Accelerated Dynamics in Active Media: From Turing Patterns to Sparkling Waves

Jorge Carballido-Landeira* and Alberto P. Muñuzuri

Group of Nonlinear Physics, Universidade de Santiago de Compostela, Santiago de Compostela E-15782, Spain

ABSTRACT: We report the destabilization of stationary Turing patterns and the subsequent emergence of fast spatiotemporal dynamics due to reactant consumption. The localized hexagonal Turing spots switch from a stationary regime to a dynamics state by exhibiting spatial oscillations with two characteristic wavelengths and one representative temporal period. These oscillatory Turing spots are not temporally stable and evolve into traveling spiral tips that, in addition to the unexpected birth of spots, rapidly transform into target patterns and originate multiple collisions and wave breakups due to their proximity, degenerating into a chaotic scenario.

INTRODUCTION

Pattern formation in chemical oscillators has been thoroughly studied since the first traveling waves reported in the Belousov–Zhabotinsky (BZ) reaction, which consists of the metal-ion-catalyzed oxidation of an organic compound (usually malonic acid) in an acidic solution by bromate ions. The BZ reaction has been frequently used as a prototype of a nonequilibrium system that exhibits nonlinear spatiotemporal behavior with the reaction–diffusion (RD) structures similar to those self-organized patterns that appear in living organisms. The possibility to generalize the results obtained from nonlinear oscillators to understand complex real phenomena has prompted the scientific community to develop new chemical reactors. Thus, the BZ reaction was proposed to be confined inside water-in-oil (w/o) microemulsions using AOT (sodium bis(2-ethylhexyl) sulfosuccinate). The relevance of the BZ-AOT system lies in the fact that the main RD mechanisms take place in nanometer-sized compartments. Meanwhile, the resultant spatiotemporal pattern is several orders of magnitude larger.

The wide variety of patterns exhibited by the BZ-AOT system has been related to the quite significant cross-diffusion coefficients obtained for the BZ reagents confined in the water nanodroplets while several nonpolar intermediates (such as bromine, the inhibitor of the reaction) are able to diffuse through the oil phase even faster than those BZ reagents residing in the AOT nanodroplets. These differences in the diffusion coefficients in addition to the high concentration of inhibitor in the oil phase are required for the appearance of stationary structures associated with the Turing instability. These structures occupy the entire reactor with a characteristic wavelength, \( \lambda \) (usually measured through 2D FFT), remain stationary for almost 1 h, and fade away slowly after that time. However, for volume droplet fractions of the dispersed phase (water plus surfactant, \( \Phi_d \)) larger than the percolation threshold (\( \Phi_d \gg \Phi_c \)), AOT microemulsions transform from spherical droplets to elongated clusters that eventually interconnect the entire system. In this regime, it is plausible to assume that the diffusion coefficients of the nonpolar intermediates and the aqueous BZ reagents become similar as a result of the fast diffusion of the water molecules into the elongated clusters. Under these conditions, the BZ-AOT system typically exhibits bulk temporal oscillations, which are homogeneous in space, with a characteristic frequency as a consequence of the prevalent Hopf instability.

Previous results across the percolation transition have shown that modifications in the volume fraction generate considerable changes in the kinetic observables of the BZ-AOT system, such as the induction period and the period of oscillations. Our study is focused in the emergence of new spatiotemporal dynamics that arise under the interaction of the Turing and Hopf modes during the onset of percolation (\( \Phi_d \approx \Phi_c \)), i.e., when spherical droplets start to convert into elongated clusters.

EXPERIMENTAL SECTION

In a typical sample preparation, a solution of 1.5 M AOT in octane was employed to prepare two AOT microemulsions (MEs) with different aqueous contents. The first microemulsion (ME1) was composed of the organic compound (malonic acid, MA) and \( \text{H}_2\text{SO}_4 \) and the second one (ME2) was loaded with sodium bromate and the catalyst (Ferroin). Both stock microemulsions ME1 and ME2 were prepared with the same droplet size, obtained through the relation \( \omega \equiv \text{[H}_2\text{O]}/[\text{[AOT]}] = 18 \), and the same droplet fraction, \( \Phi_d = \Phi_w(1 + 21.6/\omega) = 0.75 \) (where \( \Phi_w \) is the volume fraction of the water phase). To obtain

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the reactive microemulsion, we mixed equal volumes of both stock microemulsions (ME1 and ME2) and diluted with octane to acquire the desired droplet concentration. The control parameters in this study are, on the one hand, the concentration of droplets (in the range desired droplet concentration. The control parameters in this study are, on the one hand, the concentration of droplets (in the range of 0.45 ≤ Φd ≤ 0.75) and, on the other hand, the excitability of the reaction, calculated as the ratio of concentrations in the aqueous phase [H2SO4][NaBrO3]/[MA]0, where we employed [MA]0 = 0.2−0.25 M, [H2SO4]0 = 0.18−0.225 M, [NaBrO3]0 = 0.16−0.18 M, and [ferroin]0 = 4 mM. The spatially extended experiments were carried out at room temperature (T = 20 °C), the temperature at which the BZ-AOT microemulsion with Φd = 0.45 remains below the percolation threshold.20

To image the spatiotemporal patterns, a drop of the resultant microemulsion was sandwiched between two transparent windows separated by a Teflon spacer (Zelfluor membrane) of 80 μm.21 To visualize the formation of patterns, we used a camera (Guppy AVT 64 fps) with an achromatic objective (DIN × 4 Edmund Optics) connected to a personal computer. Spectrophotometric measurements were made inside 3.5 mL continuously stirred cuvettes with a Vernier spectrophotometer (Ocean Optics) connected to a computer. Spectrophotometric data were visualized and analyzed via Logger Pro software. Conductivity experiments were carried out at room temperature by using an inLab 730 measuring cell and a Mettler Toledo SevenEasy conductivity meter. Dynamic light scattering (DLS) measurements were performed at a scattering angle of 90° with a device equipped with vertically polarized incident light (λ = 488 nm, 2 W argon ion laser, Coherent Inc., Santa Clara, CA) coupled to a digital correlator (ALV λ = 488 nm, 2 W argon ion laser, Coherent Inc., Santa Clara, CA) coupled to a digital correlator (ALV 5000E, ALV GmbH, Germany). DLS experiments were conducted with microemulsions containing all BZ reagents except ferroin (to avoid solution coloration) at a constant w = 18.3 and varying the volume droplet fraction. The samples were filtered with 0.2 μm PTFE membranes (Millipore Millipore Inc., USA), and the CONTIN method was used to obtain distributions of decay rates.22,23 The hydrodynamic radius (ϕh) was calculated from the measured diffusion coefficient using the Stokes–Einstein equation (D = kBT/6πηϕh), where D is the translational diffusion coefficient at zero concentration, kB is the Boltzmann constant, T is the absolute temperature, and η is the dynamic viscosity of octane. DLS experiments were all carried out at the same temperature as for spatially extended systems (T = 20 °C) to avoid temperature-induced percolation transitions.19,20

■ RESULTS AND DISCUSSION

At the percolation edge, the dynamics of the system differs from those explained before. Initially, Turing structures displayed as hexagonal arrangements of spots remain stationary only for a short period of time (around 20–30 min). This transition state gives way to a more complex dynamics (called oscillatory Turing patterns, OTP): each individual spot (Figure 1a) starts to move toward one of its closest neighbors until they reach a gap equal to half of the initial wavelength, λT/2 ≈ 0.13 mm (Figure 1b). At this particular moment, both spots stop and turn back, moving away each other as far as 3λT/2, the instant at which they repeat the same displacement cycle. (See movie 001 in the Supporting Information.) By performing a space-time plot of the described motion (Figure 1c), we observed that the system demonstrates a frequency of oscillation and also two characteristic wavelengths coexisting simultaneously. OTP also demonstrate that spots diameter remain unaltered the whole cycle (Figure 1c), in contrast with other reported oscillatory structures (breathing modes and oscillons) where the spots or stripes periodically fluctuate their size.10,21,24

The presence of multiple wavelengths has been proven through a 2D fast Fourier transform (FFT) at a given time. Thus, it exhibits two well-defined wavelengths (Figure 1d), simultaneously demonstrating that one spot may be separated λT/2 from some neighbors while 3λT/2 from others (result also evidenced through the space–time plot in Figure 1c), recalling that the effective distance among three spatially aligned neighbors in the OTP stage is constant and equal to 2λT (as in the early Turing phase). However, a more representative FFT reveals a bandwidth spectrum (Figure 1e) indicating that a single spot can be concurrently separated via multiple gaps from the neighbors but always inside the interval of accessible values (λT/2 < λ < 3λT/2). The oscillatory demeanor of the system has been confirmed by spectrophotometric measurements of the same BZ-AOT microemulsion under continuously stirred conditions (Figure 4a) by monitoring the optical absorption maxima of ferroin (510 nm).

Oscillatory Turing spots can be easily understood in 1D systems, where an array of spots is periodically oscillating in space and time. A spatial alteration in the activator domain in relation to the inhibitor region makes each individual spot asymmetric, inducing their spatial propagation to its neighbors.25,26 However, in the usual 2D experiments, Turing
structures appear, displaying a hexagonal configuration, which means that each spot is typically surrounded by six neighbors and, consequently, has three different directions in which to propagate. Experiments showed that spots typically randomly chose one route to oscillate, presenting periodic cycles in this direction without experiencing the other alternatives (as can be observed by the space–time plot in Figure 1). However, more intricate excursions are also possible, and we even observed spots that were able to follow circular trajectories with time (Figure 2a–d and movie 002 in the Supporting Information).

In this case, after the spot reached the minimum gap $\lambda/2$ with one neighbor, it did not return but moved closer to another "fellow" located in a different angular phase; the process is repeated until completing an entire rotation (anticlockwise in Figure 2a–d). The spot repeated the same gyration consecutively as can be observed by tracking its centroid (Figure 2e). The time required to complete the full cycle is 450 ± 50 s (Figure 2f), and this result is in agreement with the case where the spot oscillates only along one direction. The complexity of this phenomenon lies in the fact that the propagation direction of one spot is delimited by its neighbors, making the BZ-AOT system composed of multiple localized individuals, which are able to decide their sense of movement without any external control, in contrast to spots moving in a globally synchronized manner.

We remark that the destabilization of Turing patterns has been previously examined by various groups. De Wit and coworkers used reaction–diffusion (RD) models to demonstrate the OTP spatiotemporal signature. This mixed state arises in the vicinity of a codimensional-two Turing–Hopf bifurcation point, specifically under subharmonic Turing instabilities, where the dynamics exhibits two wavenumbers and one frequency of oscillation. They also reported the emergence of other mixed modes, experimentally demonstrated by De Kepper et al. using oscillatory redox reactions operated in open spatial reactors. Among the variety of spatiotemporal patterns is the superimposition of traveling waves over hexagonal spots. In this case, the wave motion does not alter the Turing mode as a result of weak interactions between both instabilities. Analogous dynamics were obtained by Epstein’s group in their studies of the symmetry-breaking instability interaction. We highlight their evidence of superlattice structures switching cyclically between different spatial–periodic patterns. The double periodicity (both in time and space) of the superlattice and the shift in wavelength each half period resemble the OTP dynamics with the exception that their spatial structures change their shape with time whereas OTP does not. Furthermore, Liu et al. accounted for the possibility that more complex spatiotemporal oscillating solutions could appear by considering the nonlinearity terms in the activator–inhibitor reactions under a pure Turing unstable domain.

Bearing in mind that the BZ-AOT microemulsion is a closed reactor (i.e., there is not an income of fresh reagents), the

Figure 2. Turing spot describing a circular trajectory. (a) Centroid (green dot) of the spot case of study (circled in green). (b–d) Centroid spot localization at consecutive times separated by 125 s in the sequence of colors (green, red, blue, and purple). Images display the actual and former spot’s centroid position in movie 002 in the Supporting Information. Frame size = 0.7 mm × 0.55 mm. (e) Journey of the spot’s centroid and (f) temporal excursion calculated through the Otsu algorithm. Initial reagent concentrations: [MA]₀ = 0.21 M, [H₂SO₄]₀ = 0.2 M, [NaBrO₃]₀ = 0.17 M, and [ferroin]₀ = 4 mM, with $\Phi_d = 0.59$.

Figure 3. Sparkling waves stage. (a–d) Consecutive snapshots taken every 5 s for two spots (highlighted by red arrows), increasing their size in a wavelike shape and posteriorly colliding with each other. Frame size = 0.6 × 0.5 mm². (e, f) Sequential images of sparkling waves’ spontaneous generation taken every 2 s. (Green circles help to visualize the location of interest). Frame size = 2.5 × 1.75 mm². (i) Space–time composition (time increasing upward) highlighting the generation of unprompted waves (encircled in green) and the collision of wavelike moving spots (red arrow) as a summary of the sparkling wave stage. Initial reagent concentrations: [MA]₀ = 0.21 M, [H₂SO₄]₀ = 0.2 M, [NaBrO₃]₀ = 0.17 M, and [ferroin]₀ = 4 mM, with $\Phi_d = 0.59$. 

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chemical concentrations changed during the course of the reaction. The reactants’ consumption is the main reason for the transient state of oscillatory Turing spots which, after remaining 20−30 min (the larger the volume fraction of the droplets, the shorter the time), evolve to another dynamics system henceforth called the sparkling waves stage (SW) until the “death” of the reaction. The spatiotemporal behavior of this stage can be summarized as follows: each individual spot expands and converts into an extended propagating wave by increasing its size, resembling pairs of spiral tips (Figure 3a−c and movie 003 in the Supporting Information), a phenomenon also manifested in an active network of biological single-celled organisms.42 In an attempt to produce the spatial oscillation previously described, the recently generated tips overcome the minimum stable gap between them (λT/2), colliding with each other (Figure 3d). The generation of multiple spirals, separated initially by a small distance (λT), produces via collisions numerous breakups close to the rotational tip of the spirals. This phenomenon, also known in the literature as “core breakup”,43,44 involves dynamics faster than those displayed previously in the system (Figure 4c) and constitutes one of the possible routes to a spatiotemporal chaotic-like scenario from outwardly rotating spiral patterns.45 Earlier, Vanag et al. observed this chaotic transition by working under different initial conditions where spiral waves continuously break into segments.46 Thus, the BZ-AOT system represents experimental evidence of multiple and natural breakups, a phenomenon enhanced during the last decades because it is considered to be the mechanism underlying heart fibrillation and is systematically analyzed by numerical stability analysis.47,48 Concurrent with core breakup, unprompted spots arise interstitially, filling the empty gaps by diffusing quickly as circular target patterns (Figure 3e−h). We called them sparkling waves due to the brightness of their spontaneous appearance (Figure 3h and the movie 004 in the Supporting Information) and the rapidity of their spatial expansion (Figure 3i). SWs appear in random places and require, according to experimental observances, blank spaces larger than λT. The impossibility to characterize spatial features between SWs makes us think that they originate from the underlying oscillatory behavior associated with the Hopf mode (Figure 4a). The unpredictable location of these interstitial pulsatile patterns contrasts with spots rhythmically oscillating 2π/3 out of phase with their closest neighbor in arrangements of intertwined hexagonal lattices. These patterns,
so-called “twinkling eyes”, were obtained by modeling RD systems with two layered samples and were explained in terms of the interaction between subharmonic Turing and Hopf modes.34,35

This particular dynamical evolution has been observed only close to the percolation threshold \((\Phi_d \approx \Phi_p)\), where DLS demonstrates changes in the distribution of nanodroplets. Thus, experiments carried out at \(\Phi_d = 0.24\), \((\Phi_d \ll \Phi_p\) where only Turing patterns appear) exhibit a main peak centered at around 3 to 4 nm (solid line in Figure 4d). However, as we reach the percolation \((0.575 < \Phi_d < 0.64)\) the distribution profile differs, displaying a bimodal distribution of nanodroplets (dashed line in Figure 4d). These two subsystems represent single droplets (a small subpopulation with the same size in the case of \(\Phi_d \ll \Phi_p\), 3 to 4 nm) coexisting together with a large number of nanodroplet clusters, one order of magnitude greater (peak centered around 20–25 nm). Bearing in mind that autocatalytic rate constants depend on droplet size,49 clusters can be considered a chemical subpopulation slightly different than droplets. Moreover, conductivity measurements around the percolation transition show values 10 times greater than in the nanodroplets regime (Figure 4b), although still lower in comparison to those obtained for volume fractions at \(\Phi_d \gg \Phi_p\).\(^{49}\) The increase in conductivity suggests, according to Kataoka et al.,\(^{50}\) an increment in the interchange of the water-soluble components between slowly diffusing clusters.

The presence of nanodroplet clusters in addition to the fast exchange of mass is not favorable to the ratio of effective diffusion coefficients required for the Turing instability,\(^{2,50}\) and therefore are assumed to be the main destabilizing factor of Turing patterns.

**CONCLUSIONS**

In this article, we present a system that is able to display the interaction between spatial and time-breaking symmetries by just adjusting the dilution of the nanocompartments where the initial reagents are encapsulated. Moreover, the rich variety of spatiotemporal behaviors expected in a bifurcation point is considerably increased by considering the consumption of the chemicals in a batch reactor. Thus, by increasing the volume droplet fraction of the BZ-AOT microemulsion, the system transits from stationary Turing structures to oscillations that are homogeneous in space, with both states corresponding to samples below and above the percolation transition. However, our experiments, performed at the onset of percolation, demonstrated more striking dynamics, such as the emergence of oscillatory Turing spots and sparkling waves.

The spatiotemporal oscillations of hexagonal structures can be understood as a consequence of the mixed state obtained in the bifurcation onset, such as the patterns exhibiting the wavelength corresponding to the Turing instability and oscillating with a frequency according to the Hopf mode. This behavior contrasts with that obtained at the end of the experiments, when individual spots transform into tips of spirals propagating along the system. The proximity between the spot-converted curls produces continuous collisions of the waves and spontaneous sparkling patterns in the remaining empty gaps. This dynamical stage is much faster than those observed in the previous steps and gives way to spatiotemporal chaotic patterns through the core-breakup mechanism.

The possibility to analyze the interaction between two different instabilities by just tuning the physical properties of the microemulsion confinement represents a new tool in the achievement of complex spatiotemporal dynamics that may emerge as a consequence of mixed modes, enhancing the employment of the BZ-AOT system for such a purpose.

**ASSOCIATED CONTENT**

Supporting Information

Movies of the experimental results explained in the article. (File 001) Movie displaying oscillatory Turing spots (Figure 1). (File 002) Spot describing a circular trajectory (Figure 2). (File 003) Spot increasing in size and transforming into a tip of a wave (Figure 3a–d). (File 004) Appearance of spontaneous waves (Figure 3e–h). This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

Corresponding Author

*E-mail: jorge.carballido@gmail.com.

Present Address

(J.C.-L.) Nonlinear Physical Chemistry Unit, Service de Chimie Physique et Biologie Theorique, Faculté des Sciences, Université Libre de Bruxelles (ULB), CP231, 1050 Brussels, Belgium.

Notes

The authors declare no competing financial interest.

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**REFERENCES**

Langmuir