
Concluding Remarks

Nonlinear chemical kinetics: past, present and future

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Introduction

This has been a memorable Discussion, both for the quality of the science presented and for the tragic events that took place in New York and Washington while we were meeting.

In order to add some context to the papers presented here, I should like to begin with a brief historical overview, focusing on some of the major meetings that have shaped the study of nonlinear chemical kinetics. This approach seems particularly appropriate in view of the role (see below) that this Discussion's predecessor, Faraday Symposium 9, played in the development of the field.

Some history

Perhaps the first truly influential meeting on this topic was held in Prague in 1968.¹ The Prague meeting helped to establish glycolysis, a system about which we have heard much at this Discussion, as the prototypical biological oscillator. At least as important was the opportunity for Western scientists to learn of an obscure reaction, discovered serendipitously in the Soviet Union, that had the ability to generate both temporal oscillation and spatial pattern formation. The Belousov–Zhabotinsky reaction soon became the workhorse and the prototype for the study of nonlinear chemical kinetics, a role which it continues to hold.

After the Prague meeting, interest in these fascinating reactions grew rapidly, and in 1974, Faraday Symposium 9 was organised by Peter Gray, who is here with us today, on the topic of “Physical Chemistry of Oscillatory Phenomena”.² That Symposium generated a palpable sense of excitement, particularly among some of the younger researchers who attended. The organizers also displayed considerable perspicacity in their choice of papers. A strong case can be made that the structure of that meeting, with sessions on inorganic oscillators; thermokinetic oscillations; membranes, heterogeneous and biological systems; and theory of excitable media, laid out the structure of the field for the next several decades. In Table 1, I compare the numbers of papers in each area for Faraday Symposium 9 and Faraday Discussion 120. The similarity is remarkable; the shift away from inorganic toward biological and heterogeneous systems accurately reflects the direction of recent activity.

Two other sets of conferences deserve mention here. A series of meetings^{3–5} organized in Bordeaux in the late 1970's and early 1980's helped to solidify the international nature of the nonlinear chemical kinetics community and served as a vehicle for introducing the continuous flow stirred tank reactor as a key tool in experimental studies. The Gordon Conferences on Chemical Oscillations, the first of which was held in Plymouth, New Hampshire, USA, in 1982, have provided a regular venue for the growing number of practitioners in the field to come together, at first every third, and now every second, year to share their latest results and ideas.

Table 1 Comparison of numbers of papers given at Faraday Symposium 9 (1974) and Faraday Discussion 120 (2001)

	1974	2001
Introductory and inorganic oscillators	6	3
Thermokinetic oscillations	4	5 (3 combustion + 2 atmospheric)
Membranes, heterogeneous and biological systems	5	11 (8 biological + 3 heterogeneous)
Theory of excitable media	4	5
Total	19	24

Where we stand

Having sketched some of the past of nonlinear chemical kinetics, I turn now to the present, both the work that has been presented at this Discussion and the current state of the art. It seems clear that nonlinear chemical dynamics has grown remarkably in both breadth and depth. One might argue that in 1974 the subject stood at the margins of chemistry and had little overlap with the “core” of that discipline. I shall return at the end to the question of whether nonlinear kinetics has yet reached the core, but at this Discussion we have discussed work that touches on nearly all of the most exciting and fastest-growing areas of chemistry and related sciences. Among these are: surface science, electrochemistry, combustion, polymer science, single molecule chemistry, and biology, including neurobiology, development and metabolism. Despite this branching out of our field (or perhaps the recognition by other fields that nonlinear chemical kinetics has something to offer them), we have also continued to cultivate “our roots”. We have also heard at this Discussion about some of the topics from which nonlinear chemical kinetics sprang: the Belousov–Zhabotinsky reaction, glycolysis, traveling waves, excitability, multiple stationary states and mechanistic studies. In all cases, the work presented here represents significant advances in the depth of understanding and the sophistication of the techniques employed over what was possible a few decades, or even a few years, ago.

It is useful for those of us who have been working in this area for some time, as well as for those only recently embarked on the study of nonlinear chemical kinetics, to step back and reflect on how far we have come. The development of flow reactors, both stirred and unstirred, the application of powerful methods of spectroscopy and microscopy, the extension of our studies to membranes and catalytic surfaces, are only some of the striking experimental advances. On the theoretical side, we have benefited from the many orders of magnitude enhancement in computational capability that has occurred over the past quarter century, but we have also seen the development of new and powerful theoretical methods involving amplitude equations, bifurcation theory (analytical and numerical) and stochastic approaches. Where at one time developing a mechanism or a model that gave oscillations of any sort was considered a triumph, today we have multiple alternatives to choose from, and sophisticated experiments and algorithms are often invoked to distinguish among them.

The diversity and range of systems and phenomena that the field comprises has grown exponentially. The number of oscillating reactions, to cite just one example, has increased from two or three serendipitously discovered systems to literally dozens, most of them systematically designed. In addition to temporal oscillation and the occasional study of spiral waves or multistability, we now investigate Turing patterns, chaos, standing waves, clusters, scroll waves and many more exotic phenomena. In 1984, the organizer of the final Bordeaux meeting noted that since 1967 “over 26 meetings have been held, and their yearly number is increasing”.⁵ Pacault’s concern was well-founded. Today, there may well be 26 meetings each year on nonlinear chemical kinetics and related subjects, and it is difficult for any single meeting to have the impact of the Faraday Symposium of 27 years ago.

One feature that distinguishes this area from many others in science is a special culture, spawned, I suspect, by the fact that until recently nearly all of its practitioners were “immigrants” from other fields, who had not been trained in nonlinear chemical kinetics. To an unusual degree, the field is

interdisciplinary. A typical meeting will be attended not only by chemists, but also by physicists, mathematicians, engineers, biologists, and, occasionally, geologists, economists, astronomers or physicians. By comparison with many other fields, the atmosphere in nonlinear chemical kinetics tends to be much more one of collaboration than of competition. The number of papers that come out of multiple laboratories is striking. The degree of cross-fertilization between theory and experiment is also atypical. Theories beget experiments and *vice versa*, and people tend to have mastery of, or at least respect for, both theory and experiment to a much greater extent than is common in most other fields. Finally, a very special aspect of this field is the striking visual phenomena that characterize it. The power of an oscillating reaction or a spiral wave in a petri dish to capture the attention and the imagination of prospective students of nonlinear chemical kinetics cannot be overstated.

The future

One of the most salient lessons that we learn from tracking the progress from Faraday Symposium 9 to Faraday Discussion 120 is how perilous it is to attempt to predict the future development of a vibrant field of science. Nonetheless, while avoiding the details, which I would undoubtedly get wrong, it seems to me that the work presented here enables one to make some general statements about the likely directions in which nonlinear chemical kinetics is heading.

The future of this subject is likely to include more and more of what might be termed “chemistry plus”, that is, chemical reactions coupled to other phenomena that are typically considered to belong to the domains of physics or biology. This trend is already evident in some of the work presented here. The sorts of interactions I have in mind include hydrodynamics, surface tension and fluid flows; growth, both of living systems and of materials; mechanical forces; external fields, particularly electromagnetic and gravitational; and heterogeneous media—biological cells, membranes, micelles, emulsions, surfaces...

Our attention is increasingly likely to be focused on “big systems”. These might include systems in which many subsystems are coupled together, such as a dish full of yeast or a microemulsion containing 10^{17} nanodroplets of water; any living organism; the atmosphere; combustion problems; materials science; and the oceans. Fortunately, we may anticipate further experimental advances, and we are already becoming adept at generating and solving very large models, some containing hundreds of equations, and at developing methods to reduce those models to smaller sets of equations that offer some hope for intuitive understanding to complement the numerical results obtained from their more detailed precursors.

The future of the field will inevitably bring it into closer touch with “real world” problems. Issues that have effects outside of the laboratory not only offer increased prospects for research funding, but they are often scientifically fascinating and almost invariably challenging. Some areas in which ideas and techniques from nonlinear chemical kinetics and related fields are already beginning to be applied include the development of gels for drug delivery, meteorological analysis, the effects of weak electromagnetic fields on living tissue, and the prediction of currency fluctuations.

As was pointed out in the Introductory Lecture, further development of nonlinear chemical kinetics will necessitate a multi-scale approach to problems and the building of bridges between the micro- and macroscopic views of phenomena. Successful attack on this aspect of our field will ultimately require the development of new experimental and theoretical techniques. As one example, I cite recent work on the BZ system in a microemulsion consisting of water, oil (octane) and a surfactant, sodium bis(2-ethylhexyl) sulfosuccinate (AOT).⁶ As Fig. 1 shows, this BZ–AOT system exhibits a remarkable range of spatio-temporal phenomena. The medium consists of nanometer-sized droplets of water surrounded by a monolayer of AOT, floating in a sea of octane. Since the key species in the BZ reaction are polar and are therefore confined almost exclusively to the water, the reaction takes place in the droplets. On average, each droplet contains fewer than a dozen molecules of the ferrous phenanthroline catalyst. The chemistry is occurring in a sub-femtoliter (actually

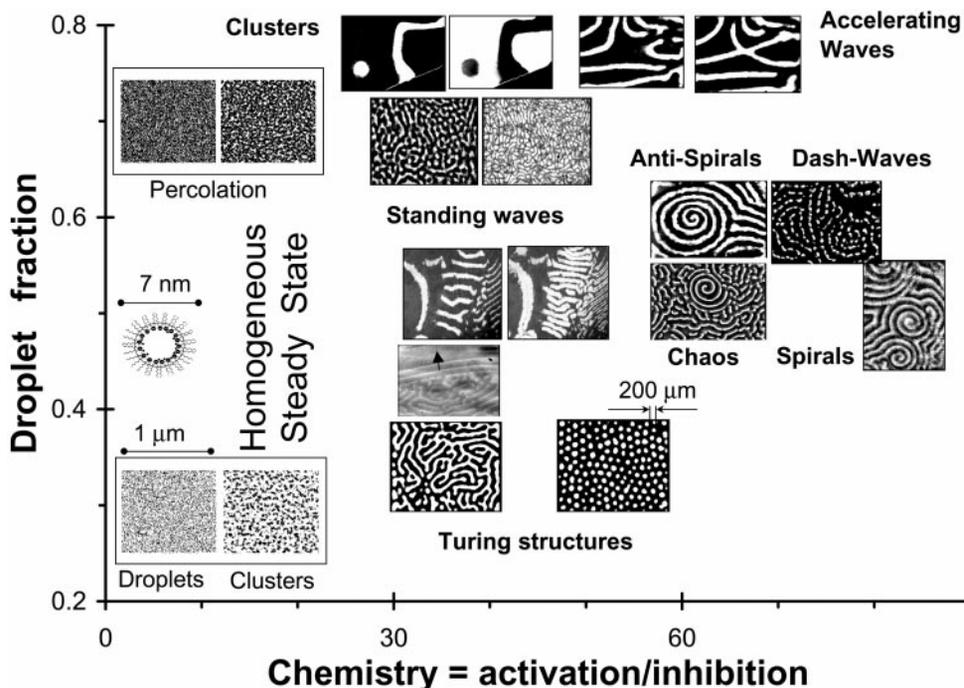


Fig. 1 A schematic phase diagram summarising complex spatio-temporal behavior in the BZ-AOT system.

micro-femtoliter) volume! This situation poses at least two fascinating challenges, one theoretical, the other experimental. The theoretical problem is to develop approaches that allow us to deal with large numbers of interacting units in which statistical fluctuations are very large without having to invoke a mean field approximation. A typical experiment in a petri dish involves 10^{17} water droplets. The structures shown in Fig. 1 have length scales of a few tenths of a millimeter, five orders of magnitude larger than the size of a droplet. It is likely that interesting structures arise at much smaller length scales than we have been able to observe thus far, but the tools remain to be developed.

I mention the BZ-AOT system merely as one example of the sorts of phenomena that are likely to arise in the years to come and the exciting problems that they will bring with them. The field is still growing and will continue to do so in directions that are impossible to predict today. One cautionary note, however, is that, to be completely honest, nonlinear chemical kinetics has still not gained a place in the central core of chemical science. For all its growth and respectability, its inclusion in textbooks, it is still considered a peripheral topic by many, perhaps most, chemistry departments. In the end, we will have become a truly central field when every major chemistry department feels that, just as it needs a spectroscopist, a crystallographer, and a synthetic organic chemist, it also needs a practitioner of nonlinear chemical kinetics. I think that day is drawing nearer, but only time will tell.

Acknowledgements and verse

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external circumstances. I offer the following sonnet as a summary of our discussions.

On Nonlinear Chemical Kinetics
This meeting we have just attended,
Deftly crafted by the great Scott.
Now we're sorry that it's ended.
We depart enlightened but not
Even close to saturated. We've
Viewed data, models, theories Steve
Chose for our illumination
In five minutes plus explication—
Surface, microgravity, BZ,
Even glycolysis in yeast.
We've had a scientific feast
Of fine nonlinear chemistry.
New insights we've received aplenty
At this, the Faraday 120.

References

- 1 *Biological and Biochemical Oscillators*, ed. B. Chance, A. K. Ghosh, E. K. Pye and B. Hess, Academic Press, New York, 1973.
- 2 *J. Chem. Soc., Faraday Trans.*, 1975, **13**.
- 3 *Far from Equilibrium: Instabilities and Structures*, ed. A. Pacault and C. Vidal, Springer-Verlag, Berlin, 1979.
- 4 *Nonlinear Phenomena in Chemical Dynamics*, ed. C. Vidal and A. Pacault, Springer-Verlag, Berlin, 1981.
- 5 *Non-Equilibrium Dynamics in Chemical Systems*, ed. C. Vidal and A. Pacault, Springer-Verlag, Berlin, 1984.
- 6 V. Vanag and I. R. Epstein, *Phys. Rev. Lett.*, 2001, **87**, 228301.