Patterns in the Belousov–Zhabotinsky reaction in water-in-oil microemulsion induced by a temperature gradient

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We investigate the effect of changing temperature in the ferroin-catalysed Belousov–Zhabotinsky (BZ) reaction dispersed in the water nanodroplets of a water-in-oil aerosol OT (AOT) microemulsion, which undergoes a temperature-induced percolation transition at about 38 °C.

We observe stationary Turing patterns at temperatures in the range 15–35 °C and bulk oscillations at \( T = 40–55 °C \). When a temperature gradient \( \Delta T \) is applied normal to a thin layer of the BZ–AOT reaction mixture, the range of patterns observed is dramatically expanded. Anti-phase oscillatory Turing patterns, leaping waves, and chaotic waves emerge, depending on the temperature gradient and the average temperature. These new patterns originate from the coupling between a low temperature Turing mode and a high temperature Hopf mode. Simulations with a simple model of the BZ–AOT system give good agreement with our experimental results.

1. Introduction

The Belousov–Zhabotinsky (BZ) reaction\(^1\) is well established as the prototype system for studies of reaction–diffusion phenomena and pattern formation, not only in aqueous solution but also in a variety of more structured media such as gels\(^2\) or membranes.\(^3\) Studies in which the reagents of the BZ reaction are encapsulated in the water droplets of a water-in-oil aerosol OT (AOT) microemulsion\(^4\) (BZ–AOT system\(^5,6\)) have generated a rich variety of new patterns, e.g., Turing structures,\(^7\) standing and packet waves,\(^8\) segmented waves,\(^9\) dashed waves,\(^10\) and oscillons.\(^11\)

Light has been used to control patterning in photosensitive variants of the BZ–AOT reaction\(^12\) as well as to manipulate transitions between different dynamic regimes in other pattern-forming systems.\(^13,14\) Recently, temperature has been utilised to control pattern formation in the BZ–AOT system.\(^15,16\)

In addition to the expected changes in the reaction rate constants,\(^17–20\) in the BZ–AOT system temperature can induce changes in the physical properties of the microemulsion, specifically a percolation transition.\(^21–24\) Increasing the temperature causes individual spherical droplets dispersed in the continuous oil phase to form aggregates (clusters) of water nanodroplets, which, on further increasing the temperature, transform to dynamical water channels that form system-spanning networks. As the system passes through this percolation transition, the viscosity, electrical conductivity, and, what is most important for pattern formation, the diffusion coefficients of water-soluble molecules increase by several orders of magnitude.\(^25,26\) In Fig. 1 we show the measured dependence of the conductivity on temperature for an AOT microemulsion loaded with the BZ reactants used in our experiments.

The possibility of working on either side of the percolation phenomenon is intriguing from the point of view of pattern formation. Usually, Turing patterns are associated with a BZ–AOT microemulsion below the percolation transition, while waves or bulk oscillations are observed above this threshold. Controlling the temperature gives us the opportunity to explore these two different behaviours, stationary Turing structures and oscillations (Hopf instability), without changing the chemical composition of the BZ–AOT system under investigation.

In our two previous studies of temperature effects on the BZ–AOT system, we explored bathoferroin\(^15\) and the ruthenium tris-bipyridine complex\(^16\) as catalysts for the BZ reaction. Here, we use ferroin as a catalyst and, as a new element, we investigate the effect of a temperature gradient normal to the thin layer of microemulsion. Having two different temperatures at the two boundaries of the BZ–AOT

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Fig. 1 Temperature-dependence of conductivity of an AOT microemulsion loaded with BZ reactants (solid line) at \( \omega = 10 \) and \( \phi_d = 0.45 \). Concentrations of BZ reactants: [malonic acid] = 0.25 M, [H\(_2\)SO\(_4\)] = 0.17 M, [NaBrO\(_3\)] = 0.16 M, [ferroin] = 0.0042 M.
layer, at which two different patterns can occur, also gives us a connection to the problem of interacting instabilities or “two coupled layers,” which has been intensively studied recently.27 In our case, we have the opportunity to investigate “Turing + Turing” and “Turing + Hopf” interacting instabilities when these instabilities, and the patterns associated with them, arise at the opposite ends of our thin layer.

2. Experimental

Two stock microemulsions (MEs), ME1 and ME2, with the same molar ratio, \([\text{H}_2\text{O}]/[\text{AOT}] = \omega (= 18)\), and the same droplet volume fraction, \(\varphi_d (= 0.72)\), were prepared by mixing aqueous solutions of the BZ reactants and a 1.5 M solution of AOT in octane. For ME1, we used solutions of malonic acid (MA) and sulfuric acid, while for ME2 we used bромate and ferroin. The reactive microemulsion was obtained by mixing equal volumes of the two MEs and diluting the mixture with octane to the desired droplet fraction \((\varphi_d = 0.576)\). A small amount of the freshly prepared reactive ME was sandwiched between two flat thermostated horizontal windows of thickness 1 mm separated by a Teflon gasket of thickness \(h = 80 \mu\text{m}\), inner diameter 25 mm, and outer diameter 47 mm, so that the ME layer had thickness \(h\) and diameter 25 mm.

The two thermostated windows are parts of our thermostated reactor described in more detail elsewhere.15,16 The reactor consists of two chambers through which water is pumped continuously at the desired temperature from a temperature-controlled bath. Our initial experiments were carried out with a zero temperature gradient, i.e., both chambers of the reactor were connected to the same bath to give a uniform temperature in the reactor. To produce a temperature difference \(\Delta T\) between the top and bottom of the ME layer, the chambers were connected to different baths at temperatures \(T_1\) and \(T_2\), with the temperature in the upper bath, \(T_1\), greater than that in the lower bath, \(T_2\), in order to avoid possible hydrodynamic convection due to the temperature gradient.

Patterns were recorded with a CCD camera mounted on an Olympus-10 stereomicroscope, connected to a personal computer, where frames were acquired and processed with IMAGE PRO-PLUS software (Media Cybernetics).

Electrical conductivity measurements of MEs were recorded with a YSI 3200 conductivity instrument. Measurements of the radius of water nanodroplets by quasi-elastic light scattering were carried out with a DynaPro, Protein Solutions, High Wycombe, UK.

3. Results

All results reported are for a microemulsion with molar ratio \(\omega = 18\), droplet fraction \(\varphi_d = 0.576\), and the following concentrations of the BZ reactants in the aqueous phase: \([\text{MA}]_0 = 0.25\text{M}\), \([\text{H}_2\text{SO}_4]_0 = 0.17\text{M}\), \([\text{NaBrO}_3]_0 = 0.16\text{M}\), and \([\text{ferroin}]_0 = 0.0042\text{M}\). First, we consider the special case with \(\Delta T = 0\), where samples are held at the same temperature at both faces. Patterns obtained at \(\Delta T = 0\) should be helpful in understanding patterns that emerge at \(\Delta T > 0\).

A \(\Delta T = 0\)

Fig. 2 shows Turing patterns found at \(T = 15\text{°C}\) (Fig. 2a), and at \(T = 35\text{°C}\) (Fig. 2b), below the percolation transition. The characteristic wavelength, \(l_T\), of Turing patterns measured via an FFT (adjacent to the corresponding snapshot) is shown in Fig. 2c as a function of temperature. The Turing patterns typically arise after the system undergoes several bulk oscillations, and they occupy the entire reactor. These patterns remain stationary in time and space for 40 min or more and then slowly disappear. Separate experiments in a continuously stirred tank reactor with the same reactive ME reveal that a homogeneous BZ–AOT system of this composition demonstrates bulk oscillations (for example, at 15 °C the period of oscillation is 330 s). Thus, Turing–Hopf interaction in this reaction–diffusion system results in Turing patterns at \(T \leq T_{cr}\). More accurate experiments with a temperature step of 1 °C in the range 35–40 °C reveal that \(T_{cr} \approx 38\text{°C}\). The wavelength, \(l_T\), decreases as the temperature increases, with \(l_T/T_1 = 1.25\) (where \(T_2 = 15\text{°C}\) and \(T_1 = 35\text{°C}\)) (see Fig. 2c).

Above \(ca. 38\text{°C}\), the BZ–AOT system demonstrates bulk oscillations (BO), illustrated in the space–time plot in Fig. 3a. Increasing the temperature to the maximum value we employed (55 °C) results in no qualitative changes in the patterns observed, yielding only an increase in the frequency of oscillations (see Fig. 3b). An analogous increase in frequency has been observed for the standard BZ oscillator in aqueous solution.17

B \(\Delta T > 0\)

Fig. 4a is a parametric diagram in which we summarise the patterns found at temperatures \(T_1\) and \(T_2\) applied to two faces of the reactive layer. This diagram can be presented in various planes, e.g., \((T)–\Delta T\) (where the average temperature \((T) = (T_1 + T_2)/2\), or \(T_1–\Delta T\), or \(T_2–T_1\). We prefer the \(T_2–T_1\) plane, where it is clearly seen that new patterns emerge only when

![Fig. 2 Stationary Turing patterns in the BZ–AOT ferroin-catalysed system, with attached FFT at (a) 15 °C and (b) 35 °C. (c) Variation of Turing wavelength with temperature. Frame size = 2.7 mm × 2.7 mm.](image-url)
This calculation, we used the ratio of heat conductivities of our glass borosilicate window $\kappa_g = 1.12 \text{ W m}^{-1} \text{ K}^{-1}$ and of the microemulsion $\kappa_{ME}$, which we treated as a mixture of water and octane (oil) with known heat conductivities ($\kappa_w = 0.598 \text{ W m}^{-1} \text{ K}^{-1}$, $\kappa_{oil} = 0.145 \text{ W m}^{-1} \text{ K}^{-1}$). $\kappa_{ME} = \kappa_w \phi_w + \kappa_{oil} \phi_{oil}$, where $\phi_w$ and $\phi_{oil}$ are the volume fractions of water and oil, respectively. Note that the ratio of slopes in Fig. 4b (temperature gradient in glass/temperature gradient in ME) is equal to $\kappa_{ME}/\kappa_g$. Using $\kappa_g/\kappa_{ME} \approx 4$, we replotted the phase diagram (shown in Fig. 4a) using the actual temperatures $T_1'$ and $T_2'$ and present the result (Fig. 4c) in the plane $(T')-\Delta T'$, where $\Delta T' = T_1'-T_2'$ and $(T') = (T_1'+T_2')/2$. As can be seen in Fig. 4a and c, the BZ–AOT system exhibits several novel patterns when a nonzero temperature gradient is applied. Six different regions can be distinguished in the diagrams.

**Turing patterns** (diamonds in Fig. 4), similar to those found in the absence of a temperature gradient, appear when both the top and bottom temperatures lie below the percolation transition. Experiments with the largest normal gradient of temperature, accessible in the Turing regime ($15 \text{ °C}$ at the bottom and $37 \text{ °C}$ at the top), were carried out to establish how the Turing wavelength depends upon the boundary temperature. We find that the system exhibits the shortest wavelength accessible for the range of temperatures in the system, i.e., the wavelength associated with the higher temperature. Such complex Turing patterns as the “black eyes” or “white eyes” observed in experiments with two coupled layers were not obtained in our experiments. It is likely that the difference between the wavelengths of patterns found at temperatures $T_1$ and $T_2$ is too small and/or that the interlayer coupling is too strong for these phenomena to emerge.

**Bulk oscillations** (open squares in Fig. 4) occur when both temperatures are in the BO region, from $39 \text{ °C}$ to $55 \text{ °C}$. The period of oscillations found is the same as that observed in the BZ–AOT system. Anti-phase oscillatory Turing patterns (APOT, circles in Fig. 4). When the temperatures $T_1$ and $T_2$ are in the regions of bulk oscillations and Turing patterns, respectively, initial bulk oscillations give way to localised APOT patterns. Fig. 5 shows a typical pattern of this type with $(T) = 35 \text{ °C}$ and $\Delta T = 25 \text{ °C}$ ($T_1 = 47.5 \text{ °C}$, $T_2 = 22.5 \text{ °C}$). The patterns in Fig. 5a to c correspond to different phases of a full cycle of an APOT pattern. Fig. 5b is a half-period away from (a) and (c).
shows an anti-phase pattern. After an additional half-period (Fig. 5c), the original pattern [shown in (a)] is recovered. This APOT pattern can be better seen in the space–time plot shown in Fig. 5d, from which we can calculate the period of oscillation and the wavelength. These APOT patterns persist for the duration of the reaction and can occupy either a portion of the medium or the entire area.

APOT + Turing patterns (open triangles in Fig. 4). In some experiments, APOT patterns arise in a different way. First, Turing structures emerge in several localised areas. Then, APOT patterns appear between islands of Turing patterns, so that both types of patterns, APOT and Turing, coexist. This configuration is shown in Fig. 6, where both structures are observed to coexist for some time. Two consecutive oscillations (Fig. 6a and b) are presented to demonstrate that while the APOT oscillates, Turing patterns continue to grow until they eventually fill the entire reactor. Note that the wavelength of the Turing patterns is half of the APOT wavelength, which suggests that the Turing instability determines the wavelength of the oscillatory APOT patterns. An alternative explanation, that a wave instability is responsible for the anti-phase oscillatory patterns, as in the case of standing waves, can probably be excluded.

Leaping waves (LW) (black squares in Fig. 4) resemble the jumping waves (JW) recently discovered in the BZ–AOT system at high temperature. We introduce here a new term, leaping waves, to emphasise the difference between LW and JW. JW are relatively narrow and look somewhat like trigger waves, while LW are much broader and resemble standing waves or APOT patterns, except that LW move, while standing waves and APOT patterns remain fixed in space. Leaping waves are observed at temperature gradients with an average temperature in the range of the transition from Turing patterns to BO, around 40 °C. Fig. 7a shows a typical example of LW, a space–time plot is given in Fig. 7b. These waves seem to propagate via discrete jumps of about 270 μm, equal to the wavelength of the APOT structures. An initial wavefront begins to propagate, but it stops, and a separate parallel wave appears a short distance ahead of the first one. This new stripe-like wave expands both forward and backward, though at different velocities. Then, the original wave disappears and only the new one remains, until another new parallel wave front begins to propagate in the same direction as the original one. In a narrow region of the parametric diagram we observed the coexistence of LW and APOT patterns.

To better understand the behavior of LW, we show how to calculate some characteristics of the system in Fig. 7b. There

Fig. 5 Snapshots of anti-phase oscillatory Turing (APOT) patterns. Wavelength, $\lambda_{\text{APOT}} = 270 \pm 10 \mu m$. Period of oscillations = 240 s: (a) first APOT observed 600 s after initiation of the reaction, (b) 120 s after (a), (c) 240 s after (a). Frame size of snapshots is 4 mm × 3 mm. (d) Space–time plot of APOT for the cross-section shown in (a). Frame size = 2.5 mm × 500 s.

Fig. 6 Snapshots of APOT coexisting with Turing patterns at arbitrary time t (a) and t + 200 s (b), where 200 s is a half-period. $T = 35 ^\circ C$ and $\Delta T = 15 ^\circ C$. Wavelength of Turing structures, $\lambda_T = 130 \pm 10 \mu m$. Wavelength of APOT patterns, $\lambda_{\text{APOT}} = 270 \pm 10 \mu m$. Frame size = 4 mm × 4 mm.

Fig. 7 (a) Snapshot of leaping waves observed in the BZ–AOT system at $\langle T \rangle = 40 ^\circ C$ and $\Delta T = 5 ^\circ C$. (b) Space–time plot corresponding to the cross-section shown in (a). Velocity of waves $v_W = 11 \pm 1 \mu m s^{-1}$ (slope of yellow line), velocity of shock point $v_{\text{shock}} = 7.6 \pm 0.6 \mu m s^{-1}$ (slope of blue line), $v_{\text{shock}}$ [calculated as $v_W (T_B - T_W)/T_W$] = 0.81 μm s⁻¹, period of bulk oscillations $T_B = 87 s$, period of waves $T_W = 81 s$, period of leaps $T_L = 24 s$; $\lambda_L = 270 \mu m$, $\lambda_W = 900 \mu m$. Frame size = (a) 2.7 mm × 1.5 mm, (b) 1.25 mm × 450 s.
are two well differentiated wavelengths: the wavelength of the leap, $\lambda_L = 270 \mu$m (red lines in Fig. 7b), and that of the wave, $\lambda_W = 900 \mu$m. Moreover, we can distinguish between the period of the leap, $T_L$, and that of the wave, $T_W$, associated with the period between leaps and the time required to generate a new wave, respectively. The velocity of LW ($v_W$) can be calculated as $v_W = \lambda_W/T_W$ (yellow line). As LW coexists with bulk oscillations, a third period, $T_B$, is also relevant. The difference between the wave and bulk periods, $T_W < T_B$, results in the occurrence of a shock point, which moves (blue line) with velocity $v_{\text{shock}} = v_W(T_B - T_W)/T_W$.15

Chaotic waves (black triangles in Fig. 4). For some experiments carried out at $T > 15 ^\circ\text{C}$, the system displays two different types of behavior at different times. Initially, the system exhibits APOT (see Fig. 8a, where the interval between oscillations is $T = 170$ s). After a few oscillations, the system evolves to chaotic waves (Fig. 8b) and remains in this regime until the end of the experiment. Similar chaotic behavior is typically observed at the final stage of reaction for all our experiments in this closed system. The transition to chaos from a well defined APOT pattern can be seen in the space–time plot of Fig. 8c.

4. Simulations

To gain further insight into the patterns found in our experiments, we performed computer simulations, focusing on several questions: (i) is it possible to explain all patterns found (a) with a simple two-variable Oregonator-like36 model, (b) by treating only the diffusion coefficients as temperature-dependent? (ii) How do patterns depend on the temperature gradient and the thickness $h$ of the layer? (iii) What is the role of the profile of the diffusion coefficient across the layer?

As a first, natural assumption, we assume that the temperature varies linearly in the ME layer as $T(y) = T_2 + (T_1 - T_2)y/h$, where $T(0) = T_2$ and $T(h) = T_1$ and $y$ is the spatial coordinate perpendicular to the layer, with $y = 0$ at the bottom face of the layer. In general, we can estimate the reaction rate constants as a function of temperature using the Arrhenius form $k = A \exp(-E_a/RT)$, where $R$ is the gas constant and $T$ is the absolute temperature. The activation energy, $E_a$, is known for many of the BZ rate constants in aqueous solution,17,20 and we, in general, can adopt these dependences for the BZ–AOT system. However some of these $E_a$ have quite different values in different works and some may differ significantly between the BZ and BZ–AOT systems. Our own experiments (see Fig. 3) reveal that frequency of oscillations increases with temperature, approximately 2.5 times per 10 degrees. Since the actual temperature difference between bottom and top faces of the ME layer does not exceed 4–5 degrees, the change in frequency should not be larger than about a factor of 1.4. To take this effect into account in our simulations, we can vary any convenient parameter of the model to achieve the same effect. Our earlier work on the effect of temperature on patterns in the BZ–AOT system15,16 suggests, however, that the temperature-dependence of the diffusion coefficient is much more important, since we were able to simulate temperature-induced pattern formation by varying only the diffusion coefficients. Indeed, changes in temperature far from the percolation point do not affect the observed BZ–AOT patterns, though the frequency of oscillations does change. Only in the vicinity of the percolation transition, when the structure of the microemulsion and, as a result, the diffusion coefficients of water-soluble molecules change significantly, do we observe new dissipative patterns.

The diffusion coefficient, $D$, of water-soluble molecules may show a behavior different from the temperature-dependence of, e.g., the conductivity shown in Fig. 1. For example, one work suggests that as the temperature increases toward the percolation point, $D$ slowly decreases and then, after passing the percolation point, significantly increases, from $ca. 10^{-7}$ cm$^2$ s$^{-1}$ at $T = 25–30 ^\circ\text{C}$ (below the percolation transition) to $ca. 10^{-5}$ cm$^2$ s$^{-1}$ at $T = 40–55 ^\circ\text{C}$ (above the transition).25 Therefore, it is not straightforward to write down the correct dependence of $D$ on the coordinate $y$. We explore two dependences, linear, which is probably correct away from the percolation transition or if the percolation transition is smooth (see Fig. 1)

$$D = D_{\text{min}} + (D_{\text{max}} - D_{\text{min}})y/h$$

(1)

and “S-shaped,” which is more appropriate in the vicinity of a sharp percolation transition

$$D = D_{\text{min}} + (D_{\text{max}} - D_{\text{min}})y^n/(y^n + h^n/2^n)$$

(2)

where $D_{\text{min}}$ and $D_{\text{max}}$ are constants, $h$ is the thickness of the layer, and $n$ is a large number, for example, $n = 20$, which gives a nearly threshold dependence of $D$ on $y$ with the
threshold point at \( y = h/2 \) (in a real microemulsion, this point, if it exists, can be anywhere within the layer), and \( D = D_{\text{min}} \) on one side and \( D = D_{\text{max}} \) on the other side of the layer.

For simplicity, we use a two-variable Oregonator-like model explored earlier:\textsuperscript{16,37}

\[
\frac{\partial u}{\partial t} = \frac{(1-q)u^2}{q+u} + u(1-z_0)(e_1 + 1 - z_0) - \frac{u^2}{e} + d\Delta u \quad (3)
\]

\[
\frac{\partial z}{\partial t} = u(1-z_0)(e_1 + 1 - z_0) - z + \Delta z \quad (4)
\]

where \( u \) and \( z \) are the dimensionless concentrations of the activator (HBrO\textsubscript{2}) and the oxidised form of the catalyst (ferroin in our case), respectively; \( z_0 \) is the total dimensionless concentration of the catalyst; \( e_1 \) is a small positive parameter; all other parameters \( e, q, \) and \( f \) are as in the standard Oregonator model; \( d = D_U/D_Z, \) \( D_Z = 1, \) \( D_U \) is \( D \) taken from eqn (1) or (2); \( \Delta \) is the two-dimensional Laplacian \( (= \partial^2/\partial x^2 + \partial^2/\partial y^2). \) The simulations are carried out in a two-dimensional coordinate system, where the (horizontal) \( x \)-axis is parallel to the layer surface and the (vertical) \( y \)-axis is the coordinate along which the temperature gradient is imposed. The parameters of system (3), (4) are chosen in such a way that it exhibits Hopf or Turing instabilities depending on \( d \) (a linear stability analysis was performed to locate both instabilities). We worked only with supercritical Turing instability, which requires that \( f > 1 \) (see, for example, ref. 20).

Among many different sets of parameters employed, we have studied most thoroughly two sets of parameters: Set 1 is \( f = 1.1, q = 0.001, z_0 = 1/130, e_1 = 0.05, \) and \( e = 0.03. \) Set 2 is \( f = 1.1, q = 0.0007, z_0 = 1/100, e_1 = 0.1, \) and \( e = 0.2. \) For Set 1, the onset of Turing instability is at \( d \approx 0.41, \) while for Set 2, \( d \approx 0.52. \) Both values of \( d \) are surprisingly close to 1, given that in many other reaction-diffusion systems the ratio between the diffusion coefficients of activator and inhibitor must be less than 0.1 for the reaction to exhibit Turing instability. Since the critical value of \( d \) is close to 0.4-0.5, we varied \( D_{\text{min}} \) and \( D_{\text{max}} \) in the range 0.1-1. Note that in model (3), (4), the diffusion coefficient of the catalyst (a relatively large molecule), \( D_Z, \) is larger than \( D_U. \) This counterintuitive choice is justified by the fact that the catalyst \( Z, \) which plays the role of inhibitor in model (3), (4), assumes the features of the actual inhibitor, Br\textsubscript{2}, which indeed diffuses much faster in water-in-oil microemulsions than any water-soluble species that resides in the relatively large water nanodroplets. This result has been demonstrated mathematically elsewhere.\textsuperscript{38}

To integrate the partial differential equations, we employ the commercial software package FlexPDE,\textsuperscript{39} with a typical error (ERRLIM) of \( 1.0 \times 10^{-5} \) for each variable in each spatial cell, zero-flux boundary conditions and, in most cases, random initial perturbations around the steady states \( u_{\text{SS}} \) or \( z_{\text{SS}} \) \( z_0 = z_{\text{SS}}(1 + 0.01\text{Random}(1)) \). However, in some simulations we also utilised spatially periodic initial conditions, \( z_0 = z_{\text{SS}}(1 + 0.01\cos(n \pi(x/L_Z))) \) with \( n = 1 \) or 2, where \( \lambda_T \) is the wavelength of the Turing instability, found by linear stability analysis as \( \lambda_T = 2\pi/k_{\text{max}}, \) where \( k_{\text{max}} \) is the wavenumber corresponding to the maximum of the dispersion curve Re(\( \lambda \)) as a function of wavenumber \( k, \) and \( \lambda \) is the eigenvalue of the linearised model (3), (4).

![Fig. 9 Typical patterns found in 2D model (3), (4). Panels (a) and (b), IPOT (in-phase oscillatory Turing) patterns; panel (b) illustrates a possibility of IPOT + wave, which is seen by a small phase shift between neighboring red-green vertical stripes; (c1) and (c2), anti-phase snapshots of APOT patterns; (d)–(f), Turing patterns, (g) chaotic pattern. For patterns in this figure (except (b)), Set 1 of parameters, linear dependence of \( D \) on \( y \) (eqn (1)), and horizontal size \( L = 6d_T \) with \( \lambda_T = 2 \) are used, \( h = 0.2d_T \) for (a), (c), (d), and (g), \( h = 0.5d_T \) for (e) and (f); for (b), Set 2, \( L = 10d_T, \) \( \lambda_T = 5, \) \( h = 0.45d_T, \) linear dependence of \( D \) on \( y, \) \( D_{\text{min}} \) and \( D_{\text{max}} \) = 0.1 and 0.5 for (a), 0.3 and 0.45 for (b), 0.3 and 0.5 for (c), 0.1 and 0.4 for ((d and (e)), 0.1 and 0.8 for (f), and 0.2 and 0.6 for (g). Color vertical bar at the right is a key for colors: red corresponds to minimum concentration and dark blue to maximum of either catalyst or activator, patterns of which are almost identical in color presentation.

Our results are presented in Fig. 9–14. Typical patterns found are shown in Fig. 9. They are in-phase oscillatory Turing (IPOT) patterns (panels a and b of Fig. 9), anti-phase oscillatory Turing (APOT) patterns (panels c1 and c2), stationary Turing patterns (panels d, e, and f), and chaotic patterns (g). We do not attempt to characterise the chaotic spatial patterns more quantitatively. To illustrate the chaotic behavior, we show in Fig. 10 the kinetics of the activator \( u \) at two points separated in space by \( \lambda_T/2. \) In the top panel, at \( t < 100, \) we see chaotic behavior that transforms to APOT patterns at \( t > 100. \) The patterns we characterise as chaotic

![Fig. 10 Kinetics of activator \( u \) in model (3), (4) at \( x = 2L/8, y = h/2 \) and \( x = 3L/8, y = h/2, L = 6d_T = 12, \) parameter Set 1. Top panel: linear dependence of \( D \) on \( y \) (eqn (1)) is used at \( D_{\text{min}} = 0.2 \) and \( D_{\text{max}} = 0.8, h = 0.2d_T, \) initial chaos transforms to APOT patterns. Bottom panel: threshold dependence of \( D \) on \( y \) (eqn (2)) is used at \( D_{\text{min}} = 0.4 \) and \( D_{\text{max}} = 0.5, h = 0.5d_T, \) chaos.
maintain chaotic kinetics (bottom panel of Fig. 10) for much longer times ($t = 500–1000$, i.e., our entire period of observation).

Six phase diagrams in the $D_{\text{min}} - D_{\text{max}}$ plane (analogous, in a sense, to the experimental diagram in Fig. 4) are shown in Fig. 11. We can compare diagrams (c) and (d) (linear dependence of $d$ on $y$) as well as (e) and (f) (non-linear dependence of $d$ on $y$) to analyse how the height, $h$, of the layer affects patterns. By analysing the pairs of diagrams (a)–(b) (Set 2, $h = 0.3\lambda_T$), (c)–(e) (Set 1, $h = 0.5\lambda_T$), and (d)–(f) (Set 1, $h = 0.2\lambda_T$), we can extract information about the role of the dependence of the diffusion ratio, $d$, on $y$ in pattern formation, while a comparison of diagrams (c) and (d) as well as (e) and (f) can give us information about the role of the thickness, $h$, with different (linear and threshold) dependences of $d$ on $y$.

The main difference between the cases $h = 0.5\lambda_T$ (c) and $h = 0.2\lambda_T$ (d) is that IPOT patterns (crosses) are not found at $h = 0.5\lambda_T$. Comparing panels (e) ($h = 0.5\lambda_T$) and (f) ($h = 0.2\lambda_T$), we see almost the same behavior, with the exception that IPOT patterns are found at $h = 0.5\lambda_T$, but only in a very narrow region around $D_{\text{min}} = 0.3$. In our experiments, we also failed to observe IPOT patterns. Since a typical Turing wavelength of our experimental patterns is $0.15–0.17$ mm, and the thickness of our layer is $0.08$ mm, our experiments should correspond to the case $h = 0.5\lambda_T$ (where $\lambda_T$ is the Turing wavelength in computer experiments calculated by linear stability analysis and confirmed by simulated patterns). In both cases (e) and (f) at $h = 0.5\lambda_T$ we found hybrid patterns, Turing + APOT (pluses). These patterns are analogous to the experimentally found patterns shown in Fig. 6. We discuss these mixed patterns below. The regions of chaotic patterns (triangles) and APOT patterns (circles) are close to one other, or even superimposed, as in the experimental diagram in Fig. 4. The regions of Turing patterns and bulk oscillations are found in the lower left and upper right corners, respectively, again in agreement with Fig. 4.

In the pairs of panels (a)–(b), (c)–(e), and (d)–(f) of Fig. 11, we analyse how the dependence of the diffusion ratio $d$ on vertical position $y$ [linear (eqn (1)) or S-shaped (eqn (2))] affects patterning. Comparing these diagrams, we see that the shape of the function $d(y)$ affects the location of the various regions, but no new patterns emerge in pairs (a)–(b) ($h = 0.3\lambda_T$) and (d)–(f) ($h = 0.2\lambda_T$), as they do in the case of changing $h$. When $h = 0.5\lambda_T$ ((c)–(e)), a narrow region with IPOT patterns emerges. In addition, a region of “bulk” oscillations with a phase shift between the oscillations at the top and bottom faces of the layer (open triangles) emerges. If such patterns are viewed from above with the CCD camera, they should look like bulk oscillations (open squares), where the entire layer is homogeneous at any moment of time. In reality, though, the layer is not homogeneous in this regime.

In addition to the layer thickness, $h$, and the dependence of $d$ on $y$, the initial conditions are also important for pattern formation.
formation. The results presented in Fig. 11 were obtained with random initial conditions. However, if we use periodic initial conditions with wavelength $\lambda_T$ corresponding to IPOT or Turing patterns, as $z_0 = z_{SS}[1 + 0.01\cos(2\pi x/\lambda_T)]$, or with wavelength $2\lambda_T$ corresponding to APOT patterns, as $z_0 = z_{SS}[1 + 0.01\cos(\pi x/\lambda_T)]$, we find, respectively, IPOT or APOT patterns. For example, for panel (b) in Fig. 11, with $D_{min} = 0.3$ and $D_{max} = 0.4$, we obtain Turing + APOT patterns starting from random initial conditions, IPOT patterns with a spatial period for $z_0$ equal to $\lambda_T$, and APOT patterns with a period of $2\lambda_T$. Thus, at least three different patterns can occur at different initial conditions for the same set of parameters.

To analyse in detail how the patterns obtained vary with $h$, we performed a series of simulations with different layer heights, shown in Fig. 12 and 13. With $D_{min} = 0.3$ and $D_{max} = 0.45$ (Fig. 12), increasing $h$ produces the following sequence: IPOT, Turing + APOT, Turing, IPOT, and again Turing patterns. With $D_{min} = 0.1$ and $D_{max} = 0.5$ (Fig. 13), increasing $h$ gives Turing patterns, horizontally arranged stationary (Turing) patterns with small-amplitude oscillations, localised Turing patterns with bulk (and also localised) oscillations, and stationary (Turing) patterns. A special case of APOT patterns found at $h \approx 0.7\lambda_T$ is shown in Fig. 14, where red stripes (corresponding to low concentration of ferroin) periodically emerge at opposite sides of the layer.

These computer experiments imply that it is not only the ferroin periodically emerge at opposite sides of the layer.

Parameter Set 2, $L = 10\lambda_T$, $\lambda_T = 5$. (A) Turing patterns at $h = (0.2 - 0.3)\lambda_T$. (B) nearly stationary patterns with small-amplitude oscillations, $h = 0.35\lambda_T$, (C) three phases of localized Turing patterns plus bulk oscillations, $h = 0.5\lambda_T$. (D) stationary (Turing) patterns at $h = (0.6 - 0.8)\lambda_T$.

The analysis presented above demonstrates that the experimentally found patterns can be simulated by taking into account the dependence of $D$ on temperature. Let us consider what happens if instead $D$ is held constant and the kinetic parameters, $e.g., \varepsilon$ or $q$, are allowed to vary with temperature. The experimental dependence (Fig. 3) of the frequency of oscillation on $T$ can be fit by making $\varepsilon$ a decreasing function of $T$. Simulations show that in general it is possible to obtain many different patterns by varying only $\varepsilon(T)$. For example, for parameter set 2 at $D_{1} = 0.4$ and $h = 0.3\lambda_T$ we found stationary Turing patterns at $\varepsilon = 0.25$, IPOT patterns at $\varepsilon = 0.22$, chaotic patterns at $\varepsilon = 0.2$ and bulk oscillations at $\varepsilon = 0.18$, when the onset of Hopf instability was at $\varepsilon = 0.22955$. If, however, the range of $\varepsilon$ lies far above the Hopf instability, as in our experiments, only a single type of pattern can be obtained at constant $D = 0.4$, namely bulk oscillations. Therefore the temperature-dependence of $D$ appears to be necessary to simulate the experimental results. Taking into account both the dependence of $D$ and $\varepsilon$ on $T$ can certainly improve the quantitative agreement between experiment and simulations.

5. Discussion and conclusions

We have systematically analysed the effect of temperature gradients on pattern formation in the BZ–AOT
reaction-diffusion system both theoretically and experimentally. When a gradient is imposed in such a way that the temperature at the top puts the system into the Hopf domain while the bottom edge has a temperature at which Turing patterns are stable, then the entire layer can exhibit complex patterns, often consisting of hybrid structures, like APOT, IPOT, leaping waves and chaotic patterns. The key parameters that determine these patterns are the temperatures of the top and bottom layers relative to the transition temperature between Hopf and Turing modes, and the layer thickness $h$ compared to the Turing wavelength, $\lambda_T$.

Our APOT patterns appear to constitute the first clear experimental observation of anti-phase oscillatory Turing patterns. Most earlier oscillatory Turing patterns\textsuperscript{16,37} were in-phase oscillatory Turing patterns; however, those experiments pointed out that APOT patterns should exist in the BZ–AOT system.

The leaping waves found experimentally in a narrow range of parameters may be a modification of jumping waves or unstable APOT patterns that propagate into a homogeneous unpatterned region that exhibits only bulk oscillations. Our simple model (3), (4) is not able to reproduce this behavior, but a more sophisticated model (with $B_2$ as an additional fast-diffusing inhibitor) does generate JW.\textsuperscript{40}

The temperature gradient utilised in this work can be used for designing and engineering dissipative patterns by treating the system as two coupled layers.\textsuperscript{27–32} It is well known that a gradient of some physical quantity can give rise to pattern formation.\textsuperscript{41} In our case, a temperature gradient is used to initiate different patterns at opposite faces of the reactive layer. The interaction of these patterns results in new patterns. The high sensitivity of the patterns to the thickness of the layer might even be used for mechanical control of patterns if we can vary the thickness across the layer by applying a nonuniform force. This idea might be tested in experiments using a wedge-shaped layer. The possibility of using mechano-chemical dynamical systems, e.g., the BZ reaction in a hydrogel that expands and contracts in response to changes in redox potential, for practical applications has been discussed in the experimental\textsuperscript{32} and theoretical\textsuperscript{43} literature.

Finally, we note that the coupling between different patterns emerging at opposite ends of a reactive layer, which we have artificially introduced in our system via a temperature gradient, occurs naturally in experiments using continuously fed unstirred reactors, where many patterns have been discovered in such chemical systems as the chlorine dioxide–iodine–malonic acid,\textsuperscript{44} ferrocyanide–iodate–sulfite,\textsuperscript{45} and thiourea–iodate–sulfite\textsuperscript{46} reactions. It may prove enlightening to analyse such patterns from the point of view of coupled layers.

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References