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# Chemical Oscillators in Structured Media

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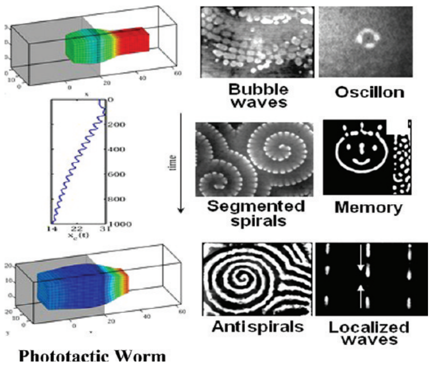
## CONSPECTUS



Evolution is a characteristic feature of living systems, and many fundamental processes in life, including the cell cycle, take place in a periodic fashion. From a chemistry perspective, these repeating phenomena suggest the question of whether reactions in which concentrations oscillate could provide a basis and/or useful models for the behavior of organisms, and perhaps even their ability to evolve.

In this Account, we examine several aspects of the behavior of the prototype oscillating chemical reaction, the Belousov–Zhabotinsky (BZ) system, carried out in microemulsions, arrays of micrometer-sized aqueous droplets suspended in oil, or hydrogels. Each of these environments contains elements of the compartmentalization that likely played a role in the development of the first living cells, and within them we observe behaviors not found in the BZ reaction in simple aqueous solution. Several of these phenomena resemble traits displayed by living organisms. For example, the nanodroplets in a BZ microemulsion "communicate" with each other through a phenomenon analogous to quorum sensing in bacteria to produce a remarkable variety of patterns and waves on length scales $10^5$ times the size of a single droplet. A photosensitive version can "remember" an imposed image. Larger, micrometer-sized droplets exhibit similarly rich behavior and allow for the observation and control of individual droplets. These droplets offer promise for building arrays capable of computation by varying the strength and sign of the coupling between drops. Gels that incorporate a BZ catalyst and are immersed in a solution containing the BZ reactants change their shape and volume in oscillations that follow the variation in the redox state of the catalyst. Using this phenomenon, we can construct phototactic gel "worms" or segments of gel that attract one another.

Whether such systems will provide more realistic caricatures of life, and whether they can serve as useful materials will largely depend on the successful integration of various properties, including communication, motion, and memory, which we observed in separate experiments. Theoretical approaches that couple reaction and diffusion processes to mechanical and other material properties are likely to play a key role in this integration, and we describe one such approach. The evolution of systems of coupled chemical oscillators presents another challenge to the development of these systems, but one that we expect to be solved.

## Introduction

> *It is often said that all the conditions for the first production of a living organism are now present, which could ever have been present. But if (and oh! what a big if!) we could conceive in some warm little pond, with all sorts of ammonia and phosphoric salts, light, heat, electricity, &c., present, that a proteine compound was chemically formed ready to undergo still more complex changes, at the present day such matter would be instantly absorbed, which would not have been the case before living creatures were found.*
>
> Charles Darwin, letter to Joseph Hooker, 1871

A chemist might conjecture that the original "warm pond" alluded to by Darwin encompassed an array of complex reactions, involving catalysis, polymerization, feedback loops, and nonlinear chemical dynamics, and that these reactions played a vital role in the emergence of compounds that ultimately paved the way for evolution. In this context, it is noteworthy that our understanding of nonlinear chemical dynamics is relatively new; one could say that the field was initiated by the discovery of oscillating chemical reactions, such as the Belousov–Zhabotinsky (BZ) reaction. With respect to the focus of this issue, it is

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interesting to consider the extent to which the latter cornerstone reaction could contribute to the emergence of lifelike functionality. The hallmarks of life include the abilities to reproduce, metabolize, communicate, and move. One might view oscillatory chemical reactions, which operate far from equilibrium and convert high free energy reactants to low free energy products in the process of generating ordered structures in time and (with the aid of diffusion) space, as performing a kind of metabolism. In this Account, we describe experimental and theoretical work on oscillating reactions in microemulsions, droplet arrays and gels (which we refer to collectively as structured media) that suggest that such systems can be harnessed to mimic other biological behaviors, such as communication and motion. Understanding how nonlinear chemical dynamics contributes to biomimetic behavior could also provide insight into the role of periodic oscillations in the emergence of early biological functionality.

Most of the studies described here employ the BZ reaction, the metal ion (or metal ion complex) catalyzed bromination, and oxidation of an organic substrate, usually malonic acid, in a strongly acidic medium.[1,2] The ability to sustain oscillations (with a period of 1−5 min) in a closed system over hundreds of cycles gives the BZ reaction its unique role in nonlinear chemical dynamics. If the catalyst is ferroin [tris(1,10-phenanthroline)iron(II)] or bathoferroin or $Ru(bipy)_3^{2+}$ [tris(2,2′-bipyridyl)ruthenium(II)], then the BZ system can be easily monitored spectrophotometrically, since the system oscillates between the reduced and oxidized states of the catalyst, which have very different absorption maxima. For example, ferroin is red in its reduced state and blue in its oxidized form. Use of $Ru(bipy)_3^{2+}$, even at relatively low concentrations as a cocatalyst, renders the system photosensitive as well, allowing for perturbation and control by light of a specific wavelength. Because it displays an astonishing variety of periodic and chaotic temporal oscillations and spatial waves, the BZ reaction has become the prototype system for studies of nonlinear chemical dynamics.[3,4] It has also been thoroughly studied from the mechanistic and modeling points of view, and a number of models, most derived from the three-variable Oregonator proposed by Field and Noyes, yield excellent agreement with a wide range of experimental results.[3]

Early studies of the BZ reaction and other chemical oscillators were carried out in aqueous solution. After it was discovered[5] that an unstirred BZ reaction could give rise to spatial pattern formation, in particular spiral waves, investigators began to examine the behavior of two or more coupled reactors, each containing an oscillating BZ solution. These simple discrete analogs of a spatially distributed system, coupled either electrically[6] or via mass transport,[7] gave rise to new dynamical behaviors and inspired efforts to look at more complicated compartmentalized configurations. In one intriguing study,[8] an array of eight coupled flow reactors containing the bistable arsenite-iodate reaction was used to create a device capable of recalling several patterns.

Compartmentalization has been suggested to play a key role in the origin of life and in evolution.[9] It has also been proposed as a means to facilitate directed evolution.[10] Recent experiments[11] on the BZ reaction occurring on 200 $\mu$m diameter cation-exchange beads in aqueous solution show evidence of the emergence of collective "quorum sensing" behavior, analogous to that exhibited by bacteria,[12] when the population density exceeds a threshold value.

Below, we describe another form of compartmentalization involving the BZ reaction; namely, we examine droplets containing the reactants and show that these droplets appear to communicate and respond to their environment in an "intelligent" manner. We then describe the lifelike behavior that can be achieved by introducing the BZ reaction into polymer gels.[13−15] These BZ gels encompass distinct forms of chemomechanical coupling, which permit the creation of "smart" autonomously moving objects.

## Reactions in Microemulsions

Suppose that the reaction takes place in a large number of distinct but interacting volumes under conditions where some signaling species can diffuse between these volumes, potentially leading to synchronization or interference between the chemical processes in different "cells". Such a configuration might arise in a mixture of water, oil, and surfactant (an emulsion) or from porous materials (e.g., zeolites). We are interested in how the size of these volumes, their density, and the rate of mass/information exchange or communication between them can affect the aggregate behavior of an ensemble of such chemically active entities. We might further imagine that, via "chemical evolution", different dynamical states of our dissipative system can regulate such physical properties as the size and density of the "cells" and the rate of mass exchange between them, and in turn these properties can influence the dynamical

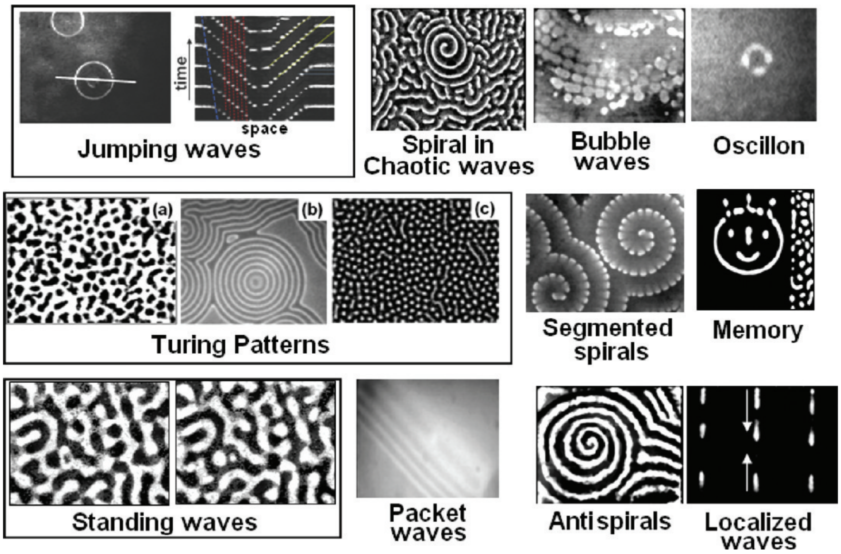

**FIGURE 1.** Patterns found in the BZ-AOT system. Jumping waves are presented as snapshots (left) and as a space-time plot (right, obtained across the white line shown in the left snapshot). Three types of Turing patterns are shown: (a) "black dots" (honeycomb), (b) "frozen waves", and (c) "white dots" (distorted hexagons). Standing waves are shown as two antiphase snapshots. "Memory" shows image briefly projected onto a photosensitive medium that exhibits localized subcritical Turing structures. Localized waves are obtained in the same manner using a striped mask. Other patterns are described in the text. Typical size of all snapshots is 5 ± 2 mm.

regimes. Such a system could perhaps display intelligent behavior, if we define intelligent behavior as a "rational" response to a changing environment. We will consider such smart materials later, but first we discuss two systems that consist of the BZ reaction incorporated into droplets.

A thermodynamically stable reverse microemulsion of water nanodroplets in oil is easily created from a mixture of water, oil and the ionic surfactant AOT [aerosol OT, sodium bis(2-ethylhexyl)sulfosuccinate].[16] We consider such a system in which a complex (e.g., oscillatory) chemical reaction occurs. Since the BZ reactants and catalyst are polar, reaction is confined to the aqueous nanodroplets, though nonpolar intermediates such as $Br_2$ and $BrO_2$ are generated during the reaction and may enter and leave the continuous oil phase, providing a means of interdroplet communication.

The polar head groups of the AOT molecules project in toward the water core, while the nonpolar tails are directed out into the oil. The average radius of the water core is determined by the ratio of water to surfactant molecules $\omega = [H_2O]/[AOT]$ and is given in nanometers by $R_w = 0.17\omega$.[17] Since we typically work with mixtures in which $\omega$ lies in the range 9–25, we are dealing with droplets that are several nanometers in diameter.

The spacing between droplets is controlled by the volume fraction $\varphi_d$ of the dispersed phase. As $\varphi_d$ increases, clusters of droplets begin to grow, and at a critical value $\varphi_p$ (around 0.5) percolation takes place, resulting in the formation of long dynamic channels of water, an increase of about 3 orders of magnitude in the conductivity of the microemulsion,[18] and an increase of 1–2 orders of magnitude in the diffusion coefficient of water molecules.[19]

Communication between droplets takes place via two distinct diffusive processes. Highly polar species (e.g., ions such as $Br^-$), which are largely confined to the water droplets, are exchanged when droplets collide and undergo fission and fusion. Less polar ($HBrO_2$) or nonpolar ($Br_2$) species diffuse through the oil as single molecules and display diffusion coefficients typical of single molecules ($\sim 10^{-5}$ cm$^2$ s$^{-1}$). The diffusion of polar molecules at $\varphi_d < \varphi_p$ is equivalent to the diffusion of water droplets, a much slower process with a diffusion coefficient around $10^{-7}$–$10^{-6}$ cm$^2$ s$^{-1}$.

By varying the structure of the AOT-microemulsion, that is, the droplet fraction $\varphi_d$ and the radius $R_w$ of droplets, as well as the chemistry of the BZ system, which can be characterized by the ratio of initial concentrations $[H_2SO_4] \times [NaBrO_3]/[MA]$ (a rough measure of the relative strengths of activation and inhibition in the reaction mixture) and the catalyst, we obtain a large gallery of patterns, many of which are presented in Figure 1.

Most of the phenomena shown in Figure 1 are unique to AOT-microemulsions; they have not been observed in experiments on the BZ reaction in simple aqueous solution or in gels. The distinctive morphologies include Turing

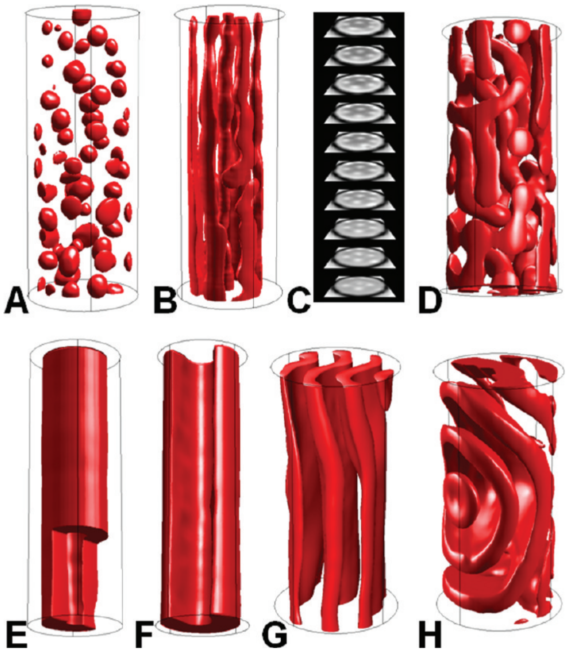

**FIGURE 2.** Tomographically reconstructed concentration fields for 3D Turing patterns. Spots (A), hexagonally packed cylinders (B), horizontal cross sections (C) taken through data array in (B), labyrinthine pattern (D), tube (E), half-pipe (F), lamellar pattern (G), and concentric hemispherical lamellae (H). [malonic acid]$_0$ = 0.30 M, [$H_2SO_4$]$_0$ = 0.18 M, [$NaBrO_3$]$_0$ = 0.23 M, [ferroin] = 5 mM, inner diameter of capillary is 0.6 mm for A−D, G, and H, and 0.3 mm for E and F. A short segment at the bottom of the front half of pattern (e) has been removed to reveal the inner structure.[29]

structures,[20] temporally stationary spatially periodic patterns first proposed as a mechanism for morphogenesis in living organisms;[21] antisprirals,[22] in which traveling spiral waves propagate inward toward the spiral center rather than outward from it; packet waves,[23] in which groups of traveling waves move through space coherently; segmented waves,[24] in which waves split into small segments transverse to the direction of propagation; and jumping waves,[25] in which circular waves propagate outward in a discontinuous, saltatory fashion. Localized patterns of the sort labeled "memory[26]" and "localized waves[27]" have been suggested[28] as a potential route to efficient information storage. More recently, we have utilized tomographic techniques to study three-dimensional Turing patterns in the BZ-AOT system.[29] An example is shown in Figure 2.

Compartmentalization at the nano level in a water-in-oil microemulsion results in quite different diffusion coefficients for the activator and inhibitor species. A nanodroplet is too small to be considered as a single oscillator. Indeed, a catalyst molecule is found on average in only one of ten nanodroplets. The characteristic wavelength of the patterns shown in Figure 1 is about 0.2 mm, 100 000 times larger than the diameter of a single nanodroplet, of which there are about $10^{17}$ in a typical experiment. The characteristic time of mass exchange between droplets, a few milliseconds, is about 10 000 times shorter than the period of oscillations. Thus, the level of organization observed in our patterns clearly results from the collective interaction of many droplets.

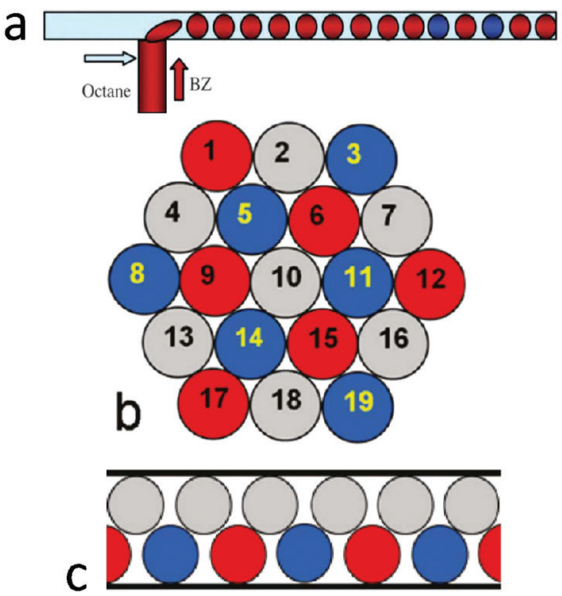

**FIGURE 3.** Pattern generation in macroemulsions produced by microfluidics. (a) Schematic rendering of method used to produce droplets. Capillary size is typically about 100 $\mu$m. (b) Schematic of two-dimensional "$\pi$-S" pattern. Gray circles represent stationary (nonoscillatory) droplets; blue and red circles show oscillatory droplets 180° out of phase with each other. (c) Schematic of "1.5 D" pattern with stationary and oscillatory droplets labeled as in (b).

Numerical simulations with models that treat the medium as homogeneous and describe the aqueous BZ chemistry augmented with species that partition into the oil phase and hence diffuse more quickly than the polar BZ species give excellent qualitative agreement with our experiments.[20,30,31] Experimentally, we are unable to see individual droplets through a microscope, nor can we control their behavior.

## Reactions in Macroemulsions: Microfluidics

Now consider what happens when the diameter of the water droplets approaches the characteristic size of the observed structures. In this case, which is more directly analogous to the compartmentalized configurations in which organisms evolve, we can no longer view the system as homogeneous and must introduce discreteness in the description of our coupled microoscillators. A closer connection can be made between theory and experiment, because we are able to produce and monitor individual microdroplets. By employing microfluidic techniques, we have been able to obtain one- and two-dimensional droplet arrays with diameters in the range 50−300 $\mu$m. Droplets with larger diameters communicate too weakly to be of interest.

Figure 3a shows schematically how the droplets are generated by flowing streams of oil and aqueous BZ solution into a narrow tube. The coupling is dominated by the inhibitory species $Br_2$. In one dimension, that is, in a capillary tube whose diameter is equal to that of the droplets, the most stable pattern is antiphase oscillation, in which neighboring droplets oscillate 180° out of phase.[32] Many more complex patterns can be obtained,[33] including mixtures of oscillatory and stationary drops. The strength of the coupling depends upon the diameter of and distance between the drops and on the malonic acid concentration.

In two dimensions, the observed patterns can be more elaborate.[34] Figure 3c shows a "1.5 D" pattern, in which the capillary is wide enough to hold two intercalated rows of droplets. In the pattern illustrated, one row of droplets is in a stationary state, while the other row contains droplets oscillating antiphase. In a wider vessel, the droplets self-assemble into a two-dimensional hexagonal lattice, and we observe many stable patterns, including the one illustrated schematically in Figure 3b, where in each triangle of droplets one is stationary and the other two oscillate antiphase. A fully oscillatory pattern with droplets oscillating 120° out of phase with their neighbors is also stable. Many less symmetric patterns are also obtained.

Our studies to date have employed arrays of identical droplets. Future experiments and simulations will explore configurations in which the sizes and/or distances of adjacent droplets are allowed to vary. If this variation can be made responsive to the state of the droplet, for example, by allowing droplets oscillating in phase to move closer together, the system would be able to tailor its interdroplet couplings in response to its chemical activity, much as neurons do with their synaptic strengths. A similar idea, aimed at implementing a Hebbian-like rule,[35] was implemented by Laplante et al.[8] in their pattern recognition experiments, but there the coupling strength was imposed directly by the experimenter rather than being allowed to evolve organically. By controlling the mix of inhibitory and excitatory coupling, it should be possible to generate complex patterns of "computational" activity.

In the above studies, the BZ reaction enabled elementary forms of metabolism, communication, and perhaps even computation. Next, we describe how this oscillating reaction can also be exploited to create "smart" materials capable of self-propelled motion.

## BZ Gels: Modeling and Experimental Prospects

Fighting, fleeing, and feeding are hallmarks of living things; these activities require some degree of mobility. By incorporating the BZ catalyst into gels, Yoshida[13] enabled the materials to exhibit a biomimetic form of chemomechanical transduction; namely, the chemical energy from the intrinsic chemical reaction is transduced into the rhythmic mechanical swelling and deswelling of the gel. These periodic volume and shape changes can lead to the directed motion of the sample. One of the challenges in designing such self-propelled gels is predicting optimal conditions that will lead to the intended movement, for example, away from a "foe" or toward "food". Recent development of a theoretical model and computational framework provides a tool suitable for simulating the dynamic behavior of BZ gels.[36−39] This approach builds on the Oregonator model for the BZ reaction in solution[40] and the two-fluid model for polymer networks[41] to describe the elastodynamics of BZ gels; the resulting governing equations are solved numerically using the "gel lattice spring model" (gLSM),[36−39] which combines finite difference and finite element methods.

With the aid of the gLSM approach, we established a number of different means of driving gels to move away from or toward specific cues.[39,42−45] A common theme in these studies is the use of spatial gradients to guide the gel's movement. Below, we describe findings from these computational studies that reveal how gradients in light, structural gradients within the gel and self-generated gradients in $u$, the activator for the BZ reaction, can be harnessed to induce the autonomous motility of the sample.

Due to the photosensitivity of ruthenium-catalyzed BZ reactions,[46] light provides a useful stimulus for controlling the behavior of BZ gels.[47] Illumination results in production of bromide ions, which act to suppress the oscillations.[47] This property was exploited in the design of millimeter-sized BZ gel "worms" that effectively flee from light;[42,48] that is, they exhibit negative phototaxis. An example of a phototaxing BZ worm is shown in Figure 4a−c, where a rectangular sample is exposed to nonuniform illumination. The light intensity is taken to be a step function, so that one-third of the sample is kept in the dark (region shaded in gray) and two-thirds is illuminated with a constant intensity. In the simulations,[42,48] the effect of light is introduced via a dimensionless parameter $\Phi$, which accounts for the additional production of bromide ions and is assumed to be proportional to the light intensity.[42,48] Above a critical value, $\Phi_c$, the chemical oscillations in the sample are completely suppressed.

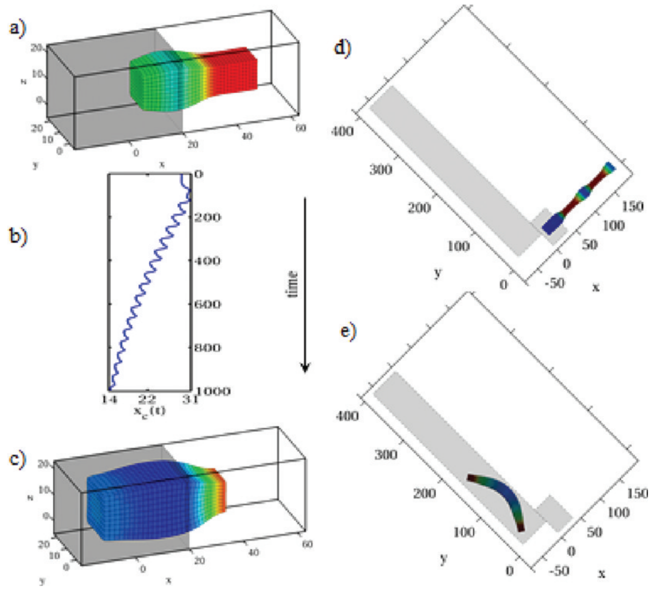

**FIGURE 4.** Phototactic "chemical worm". Gray indicates the nonilluminated regions. Panels (a) and (c) show early- and late-time positions, respectively of the BZ worm; (b) evolution of the *x* coordinate of the gel's center. Panels (d) and (e) reveal how the worm makes a turn. The velocity of these millimeter-sized worms is approximately 1.2 $\mu$m/s.[49]

For the system in Figure 4a–c, $\Phi$ is set to zero in the nonilluminated region and to $\Phi = \Phi_c$ in the illuminated area, so that oscillations are suppressed in this region. Consequently, rhythmic pulsations of the gel originate at the nonilluminated end, at the left in Figure 4a, and traveling waves continually propagate from left to right. These traveling waves effectively "push" the solvent to the right, and because of the interdiffusion of the polymer and solvent the gel is driven to the left. The gel undergoes a net displacement that is opposite in direction to the propagation of the traveling waves.

Figure 4c indicates the location of the sample at later times, showing that the worm has escaped into the dark region. Figure 4b shows the corresponding trajectory of the center of the sample; while oscillations are produced by the periodic swelling and deswelling of the gel, the systematic decrease of this point's *x*-coordinate, $x_C$, reveals the net motion of the worm along the negative *x*-direction.

In the above example, the spatially nonuniform illumination breaks the symmetry of the system and thus sets the direction for the autonomous, *unidirectional* motion. Remarkably, even after the entire sample has left the illuminated region, it keeps moving along this path. This directed motion can continue until the system is depleted of reagents (which, for millimeter-sized gels, can take hours[13,15]). Through the use of holographic techniques and masks, more complicated arrangements of light and dark regions can be achieved, permitting even more significant control over the path of the BZ gel's motion.[42] Figure 4d and e indicates how to arrange the light and dark regions in order to "instruct" the sample to make a 90° right turn. The system consists of two dark regions, A and B, which are shown in gray. The B region is offset in the *y*-direction so that its edge aligns with the center of A; initially, 20% of the gel is located in A and the remainder is exposed to light, as indicated in Figure 4d. Similar to the scenario in Figure 4a–c, the sample moves toward the dark. As the gel progresses through the dark A region, it encounters an illuminated patch, but the worm "senses" the contiguous, nonilluminated B section. Consequently, the gel bends to enter this dark area and is ultimately oriented along the length of the dark B region.

In response to different arrangements of light, the BZ worms also demonstrate an ability to make U-turns and more complex maneuvers.[42] The negative phototaxis displayed by these synthetic worms mimics the behavior of the biological worm *C. elegans*, which flees from light.[49] The ability to control the self-sustained motion of the BZ gels provides new opportunities for designing self-regulating soft robots that can navigate winding paths in order to arrive at a specific location. After the gel arrives at the designated site, it could be remotely (and noninvasively) given another set of directions by changing the arrangement of the light and hence driven to visit subsequent sites. These attributes could be utilized to create microscopic carriers that serve a "pick-up and delivery" function within microfluidic devices.

In the absence of gradients imposed by external stimuli, structural gradients within the material can be exploited to create self-propelled BZ gels. The gel in Figure 5a encompasses a systematic variation in cross-link density, $c_0$, across the width (in the *z* direction) of the sample, which is synthesized by placing the pregel solution in a transparent capillary tube and photoirradiating one side of the tube.[45] The value of $c_0$ at the top of the sample in Figure 5a is 2.5 times lower than that at the bottom. Due to these variations in $c_0$, the degree of swelling within the gel varies along *z*; the sample is relatively expanded at the top and contracted at the bottom. This oscillating BZ gel exhibits a periodic swelling and deswelling about this bent configuration, with a chemical wave propagating from the center of the sample toward the ends. The latter behavior is indicated by the color changes in Figure 5a, which pinpoint the local concentration of the oxidized catalyst. As seen in the figure, the degree of swelling is higher in areas with higher concentrations of the oxidized catalyst.

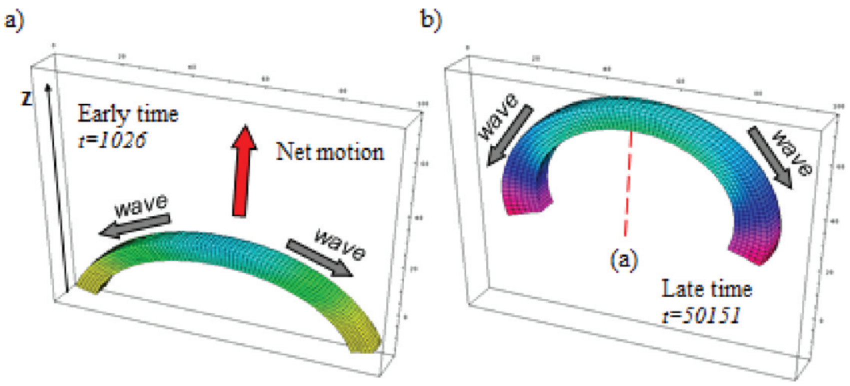

**FIGURE 5.** Simulation of a self-propelled BZ gel (see text). Color represents concentration of oxidized catalyst; yellow marks the lowest value and red the highest.

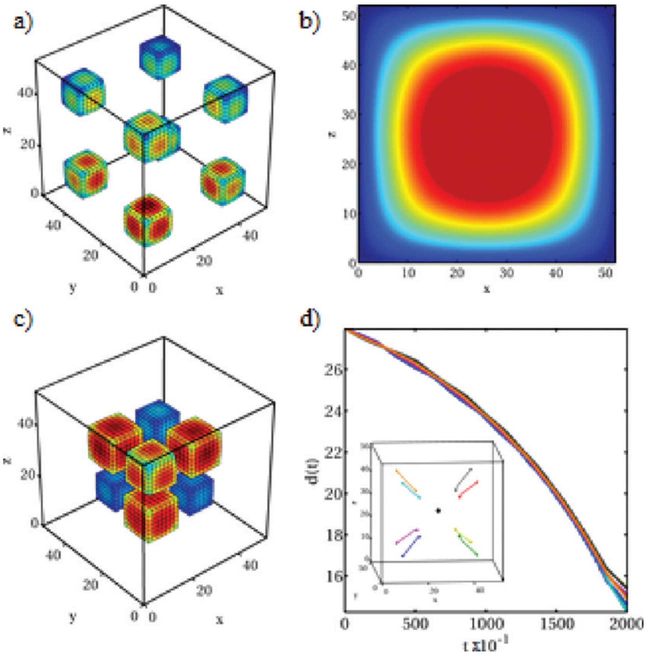

**FIGURE 6.** Simulation of an array of eight interacting cubes of BZ gel. (a) Initial location of the cubes. (b) Distribution of *u* in the solution. (c) Later location of the cubes. (d) Distance between the center of each cube and the center of the simulation box as a function of time. Color represents concentration of oxidized catalyst; blue marks the lowest value and red the highest.

These oscillations lead to a net migration of the sample in the positive *z* direction; in other words, the sample leads with its apex (Figure 5b). Thus, the net displacement of the sample is opposite in direction to the propagation of the traveling waves, which travel from the center toward the ends (as seen in Figure 5a). Recall that this mode of migratory behavior was also observed for the BZ worms. The directed motion predicted by these computational studies is consistent with preliminary experimental observations on comparable samples.[45]

The above examples illustrate means of imposing gradients to control the self-sustained motion of a *single* BZ gel unit. The images in Figure 6 reveal that multiple BZ gels in solution not only sense gradients, but also produce the gradients that dictate their collective motion. The BZ gel cubes in this scenario are structurally uniform and are placed in an initially uniform environment. Nonetheless, as evident from Figure 6, these cubes exhibit a distinct form of chemotaxis, moving toward the highest concentration of activator *u* in the solution. Chemotaxis, the ability to sense and move in response to chemical gradients, constitutes a vital function in simple organisms, enabling them to find food and flee from poisons.

Figure 6a shows the initial position of eight cubes that are located near the corners of the simulation box. The boundary condition $u = 0$ is maintained at the edges of this box. During the course of the reaction, there is a diffusive exchange of the activator *u* between the gel and fluid, resulting in a buildup of *u* in the solution. Figure 6b shows the distribution of *u* at relatively late times, revealing that the highest concentration of the activator is in the center of the box. As can be seen in Figure 6c and d, the BZ cubes migrate to this region of highest *u* concentration. In particular, Figure 6d shows the distance between the center of each cube and the center of the simulation box as a function of time, revealing that all the cubes move to this central area (Figure 6c).

The behavior of this system can be understood in the following manner.[50] For BZ gels of a certain size, the oscillation frequency, $\omega$, increases with the concentration of *u* in the outer solution. Furthermore, the propagation of the chemical wave through the BZ gel originates from the region with the highest oscillation frequency.[51] Since the concentration of *u* is higher for the "inner" surface (the surface facing the center of the box) than the outer surface, the inner surface has a higher intrinsic frequency and the direction of wave propagation is from the inner to the outer surface of each cube. Consequently, gels move in the direction opposite to the direction of wave propagation (analogous to the cases above), and thus, the cubes migrate toward the center of the box.

One could introduce structural heterogeneities into these BZ cubes to control their shapes (e.g., as in Figure 5) and to modify their collective motion. In addition, one could utilize nonuniform illumination to further control their migratory behavior. The studies on phototaxing BZ worms indicate that spatially localized light could be used to drive illuminated cubes to follow the motions of unlit pieces. In effect, one could create a school of BZ "fish" that all move in a specified direction.

## Conclusion

The experiments and simulations described here only scratch the surface of what is possible by combining nonlinear chemical dynamics with compartmentalization and well-chosen connections among the compartments. Chemical oscillators have been exploited to solve mazes,[52] to build logic gates,[53] and to construct patterns that contain self-reproducing spots.[54] They may also be capable of transducing the energy contained in environmental noise to build ordered spatial structures.[55] A key problem that remains is to integrate the various functionalities of which these systems are capable with one another. For example, living organisms not only remember and move but also are able to recall patterns of motion.

Whether the relatively simple chemical systems we have considered here are capable of even a crude form of evolution remains to be seen. Incorporation of increasingly more complex feedbacks into systems that continually receive a flow of fresh reactants and are exposed to environmental perturbations seems like a promising route. Perhaps someday, we will be able to create a series of Darwin's warm little ponds in our laboratories and watch their contents evolve!

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**Note Added after ASAP Publication.** This paper was posted to the web on December 28, 2011 with an error in the Biographical Information. The corrected version was reposted on December 30, 2011.

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BIOGRAPHICAL INFORMATION

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FOOTNOTES

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