Chaos
An Interdisciplinary Journal of Nonlinear Science

Editorial for Focus Issue: From chemical oscillations to applications of nonlinear dynamics: Dedicated to Richard J. Field on the occasion of his 80th birthday

Cite as: Chaos **32**, 100401 (2022); https://doi.org/10.1063/5.0127462
Submitted: 21 September 2022 • Accepted: 22 September 2022 • Published Online: 27 October 2022

Jason A. C. Gallas and Oliver Steinbock

Editorial for Focus Issue: From chemical oscillations to applications of nonlinear dynamics: Dedicated to Richard J. Field on the occasion of his 80th birthday

Cite as: Chaos **32**, 100401 (2022); doi: 10.1063/5.0127462
Submitted: 21 September 2022 · Accepted: 22 September 2022 ·
Published Online: 27 October 2022

Jason A. C. Gallas[1,2,3,a] and Oliver Steinbock[4,b]

AFFILIATIONS

[1]Instituto de Altos Estudos da Paraíba, Rua Silvino Lopes 419–2502, 58039-190 João Pessoa, Brazil
[2]Max-Planck Institute for the Physics of Complex Systems, Nöthnitzer Str. 38, 01187 Dresden, Germany
[3]Complexity Sciences Center, 9225 Collins Avenue Suite 1208, Surfside, Florida 33154-3001, USA
[4]Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida 32306-4390, USA

Note: This article is part of the Focus Issue, From Chemical Oscillations to Applications of Nonlinear Dynamics: Dedicated to Richard J. Field on the Occasion of his 80th Birthday.
[a]**Author to whom correspondence should be addressed:** jason.gallas@gmail.com
[b]**Electronic mail:** osteinbock@fsu.edu

https://doi.org/10.1063/5.0127462

This Focus Issue celebrates, in recognition of his 80th birthday, Professor Richard "Dick" J. Field's contributions to the field of nonlinear chemical dynamics and self-organization by presenting a kaleidoscope of modern nonlinear science that directly or indirectly relates to his accomplishments. As one of the pioneers of research on chemical oscillations, Dick laid the foundation necessary to understand limit-cycle oscillations, the Hopf bifurcation, and deterministic chaos in the Belousov–Zhabotinsky (BZ) reaction, which, thus, became the workhorse for explorations into chemical oscillations and pattern formation. Previous experimental observations of chemical oscillations were presumed to be around the point of chemical equilibrium (think pendulum) and were, thus, dismissed as some form of artifact because of the prohibition of such oscillation in chemical systems by the second law of thermodynamics. Dick's ground-breaking work with Endre Körös and Richard Noyes resulted in a detailed BZ reaction mechanism [now referred to as the Field-Koros-Noyes (FKN) mechanism[1–5]] demonstrating that the BZ oscillations occur in fact around a far-from-equilibrium steady state.

The information in the next few paragraphs is extracted from a private document provided by Dick.

Dick was born in the Fall of 1941 in Massachusetts. His infant nickname curiously was BZ. He completed his B.S. degree at University of Massachusetts in 1963, and after a mostly personal year at College of the Holy Cross, he entered the Ph.D. program at University of Rhode Island in 1964 and chose to join Professor Paul I. Abell's group. Abell was a physical organic chemist studying gas-phase chemical kinetics, radical-chain mechanisms, as well as the photoaddition of HBr to various olefins. Dick's work on the

photoaddition of HBr to $CH_3CH = CH_2$ led to the now accepted value of the allyl radical stabilization energy. He defended his dissertation in June 1968.

Dick joined Richard Noyes' chemical kinetics group at University of Oregon for his postdoctoral work. Noyes had recently published an interesting series of papers on the mechanisms (polar or radical) of binary halogen exchange reactions, e.g., $I_2 + Br_2 \rightleftharpoons 2IBr$ that attracted Dick. He and his wife Judith drove their VW bug cross-country to Eugene, Oregon in August 1968. There he started his first liquid-phase project, the experimental determination of the aqueous diffusion coefficient of $H^{\cdot}$. It was planned to use in this work the radical-chain photoreduction of H_2O_2 by H_2 in conjunction with the Photochemical Space Intermittency (PSI) method[6] developed by Noyes and his CalTech Ph.D. mentor, Roscoe Dickinson. The PSI method required the radical-chain photoreduction process to be terminated by the reaction $H^{\cdot} + H^{\cdot}$. However, Dick was not able to establish the radical chain: something was stealing his $H^{\cdot}$, and Dick now believes the thief was $2H^{\cdot} + 2H_2O_2 \rightarrow 2H_2 + 2HO_2^{\cdot}$ followed by $2HO_2^{\cdot} \rightarrow H_2O_2 + O_2$.

Dick was discouraged from ever getting the $H^{\cdot}$ diffusion coefficient when he sat down in Fall 1969 to hear University of Oregon Professor Robert Mazo's late Monday afternoon seminar on dissipative structures.[7] Mazo's talk featured a demonstration of the recently observed Busse bands[8] using what is now referred to as the Belousov–Zhabotinsky (BZ) recipe. A few days later the Noyes group meeting discussed the Busse bands. Dick first saw the BZ oscillations when he stirred a test tube containing the Busse bands while cleaning up after this meeting, which is perhaps the first observation of the BZ oscillations in North America. Mazo had only very recently carried the BZ recipe from Brussels to Eugene.

The remainder of Dick Field's career has been almost entirely devoted to the BZ reaction, its many variants, and corresponding nonlinear dynamics. Noteworthy excursions elsewhere include simulations of Earth's troposphere with Sasha Madronich that revealed interesting behaviors including bistability and chaos[9] as well as work with David Schuldberg on a psychological problem, social-support moderation of the effect of stress on individuals.[10] The interesting result here is that with some social-support, people are stable to quite high levels of stress so long as their environment does not behave periodically. Another noteworthy contribution involves the study of the honey from flowers of the New Zealand mānuka bush, which contains the nasty compound dihydroxyacetone ($C_3H_6O_3$) as does freshly prepared mānuka honey, which is, thus, not edible. However, over the course of weeks or months (depending on temperature), this dihydroxyacetone dehydrates to methylglyoxal ($C_3H_4O_2$), which is a strong antibacterial that itself dehydrates slowly to inactive products. Thus, the antibacterial action of mānuka honey passes through a maximum. Aged mānuka honey is sold around mainly Asia as a "natural" topical antibacterial. Dick and coauthors worked together at Waikato University, Hamilton, New Zealand to understand the mechanistic chemistry of the dehydration processes well enough to help New Zealand beekeepers age mānuka honey to have its greatest antibacterial strength when it arrives at market.[11–15]

The first article of this Festschrift is a historical review of the development of the FKN mechanism and the derived Oregonator model.[16] First-authored by the "sole survivor" of the FKN trio, the article also illustrates the important role of serendipity in science and the even greater importance of a prepared mind. Readers unfamiliar with the BZ reaction will find this contribution to be a valuable introduction to the chemistry of the BZ system and traveling chemical waves.

BZ oscillations and their theoretical analyses were also important for developing a better understanding of oscillations in biochemical systems for which the identification of the relevant chemical species is often ambiguous and more challenging than in the (nearly inorganic) BZ reaction. In this context, Bashkirtseva and Ryashko report results on nonlinear biochemical oscillations in noisy systems.[17] The authors analyze the creation of "phantom attractors" by multiplicative Gaussian noise and discuss the relevance of fast and slow time scales that can be found in many chemical and biological oscillators.

The contribution by Troy[18] investigates a two-variable model, the Kopell–Howard (lambda–omega) model, with a focus on rotating and stationary logarithmic spiral solutions. The first result is Theorem 1.2 where the existence of a non-oscillatory solution (0-bump solution) is proven for given parameters. Then, Theorem 2.1 is proven through a series of steps where the appropriate range of relevant parameters is also determined. The existence of more complex families of solutions could be established by combining the utilized topological shooting techniques with functional analysis approaches.

The paper by Rocha *et al.*[19] reports on the oscillatory nature of vertical growth of cobaltous silicate filaments in narrow Hele–Shaw cells. The experiments are corroborated with adequate modeling. The authors observed three different types of patterns: no filaments, single, and multiple filaments. The oscillatory origin of single filaments is discussed and compared with the results of modeling. The governing equations for the pressure and the concentration change are given, and their non-dimensionalized forms are used to determine the oscillatory regime. After appropriate scaling, the experimental and the numerical results are in very good agreement. Kumar *et al.*[20] experimentally investigated the sol-gel transition of an ethanol-containing chitosan gel and the associated self-propulsion due to interfacial tension gradients. They systematically measured a number of characteristics of the self-propelled gel including the lasting time, the speed, projection area, etc., as a function of the chitosan concentration. By tuning the volume ratio R of chitosan and water to ethanol, the authors obtained a dynamical phase diagram featuring different growth regimes and highlighted the oscillatory motion at a high ethanol content, i.e., a small R value.

The paper by Gallas and Olsen[21] investigates three four-variable subnetwork models of the peroxidase–oxidase system, the first experimental (bio)chemical reaction system to display chaotic dynamics. The aim is to determine if certain experimental behaviors can be reproduced in minimal models. High resolution dynamical phase diagrams and return maps are plotted and the models are found to display features from the full state-of-the-art model with ten coupled equations and to reproduce some of the experimental data. In particular, quint points—exceptional points where five distinct phases meet[22]—are obtained for two of the models, and experimental evidence for such elusive points is also presented. Comparison of these minimal models aids in understanding how complex behavior can be obtained in (bio)chemical systems.

The contribution by Kubodera *et al.*[23] investigates the Belousov–Zhabotinsky reaction with the aim to elucidate features of oscillations depending on the applied electrical potential, *E*. A cation-exchange resin bead loaded with the catalyst of the reaction was placed on a platinum plate as a working electrode and then *E* was applied. The authors find that global oscillations and a reduced state coexist on the bead at a negative value of *E* and that the source point of global oscillations changed depending on *E*. The thickness of the reduced state was determined by a yellow colored region, which corresponded to the distribution of Br_2. The present studies suggest that the distribution of the inhibitor, Br^-, which is produced from Br_2, plays an important role in the existence of the reduced state and global oscillations, and the source point of global oscillations.

Tang and Wang[24] describe the response of the Belousov–Zhabotinsky reaction to the presence of a grounded-Pt electrode, in terms of the creation of an electrical potential without the need for an external power source. They observed significant changes in the redox behavior of the reaction. The idea that the electrochemical perturbation may be established through the formation of a concentration battery cell is interesting, original, and might be further developed and investigated. The authors checked different experimental strategies to corroborate their hypotheses.

In Ref. 25, Dolnik and coauthors investigate pattern formation resulting from the interaction of reaction and diffusion, which is a key paradigm in the theory of morphogenesis. They study how Turing pattern formation on a growing domain is affected by discrete domain discontinuities. Using the Lengyel–Epstein reaction–diffusion model, the authors numerically simulate Turing pattern formation on radially expanding circular domains containing a variety of obstruction geometries, including obstructions spanning the length of the domain, such as walls and slits, and local obstructions such as small blocks. This generic model of chemically reacting species is useful because simulated results can be potentially reproduced in experiments with the light sensitive chlorine dioxide–iodine–malonic acid reaction. The authors demonstrate the strong influence of the domain growth and the presence of obstacles in the pattern developed. The focus of the study is on the influence of gaps in the domain, or obstructions, on pattern formation and to see how much of an effect do the obstacles have on the evolution of patterns in the growing domain compared to the static domain.

Ezzeddine and Sultan[26] explore the formation of precipitation patterns in reaction–diffusion systems and present results on the precipitation patterns in a gel medium, where the reaction–diffusion processes of multiple sources develop distinct precipitation regimes and create polygonal boundaries. The authors describe a 2D analog of the Liesegang phenomenon that also offers the ability to control the precipitation patterns with precise detail. The method is generalizable to multiple precipitation systems (lead chromate and cobalt hydroxide) and offers interesting polymorph selection in the cobalt case. The dynamics and structure of precipitate formation are analyzed.

Doedel and Pando Lambruschini[27] investigate mixed-mode oscillations that arise in CO_2 lasers coupled symmetrically through saturable absorbers, a procedure that has been implemented both theoretically and experimentally in the literature. They consider the two lasers in which mixed-mode oscillations arise in the absence of coupling and show that dynamical transitions among resonances in the chaotic regime may be explained by the overlap of certain resonances. They find that the overlap of resonances can explain the onset of two different scaling regions in the dimension correlation sum, which display an explicit dependence on the optical coupling strength. For very small coupling ranges, they report larger scaling regions, which look analogous to the ones for the uncoupled laser system. For larger coupling, but still well below the synchronization threshold, they find steeper and larger scaling regions.

The contribution of Romano *et al.*[28] considers experimentally two non-identical electrocatalytic periodic oscillators coupled unidirectionally (master → slave) through the applied potentials. These coupled oscillators were studied by considering compositionally identical M(methanol)–S(methanol) and non-identical M(methanol)–S(formic acid) organic molecule components. For the master, the applied potential is kept constant and for the slave, the applied potential is continuously adjusted through the perturbation term. The authors identify different synchronization domains (no sync, phase, and lag) as a function of the coupling strength parameter. A particularly interesting novelty is the consideration of non-identical dynamical systems.

The paper by Battogtokh and Tyson[29] provides a nice comparison of two types of mechanisms proposed for localization of the shoot apical meristem (SAM)—classical Turing reaction–diffusion and a bistable switch controlling a fast-diffusing hormone. The authors argue that the bistable switch exhibits better localization of the transcription factor WUSCHEL domain and shows a better response to SAM ablation than does the Turing model, namely, the bistable reaction–diffusion model can better explain the development of certain plant structures, as compared to the Turing instability models previously discussed.

Liu *et al.*[30] investigate the synchronization of active chemical oscillators in the presence of an electrochemical coupling. Two chemical oscillators are passively coupled through the use of a wire connecting two batch reactors with a Pt-mesh electrode. The authors show that a redox oscillatory chemical reaction can spontaneously synchronize with a connecting metal wire in a closed system. The coupling takes place by mediating electrochemical reactions on the two ends of the metal wire. The results were reproduced in simulations with the Oregonator model with a coupling term that affected the oxidized form of the catalyst in each cell, based on the Nernst equation. The results demonstrate the use of synchronization theories in a highly drifting system (as the equilibrium is reached) and set the stage for the design of large sets of coupled chemical reactions, e.g., for chemical computations.

While the cross section of current nonlinear science presented in this issue is obviously far from complete, the collected papers illustrate the relevance of Dick's work to the field of nonlinear science which, during the past 50 years, has grown in innumerable directions. In a time of rapid metrics, Dick's work reminds us of how a small number of key papers can have long-lasting impact on a research field that around 1970 was just beginning to define itself. We are grateful for Dick's achievements and his commitment to science and our future.

Lastly, we have to share the sad news of the passing of Harold M. Hastings last May 2, who was one of the three guest editors organizing this Festschrift. He was actively involved in most of this process and the news of his death reached us unexpectedly. Harold

received his education at Yale and Princeton Universities. After many years on the faculty of Hofstra University, he continued to work at Bard College at Simon's Rock, the last 12 years as Professor and Chairperson of the Department of Physics and Astronomy and Professor of Mathematics. Harold's scientific interests were very broad ranging from fractals and excitation waves to the evolutionary stability of food chains and cardiac arrhythmia. He always showed a sincere and deep interest in the work of others, regardless of the topic. Harold will be missed by his many former students and colleagues.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Jason A. C. Gallas: Writing – review & editing (equal). **Oliver Steinbock:** Writing – review & editing (equal).

REFERENCES

[1] R. M. Noyes, R. J. Field, and E. Korös, "Oscillations in chemical systems. I. Detailed mechanism in a system showing temporal oscillations," J. Am. Chem. Soc. **94**, 1394–1395 (1972).
[2] R. J. Field, E. Korös, and R. M. Noyes, "Oscillations in chemical systems. II. Thorough analysis of temporal oscillation in the bromate-cerium-malonic acid system," J. Am. Chem. Soc. **94**, 8649–8664 (1972).
[3] R. J. Field and R. M. Noyes, "Explanation of spatial band propagation in the Belousov reaction," Nature **237**, 390–392 (1972).
[4] R. J. Field and R. M. Noyes, "Oscillations in chemical systems. IV. Limit cycle behavior in a model of a real chemical reaction," J. Chem. Phys. **60**, 1877–1884 (1974).
[5] R. J. Field and R. M. Noyes, "Oscillations in chemical systems. V. Quantitative explanation of band migration in the Belousov-Zhabotinskii reaction," J. Am. Chem. Soc. **96**, 2001–2006 (1974).
[6] G. A. Salmon and R. M. Noyes, "Evidence for photochemical space intermittency," J. Am. Chem. Soc. **84**, 672–673 (1962).
[7] P. Glansdorff and I. Prigogine, *Thermodynamic Theory of Structure, Stability and Fluctuations* (Wiley-Interscience, New York, 1971).
[8] H. G. Busse, "A spatial periodic homogeneous chemical reaction," J. Phys. Chem. **73**, 750 (1969).
[9] R. J. Field, P. G. Hess, L. V. Kalachev, and S. Madronich, "Characterization of oscillation and a period-doubling transition to chaos reflecting dynamic instability in a simplified model of tropospheric chemistry," J. Geophys. Res. **106**, 7553–7565 (2001).
[10] R. J. Field, J. A. C. Gallas, and D. Schuldberg, "Periodic and chaotic psychological stress variations as predicted by a social support buffered response model," Commun. Nonlin. Sci. Numer. Simulat. **49**, 135–144 (2017).
[11] M. N. C. Grainger, M. Manley-Harris, J. R. Lane, and R. J. Field, "Kinetics of the conversion of dihydroxyacetone to methylglyoxal in New Zealand Mānuka honey: Part I—Honey systems," Food Chem. **202**, 484–491 (2016).
[12] M. N. C. Grainger, M. Manley-Harris, J. R. Lane, and R. J. Field, "Kinetics of the conversion of dihydroxyacetone to methylglyoxal in New Zealand Mānuka honey: Part II—Model systems," Food Chem. **202**, 492–499 (2016).
[13] M. N. C. Grainger, M. Manley-Harris, J. R. Lane, and R. J. Field, "Kinetics of the conversion of dihydroxyacetone to methylglyoxal in New Zealand Mānuka honey: Part III—A model to simulate the conversion," Food Chem. **202**, 500–506 (2016).
[14] M. N. C. Grainger, A. Owens, M. Manley-Harris, J. R. Lane, and R. J. Field, "Kinetics of the conversion of dihydroxyacetone to methylglyoxal in New Zealand Mānuka honey: Part IV—Formation of HMF," Food Chem. **232**, 648–655 (2017).
[15] A. Owens, J. R. Lane, M. Manley-Harris, A. M. Jensen, and S. Jørgensen, "Kinetics of the conversion of dihydroxyacetone to methylglyoxal in New Zealand Mānuka honey: Part V—The rate determining step," Food Chem. **276**, 636–642 (2019).
[16] R. J. Field, R. M. Mazo, and N. Manz, "Science, serendipity, coincidence, and the oregonator at the University of Oregon, 1969–1974," Chaos **32**, 052101 (2022).
[17] I. Bashkirtseva and L. Ryashko, "Slow-fast oscillatory dynamics and phantom attractors in stochastic modeling of biochemical reactions," Chaos **32**, 033126 (2022).
[18] W. C. Troy, "Logarithmic spiral solutions of the Kopell–Howard lambda–omega reaction–diffusion equations," Chaos **32**, 053104 (2022).
[19] L. A. M. Rocha, J. H. E. Cartwright, and S. S. S. Cardoso, "Filament dynamics in vertical confined chemical gardens," Chaos **32**, 053107 (2022).
[20] P. Kumar, D. Horváth, and A. Tóth, "Sol-gel transition programmed self-propulsion of chitosan hydrogel," Chaos **32**, 063120 (2022).
[21] J. A. C. Gallas and L. F. Olsen, "Complexity in subnetworks of a peroxidase–oxidase reaction model," Chaos **32**, 063122 (2022).
[22] R. J. Field, J. G. Freire, and J. A. C. Gallas, "Quint points lattice in a driven Belousov–Zhabotinsky reaction model," Chaos **31**, 053124 (2021).
[23] Y. Kubodera, M. Horisaka, M. Kuze, N. J. Suematsu, T. Amemiya, O. Steinbock, and S. Nakata, "Coexistence of oscillatory and reduced states on a spherical field controlled by electrical potential," Chaos **32**, 073103 (2022).
[24] A. Tang and J. Wang, "Drastic effects of an inert Pt wire on the redox behavior of the Belousov–Zhabotinsky reaction," Chaos **32**, 073111 (2022).
[25] M. Dolnik, C. Konow, N. H. Somberg, and I. R. Epstein, "Effect of obstructions on growing Turing patterns," Chaos **32**, 073127 (2022).
[26] D. Ezzeddine and R. Sultan, "Polygonal boundary gaps in multiple diffusion source precipitation systems in gel media," Chaos **32**, 083107 (2022).
[27] E. J. Doedel and C. L. Pando Lambruschini, "Correlation sum scalings from mixed-mode oscillations in weakly coupled molecular lasers," Chaos **32**, 083132 (2022).
[28] R. L. Romano, L. P. Damaceno, D. V. Magalhães, P. Parmananda, and H. Varela, "Electrical coupling of individual electrocatalytic oscillators," Chaos **32**, 083139 (2022).
[29] D. Battogtokh and J. J. Tyson, "Nucleation of stem cell domains in a bistable activator-inhibitor model of the shoot apical meristem," Chaos **32**, 093117 (2022).
[30] Y. Liu, J. Pérez-Mercader, and I. Z. Kiss, "Synchronization of Belousov-Zhabotinsky oscillators with electrochemical coupling in a spontaneous process," Chaos **32**, 093128 (2022).