Introduction: Nonlinear pattern formation in surface science

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(Received 9 January 2002; accepted 9 January 2002; published 21 February 2002)

[DOI: 10.1063/1.1455646]

This issue of Chaos is focused on experimental and theoretical problems of nonlinear pattern formation in surface chemical reactions and in electrochemical systems. Surface chemical reactions play a central role in the processes of heterogeneous catalysis, which are broadly used in chemical industry and environmental technology. In a typical catalytic process, the molecules of reactants are adsorbed from the gas phase onto a metal surface, diffuse on it, and react to form a product that goes back to the gas phase. Thus, the reaction proceeds within an atomically thin adsorbate layer on the surface of a metallic catalyst. The concentration patterns developing on the surface are observed using various methods of optical and electron microscopy. Scanning tunneling microscopy (STM) and field-ion microscopy (FIM) allow to view such reactions with an atomic resolution, tracing diffusive motions of single atoms and monitoring individual reaction events.

Nonlinear phenomena are essential in surface chemical reactions. Besides nonlinear reaction kinetics, a number of other effects may be involved here. Adsorption of molecules can, for example, induce a structural surface phase transition in a metal catalyst, accompanied by a rearrangement of atoms in its top layer. When the surface structure is modified, this in turn influences adsorption and diffusion of reactants, and thus the local reactivity of the surface. On the other hand, lateral interactions between adsorbed molecules are typically present. Attractive interactions can lead to a condensation phase transition inside an adsorbate, converting it into a two-dimensional reactive liquid or solid. Some reactants, such as oxygen, may penetrate from the surface to the lower layers and into the bulk of the catalyst, forming sub-surface species. Finally, nonlinear thermal effects may be significant.

The mechanisms of surface chemical reactions are often relatively simple. The Belousov–Zhabotinsky reaction, which is frequently used in experiments on nonlinear pattern formation, involves tens of different intermediate products and its detailed kinetics is not yet completely understood. In contrast to this, in a catalytic reaction, such as the oxidation of CO molecules on platinum, only a few species are participating. The atomic reaction mechanisms are well known here. They are confirmed by independent experiments, including direct observations of reaction processes on atomic scale by STM. Mathematical models of surface chemical reactions yielding quantitative agreement with the observations have been constructed and investigated. Depending on the choice of reaction parameters, all basic regimes of bistability, excitability, and oscillations can be realized in such systems. Propagation of fronts and pulses, as well as the formation of complex patterns of rotating and standing waves, are being investigated. Chemical turbulence characterized by spontaneous generation of spiral waves and development of chaotic spatiotemporal concentration patterns is also observed in these reactions.

Nonlinear pattern formation in surface chemical reactions can be controlled and manipulated. Using lithography methods, microscopic reactive regions with various configurations can be created on the surfaces. Thus, nonlinear chemical kinetics and pattern formation in microreactors may be investigated. The local reactivity of catalytic surfaces can also be dynamically modified by applying focused laser beams. Artificial global feedbacks can be furthermore introduced by making the supply rates of reactants dependent on the global properties of the monitored concentration patterns. Employing such feedback methods, experimental control of turbulence has recently been demonstrated for the first time in a chemical system.

Electrochemistry is another field providing interesting examples of nonlinear pattern formation. In this case the patterns are developing in the presence of reactions on surfaces of metal electrodes. In addition to nonlinearities due to reactions, electrical fields play a significant role here. They lead to migration of reactants and result in nonlinear interactions between distant parts of a medium. Various spatiotemporal regimes, including stationary Turing-like structures, waves, and chaotic oscillations, have been observed in electrochemical systems. Chaotic electrochemical oscillators can be combined to form periodic arrays and artificial global feedbacks can then be introduced. In this way, effects of synchronization and dynamical clustering in populations of globally coupled chaotic oscillators become accessible to experimental and theoretical investigations.