Chemical waves in a continuously fed reactor: Numerical studies of the chemical pinwheel

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The Belousov–Zhabotinskii reaction in an annular gel reactor [Z. Noszticzius et al., Nature 329, 619 (1987)] is modeled by the reduced two-variable Oregonator with radial gradients in the concentration of bromate and malonic acid. This model is found to produce a wave shape and dispersion relation that are in satisfactory agreement with the experimental data. The numerical studies also reveal that the pinwheel dynamics can be understood in terms of the local chemistry in the reactor.

I. INTRODUCTION

During the last few years, continuously fed unstirred reactors (CFURs)1–5 have been developed to overcome the limitations of earlier experiments on the formation of chemical spatiotemporal structures. Those experiments,6 yielding spiral waves and concentric ring patterns (target waves), were conducted in closed systems. As a consequence, the systems evolved irreversibly towards thermodynamic equilibrium and any observed patterns were of a transient nature. CFURs overcome this problem; they can be maintained at a fixed distance away from equilibrium by the continuous feed of reagents so that spatiotemporal patterns can be sustained indefinitely. CFURs have made it possible to study the stability of spatial patterns and the transitions between well-defined states with different patterns.6–9

CFURs have also led to the observation of new spatiotemporal states, e.g., the chemical pinwheels. These structures are observed in the Belousov–Zhabotinskii reaction conducted in an annular gel reactor. In this reactor, an annular inert gel (polyacrylamide, inner radius 1.2 cm, outer radius 1.8 cm, thickness 0.6 mm) separates two continuously fed, stirred reservoirs. The reservoir in contact with the inner rim of the gel annulus is fed with malonic acid (0.1 M), sulfuric acid (0.24 M) and ferroin (0.006 M). The feeds to the outer reservoir are potassium bromate (0.1 M) and sulfuric acid (0.24 M). The purpose of the gel is to inhibit convective motion that interferes with the chemical patterns. A pacemaker, which can appear spontaneously or can be generated artificially (spot illumination or local chemical perturbation), sends out wave fronts in opposite directions. Left alone, these fronts travel half-way around the annulus, collide and annihilate. A chemical pinwheel is obtained by eliminating either the clockwise or counterclockwise fronts. (Further details of the experiments can be found in Refs. 1 and 5.) The number of waves within a pinwheel can be adjusted by changing the duration while the pacemaker is active. As expected, the wave speed decreases as the number of waves in the annulus is increased. (This relation between speed and period is known as the dispersion relation.) For instance, with 7 waves in the annulus the wave speed is 2.08 mm/min, while with 12 wave it is 1.69 mm/min.7

The aim of this paper is to provide an understanding of the characteristic features of the pinwheel, viz., the wave shape and the dispersion relation. In Sec. II we introduce a model of the Belousov–Zhabotinskii reaction in an annular gel reactor. This model is based on the two-variable Oregonator, also known as the Tyson–Fife model. We discuss the numerical treatment of the resulting spatially two-dimensional reaction–diffusion system. The results of our numerical studies are presented in Sec. III. This section also contains an analysis of the pinwheel in terms of the local chemistry. We conclude by summarizing our main results in Sec. IV.

II. MODELING CHEMICAL PINWHEELS

The thickness of the gel is small compared to its width and circumference; thus the reactor can be modeled as a spatially two-dimensional system. Experimental evidence suggests that the curvature of the reactor has, if any, only a minor effect on the wave features; we approximate the reactor by a rectangular strip with periodic boundary conditions on the short edges of the rectangle. We choose the length of the strip to be equal to the average circumference, i.e., 9.42 cm. The width of the strip is set equal to the difference between the outer and inner radius, i.e., 0.6 cm. On the sides that correspond to the inner and outer rim of the annulus, i.e., the long sides of the rectangle, we impose Dirichlet boundary conditions. We keep the values of the variables fixed at the values of the local steady state of the chemistry, i.e., the zeroes of the right-hand side of (1) and (2) with D = 0. This models the uniform feed of the inner and outer rim.
To model the chemistry in the gel reactor, we use Tyson and Fife's two-variable reduction of the Oregonator. This model has proven very satisfactorily in capturing the essential features of chemical waves in the Belousov–Zhabotinskii reaction and is given by the following two coupled reaction–diffusion equations:

\[ \frac{\partial u}{\partial t} = D \nabla^2 u + \frac{1}{\epsilon} [u(A - u) + fB(u - qA - u)/(qA + u)] \]
\[ = D \nabla^2 u + f(u,v), \quad (1) \]
\[ \frac{\partial v}{\partial t} = D \nabla^2 v + Au - Ru = D \nabla^2 v + g(u,v). \quad (2) \]

We have followed Vastano's scaling to be able to account for the gradients in the radial direction of the annulus, set up by the asymmetric feeds of the inner and outer reservoir. The variable \( u \) corresponds to the concentration of the bromous acid and \( v \) to the concentration of the oxidized form of the metal ion catalyst. The coefficient \( f \) is twice the stoichiometric factor \( h \) of the original three-variable Oregonator. The pinwheels observed in the experiment correspond to waves of oxidation in a reduced excitable medium. Values of \( h \) in the vicinity of 1.5 are representative for such a situation. The coefficient \( q \) is a combination of rate constants of the three-variable Oregonator, and \( \epsilon \) involves rate constants as well as the concentration of \( H^+ \). Since the feeds of the inner and outer reservoir both contain sulfuric acid, we assume that \([H^+]=0.312 \text{ M}^5\) and Tyson's "Lo" values for the Oregonator rate constants, we find \( \epsilon = 3.2 \times 10^{-2} \) and \( q = 2.002 \times 10^{-4} \), respectively.

In the Vastano scaling, the kinetic equations also include bromate (labeled \( A \)) and the organic substrate (labeled \( B \)). In the experiments, bromate is fed only to the outer reservoir, while malonic acid is fed only to the inner reservoir. Thus, we expect \( A \) and \( B \) to have gradients across the annulus. In numerical studies of well-stirred reactors, \( A \) and \( B \) do not vary much in one oscillation of the reaction. For the annular gel reactor this translates into the assumption that the gradients of \( A \) and \( B \) are solely determined by diffusion. Therefore we use a linear profile for the spatial variation in the concentration of \( A \) and \( B \) across the rectangular strip. Ideally we should require that \( A \) and \( B \) vary from the feed concentration at one rim to zero at the other rim. However, the Tyson–Fife model produces unphysical results in this case. To avoid these problems, Vastano set the values of \( A \) and \( B \) on the opposite boundary to one sixth of the feed values. In our spatially two-dimensional case it is necessary to choose these values to be one half of the feed concentrations; attempts to trigger waves with smaller values were unsuccessful. As in Ref. 3 and 12, we also impose a linear gradient on the stoichiometric factor \( h \), since it depends on the ratio of malonic acid to brominated malonic acid. In our numerical simulations, \( h \) varies from 1.5 to 1.55. A simulation with a larger gradient in \( h \), from 1.4 to 1.6 was conducted; the wave speed changed by less than 1% and no significant change in the shape of the waves was observed.

The value of the parameter \( q \) poses a problem for numerical studies, as noted by Jahnke, Skaggs and Winfree. If the value corresponding to Tyson's Lo values of the rate constants is used, the computer time necessary to integrate the equations becomes too long. To avoid this problem, Jahnke et al. raised \( q \) by a factor of 10. We have followed their procedure and used \( q = 3.5 \times 10^{-3} \) in our numerical studies. We find that the wave speeds obtained with this modified value of \( q \) are in satisfactory agreement with the experimental values. In contrast, waves obtained with the Lo value of \( q \) have speeds that are 30% higher than those with the modified value, which is a larger discrepancy with the experiment. Since the Tyson–Fife model is a highly reduced model of the Belousov–Zhabotinskii chemistry, it is clearly inappropriate to insist on the use of an "exact" value of \( q \), if modifications of this parameter value produce a more satisfactory agreement with experimental results.

Due to the smallness of \( \epsilon \), the variables \( u \) and \( v \) evolve on different time scales, in other words, the equations are stiff. We solve the reaction–diffusion equations (1) and (2) numerically by Euler's method, as advocated by Lugosi and Winfree. The use of a stiff integrator for the kinetics provides no advantage for the case of spatially extended systems, since every stage of the stiff kinetics will be present at some point in the system; the integrator would thus always choose the smallest time step for integration. We also note that the primary source of stiffness is the reaction term and not the discretized diffusion operator. It is thus unnecessary to use an implicit method for the diffusion term; the time step required to integrate the reaction part of the equation accurately is small enough to ensure numerical stability for the diffusion part. The time step used in our integrations was 0.001 time units.

The waves in the chemical pinwheel, for experimental conditions of Ref. 1 and similar ones, are identical and evenly spaced. We take advantage of this symmetry for our numerical studies; we divide the length of the strip by the number of waves to be studied and impose periodic boundary conditions on the sides parallel to the short sides of the rectangle for each subdivision. There will be only one wave in each subdivision. In this way, the numerical integration has to be carried out for a smaller spatial region, which improves the accuracy and speed of the computations. (Clearly, symmetry breaking in a chemical pinwheel cannot be studied in this way. Preliminary studies of this phenomenon have been conducted by our collaborators in Bordeaux.) For instance, in the case of eight waves in the reactor we divide the total length of 9.42 cm by eight and study a subdivision of 1.775 x 0.6 cm with only one wave in it. We impose a spatial grid of 100 x 50 points on this subdivision. For different number of waves, we vary the mesh size such that the length of every mesh interval, measured in centimeters, remains constant. In other words, the spatial resolution is the same for all pinwheel states. For example, in the case of four waves the subdivision is 2.355 x 0.6 cm and a grid of 200 x 50 points is used. The spatial derivatives were approximated by second-order differencing on the spatial grid and the result-
The system of equations was integrated on the Cray XMP of the University of Texas Center for Higher Performance Computing.

III. RESULTS

To generate a pinwheel in the numerical simulations, we mimic the experimental procedure. A pacemaker is created by setting the variables $u$ and $v$ at a point in the middle of the strip to a value beyond the excitability threshold, while at all other points the variables are set to the local steady state, given by $f(u,v) = 0$ and $g(s_1,u) = 0$. This initial condition produces an oxidation front as shown in Fig. 1(a). The front travels to the outer rim of the reactor and then splits into two fronts moving in opposite directions, see Fig. 1(b). If the fronts are left alone, they will collide with each other, due to the periodic boundary conditions on the short sides of the rectangle, and annihilate. Thus one of the fronts has to be destroyed, as in the experiment. In the numerical simulations this is done by replacing one front with the values of the local steady state. As a result, a single front moves around the strip, the subdivision to be precise, with constant velocity, see Fig. 2. The shape of the wave is in good agreement with experimental observations. The wave speed is determined by counting the number of time steps necessary for the absolute concentration maximum to move from one grid point to the next. With the above choice of parameter values, we obtain a speed of 2.29 mm/min for sixteen waves in the reactor. For a pinwheel with eight waves we find a speed of 2.53 mm/min. The agreement between numerical and experimental values of the wave speed is quite satisfactory for such a highly reduced model as the two-variable Oregonator. To obtain the wave speed as a function of the number of waves in the reactor is equivalent to determining the relation between speed and period, i.e., the dispersion relation. The dispersion relation for the numerical simulations is shown in Fig. 3. We see that for small periods, i.e., large number of waves, the velocity decreases significantly. This result agrees qualitatively with experimental observations, though quantitatively the change in wave speed is greater in the experi-
ment: from 1.69 mm/min for 12 waves to 2.08 mm/min for 7 waves.

Previous studies have been shown that chemical waves are essentially due to the local, excitable kinetics of the medium. We will now show that this is also true for chemical pinwheels; their essential features are determined by the local chemistry. We define a local description in the following way: Consider a spatially one-dimensional system whose value of \( A, B, \) and \( f \) corresponds to their respective value at a particular radius \( r \) in the annular gel reactor. The wave in such a system is called the local plane wave at radius \( r \). We solve numerically the spatially one-dimensional version of (1) and (2) to determine the front height, the maximum value of \( u \), and the wave speed of the local plane wave. We call these values the local plane front height, \( u_{\text{max}}(r) \), and the local plane wave speed \( c(r) \).

In Fig. 4 we compare the local plane front height with the maximum value of \( u \), at a given radius, for the pinwheel wave. Note that over much of the width of the wave region, the latter value is very close to the local plane front height. The exception is the vicinity of the outer and inner rim. Here the boundary conditions at the rims, which the local plane wave cannot fulfill, come into play: The sudden decrease at the outer rim is due to the fixed boundary conditions imposed here. Towards the inner rim is a region where the local description has kinetics that are not excitable and no waves can propagate.

We have shown that the height of the wave is essentially determined by the local chemistry of the system. We will now show that the same is true for the wave shape. The experiments show that in the long time limit the entire wave front propagates without distortion through the system. Imposing this condition generates a relation between the local normal velocity of the wave front, \( N(r) \) and the shape of the wave front. This relation follows from simple geometric considerations. In a chemical wave front, each portion of the front moves normal to the front at a speed determined by the local plane wave speed and the local curvature, \( N(r) = c(r) + DK(r) \). The local curvature \( K(r) \) is typically a small quantity and the curvature term can be neglected, except near cusps in the wave front or near the core of a spiral wave. For the Belousov–Zhabotinskii reaction in the annular gel reactor, the curvature term will become important for a radius of curvature smaller than about 60 \( \mu \)m, see also Ref. 11. Such a situation does not arise in the pinwheel waves and it is therefore legitimate to approximate the local normal velocity by the local plane wave velocity, \( N(r) \approx c(r) \), which considerably simplifies the treatment.

The physical mechanism by which the front propagates without deformation can now be understood by referring to Fig. 5. For the velocity profile shown at left, the front has reached its long time asymptotic shape. While the pieces of the front near the leading edge move faster than the pieces on the flanks, they have further to go in order not to deform the front. A close up view of a small section of the front is shown in Fig. 6. The whole front is moving in the \( x \)-direction with velocity \( c_0 \), while the small portion of the front shown, is moving with a velocity \( c(r) \) in a direction normal to its front. For a given value of \( r \), the front is located at a position \( x = f(r,t) \). The angle between the tangent to the front and the direction of gradient in the velocity (the \( r \)-axis) is defined as \( \theta \), which is also the angle between the displacements \( c_0 \Delta t \) and \( c(r) \Delta t \).

From the leftmost of the right triangles in the figure, we obtain
\[
c(r) = c_0 \cos[\theta(r)] ,
\]  
while from the other right triangle, we find
\[
dr = \cos[\theta(r)] \sqrt{\frac{df}{dr}}\cdot dr.
\]  
Eliminating \( \cos(\theta) \) from Eqs. (3) and (4), we obtain the following differential relation between \( f(r) \) and \( c(r) \).
FIG. 6. An expanded view of a part of the wave front, showing the front position \( f(r,t) \) at time \( t \), and then a short time \( \Delta t \) later. Note that the direction of propagation is vertical in this figure.

\[
c(r) = c_0 \sqrt{1 + (df/dr)^2},
\]
or, equivalently,

\[
df/dr = \pm \sqrt{\left( \frac{c_0}{c(r)} \right)^2 - 1}.
\]

Note that since the wave shape profile \( f(r) \) is a real function, \( c_0 > c(r) \), and \( c_0 = c(r) \) only where \( df/dr = 0 \), that is, at the leading edge of the wave front. Also, at values of \( r \) where the wave speed goes to zero, \( df/dr \) becomes singular. Specifically, as \( c(r) \to 0 \), \( |df/dr| \to \infty \), so that the wave front will asymptotically approach that value of \( r \), but not reach it. Meanwhile, it will be trailing out indefinitely far in the direction opposite to the direction of propagation, resulting in very long tails of the wave. In our model, these tails are truncated: The wave branch becomes unstable before reaching the point at which \( c = 0 \), so that the front will not persist in regions where \( c \approx 0 \).

To obtain the wave shape \( f(r) \), we can integrate Eq. (5) with respect to \( r \):

\[
f(r) = f(r_0) \pm \int_{r_0}^{r} \sqrt{\left( \frac{c_0}{c(r)} \right)^2 - 1} dr.
\]

Since this equation was formulated directly for the asymptotic state, the long-time limit, it contains no dynamics. Thus it is not possible within the framework of this treatment to determine which of the “plus” or “minus” solution is stable. Using a time evolution method, we find that the plus solution generates the dynamically stable wave front shape.

To simplify Eq. (6), choose \( r_0 \) to be at the maximum of \( c(r) \), i.e., at the leading edge, and set \( f(r_0) = 0 \). Then Eq. (6) becomes

\[
f(r) = \int_{r_0}^{r} \sqrt{\left( \frac{c_0}{c(r)} \right)^2 - 1} dr.
\]

Since the local wave speed profile is available only numerically, this expression must be evaluated numerically. The shape given by Eq. (7) is shown in Fig. 7 and agrees well with the results from the two-dimensional numerical simulations, except near the boundaries. Discrepancies near the inner and outer rim are again due to the fact that a local description cannot account for the boundary conditions there.

The good agreement of the wave shape predicted by the local description with that of the full two-dimensional simulation and of the experiment shows that the local chemistry dominates the behavior. The essential features of pinwheel waves can indeed be understood by the local picture adopted above, namely, each piece of the front propagates normal to the front with a velocity that is determined by the local concentration of bromate and malonic acid and that is little affected by diffusion tangential to the front.

IV. CONCLUSIONS

We have shown that the reduced two-variable Oregonator, the Tyson–Fife model, can successfully describe a new spatiotemporal structure of the Belousov–Zhabotinskii reaction, namely the chemical pinwheel observed in an annular gel reactor. Our results establish that this structure belongs to the same category of patterns as the target and spiral waves. Indeed, the essential features of pinwheel waves can be understood in terms of the local chemistry of the system, as is the case for the other chemical wave phenomena. The spatial variations of the excitability of the medium, due to gradients of bromate and malonic acid, can account for the shape of the wave. The calculated dispersion relation also agrees qualitatively with the experimental data.

FIG. 7. The fronts as obtained from the local velocities (dotted line) and from the 2D simulation (solid lines). Fronts have been offset by an arbitrary amount for ease of comparison.
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7N. Kreisberg (private communication). The conditions studied in this paper correspond to current experiments and differ somewhat from those of Ref. 1.
13The Vastano scaling is based on the Oregonator scheme (Refs. 9 and 10):

\[ A + W \rightarrow U + P, \quad U + W \rightarrow 2P, \quad A + U \rightarrow 2U + 2V, \quad 2U \rightarrow A + P, \]

\[ B + V \rightarrow hW, \] where \( A = [\text{BrO}_3^-] \), \( B = [\text{organic species}] \), \( V = [\text{Fe}^{3+}] \), \( U = [\text{HBrO}_2] \), \( W = [\text{Br}^-] \), \( P = [\text{HO}_2^-] \), and \( h \) is the stoichiometric factor, and corresponds to:

\[ u = (2k_5/k_2) U, \quad v = (k_6/(k_5^2)) V, \]

\[ w = (k_5/k_2) W, \quad e = k_7/k_5, \quad \epsilon' = (2k_5/k_3^2/k_7), \quad q = (2k_5/k_3^2), \]

\[ f_0 = 2k_0, \quad f_1 = k_0, \quad f_2 = 2k_0^2/k_1, \quad f_3 = 4k_0^2/k_1^2, \quad f_4 = 2k_0^3/k_1^3. \]

The unscaled value of the diffusion coefficient is chosen to be \( D' = 2 \times 10^{-5} \text{cm}^2/\text{s} \). Note that the Vastano scaling simplifies the kinetic equations by identifying the relevant combinations of rate constants, but that it does not nondimensionalize them. We work with dimensioned quantities in our numerical integrations; space is in cm.

18Since an exhaustive search of the parameter space (\( \epsilon, \alpha, \) gradients of \( A, B, \) and \( f \)) is very time consuming, it was not deemed worthwhile for such a highly reduced model to make a systematic attempt at optimizing the quantitative agreement between the experimental and theoretical values of the wave speeds.