Mini-Symposium

Dynamic self-organization in chemistry - oscillatory chemical reactions

Program and abstracts

Polish Chemical Society
The Katowice Branch

http://www.ptchem.katowice.us.edu.pl/

Katowice, March 21st, 2022

Program

1:00 pm – 1:05 pm; Opening (Prof. Jacek Nycz, chair, Polish Chem. Soc., The Katowice Branch; Prof. Mieczysław Sajewicz)

1:05 pm – 2:05 pm; On the origin and manifestations of dynamic self-organization in selected chemical and electrochemical systems (Prof. Marek Orlik, Faculty of Chemistry, University of Warsaw, Warsaw, Poland)

Moderator: Prof. David Hochberg

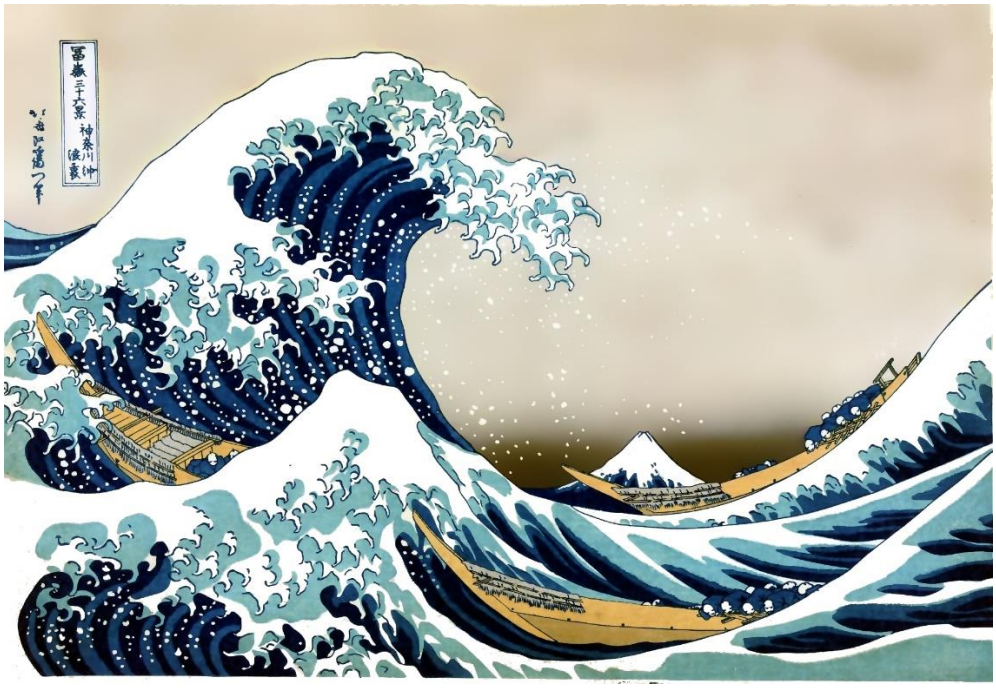
2:05 pm – 3:05 pm; Chaotic oscillations in chiral hypercycles: Mirror symmetry breaking and entropy production (Prof. David Hochberg, Spanish Science Research Council (CSIC) and Center of Astrobiology (CAB), Madrid, Spain)

Moderator: Prof. Marek Orlik

3:05 pm – 4:05 pm; Oscillatory chemical reactions for advanced healthcare (Dr Katarina Novaković, Faculty of Engineering, University in Newcastle, Newcastle, UK)

Moderator: Prof. Emer.Teresa Kowalska

16:05 – 16:10 Closing remarks (Prof. J. Nycz, Prof. M. Sajewicz)



The great wave off Kanagawa and the view of Mount Fuji (the woodblock print); Hokusai, ca. 1831

Speaker CVs and abstracts

Prof. Marek Orlik

Professor Marek Orlik, Ph. D. D.Sc. graduated at the Faculty of Chemistry, University of Warsaw. His research conducted initially under supervision of Prof. Zbigniew Galus, was focused on classical electrochemistry of coordination compounds and kinetics of fast electrode processes, studied experimentally and with numerical modelling, both at the home Faculty and in the research group of Prof. Gerhard Gritzner at the University of Linz (Austria). Later he switched to nonlinear dynamics in electrode processes and homogeneous chemical reactions. As a scholarship holder of the Humboldt Foundation, prof. Orlik worked for two years (1996 – 1998) at the Fritz Haber Institute of the Max Planck Society in Berlin, with Dr. Karl Doblhofer and Prof. Gerhard Ertl (a 2007 Nobel laureate in chemistry), where he studied experimentally and numerically the self-organized electrohydrodynamic convection. Later, he studied nonlinear dynamic phenomena (oscillations and multistability) in electrode reactions of the pseudohalogenide complexes of nickel. In recent years he is dealing with the analysis of kinetic mechanisms and sources of dissipative spatiotemporal patterns in H_2O_2-based chemical oscillators. He is, among others, an author or coauthor of ca. 60 original and review scientific papers, an author of the first in the world literature two-volume monograph "Self-organization in electrochemical systems" (Springer, 2012) and the Polish book “Oscillatory reactions – order and chaos” (WNT, 1996). Prof. Orlik shares his research with intensive teaching activity at various levels of chemistry education, for which he has recently been awarded the Jan Harabaszewski medal by the Polish Chemical Society. In addition to many years of teaching at the home Faculty, he is also a Chairman of the Polish Chemistry Olympiad Committee. For many years he has also been the editor-in-chief of a magazine for chemistry teachers. He is a member of Polish Chemical Society since 1978. More information available at: http://beta.chem.uw.edu.pl/people/MOrlik/

On the origin and manifestations of dynamic self-organization in selected chemical and electrochemical systems

Despite the extremely visually stunning course of oscillatory chemical reactions and the huge progress in understanding, in the second half of the twentieth century, the mechanisms of these processes, showing close correlations with the basics of the functioning of living organisms, the ideas of nonlinear dynamics still cannot find a prominent place in chemical education, and consequently remain little-known to chemists around the world. Even the Nobel Prize in Chemistry, awarded in 1977 to I. Prigogine "for his contributions to non-equilibrium thermodynamics, particularly the theory of dissipative structures" did not change this. One of

the reasons for this situation may be the interdisciplinarity of nonlinear dynamics, which require a certain mathematical description and numerical modeling skills. Moreover, the essence of nonlinear dynamics is the study of systems that lose their stability in various ways, which is the domain of non-classical chemical kinetics. Therefore, chemists dealing with nonlinear dynamics have a great obligation to inform about these fascinating phenomena, which is the purpose of the current lecture. First of all, the concept of stability od states and possible example consequences of its loss to other behaviors will be introduced. On the example of model reaction mechanisms, qualitative and quantitative criteria for oscillatory dynamics will be shown. The next part of the lecture will be devoted to the review of - studied over many years by the author and his coworkers - selected, different electrochemical and chemical dynamical systems, in which spontaneous oscillations of the state of the system and/or spatiotemporal dissipative structures were observed, taking into account recently published research. Finally, an attempt will be made to answer the question – whether the system must be very complicated to behave in a complex or even unpredictable way, which leads directly to the concept of deterministic chaos.

Prof. David Hochberg

Prof. David Hochberg is a theoretical physicist, with a B.A degree from the University of California, Berkeley, a Masters in Science and a Ph.D in physics from the University of Chicago. After postdoctoral research positions held in the UK (Theory Group, Rutherford Appleton Laboratory), in the USA (Bartol Research Institute, and Vanderbilt Universty) and in Spain (University of Valencia, and the Autonomous University of Madrid), he was appointed a permanent Scientific Researcher in the Spanish Science Research Council (CSIC), and is a founding member of the Centro de Astrobiología (CAB) since 1999. His interests have been devoted to applying methods of theoretical physics to a wide variety of problems from particle physics, general relativity, and stochastic processes in chemistry and physics, among others. His current research interest involves the non-equilibrium thermodynamics of the physics and chemistry of complex nonlinear systems, with a specialty in mirror symmetry breaking in chemical systems and the origins of biological homochirality. Prof. Hochberg has served as head of the Chirality Working Group during the COST Action CM0703 "Systems Chemistry", and was a member of its Management Committee. He has been principal investigator on a number of nationally funded research projects devoted to theoretical and experimental chemical models for the origins of biological homochirality. He is head of the Prebiotic Chemistry and Physics of Complex Systems group at CAB.

Chaotic oscillations in chiral hypercycles: Mirror symmetry breaking and entropy production

Catalytic reaction networks consist of molecular arrays interconnected by autocatalysis and cross catalytic pathways among the reactants, and serve as bottom-up models for the design and understanding of molecular evolution and emergent phenomena. An important example of the latter is the emergence of homochirality in biomolecules during chemical evolution. This chiral symmetry breaking is triggered by bistability and bifurcation in networks of chiral replicators. Spontaneous mirror symmetry breaking (SMSB) results from hypercyclic connectivity when the chirality and enantioselectivity of the replicators are taken into account. Heretofore, SMSB has been generally understood as involving chemical transformations yielding scalemic or stable chiral outcomes as non-equilibrium *steady states* (NESS). In this lecture, we consider instead the chaotic regime, in which steady states do not exist. The dissipation, or *entropy production*, is chaotic as is the entropy exchanged with the environment. The rate of change of the total system entropy, governed by the entropy balance equation, is

likewise chaotic. Subsequent to the mirror symmetry breaking transition, the time averaged entropy production is minimized in the final chaotic chiral state with respect to the former chaotic racemic state. The chemical forces evolve in time so as to lower the sum of the entropy production and the exchange entropy, in compliance with the General Evolution Criterion extended to reactions subject to volumetric open flow in well mixed reactors.

Dr Katarina Novaković

Dr Katarina Novakovic, Senior Lecturer in Chemical Engineering, at the School of Engineering, Newcastle University, UK, is a leading expert in Oscillatory Carbonylation Reactions (OCRs) with a core interest in their applications to intelligent materials for novel healthcare technologies and other interdisciplinary uses. Katarina graduated from the University of Belgrade, Serbia (1997) with a degree in Chemical Engineering, specialising in Organic Chemical Technology and Polymer Engineering. Following, she worked in the pharmaceutical industry (1997-2000) at Solid Forms Plant, Hemofarm. Katarina obtained her PhD (2000-2004) from the School of Chemical Engineering and Advanced Materials, Newcastle University, where she gained expertise in the area of mathematical modelling and simulation of polymerisation processes in a Spinning Disc Reactor. Subsequently, Katarina continued working at Newcastle University and began to study the oxidative carbonylation reaction and achieved reproducible oscillations in both pH and heat output. Katarina's efforts in this area resulted in a five year EPSRC Career Acceleration Fellowship awarded in 2009 (CAF2009). Building on the outcomes from CAF2009, in 2012 Katarina was awarded further funding via the EPSRC Developing Leaders award. At that time Katarina entered the area of stimuli responsive hydrogels, her research group now pursues as injectable, implantable, and transdermal forms. EPSRC support enabled Katarina to establish new directions in the area of intelligent polymeric materials and discover the world's first oscillatory chemical reaction employing a polymeric substrate. These findings accelerated to further developments and EPSRC Healthcare Technologies Impact Fellowship (2016) where Novakovic group achieved a proof-of-principle rhythmic material envisioned for application in hands-free drug delivery and mechanoresponsive tissue regeneration. Recent studies expanded a range of materials studied to include investigations of bioglass-hydrogel scaffolds for tissue regeneration and hydrogel based materials for immunomodulatory applications.

Oscillatory chemical reactions for advanced healthcare

Polymeric oscillators under lab conditions are a new concept primarily associated with only two research groups worldwide, Professor Ryo Yoshida's research group, Tokyo University and the Novakovic research group, Newcastle University. The ultimate aim in linking oscillatory chemical systems with polymer science is the development of useful materials and devices that otherwise would not be feasible. The vision includes fully self-oscillatory materials, materials that act life-like, materials that are able to carry and dispense their content in predefined rhythms, and materials which can generate environment which favours cell self-assembly into functional tissue, e.g., healing of a heart tissue following myocardial infarction. The talk will showcase progress in this area so far and present most recent developments in

Novakovic lab ranging from first ever mono- and poly-functional polymeric substrate oscillatory chemical reactions (employing alkyne-terminated poly(ethylene glycol)) to recently expanded family of polymeric catalysts successfully applied to oscillatory systems (using polymer-bound palladium catalysts). Moving to all polymeric oscillatory systems and further to oscillatory materials enables containment of the active chemical species within the scaffold, crucial to reduced toxicity and biocompatibility of these systems.