Introduction to Focus Issue: Oscillations and Dynamic Instabilities in Chemical Systems: Dedicated to Irving R. Epstein on occasion of his 70th birthday

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(Received 4 June 2015; published online 25 June 2015)

[http://dx.doi.org/10.1063/1.4922594]

“Oscillations and Dynamic Instabilities in Chemical Systems” is the title of the Gordon Research Conference inaugurated in 1982 by Irving R. Epstein, whom we honor with this Focus Issue. Oscillations and dynamic instabilities in chemical systems comprise the study of dynamical phenomena in chemically reacting systems far from equilibrium. Systematic exploration of this area began with investigations of the temporal behavior of the Belousov-Zhabotinsky oscillating reaction, discovered accidentally in the former Soviet Union in the 1950s. The field soon advanced into chemical waves in excitable media and propagating fronts. With the systematic design of oscillating reactions in the 1980s and the discovery of Turing patterns in the 1990s, the scope of these studies expanded dramatically. The articles in this Focus Issue provide an overview of the development and current state of the field with special emphasis on the contributions of Irving Epstein.

In The Great Gatsby, the gambler Meyer Wolfsheim tells the young Nick, “Let us learn to show our friendship for a man when he is alive….” With this Focus Issue, we are pleased to show our friendship, and the friendship of many, many researchers around the world, for Irving R. Epstein while he is not only alive but very scientifically active.

Irving Robert Epstein was born August 9, 1945 in New York City. He received his A.B. (artium bacalaureus) summa cum laude in Chemistry and Physics from Harvard College in 1966. In 1967, he was a Marshall Scholar and received a Diploma in advanced mathematics with C. A. Coulson from Oxford University. The first paper he published, as sole author, was in 1967 on “1–4 Bond Orders—A Static Reactivity Index for Diels-Alder Reactions.”¹⁴ He then returned to Harvard for graduate school and earned an A.M. (artium magister) in 1968 and a Ph.D. in chemical physics in 1971 with W. N. Lipscomb, who received the Nobel Prize in Chemistry in 1976.

He started his scientific career at Brandeis University in 1971. In the spring of 1973, he had a couple of very bright undergraduate students who had taken General Chemistry from him and were interested in summer research. Because his research at that time was in quantum chemistry, which was not well suited to sophomores, he went to the library to look for possible projects. He came across an article by Dick Field, in which he described oscillations and pattern formation in the BZ reaction.⁵ After reading the Field article, he found the classic Field-Körös-Noyes paper, which had recently appeared in JACS,³⁴ and decided that this system was perfect for an undergraduate research project. He persuaded Ken Kustin to give him a bit of space and equipment because as a theorist, Irv had no lab space of his own. This research led to Irv’s first paper on oscillating reactions in 1976.⁵

Irv has made many significant contributions to the field of nonlinear chemical dynamics but his arguably most significant was the systematic design of oscillating reactions. Irv explained how he came to work on the systematic design of oscillating reactions:

“It always bothered me that all the oscillating reactions that were known when I started working on them had been discovered by accident. There is a quote from Richard Feynman to the effect that ‘What I cannot create, I do not understand.’ So when I gave talks on oscillating reactions, I would often throw in a line at the end that if we truly understood chemical oscillators, we should be able to build one, just like if I really understood how a TV set works, I should be able to build one (I can’t). Pretty soon, I began thinking about this more and more, and started writing proposals to NSF to design chemical oscillators. The first three were rejected (some reviewers thought it was a great idea, others said ‘interesting, but it will never work’). On the fourth try, a kind program director took pity on me and funded us, which enabled me to bring Patrick De Kepper and Miklós Orbán to Brandeis. Combining my ideas, Ken Kustin’s and theirs, the project worked within months, and we had the first deliberately designed chemical oscillator.” That system was the arsenite-iodate-chlorite system, which Irv says is his favorite chemical system.⁶ Another of Irv’s significant accomplishments was explaining how Turing patterns occur in the CIMA system.⁷⁸

As of May 2015, Irv has published over 400 peer-reviewed papers. In 1998, he and John Pojman published an Introduction to Nonlinear Chemical Dynamics,⁹ which has not been a best seller but has been cited over 1000 times. Irv has done more than publish in the field; he has trained many, many of the current generation of researchers. He has mentored sixteen Ph.D. students, fifty-nine postdoctoral researchers, and over one hundred undergraduate researcher students.

In 1982, he started the Gordon Research Conference on “Oscillations and Dynamic Instabilities in Chemical Systems” from which this Focus Issue takes its name.
Irv has also served Brandeis University as Chair of the Chemistry Department (1983–1987; 2007–2010), Dean of Arts and Sciences (1992–1994), and Provost and Senior Vice President for Academic Affairs (1994–2001), all the while directing a tremendously successful research program. From 1989 to 1994, he was the Helena Rubinstein Professor and since 2006 he has been the Henry F. Fischbach Professor of Chemistry.

He has served as an Associate Editor of this journal since 1991 and joined the Editorial Board of the Journal of Systems Chemistry in 2009. Irv has served on the Board of Directors of the New England Complex Systems Institute since 1996 and Chair of its Board since 2005. In 2006, he was awarded a Howard Hughes Medical Institute Professorship. He founded the “STEM Posse,” a program to identify, recruit, and retain bright disadvantaged students in the sciences and a program of which he is especially proud.

IN THIS ISSUE

Reactions and mechanisms

The explanation of the oscillations in the Belousov-Zhabotinsky reaction called for a detailed kinetic mechanism consistent with both the chemistry of the substances and with the mathematical description of the reaction. In this process, identification of the simplest reaction system underlying the BZ and related bromate-based oscillators played a central role, which was accomplished by Irv Epstein and long-term collaborators and friends Miklós Orbán and Patrick de Kepper. The hunt for the new oscillatory reactions started, and new reactions systems, many of the group of Miklós Orbán, were discovered; the taxonomy of chemical oscillatory systems can be found now in textbooks. Systematic design of oscillatory reactions, which is based on general design guidelines and the mechanistic and parametric requirements of oscillations, was instrumental in the tedious process. The methodology was also applied to the design of pH oscillations. In this issue, Miklós Orbán and his co-authors report that the simplest bromate oxidation-based pH oscillator can now be conducted in semi-batch and gel-fed batch reactors. Such arrangement could facilitate the application of oscillatory chemical reactions in many other systems, because pH oscillators can be applied to drive the equilibrium point of other, pH sensitive reactions.

Chlorite-based systems served as a great resource for nonlinear chemical dynamics. István Nagypál and Attila K. Horváth report that three independent but cross-coupled reactions of the chlorite ions can be unified through short-lived intermediates to describe the kinetic curves in the chlorite-thiosulfate reaction in a complex, 39 step kinetic model. However, a complex mechanism is not necessary for generation of complex oscillations. M. Gallas and J. A. C. Gallas show that instead of the complex, 10-equation, 14-parameter enzyme model for the non-chaos-mediated mixed-mode oscillations, a greatly simplified, four-variable, nine-parameter model can also be used; in addition, the model also exhibits a nested arithmetic progression of oscillatory phases.

Turing patterns

A major breakthrough in nonlinear chemical dynamics was the discovery of formation of stationary spatial patterns through the Turing mechanism in the De Kepper laboratory. Irv Epstein with István Lengyel interpreted the patterns with a model that was reduced to two variables and has become the Lengyel-Epstein model. (Two contributions on Turing patterns use this model in the issue.) Reversible complexation of an activator species to form an unreactive, immobile complex was shown to facilitate the formation of Turing patterns. This idea is further elaborated in the work of Tóth and Horváth in this issue by immobilizing autocatalysts in ionic systems though selective binding, even for ions with equal mobilities. Turing patterns turned out to be rather peculiar patterns; only two clear examples had been demonstrated until 2009 when the De Kepper group developed an operational design method. In the issue, De Kepper and his co-authors elaborate on the journey of discoveries of Turing patterns in new reaction systems from the perspective of the design method. The Turing instability can also play an important role in standing wave oscillatory patterns: Berenstein shows in a newly proposed mechanism that a system exhibiting defect-mediated turbulence for equal diffusivities and Turing instability can create standing waves even with a two-variable model instead of the common scenario with a short-wavelength bifurcation of three-variable systems.

Effects of light modulation

Light can affect the BZ reaction with a proper catalyst. The Gao group, in collaboration with Irv Epstein, reports that there is a non-monotonic relationship between the oscillation frequency and photointensity due to the essential mechanistic step related to reduction of BrO$_3^-$ to HBrO$_2$. The light sensitivity of BZ reaction allows external perturbation of the system to create even more complex patterns. The group of Irv Epstein showed oscillatory cluster patterns that arise in a homogenous chemical system with global feedback. In the issue Schmidt and Krasner show that with nonlinear global coupling, a chimera state can be obtained where synchronous and desynchronous states co-exist in a medium. Irv Epstein also showed that Turing patterns can be manipulated and controlled by light.

In this issue, simulations by the group of Ehud Meron show a non-monotonic resonance in the Lengyel-Epstein model due to spatially periodic illumination. Although not directly related to light modulation, but rather to the general periodic perturbation of the simplified model of the BZ reaction (the Oregonator), the Rotstein group reports complex oscillatory patterns in which middle-amplitude oscillations play important role in addition to the common small and large amplitude oscillations observed in the BZ system.

Patterns in 3D

With an increase of spatial dimensions, more complicated spatiotemporal phenomena can be expected: traveling waves in 1D can transform to spiral motion in 2D, which in
turn can give scroll waves in 3D. Imaging chemical reactions in 3D proved to be a great challenge; however, in the past decade MRI techniques and tomography allowed analysis of very complex patterns. Such three-dimensional patterns become forefront research in nonlinear chemical dynamics. Irving Epstein with Vladimir Vanag and Tamás Bánási showed that Turing structures can also develop in 3D. In this issue, Tamás Bánási and Annette Taylor investigate helical Turing patterns that form in cylindrical layers using the Lengyel-Epstein model. The group of Oliver Budroni tests the prediction that scroll waves can rotate around one-dimensional phase singularities, experimentally controlled by steps, troughs, and corners. Stable, complex, 3D convection-driven fronts arising in the chlortetrathionate reaction as a result of antagonistic thermal and solutal contribution to the density charge are reported by the group of Jerzy Maselko.

Precipitation patterns, which underlie the formation of “chemical garden” experiments, received considerable attention in the past years because of their potential in creating nanostructures. The group of Kenneth Showalter presents a model for the circular and spiral propagation of 3D waves in the AlCl$_3$/NaOH and NaAl(OH)$_4$/HCl system. Self-constructing and evolving 3D structures made from elastic membranes in an aluminum-hydroxide-carbonate system are reported by the group of Ágota Tóth.

Anisotropy

Irv Epstein, in collaboration with István Nagy-Pál and György Baza, demonstrated anisotropy in the propagation of chemical waves because of gravity. In this issue, a collaborator of Irv Epstein, Alberto P. Munuzuri and his co-authors show that an anisotropy induced through centrifugal forces can also affect reaction-diffusion systems in simulations with the Oregonator model.

Coupled systems

Irving Epstein with Michael Crowley discovered that coupling of chemical oscillations can cause the oscillations to disappear (or to appear) and can lead to multiple modes of entrained oscillations. These results initiated extensive research on coupling of discrete chemical reaction units. The simplest way to compartmentalize the reaction is to use many CSTRs with mass transfer or electrical coupling. These techniques were greatly refined, for example, to demonstrate the role of inhibitory and excitatory pulse coupling of chemical oscillators. The group of Vladimir Vanag reports that the dynamical regimes of two pulse-coupled non-identical BZ oscillators with delay can exhibit amplitude death and higher-order entrainments depending on the coupling strength and time delay. Irving Epstein demonstrated biorhythmicity (two different modes of oscillations under the same conditions) in chlorite-bromate-iodide system with Mohammed Alamgir. Now Nagy et al. report that when an oscillatory electrochemical reaction is coupled to itself with a delay (through a feedback mechanism) bi- and trirhythmicity can be observed.

Patterns in structured media

The nanoscale encapsulation of the BZ media with AOT microemulsions, developed by Irv Epstein with Vladimir Vanag, produced incredibly rich dynamical phenomena; perhaps the most striking example is the inward rotating spiral. It was proposed that some of the complex phenomena can be interpreted by the peculiar cross diffusion effect. Budroni et al. report that cross-diffusion effects in AOT water-in-oil microemulsion solution with different water or AOT compositions can induce buoyancy-driven convective instabilities at the interface between the two solutions.

Microscale encapsulation of the BZ reaction was developed by the group of Irv Epstein with microfluidic droplet technology. The system displayed rich in and anti-phase synchronization patterns and was recently used to confirm all predictions of Turing for a ring of six coupled drops, in particular, related to the differential growth of the droplets due to the formation of the spatial pattern. In this issue, the group of Seth Fraden reports creation of planar networks of chemical oscillators using programmable illuminations that can create Dirichlet (constant-concentration) or Neumann (no-flux) boundary conditions for the droplets. Using light, the period of the individual droplets can be controlled to cause one-time phase delay or constant period elongation. In an innovative paper, Amemiya et al. show that the microencapsulation technique is a useful tool to investigate how cell-to-cell communication during glycolytic oscillations depends on density and spatial distribution of yeast cells: The yeast cells were encapsulated into alginate microparticles using a centrifuge-based droplet method.

Polymers and chemomechanical systems

Application of nonlinear dynamics to polymer systems attracted attention because of the potential practical importance and the presence of strong nonlinearities (e.g., the thermochemical feedback due to the strongly exothermic reactions accelerating the rate). Earlier efforts of Irv Epstein in polymer systems focused on patterns that arise during the polymerization of acrylamide. In this issue, the group of Tran-Cong-Miyata shows how competition between photocross-linking and phase separation can provide useful methods of material design in the micro- and sub-micrometer scales. Combination of oscillating BZ reaction and specially designed polymer materials resulted in self-oscillating gels. Structural modification of the polymers to tailor behavior is a challenging task. The Yoshida group reports the preparation of an AB diblock copolymer composed of hydrophilic poly (ethylene oxide) (PEO) segment and self-oscillating polymer segment (N-isopropylacrylamide that contains ruthenium tris(2,2’-bipyridine) (Ru(bpy)$_3$), a catalyst of the BZ reaction). In another paper of the issue, the group of Anna C. Balazs shows in numerical simulations that the oscillating polymer gels can entrain to periodic mechanical deformation.

Oscillating chemomechanical systems remain an important research field and potential application of nonlinear chemical dynamics. In the issue, Nakata et al. investigate the oscillatory motion of a camphor boat and identifies mode-
bifurcations as a function of the diffusion length of camphor molecules, e.g., multiple accelerations during oscillation, period-2 or irregular oscillatory motion, and reciprocating oscillation. In another contribution, the group of Parmananda reports that coupled mercury beating heart systems can synchronize in a similar manner to the Kuramoto transition of phase oscillators.

ACKNOWLEDGMENTS

I.-Z. K. acknowledges support from the National Science Foundation under Grant No. CHE-0955555.