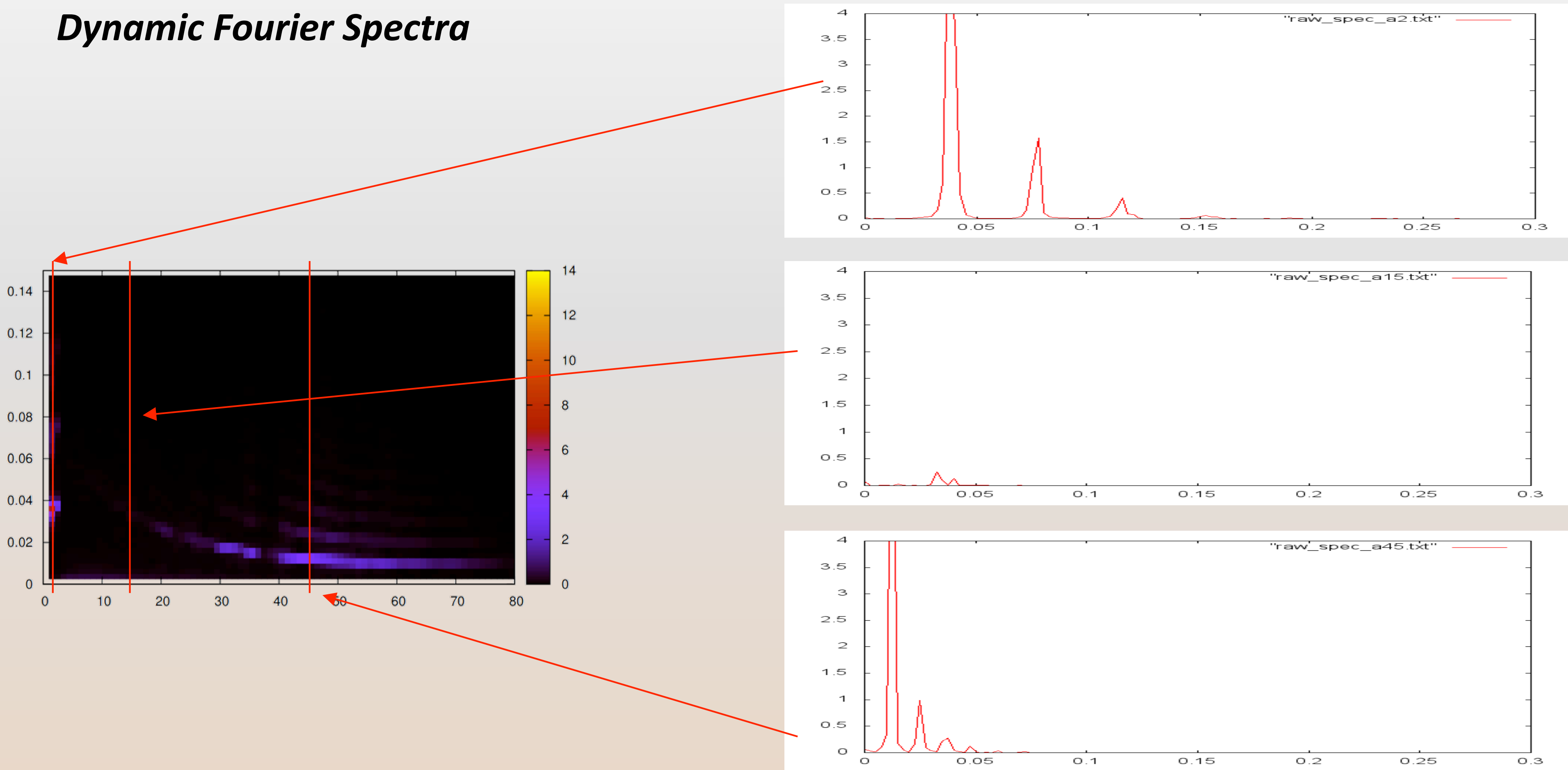
"Dynamic" Fourier Spectra



The Belousov Zhabotinsky Reaction

Charactarisation of the Transient

Dynamic Fourier Spectra



The 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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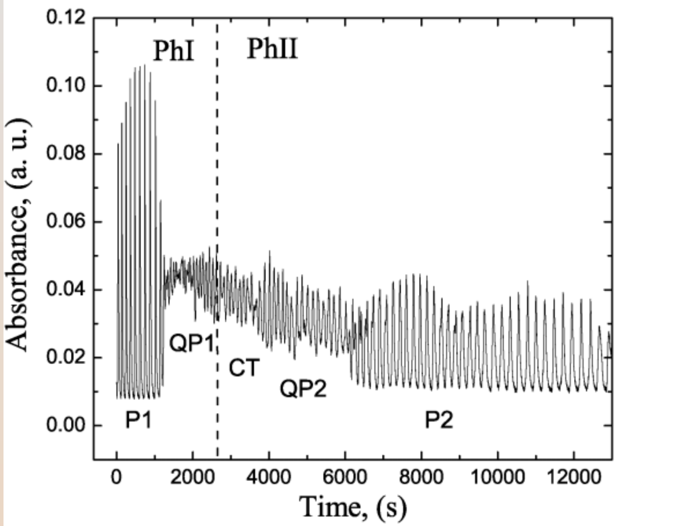
Received 1 August 1996; in final form 13 September 1996

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

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



Spectrophotometric time series at $\lambda = 320$ nm of a cerium

ELSEVIER Chemical Physics Letters 293 (1998) 145–151

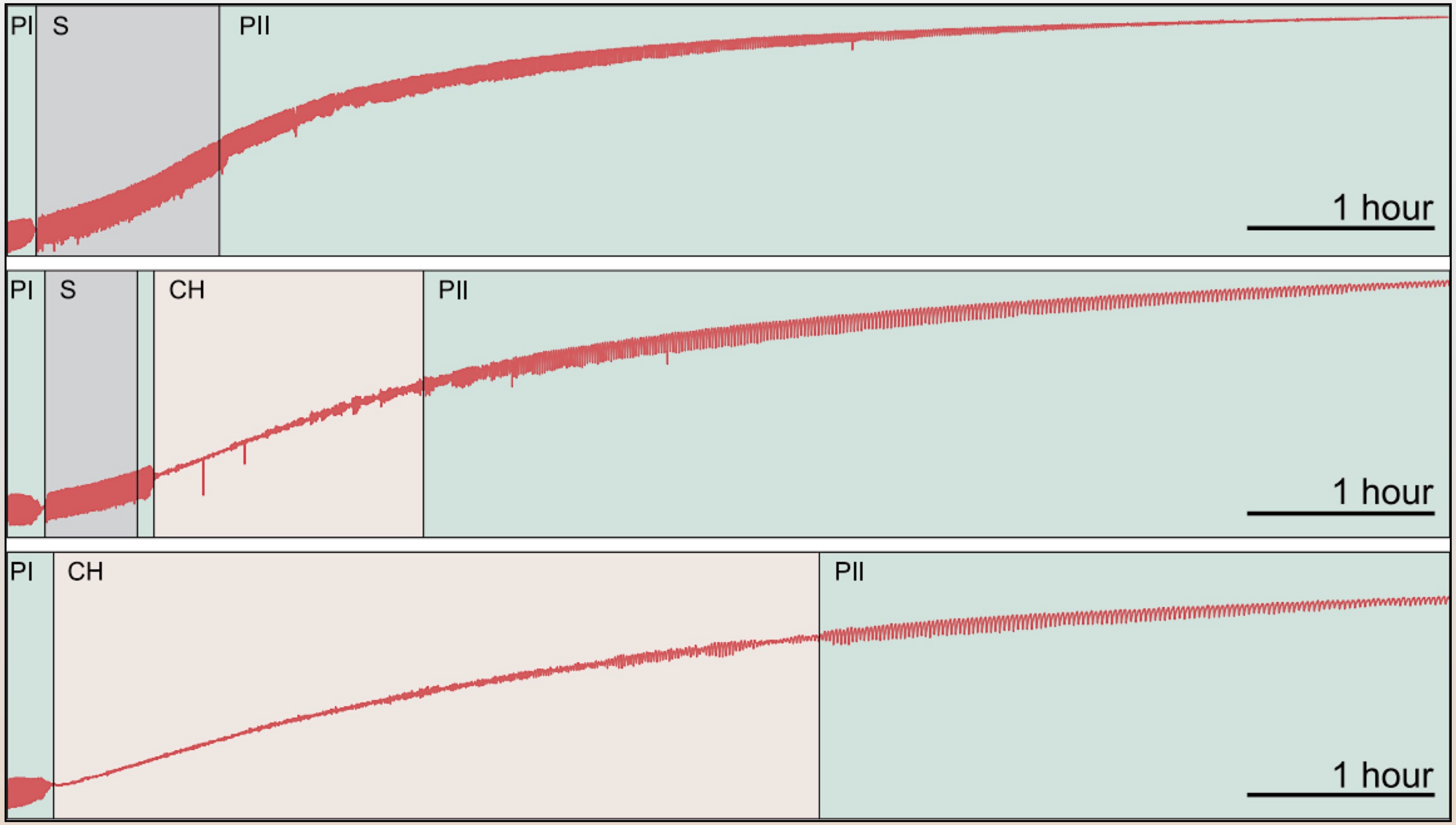
Inverse Ruelle–Takens–Newhouse scenario in a closed unstirred cerium-catalysed Belousov–Zhabotinsky system

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

Inverse Ruelle-Takens-Newhouse Scenario

The Belousov Zhabotinsky Reaction

Hydrodynamic Control of the Chaotic Transient



Florian Wodlei, Mihnea R. Hristea
Effect of Limited Stirring on the Belousov Zhabotinsky Reaction
Proceedings of the European Conference on Complex Systems 2012 (September 2013) | ISBN: 978-3-319-00394-8

The Belousov Zhabotinsky Reaction

Reaction Consumption and the Chaotic Transient

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.

PAPER www.rsc.org/pccp | Physical Chemistry Chemical Physics

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

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DOI: 10.1039/c0cp00109k

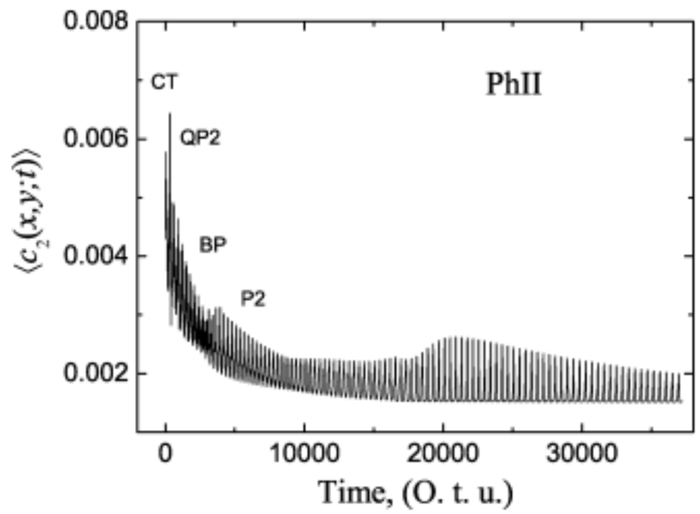

Fig. 2 Evolution of the catalyst ($\langle c_2(x,y;t)\rangle$) in the region PhII.

Chemical Kinetics vs. Diffusion vs. Convection

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

The Belousov Zhabotinsky Reaction

Reaction Consumption and the Chaotic Transient

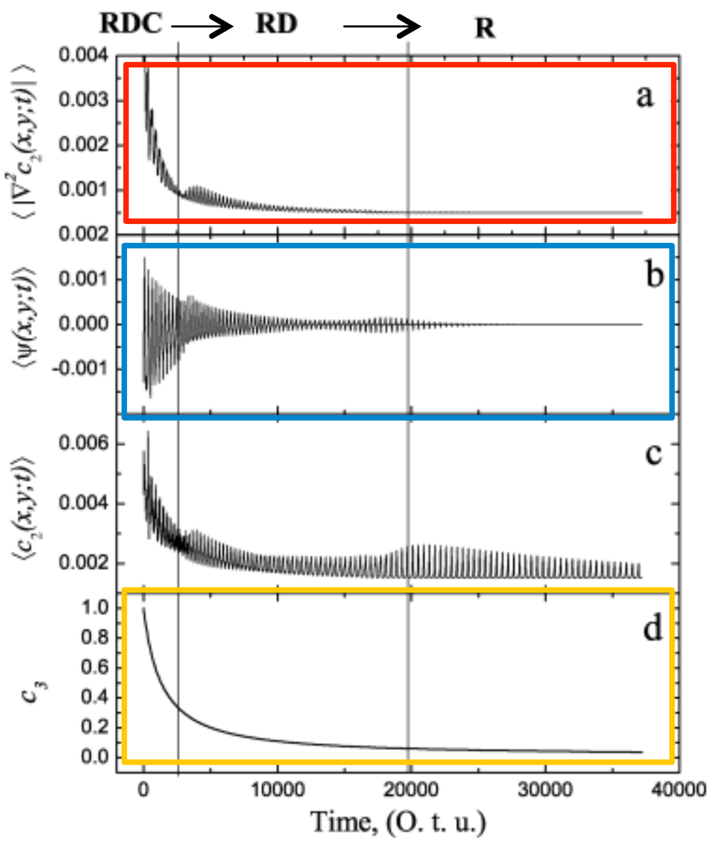

Fig. 4 Direct comparison between the time evolution of: (a) the spatial average of the diffusive contribution, $\langle|\nabla^2 c_i(x,y;t)|\rangle$, (b) the spatial average of the stream function $\langle\psi(x,y;t)\rangle$ (related to the velocity field according to 4–5) and (c) the catalyst mean concentration, $\langle c_2(x,y;t)\rangle$, (d) the concentration of bromate ions, $c_3(t)$. As the concentration c_3 decreases, the diffusive and the hydrodynamical contribution decay to zero.

Chemical Kinetics vs. **Diffusion** vs. **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^-)

Our Group

Living Systems Research

LIVING SYSTEMS
RESEARCH

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

Mihnea R. Hristea
Theory (Reaction-Diffusion-Convection, Graph Theory, Mathematical Statistics)

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Social Insects

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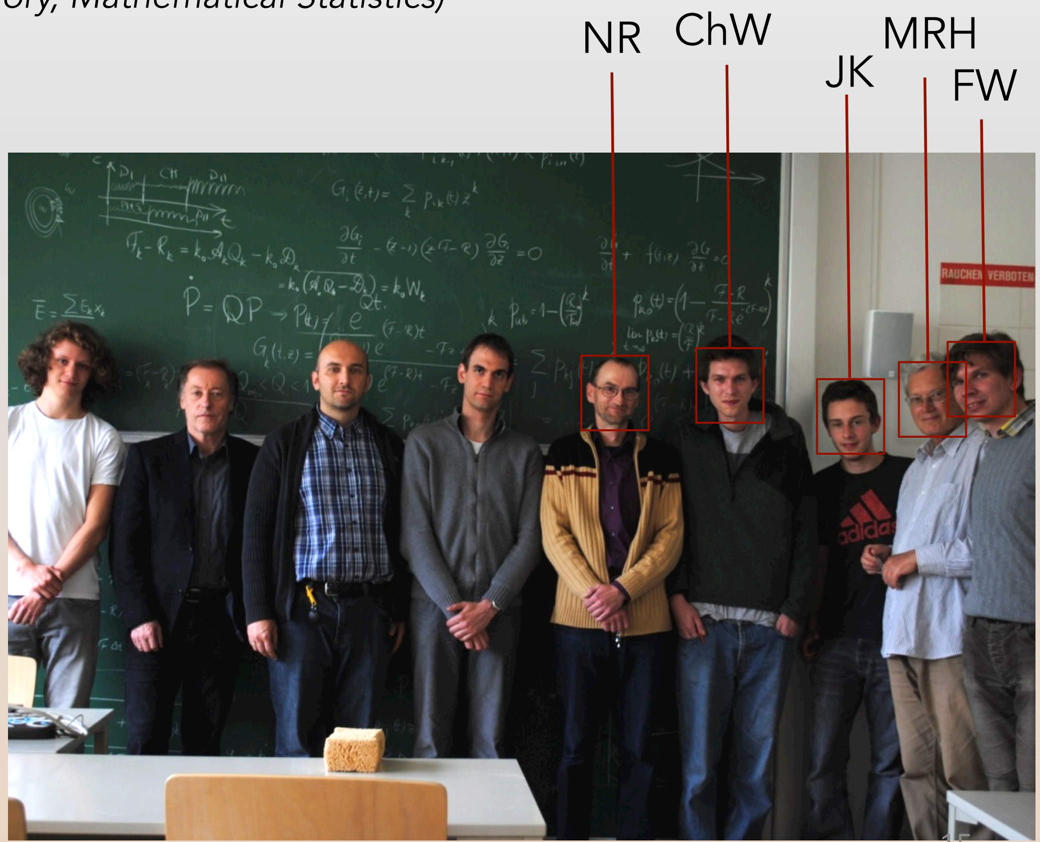
Photography, Graphic-Design, Illustrations



10th Seminar (24/4/14) held at University Klagenfurt mit Lauro Langosco, Günther Pilz, Wilfried Elmenreich, Istvan Fehervari, Norbert Reichmann, Christian Wodlei, Jakob Klien, Mihnea Hristea und Florian Wodlei (von links)

Our Group

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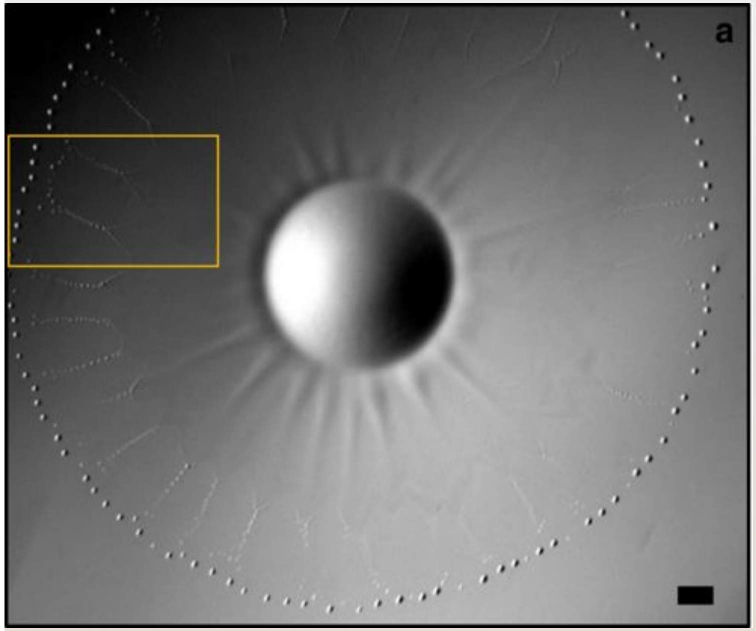
Chemical Self-Organization



Self-Organization of a Dichloromethane Droplet
Belousov-Zhabotinsky Reaction

Social Insects

Carinthian Honey Bees
Ants

F. Wodlei, J. Sebilleau, J. Magnaudet and V. Pimienta: *Marangoni-driven flower-like patterning of an evaporating drop spreading on a liquid substrate.* ***Nature Communications*** **volume 9**, 820 (2018)

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SELF-ORGANIZING SYSTEMS
RESEARCH CLUSTER OF THE ALPEN-ADRIA UNIVERSITY KLAGENFURT

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