Chemical Complexity: Spontaneous and Engineered Structures

István Z. Kiss and John L. Hudson
Dept. of Chemical Engineering, University of Virginia, Charlottesville, VA 22904

Introduction

Complexity abounds in chemically and biologically reacting systems: concentration waves and other complicated time-varying patterns form on the surface of a single crystal catalyst under isothermal, ultra-high vacuum conditions and patterns of concentrations and electrical potential occur in electrochemical reactions; neurons interact through the transmission of electrical and chemical signals; spiral waves and turbulent concentration motion occur in cardiac tissue; and complex calcium waves including spirals form in frog oocytes. To chemical engineers, this may be hardly surprising: in many traditional examples, such as a fixed-bed reactor, concentrations and temperature vary throughout the bed and change with time. In some other fields, however, the importance of spatiotemporal dynamics is more recent news.

Each of the above examples is a complex system made up of a number of coupled interacting, nonlinear processes. Over a period of years beginning in the 1950s sophisticated contributions of many groups appeared on the nonlinear behavior obtainable in a stirred open reactor (the CSTR) and on the bifurcation structure leading to multiple steady states and oscillations (Aris and Amundson, 1958). This reactor type was subsequently used to show the existence, characterization, and control of chaotic behavior in chemical systems.

In chemically reacting systems the reaction rate is typically a function of both space and time, and greater complexities set in when spatial variations are allowed. We discuss in this perspective the spatiotemporal patterns that occur in dissipative distributed chemically reacting systems, how the interaction of nonlinear reaction and coupling among reaction sites determines structure, and how such structure can be controlled and engineered through external signals (pacemakers), feedback, and patterned catalytic structure.

Spontaneous and Engineered Pattern Formation

The degree of interaction among reacting sites is influenced both by the local reaction rate and the range and strength of the coupling. The synchronization theories of Winfree and Kuramoto on the emergence of coherence as coupling is imposed have played a fundamental role in the development of the field of nonlinear science dealing with collective dynamics (Winfree, 1980; Kuramoto, 1984). Even weak coupling can produce significant changes in the collective, or overall, behavior of a system. Strong interactions produce not only spatial patterns, but also changes of the dynamics of the individual sites. A classic example of the change in local dynamics through interactions is diffusion induced chemical turbulence in which local coupling of periodic oscillators produces chaos.

In chemically reacting systems both the local and overall reaction rates can be influenced by synchronization of reaction sites. Other engineering applications of synchronization include microwave communications, high-power laser devices, and superconducting electronic systems. Visual and audio interactions make crickets chirp, fireflies flash, and audiences clap in synchrony. Mutual synchronization has been shown to be important in interpreting glycolitic oscillations, alpha rhythms in the brain, and aggregate beating of heart cells.

Considerable progress has been made in the engineering or control of spatiotemporal patterns and in the quest for improved reactivity and selectivity, as well as control of biological activity. A host of imaginative techniques have been developed that increase the rate of transport of one reactant component relative to that of others, for example, through the use of emulsions, immobilized reactants, flow, or electric fields.

Heterogeneity or nonuniformity is ubiquitous in surface reaction systems. The heterogeneity arises due to variations in local surface and/or transport properties. Heterogeneities play the role of nucleation centers and induce the collapse of long-range order in solid-gas phase reactions. Nonuniformity increases the number of possible patterns and affects the sensitivity of patterns to changes in initial conditions or perturbations. Investigators have developed creative ways to take advantage of the effects of heterogeneities, that is, they have designed and manufactured heterogeneous surfaces that produce desired structure and reaction rates. Carefully designed inert boundaries and active catalytic areas have been used to confine reaction structure and to influence rates of reaction.

One of the most exciting developments in controlling reaction patterns is in the use of local and global external signals, either open-loop or closed-loop, to produce desired patterns (rhythms and spatial length scales) and rates of reaction. Examples are given in the next section.

Some Examples

We choose a few examples of experimental studies to illustrate a broad spectrum of investigations on pattern formation in chemical systems. Only a very small fraction of the large number of significant contributions has been included. Some entire fields had to be omitted, and in others only a few key articles are cited. Pattern formation can best be seen through figures. We show patterns

---

Correspondence concerning this article should be addressed to J. L. Hudson.

obtained in fluid (gas and liquid) phase reactions and on gas/solid and electrochemical surfaces. Solid-phase and polymerization reactions are discussed briefly, however, due to space limitations, no patterns are shown. We do treat biological examples because of their importance and because chemical systems can often serve as model systems; however, the sampling rate here is even lower. Similarities and differences in pattern formation in the diverse areas will be evident from the figures. We hope that the examples give the general reader an idea of the status of the field.

Liquid and gas-phase reaction systems

The combination of chemical reaction and transport yields a wide variety of concentration patterns. Flames exhibit both stationary and moving patterns, some examples of which are shown in Figure 1a. The configurations of patterns of concentric rings of stationary or rotating cells depend on system parameters, e.g., fuel composition, pressure, and total flow. The propagation velocity and maximum temperature are determined by the mode of propagation of the combustion wave.

A liquid-phase system, the Belousov-Zhabotinsky (BZ) reaction (catalytic oxidation of malonic acid), exhibits target and spiral patterns in a thin layer of solution. In Figure 1b it is shown that the tip of a spiral follows a meandering, rather than a circular, path; meandering has been extensively studied, as it could provide a clue to the cause of cardiac arrhythmias which lead to ventricular fibrillation (Winfree, 1998). Methods have been developed to control the motion of the spiral patterns because of the potential biological applications. Under constant illumination of a light sensitive BZ reaction, the shape of the trajectory of a spiral wave core depends on the applied light intensity (Braune and Engel, 1993). With a periodic variation of illumination, a wide range of open and closed hypocycloidal trajectories of the spiral tip has been observed; one example is shown in Figure 1c. Stronger forcing or feedback (Figure 1d) destroys the spiral structures, and standing-wave oscillations are obtained. Control of wave propagation by feedback-regulated excitability gradients has also been achieved (Figure 1e). The wave of activity is guided with light to propagate in controlled directions.

In a classical article Turing showed that stationary structures are possible in reaction-diffusion systems if key species have very different rates of diffusion (Turing, 1952). A wide range of diffusion coefficients is common in biological systems where molecular weights span several orders of magnitudes, and transport may be facilitated by membranes, filaments, or other structural elements. However, the similar values of diffusion coefficients of simple molecules inhibit the formation of Turing patterns. Turing patterns have been seen using a large molecule (starch) to bind tri-iodide ion in the chlorite-iodide-malonic acid system (Castets et al.,

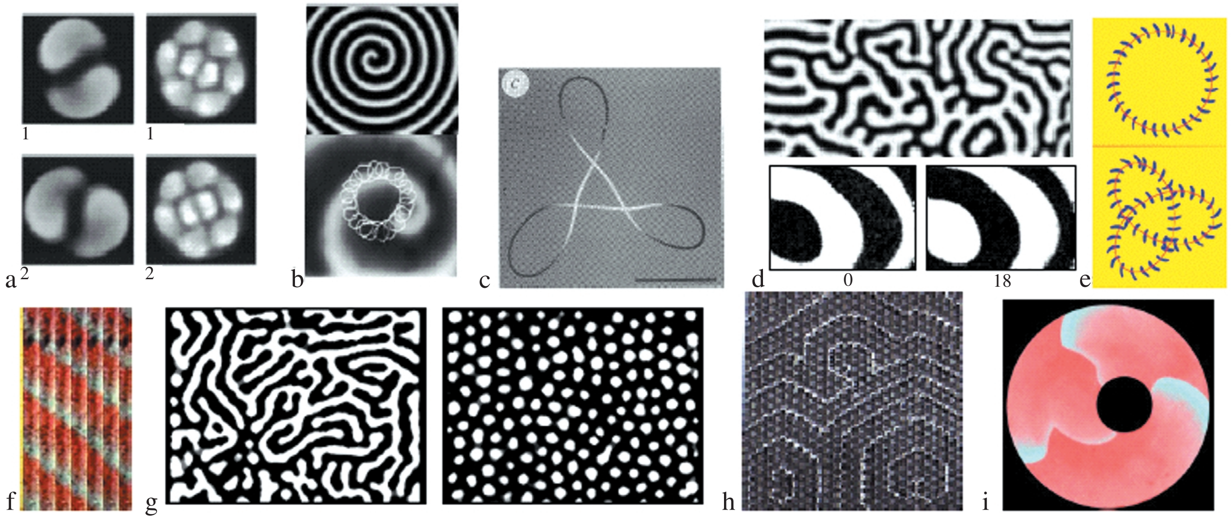

Figure 1. Liquid- and gas-phase reactions.
(a) Cellular flames on a circular porous plug burner (isobutene-air combustion). (Left) snapshots of two rotating cells. (Right) counter-rotating cells. (Shading shows emitted chemiluminescence) (Palacios et al., 1998). (b) Spiral formation in quasi 2-D BZ reaction. Top: fully developed spiral (Petrov et al., 1997). Bottom: Meandering spiral with outward petals. The white lines in the images show the trajectories of spiral tip (Ge et al., 1996). (c) Control of spiral wave dynamics by periodic modulation of light intensity and, thus, excitability. Sequence of tip trajectories (Steinbock et al., 1993). (d) Pattern formation with periodic forcing (top) and global feedback (bottom) of spirals of BZ reaction shown in 1b. (Top) Resonant labyrinthine standing wave oscillatory pattern with light pulsed at twice the natural frequency of the reaction (Petrov et al., 1997). (Bottom) Oscillatory cluster pattern with global feedback (Vanag et al., 2001). (e) Design and control of wave propagation patterns in the excitable BZ system. Circular (top) and three lobed hypotrochoid (bottom) trajectories resulting from wave propagation control (Sakurai et al., 2002). (f) Differential flow induced chemical instabilities in the BZ reaction. Downward propagating blue oxidation waves are seen on a cation exchange column on which the catalyst (ferriin) was immobilized (Tóth et al., 2001). (g) Pattern formation in a tunable medium: the BZ reaction in a microemulsion. (Left) labyrinthine (left) and hexagonal (right) Turing patterns (Vanag and Epstein, 2001). (h) Wave propagation in patterned excitable BZ media. Propagating waves with cellular inhomogeneities (catalyst patterns appear as the background) (Steinbock et al., 1995). (i) Rotating waves around a circular obstacle which is surrounded by two homogeneous wave conducting regions with different wave velocities (Volford et al., 1999).

1990). Structures have also been obtained with immobilized catalysts on ion-exchange resins (Rovinsky and Menzinger, 1993); a propagating reaction zone in a packed tubular reactor can be seen in Figure 1f. Water in oil microemulsions have been used to generate a wide range of structures including Turing patterns (Figure 1g), inwardly moving spirals, and waves (anti-pacemakers); bromine diffuses rapidly through the oil and inhibits the BZ reaction by generating Br- ions. The modification of patterns through the influence of motion of charged species can be obtained with the use of electric fields (Sevcikova et al., 1992).

The cellular nature of living systems gives rise to inhomogeneities and anisotropy, and these may play an important role in the behavior of biological media such as the heart muscle. The cellular structure of cardiac tissue can cause local variations in wave velocity and also gives rise to propagation failure. BZ membranes with fabricated inhomogeneities provide a convenient way to explore and control wave propagation. Cellular inhomogeneities of BZ catalyst have been printed on a membrane; anisotropies occur in wave propagation (Figure 1h) and spiral waves, not seen on homogeneous membranes, can develop spontaneously. An experimental model system of attrial flutter arrhythmia has been implemented: a central hole cut into the membrane plays the role of an obstacle and a "chemical pinwheel" system of wavefronts rotating around the hole can be created (Figure 1i).

Solid phase reactions

In self-propagating high-temperature synthesis (SHS) a high-temperature front propagates through a solid mixture to produce desired products. The technology has been developed such that slowly moving, high-temperature fronts produce a variety of advanced materials including ceramics, intermetallics, and composites (Merzhanov, 1992). The behavior of the propagating front has been investigated with the use of high-speed video recordings (Varma et al., 1998; Nersesyan et al., 2002).

Polymerization

Polymerization reactions are often highly exothermic such that nonlinear effects become important and produce temporal and/or spatial structure. A recent review discusses steady-state multiplicity, sustained oscillations, and traveling waves and their occurrence in industrial reactors including stirred tanks, loop reactors, and fluidized beds (Ray and Villa, 2000). Several interesting examples are discussed: a loop reactor at high circulation rates normally operates stably. However, if the recirculation rate should drop, wall heat transfer is reduced and oscillations set in; if the recirculation rate drops further, heat-transfer area is poorly utilized and traveling waves can arise.

Frontal polymerization is a well-known example of propagating reaction waves; patterns (functionally gradient materials) can be produced by programming the concentration of the monomer feedstream (Chekanov and Pojman, 2000).

Heterogeneous gas/solid reactions

Patterns have been studied in heterogeneous systems on scales from industrial reactors to supported catalysts to small single crystal catalyst surfaces. On the reactor scale, hot zones, where temperatures are much higher than that of adjacent regions, form in

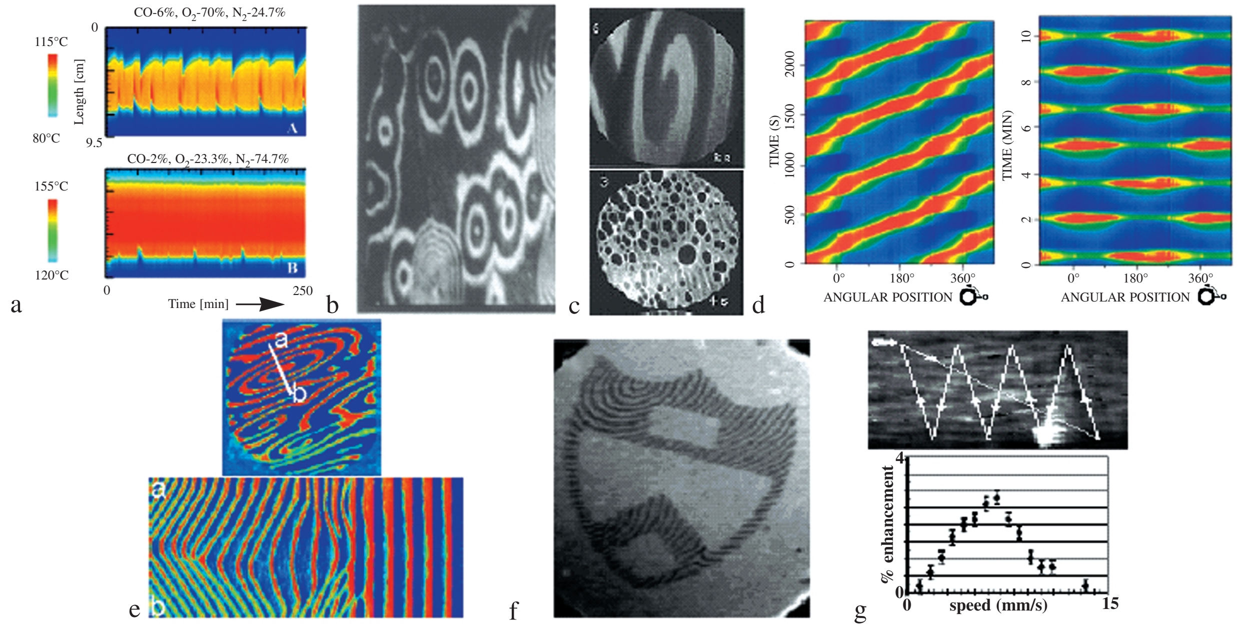

Figure 2. Heterogeneous (gas-solid) reactions.
(a) Hot zones with single front and dual front motions during CO oxidation in a radial flow reactor (Marwaha and Luss, 2002). (b) Autonomous target patterns of traveling waves (PEEM) (Jakubith et al., 1990). (c) Autonomous spiral (top, LEEM) and cellular (bottom, MEM) structures (Rose et al., 1998). (d) Spatiotemporal patterns during hydrogen oxidation on a Ni ring. Effect of global coupling (Graham et al., 1993). (e) Control of spatiotemporal patterns with global delayed feedback: suppression of spiral-wave turbulence (Kim et al., 2001). (Top) snapshot before control; (bottom) space-time plot with control. (f) Pattern formation during CO oxidation on Pt(110) in microdesigned catalytic domains (Wolff et al., 2001). (g) Improved surface activity with spatio-temporally variable operation (Papathanasiou et al., 2002). CO oxidation on Pt(110).

packed-bed reactors and on catalyst gauzes. The dynamics of the oxidation of carbon monoxide have been studied with the use of an infrared camera arranged to observe hot zones normal to the flow direction in a radial flow reactor. With this novel apparatus, a variety of motions of the hot zones could be studied, two of which can be seen in Figure 2a.

Considerable progress in investigating autonomous patterns in gas-solid systems has come with the use of single crystals of pure metals as catalysts under low-pressure conditions where thermal effects of the reactions are minimized. Since the reactants and products adsorb on the single crystal catalyst surface, microscopy methods can be used to observe pattern formation. Photoemission electron microscopy (PEEM) has been used to observe structure on scales from several micrometers to hundreds of micrometers; these length scales arise through the interaction of reaction and diffusion on the catalyst surface. Spatiotemporal patterns including waves, both standing and traveling, spirals, and chaos have been observed. An example of a target pattern formed during the oxidation of carbon monoxide on a Pt(110) surface is given in Figure 2b. Other microscopy methods, with high resolution and rich contrast, have been used to study CO oxidation; examples of a spiral obtained with low energy electron microscopy (LEEM) and of a cellular structure obtained with mirror electron microscopy (MEM) can be seen in Figure 2c, top and bottom, respectively.

Global coupling through the gas phase can also play an important role in the development of structure. The effects of this global coupling have been demonstrated in a study of the oxidation of hydrogen on a polycrystalline nickel ring under atmospheric conditions in a well-stirred reactor. A traveling pulse and a more complicated pattern are shown in Figure 2d. The stirring in the gas phase produces a global coupling since reaction at any location on the ring influences conditions in the stirred gas phase and this gas phase feeds back to all locations on the reaction surface.

Several techniques have been used to control the spatiotemporal structure on catalytic surfaces. One of these is a global delayed feedback that has been used to suppress spiral wave turbulence (Figure 2e). The model reaction, carbon monoxide oxidation on Pt (110), was used under ultra-high vacuum conditions; a PEEM signal was integrated over the observational area to obtain a global signal that was fed back to the dosing rate of carbon monoxide. Thus, a delayed global feedback was used to control the surface patterns and to stabilize uniform oscillations on the catalyst surface.

Control of pattern formation can be accomplished in gas-solid reacting systems by the appropriate design of a heterogeneous surface in which the scale of the autonomous patterns is the same order as that of the heterogeneities. An example of the reaction on such a heterogeneous surface is seen in Figure 2f. The reactive surface domain is the portion exhibiting waves. The surrounding surface is covered with inert titanium; the height of the shield pattern is 350 micrometers. A target pattern from the CO oxidation is thus restricted to the complex, reacting surface. By varying the size of the reactive domains, the spontaneous spatial scales of the patterns are controlled. Similar experiments were also carried out with two catalytically active materials, Pt and Rh; thus, the geometries of the two regions can influence both local and overall reactivity.

Control of spatial structure via spatiotemporally varying operation can also lead to enhanced overall reactivity. A result of a novel experiment in which a focused laser beam was used to control the reaction rate is shown in Figure 2g. Conditions were chosen for the CO oxidation reaction near the boundary between a CO-poisoned state and an excitable region where reaction pulses travel on the catalyst surface. By moving the laser spot across the surface, local activity is enhanced and overall reaction is increased.

Electrochemical

Nonlinearities are ubiquitous in electrochemical systems. In most electrochemical systems that exhibit oscillations and pattern formation the electrode potential is an essential variable, that is, the potential is part of a required feedback loop. It is rare in electrochemistry, in contrast to gas-liquid or gas-solid reaction systems, for instabilities to arise solely through nonlinear kinetic factors; the potential drop in the electrolyte is necessary for the instabilities and spatial structure to occur. (The reaction rate, proportional to the current, depends exponentially on the potential, but can be inhibited at large overpotentials by oxide and salt layers on the electrode surface.) Coupling among reacting sites is dominated by migration currents and the geometry of the reactor plays a major role in observed behavior; both short- and long-range coupling can be obtained.

An example of the effects of the range of coupling can be seen in Figure 3a. A front (top) moves at a constant velocity across the electrode surface; this is obtained by placing the counter electrode close to the surface of the working electrode so that coupling is short-range. By changing the geometry so that the reference electrode is far from the working electrode, accelerating fronts (Flätgen and Krischer, 1995; Otterstedt et al., 1996) are obtained as seen in the lower portion of the figure.

In Figure 3b the effect of geometry is shown in the electrocatalytic oxidation of hydrogen carried out on a platinum ring electrode in the presence of Cu^{2+} and Cl^{-} ions that block surface sites. The simple uniform pulses seen in the top panel were obtained under conditions where the coupling is largely diffusive. As the effects of global coupling are added through changes in cell geometry, target and complex patterns are produced.

A feature of electrochemical reactions is the occurrence of negative coupling, that is, an effect at one location produces a counter effect at another location. The reference electrode is brought close to the surface of the working electrode; this is commonly done in electrochemical experiments in order to minimize the effects of a potential drop in the electrolyte on the measured potential. As seen in recent experiments, this can also produce a negative coupling, qualitatively similar to a teeter-totter, in which, when one side goes up, the other goes down. The rotating wave of Figure 3c was obtained with a disk cobalt electrode with a reference electrode placed close to the center of the disk. A second example, standing wave oscillations obtained during formic acid oxidation on a platinum ring, is shown in Figure 3d.

Images obtained with surface plasmon microscopy applied to patterns obtained in the periodate reduction reaction on Au(111) in the presence of camphor adsorbate can be seen in Figure 3e. The work showed that, in agreement with the theory on Turing structures, the wavelength of the pattern depended on the parameters of the experiment, but not on the size of the electrode.

Electrode arrays have been used to study patterns on spatially distributed electrochemical reactions. The current can be measured at each of the elements of the array and, thus, reaction rate obtained as a function of both time and space. An example of emerging coherence with the addition of weak global coupling to a set of electrochemical oscillators is shown in Figure 3f. In weak coupling only the frequencies, but not the amplitudes of the oscillations, are changed with coupling. At low coupling strength, the order is independent of coupling; the non-zero values seen at low K in Figure 3f are due to finite size effects. At a critical value of coupling strength, a second-order phase transition occurs at which some of the oscillators synchronize. As the coupling strength is further increased, more of the oscillators join the synchronized group. The data shown in the figure were obtained for smooth oscillators; similar results have also been seen with relaxation and chaotic oscillators.

An example of the effects of stronger coupling on an array of chaotic electrochemical oscillators is shown in Figure 3g. Strong global coupling leads to identical synchronization of the oscillators. At intermediate coupling strength, dynamical condensation or clustering occurs in which groups of elements synchronize. The results of two experiments carried out under identical conditions are shown in the top row of the figure. Depending on initial conditions, both the arrangements and the numbers of elements in the stable clusters can change. The system is complex and the number of possible states is very large; even for a modest number of, say, 100 reacting sites, the number of possible states would be larger than Avogadro's number. For both weaker and stronger coupling, intermittent clustering occurs in which nonstable clusters form and break up. Clustering can also be obtained with global forcing and feedback. An example of stable clustering in each of these cases is shown in the bottom left (four stable clusters) and right (three stable clusters), respectively.

Selected biological examples

Self-organized spatiotemporal patterns form commonly in biological systems and play a fundamental role at a variety of scales. Heterogeneities are widespread and important.

A well-known example of pattern formation in biological systems is that produced by colonies of the slime mold Dictyostelium discoideum bacteria, as seen in Figure 4a. When deprived of heat or moisture, the microorganisms aggregate into multicellular bodies that are more fit to survive hardship. Some of the cells release an attractant that nearby cells follow to its source. The slime mold colony undergoing chemotaxis behaves as an excitable medium and can exhibit target and spiral patterns as in chemical systems.

Cardiac fibrillation, studied extensively because of the importance to life-threatening rhythm disturbances, can be understood based on the theory of excitable media; self-organized three-dimensional (3-D) rotor yield scroll waves that move through the heart. A rotating spiral wave in the cardiac muscle of a dog can be

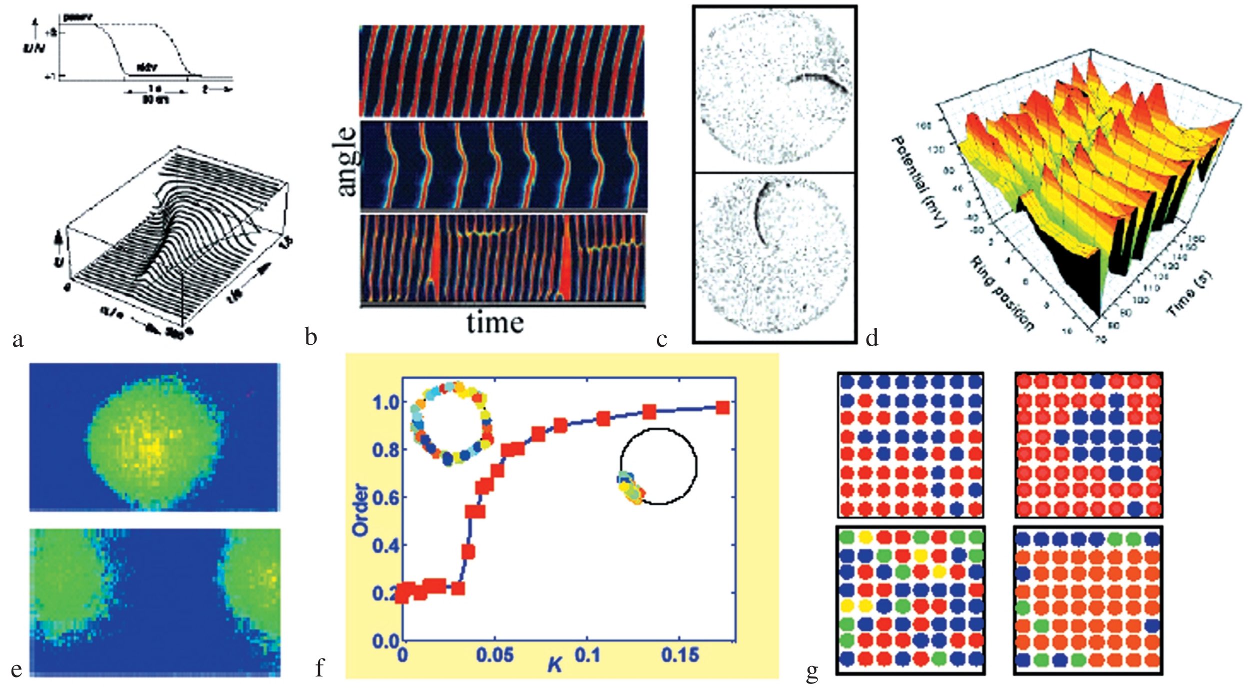

Figure 3. Electrochemical reactions.
(a) (Top) constant speed potential front profile on a gold wire in a concentrated HCl/NaCl solution (Franck, 1958). (Bottom) accelerating potential front during the reduction of $S_2O_8^{2-}$ on a silver ring electrode (Flätgen and Krischer, 1995). (b) Pattern formation during the oscillatory oxidation of H_2 on Pt ring-electrodes in the presence of electrosorbing ions (Cu^{2+} and Cl^-). (Top panel) uniform pulses. (Middle panel) target pattern waves; (Bottom) Complex pattern (Grauel et al., 2001). (c) Rotating wave of active region on a passivated Co electrode (Otterstedt et al., 1996). (d) Standing wave potential oscillations in the electrocatalytic oxidation of formic acid on Pt ring electrode (Strasser et al., 2000). (e) Stationary potential (and adsorbate) patterns during the periodate reduction on Au(111) electrodes in the presence of camphor adsorbate. ((Blue) camphor free area; (orange and yellow) high camphor coverage) (Li et al., 2001). (f) Emerging coherence of an array of 64 periodic oscillators with heterogeneity. Order function vs. global coupling (*K*). Insets show snapshots of individual oscillators in state space. Ni dissolution in sulfuric acid (Kiss et al., 2002). (g) Cluster formation of globally coupled array of chaotic oscillators. (Top) two cluster configurations with global coupling (Wang et al., 2000). (Bottom) cluster configurations with forcing (left) and feedback (right) of the potential (Wang et al., 2001).

seen in Figure 4b. Wave patterns in the heart can be influenced by the imposition of external electrical signals; a standing wave induced by alternating electric fields is shown in Figure 4c.

Both inter- and intracellular calcium signaling are important in biological systems. An example of a spiral in a frog oocyte, obtained with a confocal microscope, is shown in Figure 4d. Energization of mitochondria alters the pattern of wave activity; the number of pulsatile foci is reduced and spiral waves are no longer observed, but target patterns predominate.

Microfabricated slime mold structures are shown in Figure 4e. A living coupled oscillator system was made by a patterning method, and parameters, such as distance between the cells and, thus, coupling strength, varied. At a given distance, anti-phase oscillations are seen.

Neurons can interact via electrical coupling. The mechanism of the interaction is complicated because of the different time scales involved in the process, i.e., slow variations and fast spikes or bursts. An experimental study of the coupling of two neurons from the California spiny lobster has shown that the natural coupling synchronizes the slow oscillations, but not the fast spikes of the membrane potential. Time series of synchronous, unsynchronized, and anti-phase synchronized behavior are seen in Figure 4f.

Outlook

The rate of development in the area of nonlinear dynamics applied to chemically reacting systems has been, not surprisingly, highly nonlinear. The field has seen spurts of activity, such as the early studies of stability and oscillations, in developments on wave propagation and pattern formation, in the studies of chaotic behavior, both temporal and spatiotemporal, interspersed with resting periods not unlike the refractory period of a firing neuron or the excitable behavior of a chemical reaction. So, predictions on developments in the field should be made with caution.

Advancements in chemical structure formation will occur in parallel and in cooperation with developments on spatiotemporal-temporal dynamics in other fields. For example, new techniques are being explored for structural health monitoring of complex mechanical structures with vibration-based damage detection using chaotic forcing signals (Todd et al., 2001). Injection-locking techniques with mutually synchronized microwave oscillators have been used to achieve synchronous operation of a number of integrated antenna oscillatory circuits (York and Compton, 1991). Pressure oscillations in a rat kidney are attributed to the interaction of nephrons (Sosnovtseva et al., 2003). The growth and spread of viral diseases within a human population are also influenced by the interactions among individuals.

The understanding and the ability to manipulate the behavior of large numbers of interacting nonlinear chemically reacting sites are still at their beginnings. As progress is made on the unraveling of the mechanisms of both the local dynamics and the coupling among sites, the ability to design and operate chemical systems in an optimal fashion will grow. It is reasonably certain that the progress will encompass activity in the following areas, as well, of

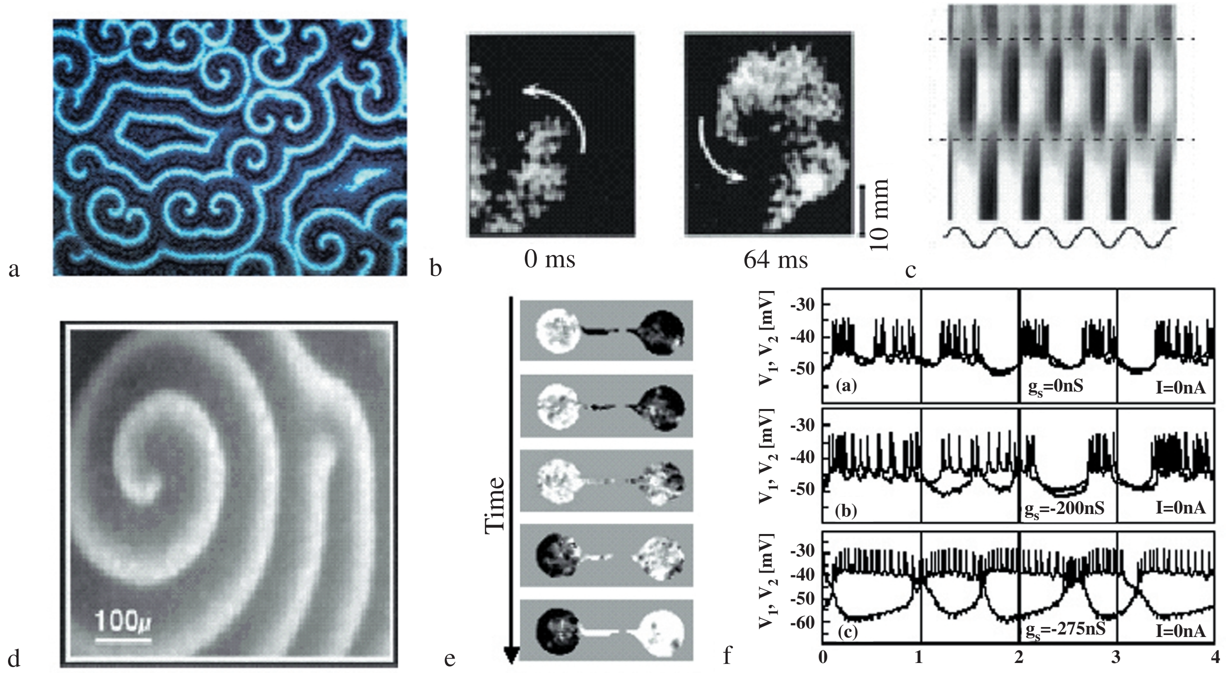

Figure 4. Selected biological examples.
(a) Spiral wave structure in colonies of slime mold Dictyostelium discoideum bacteria (Siegert and Weijer, 1989). Copyright: Dr. Florian Siegert. (b) Spiral waves visualized by a voltage sensitive dye in a thin sheet of dog cardiac muscle. (Jalife et al., 1998). (c) Space time plots of standing wave patterns in cardiac tissue of rabbit with (10 Hz) sinusoidal electric stimulation (Gray et al., 2001). (d) Intracellular Ca^{2+} waves of Xenopus oocytes forming a spiral structure (Falcke et al., 1999). (e) Antiphase oscillating thickness (indicated by black and white shadings) in plasmoidal slime mold microfabricated structures (Takamatsu et al., 2000). (f) Synchronous (top), unsynchronized (middle), and antiphase synchronized (bottom) potential time traces of a pair of electrically coupled neurons from the California spiney lobster (Elson et al., 1998).

course, in others that have not yet been explored. This work will be interdisciplinary and will involve chemical engineers, often in cooperation with investigators from other engineering areas, chemistry, biology, physics, and medicine.

Some examples:

- *Nanoscale self-organized reactors.* The spatial scales over which control can be obtained will continue to decrease. Reactors with length scales down to the nanometer range can spontaneously develop in gas-solid surface reactions by means of nonequilibrium self-organization (Hildebrand et al., 1999). Design of chemical reactors at the nanometer scale will allow control of reaction conditions and improved selectivity. Statistical fluctuations become significant in the formation of structure and should be included in the description and as a means of improving conditions. Self-organized microreactors will be developed in which size is altered by control of adsorption and reaction rates.

- *The efficient operation of ultra-small-scale networked reactors.* Several aspects of interactions in complex network systems have been recently reviewed (Ottino, 2003).

- *Design of networks of controllable and time-varying coupling strengths to optimize structure and reactivity.* Techniques similar to those of neural networks will be used to optimize reactor conditions. In electrochemical systems both active and negative coupling can be introduced to control patterns and optimize reaction rates.

- *Optimized reaction conditions through the formation of dynamical clustering or synchronously operating groups of elements in a population of reacting sites.* Such clusters can be used as a mechanism of partition of steps in complicated reaction systems. By appropriate manipulation of subgroups, highly efficient hierarchically structured interactions can be developed.

- *Optimization and control of reacting systems with different time scales.* Applications are to a variety of systems from bursting neurons to industrial chlorination reactors.

- *The use of heterogeneities on catalyst surfaces to influence the local and global rates of reaction.* Carefully designed microfabricated heterogeneous surfaces consisting generally of a spectrum of catalyst materials will be designed to produce an overall optimum reaction. The development and characterization of anisotropic surfaces on which rates of transport are dependent on direction to control transport rates and pattern formation; such studies will also have biological implications such as, for example, in cardiac muscle and heart fibrillation.

- *The development of other tunable media.* Increased use will be made of multiphase systems such as emulsions of liquid droplets to control selected rates of transport and interaction. The microstructure of the medium is controlled by the size and concentration of the droplets.

- *The use of active motion using concepts from biological organisms and species that move actively through media and in response to signals from other members of the population.*

- *Open-loop and closed-loop (through spatiotemporal feedback) operation to optimize structure and reactivity.* This can include reaction wave design: the sensing and local activation to guide reaction waves over a catalyst surface and reactivation of inactive surfaces. Applications will be to catalytic and electrocatalytic systems including fuel cells.

- *Optimal synchronization of reacting sites by means of external signals or feedback.* Conversely, in some cases, carefully designed signals such as phase resetting pulses to desynchronize elements will be developed in order to induce breakup of undesired synchronization in the brain responsible for Parkinson's disease.

- *Designing activity waves with biological applications such as the use of electrical stimuli for cardiac defibrillation methods.*

Although the above list is certainly incomplete and, perhaps, in places incorrect, it is likely an indication of the major developments expected in the next few years. Chemical Engineers will play a major role in these activities since they involve concepts that are fundamental elements of the profession: reaction kinetics, coupling through mass and heat transfer, and control of chemical processes.

Acknowledgments

A portion of the work discussed in this perspective was supported by the National Science Foundation (CTS-0000483). We thank Julio Ottino for his insightful suggestions and comments.

Literature Cited

Aris, R., and N. R. Amundson, "An Analysis of Chemical Reactor Stability and Control—I: The Possibility of Local Control with Perfect or Imperfect Control Mechanisms," *Chem. Eng. Sci.*, **7**, 121 (1958).

Braune, M., and H. Engel, "Compound Rotation of Spiral Waves in a Light-Sensitive Belousov-Zhabotinsky Medium," *Chem. Phys. Lett.*, **204**, 257 (1993).

Castets, V., E. Dulos, J. Boissonade, and P. DeKepper, "Experimental-Evidence of a Sustained Standing Turing-Type Nonequilibrium Chemical-Pattern," *Phys. Rev. Lett.*, **64**, 2953 (1990).

Chekanov, Y. A., and J. A. Pojman, "Preparation of Functionally Gradient Materials Via Frontal Polymerization," *J. Appl. Polym. Sci.*, **78**, 2398 (2000).

Elson, R. C., A. I. Selverston, R. Huerta, N. F. Rulkov, M. I. Rubinovich, and H. D. I. Abarbanel, "Synchronous Behavior of Two Coupled Biological Neurons," *Phys. Rev. Lett.*, **81**, 5692 (1998).

Falcke, M., J. L. Hudson, P. Camacho, and J. D. Lechleiter, "Impact of Mitochondrial Ca^{2+} Cycling on Pattern Formation and Stability," *Biophys. J.*, **77**, 37 (1999).

Flätgen, G., and K. Krischer, "Accelerating Fronts in an Electrochemical System due to Global Coupling," *Phys. Rev. E*, **51**, 3997 (1995).

Franck, U. F., "Instabilitätserscheinungen an passivierbaren metallen," *Zeit. Elecktrochem.*, **62**, 649 (1958).

Ge, L., O. Y. Qi, V. Petrov, and H. L. Swinney, "Transition from Simple Rotating Chemical Spirals to Meandering and Traveling Spirals," *Phys. Rev. Lett.*, **77**, 2105 (1996).

Graham, M. D., S. L. Lane, and D. Luss, "Temperature Pulse Dynamics On a Catalytic Ring," *J. Phys. Chem.*, **97**, 7564 (1993).

Grauel, P., H. Varela, and K. Krischer, "Spatial Bifurcations of Fixed Points and Limit Cycles during the Electrochemical Oxidation of H-2 on Pt Ring-Electrodes," *Faraday Discuss.*, **120**, 165 (2001).

Gray, R. A., O. A. Mornev, J. Jalife, O. V. Aslanidi, and A. M. Pertsov, "Standing Excitation Waves in the Heart Induced by Strong Alternating Electric Fields," *Phys. Rev. Lett.*, **87**, 168104 (2001).

Hildebrand, M., M. Kuperman, H. Wio, A. S. Mikhailov, and G. Ertl, "Self-Organized Chemical Nanoscale Microreactors," *Phys. Rev. Lett.*, **83**, 1475 (1999).

Jakubith, S., H. H. Rotermund, W. Engel, A. Vonoertzen, and G. Ertl, "Spatiotemporal Concentration Patterns in a Surface-Reaction—Propagating and Standing Waves, Rotating Spirals, and Turbulence," *Phys. Rev. Lett.*, **65**, 3013 (1990).

Jalife, J., R. A. Gray, G. E. Morley, and J. M. Davidenko, "Self-Organization and the Dynamical Nature of Ventricular Fibrillation," *Chaos*, **8**, 79 (1998).

Kim, M., M. Bertram, M. Pollmann, A. von Oertzen, A. S. Mikhailov, H. H. Rotermund, and G. Ertl, "Controlling Chemical Turbulence by Global Delayed Feedback: Pattern Formation in Catalytic CO Oxidation on Pt(110)," *Science*, **292**, 1357 (2001).

Kiss, I. Z., Y. M. Zhai, and J. L. Hudson, "Emerging Coherence in a Population of Chemical Oscillators," *Science*, **296**, 1676 (2002).

Kuramoto, Y., *Chemical Oscillations, Waves and Turbulence*, Springer, Berlin (1984).

Li, Y. J., J. Oslonovitch, N. Mazouz, F. Plenge, K. Krischer, and G. Ertl, "Turing-Type Patterns on Electrode Surfaces," *Science*, **291**, 2395 (2001).

Marwaha, G., and D. Luss, "Formation and Dynamics of a Hot Zone in Radial Flow Reactor," *AIChE J.*, **48**, 617 (2002).

Merzhanov, A. G., "Combustion: New Manifestations of an Ancient Process," *Chemistry of Advanced Materials*, C. N. R. Rao, ed., Blackwell Scientific Publication, Cambridge, MA, p. 19 (1992).

Nersesyan, M. D., J. T. Ritchie, I. A. Filimonov, J. T. Richardson, and D. Luss, "Electric Fields Produced by High-Temperature Metal Oxidation," *J. Electrochem. Soc.*, **149**, J11 (2002).

Otterstedt, R. D., P. J. Plath, N. I. Jaeger, and J. L. Hudson, "Rotating Waves on Disk and Ring Electrodes," *J. Chem. Soc. Faraday Trans.*, **92**, 2933 (1996).

Otterstedt, R. D., P. J. Plath, N. I. Jaeger, J. C. Sayer, and J. L. Hudson, "Accelerating Fronts During the Electrodissolution of Cobalt," *Chem. Eng. Sci.*, **51**, 1747 (1996).

Ottino, J. M., "Complex Systems," *AIChE J.*, **49**, 292 (2003).

Palacios, A., G. H. Gunaratne, M. Gorman, and K. A. Robbins, "Karhunen-Loeve Analysis of Spatiotemporal Flame Patterns," *Phys. Rev. E*, **57**, 5958 (1998).

Papathanasiou, A. G., J. Wolff, I. G. Kevrekidis, H. H. Rotermund, and G. Ertl, "Some Twists and Turns in the Path of Improving Surface Activity," *Chem. Phys. Lett.*, **358**, 407 (2002).

Petrov, V., Q. Ouyang, and H. L. Swinney, "Resonant Pattern Formation in a Chemical System," *Nature*, **388**, 655 (1997).

Ray, W. H., and C. M. Villa, "Nonlinear Dynamics Found in Polymerization Processes—A Review," *Chem. Eng. Sci.*, **55**, 275 (2000).

Rose, K. C., W. Engel, F. Meissen, A. J. Patchett, A. M. Bradshaw, and R. Imbihl, "LEEM and MEM Studies of Spatiotemporal Pattern Formation," *Surf. Rev. Lett.*, **5**, 1233 (1998).

Rovinsky, A. B., and M. Menzinger, "Self-Organization Induced By the Differential Flow of Activator and Inhibitor," *Phys. Rev. Lett.*, **70**, 778 (1993).

Sakurai, T., E. Mihaliuk, F. Chirila, and K. Showalter, "Design and Control of Wave Propagation Patterns in Excitable Media," *Science*, **296**, 2009 (2002).

Sevcikova, H., M. Marek, and S. C. Müller, "The Reversal and Splitting of Waves in an Excitable Medium Caused By an Electrical-Field," *Science*, **257**, 951 (1992).

Siegert, F., and C. Weijer, "Digital Image-Processing of Optical-Density Wave-Propagation in Dictyostelium-Discoideum and Analysis of the Effects of Caffeine and Ammonia," *J. Cell Sci.*, **93**, 325 (1989).

Sosnovtseva, O. V., D. E. Postnov, E. Mosekilde, and N. H. Holstein-Rathlou, "Synchronization. of Tubular Pressure Oscillations in Interacting Nephrons," *Chaos Solitons Fractals*, **15**, 343 (2003).

Steinbock, O., P. Kettunen, and K. Showalter, "Anisotropy and Spiral Organizing Centers in Patterned Excitable Media," *Science*, **269**, 1857 (1995).

Steinbock, O., V. Zykov, and S. C. Müller, "Control of Spiral-Wave Dynamics in Active Media By Periodic Modulation of Excitability," *Nature*, **366**, 322 (1993).

Strasser, P., J. Christoph, W. F. Lin, M. Eiswirth, and J. L. Hudson, "Standing Wave Oscillations in an Electrocatalytic Reaction," *J. Phys. Chem. A*, **104**, 1854 (2000).

Takamatsu, A., T. Fujii, and I. Endo, "Time Delay Effect in a Living Coupled Oscillator System with the Plasmodium of Physarum Polycephalum," *Phys. Rev. Lett.*, **85**, 2026 (2000).

Todd, M. D., J. M. Nichols, L. M. Pecora, and L. N. Virgin, "Vibration-based Damage Assessment Utilizing State Space Geometry Changes: Local Attractor Variance Ratio," *Smart Mater. Struct.*, **10**, 1000 (2001).

Tóth, R., A. Papp, V. Gáspár, J. H. Merkin, S. K. Scott, and A. F. Taylor, "Flow-Driven Instabilities in the Belousov-Zhabotinsky Reaction: Modelling and Experiments," *Phys. Chem. Chem. Phys.*, **3**, 957 (2001).

Turing, A. M., "The Chemical Basis of Morphogenesis," *Philos. Trans. R. Soc. B. London*, **237**, 37 (1952).

Vanag, V. K., and I. R. Epstein, "Pattern Formation in a Tunable Medium: The Belousov-Zhabotinsky Reaction in an Aerosol OT Microemulsion," *Phys. Rev. Lett.*, **87**, 228301 (2001).

Vanag, V. K., A. M. Zhabotinsky, and I. R. Epstein, "Oscillatory Clusters in the Periodically Illuminated, Spatially Extended Belousov-Zhabotinsky Reaction," *Phys. Rev. Lett.*, **86**, 552 (2001).

Varma, A., A. S. Rogachev, A. S. Mukasyan, and S. Hwang, "Combustion Synthesis of Advanced Materials: Principles and Applications," *Adv. Chem. Eng.*, **24**, 79 (1998).

Volford, P., P. L. Simon, H. Farkas, and Z. Noszticzius, "Rotating Chemical Waves: Theory and Experiments," *Physica A*, **274**, 30 (1999).

Wang, W., I. Z. Kiss, and J. L. Hudson, "Experiments on Arrays of Globally Coupled Chaotic Electrochemical Oscillators: Synchronization and Clustering," *Chaos*, **10**, 248 (2000).

Wang, W., I. Z. Kiss, and J. L. Hudson, "Clustering of Arrays of Chaotic Chemical Oscillators by Feedback and Forcing," *Phys. Rev. Lett.*, **86**, 4954 (2001).

Winfree, A. T., *The Geometry of Biological Time*, Springer-Verlag, New York (1980).

Winfree, A. T., "Evolving Perspectives during 12 years of Electrical Turbulence," *Chaos*, **8**, 1 (1998).

Wolff, J., A. G. Papathanasiou, I. G. Kevrekidis, H. H. Rotermund, and G. Ertl, "Spatiotemporal Addressing of Surface Activity," *Science*, **294**, 134 (2001).

York, R. A., and R. C. Compton, "Quasi-Optical Power Combining Using Mutually Synchronized Oscillator Arrays," *IEEE Trans. Microw. Theory Tech.*, **39**, 1000 (1991).