Complex organizing centers in groups of oscillatory particles

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We investigate the origin and evolution of spatiotemporal complexity in a system of locally coupled Belousov–Zhabotinsky chemical oscillators. Using a combination of high resolution microscopy and fine grain numerical modeling, we demonstrate that the behavior arises from an initial phase heterogeneity of the oscillators. This heterogeneity produces wave breaks in the system with the free ends becoming pinned to holes in the medium. The fastest of these pinned tips behave as reentrant circuits that phase set the rest of the medium. The slower tips are repeatedly destroyed and then re-created by the central circuit. The resulting spatiotemporal pattern repeats with the frequency of the reentrant circuit, with its spatial structure depending on the location of the initial wave breaks.

1. Introduction

Local coupling within groups of oscillators often gives rise to propagating waves of activity. The resulting spatiotemporal behaviors have generated great interest due to their functional role in biological systems, such as electro-mechanical wave propagation through heart tissue1 and cAMP waves directing the movement of starving Dictyostelium discoideum cells.2,3

The Belousov–Zhabotinsky (BZ) reaction4,5 is an experimentally tractable oscillatory system that has been widely used to develop an understanding of spatiotemporal patterns.6–8 The reaction is typically studied in quasi-2D continuous media,9 however, many spatiotemporal systems are composed of discrete cellular oscillators. A discretized chemical oscillator system has been developed from the BZ reaction,10 in which the catalyst for the oscillators. A discretized chemical oscillator system has been developed from the BZ reaction,10,15,16 and synchronization in globally and locally coupled oscillators.17–20

Biological systems of coupled oscillators are typically heterogeneous. The role of different types of heterogeneities in wavebreakages, such as spatial variations of cell density or cellular coupling, has been extensively studied in heart tissue to better understand cardiac arrhythmias.21–23 Early experiments on layers of catalyst particles in the BZ system reported increasing complexity of the spatiotemporal patterns with increasing bromate concentration.10

2. Experimental details

The particles used in the experiment are porous cation-exchange beads (Biorad 50WX-100, mean diameter ~280 µm) that are loaded with the BZ catalyst ferroin ([Fe(phen)3]3+) = 1.7 × 10^-5 mol g^-1 particles). The loaded particles are placed into a Petri dish and covered with catalyst-free BZ solution,27,25 with [NaBr] = 0.1 M, [CH3COO]2- = 0.2 M, [H2SO4] = 0.6 M, and varied bromate concentration. The particles are uniformly illuminated from below and viewed from above using a microscope fitted with a digital camera. The bromate concentration is selected so that the individual particles are oscillatory, [BrO3^-] ≥ 0.42 M, with the mean period of the particles

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Fig. 1 Low bromate (0.42 M) single spiral pattern. (a) The five panels show the temporal evolution of the spiral pattern. (b) Close-up of the reentrant circuit region, shown by a red box in (a). The arrows in the first panel indicate the path of the wave around the circuit. The propagation of the wave perpendicular to the contact tangent between the particles can be seen in the successive images. Images are constructed by subtracting consecutive images and then adding the image difference (3×) to a wave-free particle image. The images are taken every 5 s, where each close-up image in (b) is taken from the corresponding panel in (a).

demonstrated by constructing a map that shows the number of particles that are close but not in contact. This also occurs in the case of particles moving around a hole in a continuous field. This behavior is dynamically similar to a pinned spiral tip moving around a hole in a continuous field. This tip originates as a pinned spiral tip rotating around a hole, serving as a wave source. However, such centers are transformed into defects when overtaken by incoming waves from a higher frequency source. The defect is a pinned spiral tip that is periodically destroyed and then recreated by the incoming waves.

The group behavior of the oscillatory particles is studied in quasi-circular monolayers of particles in the catalyst-free BZ solution. Each particle is positioned to be less than one particle diameter away from a neighboring particle. Fig. 1a shows a typical spiral pattern that spontaneously formed under low bromate concentration conditions. The spatiotemporal activity in groups of particles consists of waves propagating across the surface of the particles. This contrasts with the behavior of isolated particles, which oscillate quasi-homogeneously. The propagation process can be seen clearly in the close-up shown in Fig. 1b. A wave is initiated on the surface of a particle at the point of contact with another particle. The wave then travels normal to the tangent line of the point of contact across the surface of the particle. This also occurs in the case of particles that are close but not in contact.

The set of five particles marked by the arrows in Fig. 1b, first panel, constitute a reentrant circuit. Waves travel around this circuit, moving on each particle normal to the contact tangent. This behavior is dynamically similar to a pinned spiral tip moving around a hole in a continuous field. We describe these types of structures as reentrant circuits or spiral waves. Away from the center, the waves travel outward from one particle to the next. On each particle, the wave is initiated at the contact (or near contact) point, grows in size and then shrinks as it travels to the contact point of the next particle. All of the waves shown in Fig. 1a originate from the reentrant circuit.

The reentrant circuit is an organizing center that frequency synchronizes and phase sets the other oscillators. This can be demonstrated by constructing a map that shows the number of particles a wave has travelled across since leaving the central circuit in order to reach the current particle—a network-distance map. All particles are labeled according to the number of particles a wave has traveled across from an arbitrary particle in the reentrant circuit, designated as the reference (0th) particle. This labeling scheme, shown in Fig. 2a, may be interpreted as the accumulative relative phase of the particle or the network distance of a particle from the reference particle. We note that the actual wave propagation distance will differ slightly from the network-distance map shown in Fig. 2a due to heterogeneities in particle size and variations in wave velocity.

As the bromate concentration is increased, the spatiotemporal behavior becomes more complex. Fig. 3a shows an example of the patterns for medium bromate concentration. Close-ups of two different dynamical structures embedded within this pattern are shown in Fig. 3b and c. The reentrant circuit, shown in Fig. 3b, is composed of a wave propagating around three particles. The structure shown in Fig. 3c is of a different dynamical form. It originated as a pinned spiral tip rotating around a hole, serving as a wave source. However, such centers are transformed into defects when overtaken by incoming waves from a higher frequency source. The defect is a pinned spiral tip that is periodically destroyed and then recreated by the incoming waves (see Section 4 for further details). A detailed examination of Fig. 3a shows that all of the spiral tips and defects are pinned to holes between the particles.

A quantitative measure of the complexity of a spatiotemporal pattern can be obtained by determining the total number of spiral tips. The presence of a tip is indicated when the winding number around a closed loop encircling an arbitrary point is nonzero. The winding number is defined as \( \int \nabla \phi \cdot ds \), where, in the particle system, the closed loop \( L \) is drawn through the contact points between the particles immediately adjacent to a hole, and \( \phi \) is the phase on the loop. Based on this definition of a spiral tip, the spatiotemporal pattern shown in Fig. 1a has one tip, whereas the pattern shown in Fig. 3a has 10 tips. The pinned tip shown in Fig. 3b is of special importance in the second case because it forms the spiral with the highest frequency. Image analysis shows that waves from this reentrant circuit
govern the rest of the oscillators in the group by setting the synchronization frequency and establishing the pattern that defines the network-distance map shown in Fig. 2b.

At still higher bromate concentrations, a new form of organizing center is exhibited: a spiral wave on the surface of a single particle. This behavior has been observed only at high bromate concentrations and with larger particles (≥ 0.32 mm). This particle size is relatively small compared to the critical particle size (≥ 0.6 mm) reported necessary to support spiral behavior. A possible explanation of this might be the close proximity of the other particles, which can change the dynamics of the individual particles due to the additional sources of bromide and bromous acid in the surrounding solution. Fig. 4a shows an example of a group of particles in which there are three organizing centers, one reentrant circuit, Fig. 4b, and two individual particle spiral centers, Fig. 4c, each of which sets the phase of a spatiotemporal domain in the group. All three organizing centers have the same frequency, where the two individual particle spiral centers are apparently entrained. The reentrant circuit has two tips rotating around a four-particle circuit, analogous to a two-armed spiral. The network-distance map for this group is shown in Fig. 2c. Network-distance maps are generally stable, with little change over the one-hour duration of an experiment; however, the domains containing individual particle spiral centers display more variation. The phase map in Fig. 2c shows an average of the spatiotemporal domains over the course of the experiment.

3. Modeling study

Models that have been previously developed to investigate the interactions between catalyst loaded BZ particles have treated each individual particle as a zero-dimensional point. Here, we introduce a finer resolution representation of the individual particles in order to allow
for local wave activity and to better describe the holes between the particles. Each particle is represented as part of a 10 × 10 unit of cells, with the corner cells making up the holes between the particles. Fig. 5 shows a collection of four such particles with regular holes between them. Each cell of a given particle p has the same value of the total catalyst concentration \( C_p \). Cells that make up the holes have \( C = 0 \). The chemical kinetics of the BZ reaction is modeled with the three-variable ZBKE model,\(^{17,34}\) where the variables \( X_{ij} \), \( Y_{ij} \) and \( Z_{ij} \) represent \([\text{HBrO}_2] \), \([\text{Br}^-] \), and the oxidized form of the catalyst in the \((i, j)\) cell (see model details in Appendix A). A typical simulation consists of 100 particles each arranged in a regular 10 by 10 lattice, which corresponds to a simulation with 100 × 100 cells. Diffusive coupling of \([\text{HBrO}_2] \) and \([\text{Br}^-] \) between neighboring cells is modeled using a six-point Laplacian with noflux boundary conditions. Frequency heterogeneity in the particle population is included by assigning the value of \( C_p \) from a distribution of values.

Model parameters are chosen so that isolated individual particles are oscillatory, with bromate concentration \( A \) in the range 0.39 M ≤ \( A \) ≤ 0.55 M. For simulations of homogeneous particles, the total catalyst concentration is set to \( C_p = 0.01 \) M for all \( p \), which results in oscillatory periods between 90 s \((A = 0.39 \text{ M})\) and 14 s \((A = 0.55 \text{ M})\). Details of the distributions of \( C_p \) used in the construction of heterogeneous populations are given in the appropriate figure legends.

### 4. Origin of spiral tips

We have carried out model studies to investigate different possible origins of spiral tip formation in the system, including the role of initial conditions and frequency heterogeneity. After immersion into the catalyst-free BZ solution, each particle will begin to undergo oscillations. The initial phase of the particles is modeled either by setting all particles to the same initial phase or by setting each particle to a random initial phase. In groups of homogeneous particles, the first results in uniform oscillations across the group, while the second results in broken waves and the formation of spiral tips. Fig. 6a shows that the number of tips formed increases with increasing bromate concentration.

In contrast to homogeneous particles, particles with a heterogeneous distribution of \( C_p \) typically produce target patterns when started at the same initial phase. Under these conditions, we have also observed a very small range of bromate concentration where spiral tip formation is observed, shown in Fig. 6a. At lower bromate concentrations, non-oscillatory particles must be included in order to produce spiral tips. At higher bromate concentrations, the faster oscillators have a shorter period than the time taken for a tip to circuit a hole, resulting in a mixed pattern of broken and target waves.
We have not observed target patterns, nonoscillatory particles, or mixed target and broken wave patterns in our experiments with groups of oscillatory particles. This suggests that frequency heterogeneity is not an essential element of the wave breaking mechanism of our system. In support of this, we find that introducing random initial phases into a group of particles with a heterogeneous distribution of \( C_p \) results in qualitatively similar behavior to that seen using groups of homogenous particles, as described above.

We now describe a mechanism for the development of a spiral tip, based upon the initial phase of a particle. The ability of a wave to propagate onto a particle depends on the phase of the particle when the wave is incident. Fig. 6b shows phase response curves of an individual cell to the firing of a neighboring stimulus cell to which it is diffusively coupled. Here, zero phase corresponds to the peak in the autocatalyst concentration. Each point on the graph corresponds to the stimulus cell firing at a different phase of the second cell, indicated on the x-axis. This results in a phase advance or delay of the oscillator relative to the time the cell would have fired in the absence of the stimulus cell. When the stimulus cell fires early in the phase cycle of the oscillator, the stimulus cell fires later, the oscillator is phase advanced, which corresponds to the inability of a reaction-diffusion wave to propagate across a particle. When the stimulus cell fires later, the oscillator is phase delayed, which corresponds to the propagation of a reaction-diffusion wave. Non-propagation results in the creation of a free end in the system, which then has the possibility of forming a spiral tip.

A typical birth of a spiral tip in a system of six homogeneous particles initiated at random phases is shown in Fig. 7. The top middle particle fires first, panel (a), resulting in a wave propagating down and to the right, panel (b). The wave is unable to propagate onto the upper left particle because it is in an unexcitable state. The wave propagates further on the particles, panel (c), and finally returns to the upper left particle, panel (d), which is now ready to support wave activity. The broken wave becomes a spiral tip pinned to the left central hole, with a rotational period of 19.2 s. This period is shorter than the intrinsic period of the individual particles.

Spiral tip formation in a group of particles with random initial phases requires two neighboring particles to have an appropriate difference in phases, such that when one fires, a wave fails to propagate on the other. At low bromate, the necessary phase difference range is small, as shown in Fig. 6b, and the likelihood of two neighbors with the appropriate phase difference is also small. At higher bromate concentrations, the probability of an appropriate phase difference
increases owing to a larger range of the unexcitable phase of the oscillator.

Geometric heterogeneities in groups of oscillatory particles might also play a role in the spatiotemporal behavior. Such heterogeneities arise in the experiments from nonuniform packing of the particles as well as a distribution of particle sizes. This leads to variations in the hole sizes between particles and breaks in the packing across which waves cannot propagate. A convenient approach for incorporating this geometric heterogeneity into the model is to allow small variations in the hole size in the regular particle lattice along with occasional breaks between connecting particles, as shown in Fig. 5(b).

Comparisons between simulations with regular and irregular geometries can be made by using the same set of random initial phases for the particles in each case. We find that spiral tips typically form around the same holes in the two cases, but the sizes of the holes may be different in the irregular geometry case. Since the period of circulation of a tip around a hole depends on the hole size, the spiral frequencies generally differ between the regular and irregular packing cases.

In a continuous medium, a high frequency source will always overtake a lower frequency source, and the medium will eventually become dominated by the highest frequency source. However, spirals that are pinned to holes tend to be removed only when the incoming wave train is of sufficiently high frequency and the size of the hole is below a critical radius. The experimental behavior shown in Fig. 3c is an example where unpinning is unsuccessful; the tip around the hole is regenerated with each new incoming wave to form a defect. This process is illustrated numerically in Fig. 8, where an approaching wave collides with a pinned tip and the wave annihilation forms a free end. The remaining segment of the wave then reforms the tip.

5. Discussion

The origin of the complex spatiotemporal behavior, represented by the network-distance maps, can now be described. In our simulations, spiral tips are formed primarily due to variations in the initial phases of the different particles. Following the phase-dependent initiation events, a number of broken ends pin to holes in the vicinity of the initiations. The spiral tip circulating the smallest hole has the highest frequency and becomes a reentrant circuit, feeding waves into the system. These waves fail to unpin other spiral tips but instead continuously destroy and then re-form them at the frequency of the reentrant circuit, resulting in the formation of defects. The result is one or more (in the case of circuits having the same frequency) reentrant circuits, which entrain the entire system. The spatiotemporal pattern repeats with the frequency of the reentrant circuit. Higher bromate concentrations are associated with an increase in the initial number of wavebreaks in the system, leading to an increase in the complexity of the network-distance map, as illustrated in Fig. 2.

A second type of organizing center has been observed in our experiments: a spiral on the surface of an individual particle. This type of organizing center involves 3D geometries in groups of oscillatory particles might also play a role in the spatiotemporal behavior. Such heterogeneities arise in the experiments from nonuniform packing of the particles as well as a distribution of particle sizes. This leads to variations in the hole sizes between particles and breaks in the packing across which waves cannot propagate. A convenient approach for incorporating this geometric heterogeneity into the model is to allow small variations in the hole size in the regular particle lattice along with occasional breaks between connecting particles, as shown in Fig. 5(b).

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catalyst, \([\text{Fe(phen)}_3^{3+}] + [\text{Fe(phen)}_3^{2+}]\), in cell \((i, j)\) that is a component of particle \(p\). For cells which represent holes in the medium, the above rate equations are solved with \(C = 0\). All other constants and \(U_{ss} = f(X_{ij}, Y_{ij}, Z_{ij})\) as in Zhabotinsky et al.\textsuperscript{34} The equations are integrated using a Euler scheme with time step 0.004 s.

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