

# Oscillations and waves in the Belousov–Zhabotinskii reaction in a finite medium

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Received 9 August 1993

Travelling reaction-diffusion waves are considered in a finite medium. The model considered is a simplified model of the Belousov–Zhabotinskii reaction, described mathematically by the two-variable Oregonator. A one-dimensional problem consisting of three regions is considered. Regions I ( $x \leq 0$ ) and III ( $x \geq 1$ ) act as reservoirs with fixed concentrations of the reactant X (the autocatalyst, hypobromous acid ( $\text{HBrO}_2$ )), where the concentration of X in regions I and III may be different. Region II represents a catalyst-loaded membrane, within which species X can diffuse while species Z (the oxidized form of the metal-ion catalyst ( $\text{Ce(IV)}$ )) is fixed spatially. The large time behaviour of the system is considered and both stable steady states and periodic spatio-temporal structures are seen.

## 1. Introduction

In this paper the reduced two-variable Oregonator model for the Belousov–Zhabotinskii (BZ) reaction [1,2] is considered. This model was used previously to discuss the initiation and propagation of reaction-diffusion waves travelling along membrane interfaces in the Belousov–Zhabotinskii reaction by Leach et al. [3]. The work described in detail in [3] was motivated by the recent experimental observations reported by Showalter and his co-workers, see, for example, Winston et al. [4]. Here the metal-ion catalyst ( $\text{Ce(IV)}$ ) in the BZ reaction is immobilized in gel form within a Nafion membrane, inhibiting the passage of the ionic species, and the whole is bathed in a solution of the other reactants. Thus the reaction can take place only along the interface between the membrane and the surrounding solution.

The present paper is a preliminary numerical investigation of a new experimental configuration. The reaction system under investigation here consists of three regions. Regions I and region III are essentially inert and act only as reservoirs with fixed concentrations of the reactant X (the autocatalyst, hypobromous acid ( $\text{HBrO}_2$ )), where the concentrations of X in regions I and III may be different. The

reaction is confined to region II which represents a catalyst-loaded membrane, within which species X can diffuse while species Z (the oxidized form of the metal-ion catalyst) is fixed spatially in the form of a gel. It is assumed that the reservoir regions I and III are sufficiently large and well-stirred so that the very small loss of Z across the reservoir-membrane interfaces into these regions does not alter the concentration of X there. A one-dimensional model is considered, with the concentrations  $u(x, t)$  and  $v(x, t)$  of autocatalyst X and the oxidized form of the metal-ion catalyst Z, respectively, being the dependent variables and where the coordinate  $x$  is normal to the interfaces. Region II is scaled so that it is a finite region of unit length extending over the range  $0 \leq x \leq 1$ . Under such scalings the equations for the reduced Oregonator become, from [3],

$$\varepsilon \frac{\partial u}{\partial t} = D \frac{\partial^2 u}{\partial x^2} + u(1 - u) + f \frac{(q - u)}{(q + u)} v, \quad (1a)$$

$$\frac{\partial v}{\partial t} = u - v \quad (1b)$$

in  $0 \leq x \leq 1$ ,  $t \geq 0$ , with boundary conditions

$$\left. \begin{array}{l} u = u_0 \quad \text{on} \quad x = 0 \\ u = u_1 \quad \text{on} \quad x = 1 \end{array} \right\} t \geq 0, \quad (2a)$$

and initial condition

$$u = v = 0 \quad \text{in} \quad 0 \leq x \leq 1 \quad \text{at} \quad t = 0. \quad (2b)$$

Equations (1) have been made dimensionless in essentially the same way as described in [3] except that here we use  $l$ , the width of the membrane, as the scale for the space co-ordinate  $x$ . This leads to the extra non-dimensional parameter  $D$  (the diffusion parameter), which is given by

$$D = \frac{D_x}{k_5 A l^2}, \quad (3)$$

where  $D_x$  is the diffusion coefficient of autocatalyst X and where  $k_5$  is the rate constant which determines the rate of production of Z in the Oregonator model. This diffusion parameter is considered small.

Equations (1) contain three other non-dimensional parameters, namely  $q$ ,  $\varepsilon$  and  $f$  (as defined in [3]). The parameter  $q$  is thought to be small (we take  $q = 0.0008$  throughout). The parameter  $\varepsilon$  is generally taken to be small and certainly within the range  $0 < \varepsilon \leq 1$ , while the parameter  $f$  can take all (positive) values. The remaining two parameters  $u_0$  and  $u_1$  are non-dimensional (constant) concentrations of the autocatalyst on the boundaries  $x = 0$  and  $x = 1$ , respectively.

The two-variable Oregonator model in a well-stirred system is given by eqs. (1) with the diffusion term put to zero. This system has two, physically acceptable, (i.e. non-negative) stationary states  $(u_s, v_s)$  given by

$$u_s = v_s = 0, \tag{4a}$$

$$u_s = v_s = \frac{1}{2} \left\{ 1 - (f + q) + \sqrt{(f + q - 1)^2 + 4q(f + 1)} \right\}. \tag{4b}$$

Stationary state (4a) corresponds to the initial conditions for the unreacted state and is a saddle point (and thus unstable) for all parameter values. Stationary state (4b) can be both stable and unstable with Hopf bifurcations occurring at the change of stability. The conditions for which are given parametrically by

$$\varepsilon = 1 - 2u_s \left( 1 + \frac{fq}{(q + u_s)^2} \right), \tag{5}$$

## 2. Numerical results

The initial-boundary value problem given by eqs. (1) and conditions (2) was solved numerically using essentially the same method as used to solve the initial-value problem described by Leach et al. [3], this method being based on the scheme used by Merkin and Needham [5].

The numerical scheme is a modified Crank–Nicolson method, in which the derivatives in the  $t$ -direction are replaced by forward differences and all the other terms averaged over the time-step from  $t$  to  $t + \Delta t$ . This results in two coupled ordinary differential equations in  $x$  which are then differenced using central differences. The resulting sets of nonlinear algebraic equations are solved by Newton–Raphson iteration, a process which was found to converge very quickly for the present problem.

In the numerical results presented below, the parameter  $q$  was fixed at  $q = 0.0008$ , which is sufficiently small to allow both single travelling waves and wave trains to be observed. The parameters  $u_0$  and  $u_1$  (the dimensionless concentrations of the autocatalyst on the reservoir membrane boundaries at  $x = 0$  and  $x = 1$ , respectively) were fixed at the same values,  $u_0 = u_1 = 1.0$  for most of the calculations. This value can be chosen arbitrarily, since there is no minimum value of the autocatalyst on the boundary below which travelling waves are not initiated, as was shown in Leach et al. [3]. However the magnitude of the non-dimensional concentration of the autocatalyst on a boundary does have a weak effect on the time scale over which travelling waves are first seen. When  $u_0 = u_1$ , the solution in the finite region  $0 \leq x \leq 1$  is symmetric about  $x = \frac{1}{2}$ . However, for  $u_0 \neq u_1$  a wave will be initiated from the boundary with the larger concentration of the autocatalyst before a wave is initiated from the other boundary. Consequently the point of collision of the two waves will no longer be at  $x = \frac{1}{2}$ , but will be shifted slightly towards the boundary with the lower autocatalyst concentration.

The parameter  $D$  is considered small ( $D \ll 1$ ), ensuring that there are boundary-layer regions in the membrane (region II) at the interfaces with the reservoirs of

thickness of  $O(D^{1/2})$ . In the results presented below two values of  $D$  are considered, namely  $D = 0.001$  and  $D = 0.00001$ . Decreasing the value of  $D$ , allows a larger number of waves in the wave train to be observed clearly. The values of the parameters  $\varepsilon$  and  $f$  are chosen so as to illustrate the distinct types of behaviour encountered.

Firstly, consider values of the parameters  $f = 0.4$ ,  $\varepsilon = 0.3$  and  $D = 0.001$ . These values exemplify the situation where stationary state (4b) is stable, ( $u_s = v_s = 0.60106$ ). Figure 1 shows the situation after sufficient time has elapsed for the solution to have settled down to a steady state. The initial development in this case shows two travelling waves, one emerging from each boundary-layer region close to the membrane-reservoir interfaces and converting the initially unreacted state to the stable fully reacted stationary state (4b) as they travel towards the centre. These waves then collide at the centre and leave behind the steady state shown in fig. 1, with the concentrations of both X and Z being equal. No further time-dependent behaviour is generated.

Next, consider values of the parameters  $f = 1.0$ ,  $\varepsilon = 0.3$ . In this case stationary state (4b) is unstable and only wave trains are observed in the reaction-diffusion system. Although, this value of  $\varepsilon$  is somewhat larger than is generally regarded as being physically realistic for the BZ reaction, this choice of  $\varepsilon$  exemplifies the features of the wave profiles. It allows a large number of waves to be depicted clearly in the wave trains for the expenditure of a reasonable amount of computational effort. A more physically realistic value for  $\varepsilon$  (say  $\varepsilon = 0.05$ ) requires much larger amounts of computational effort to generate the wave profiles due to the much increased wave speed.

Figure 2 illustrates a sequence of profiles of the autocatalyst concentration  $u$  plotted against  $x$ . The data was sampled after a substantial time had elapsed, allowing the transitory behaviour to die out and ensuring that any non-steady behaviour

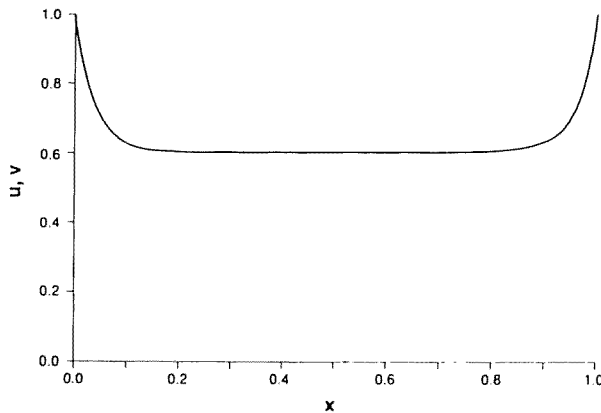


Fig. 1. Concentration profile of  $u$  and  $v$  plotted against  $x$ , for  $\varepsilon = 0.3$ ,  $f = 0.4$ ,  $D = 0.001$ ,  $q = 0.0008$  and  $u_0 = u_1 = 1.0$ .

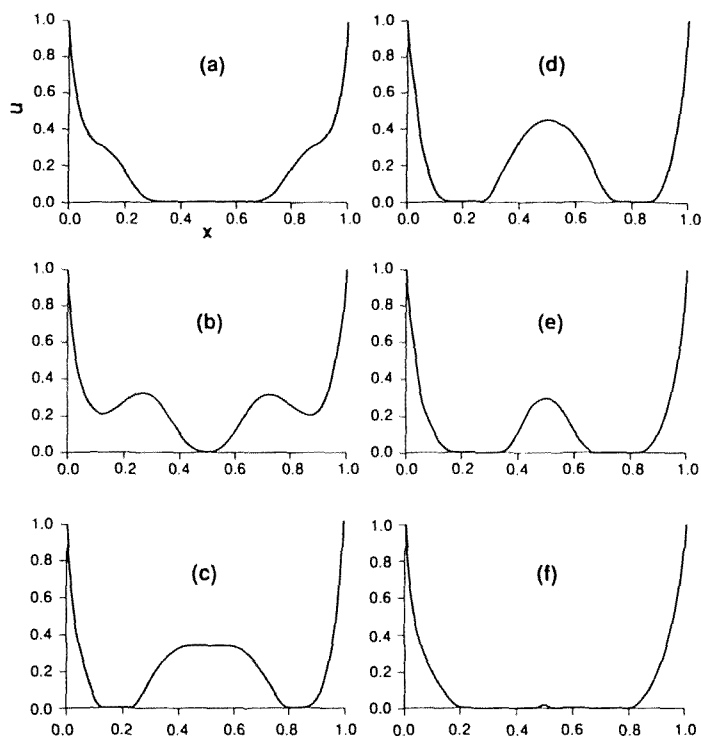


Fig. 2. Concentration profiles of  $u$  plotted against  $x$ , for  $\varepsilon = 0.3, f = 1.0, D = 0.001, q = 0.0008$  and  $u_0 = u_1 = 1.0$ .

was truly repetitive. Figure 3 illustrates the corresponding sequence for concentration  $v$  (sampled at the same times as the sequence in fig. 2). Fig. 2(a) shows the waves just being born from the boundary-layer regions, with fig. 2(b) showing the waves starting to become detached from the boundary-layer regions. Ahead of these waves the medium is excitable allowing both waves to travel towards the centre of the region. Figures 2(c)–(f) then show in sequence the collision at the centre and the final collapse of the waves, leaving the region at first refractory to further excitation at the rest state  $u = q$ . The finite region then gradually recovers excitability ready for the whole process to be repeated. Note that behind the waves the concentration of  $u$  sharply decreases to a value close to  $q$ , while the structure of  $v$  (fig. 3) is much more ramp-like. This whole process is repeated on a (non-dimensional) time period of  $t = 5.39$ , being made up of times  $t = 3.80$  in the active state and  $t = 1.59$  in the rest state.

On decreasing the parameter  $D$  the structure of the travelling waves can be seen more clearly. Figure 4 illustrates this by displaying a sequence of concentration profiles of  $u$  plotted against  $x$ , again after the transients had died out, for  $\varepsilon = 0.3$  and  $f = 1.0$  but now with  $D = 0.00001$ . Figure 4(a) shows a pair of wavetrains of increasing amplitude generated from the boundary-layer regions (which are now

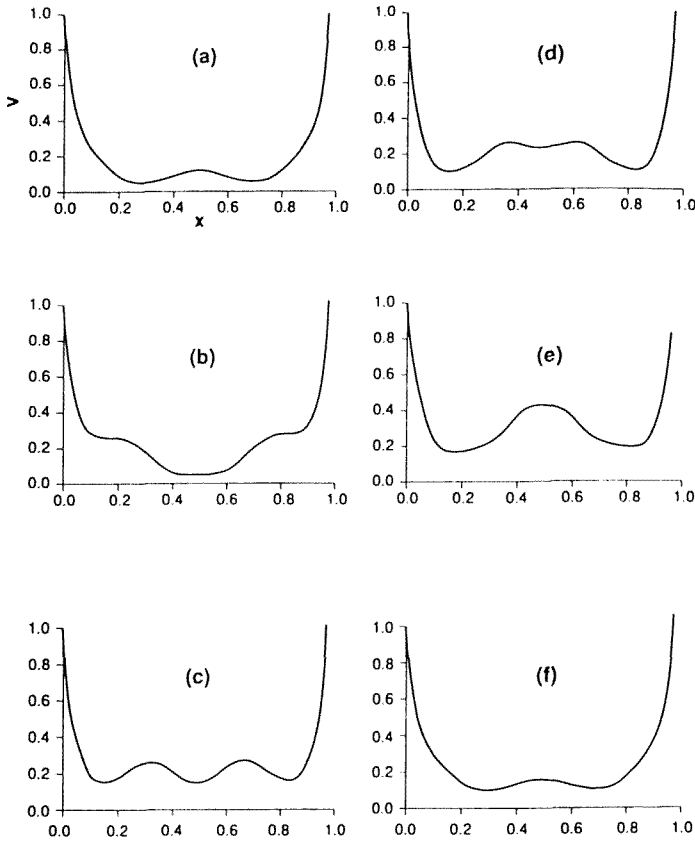


Fig. 3. Concentration profiles of  $v$  plotted against  $x$ , for  $\varepsilon = 0.3, f = 1.0, D = 0.001, q = 0.0008$  and  $u_0 = u_1 = 1.0$ .

very thin), travelling towards the centre. The picture is much clearer in this case. The leading waves in each of the wave trains collide at the centre initially increasing the concentration  $u$  of autocatalyst X there before annihilating each other. At the same time further wavelets are born in the boundary-layer regions. These quickly increase in amplitude to form part of the wave trains. This process is repeated indefinitely with further waves colliding at the centre and further waves being formed near the boundaries to replenish the wave trains.

As was seen in Leach et al. [3], it is possible for wave pulses to be generated for values of the parameters for which stationary state (4b) is stable. This situation can occur for values of the parameters satisfying the conditions  $q < q_*$  (the value of  $q$  above which the well-stirred system is non-oscillatory for all parameter values),  $f > f_H$  (the value of  $f$  corresponding to the upper Hopf bifurcation) and  $\varepsilon < \varepsilon_C \ll 1$  (this critical value of  $\varepsilon = \varepsilon_C$  has not been determined exactly, though further calculations suggest that it lies between  $\varepsilon = 0.05$  and  $\varepsilon = 0.15$ ). Figure 5 illustrates this phenomenon for values of the parameters  $f = 3.0, \varepsilon = 0.05$  and  $D = 0.00001$ , by

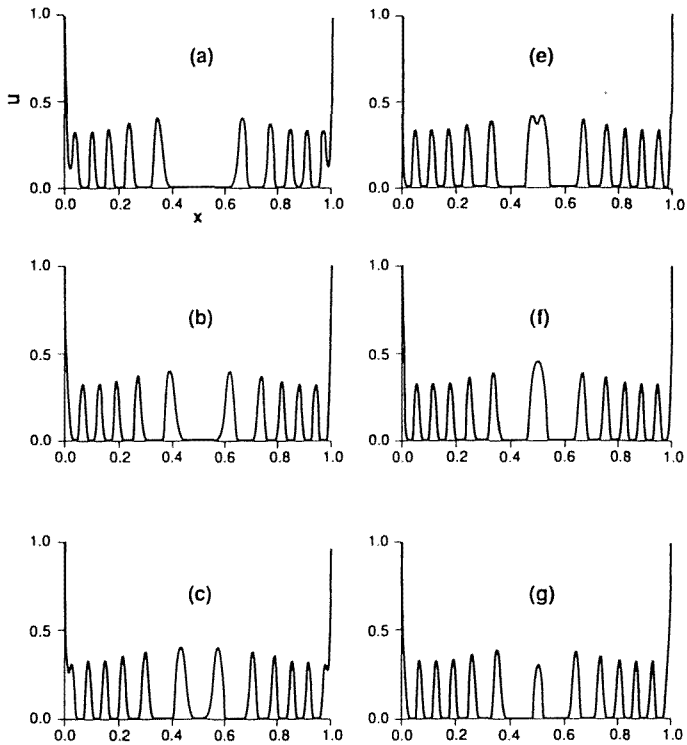


Fig. 4. Concentration profiles of  $u$  plotted against  $x$ , for  $\varepsilon = 0.3, f = 1.0, D = 0.00001, q = 0.0008$  and  $u_0 = u_1 = 1.0$ .

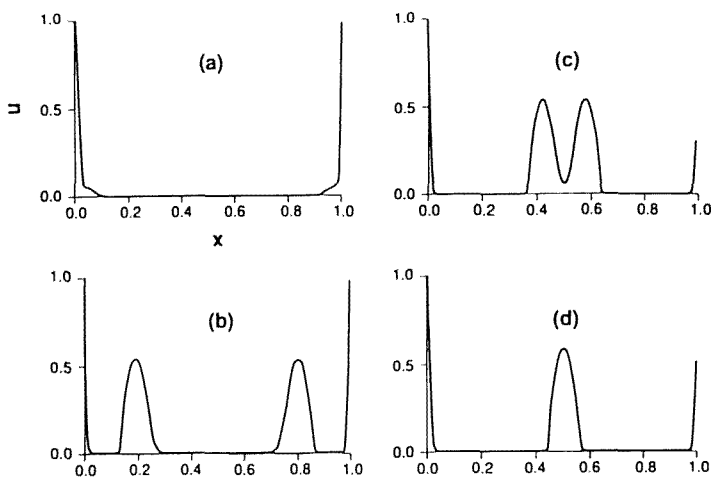


Fig. 5. Concentration profiles of  $u$  plotted against  $x$ , for  $\varepsilon = 0.05, f = 3.0, D = 0.00001, q = 0.0008$  and  $u_0 = u_1 = 1.0$ .

presenting a sequence of profiles of the concentration of autocatalyst  $u$  plotted against  $x$  (again after sufficient time for the transients to have died out). Figure 5(a) shows two waves being born out of the boundary-layer region with the central region being in its refractory phase,  $u = q$ . Figure 5(b) shows that two travelling pulses have formed, completely detached from the boundaries, travelling towards the centre, leaving behind a refractory region in which  $u = q$  (even though stationary state (4b) is stable, having the steady state value  $u_s = 0.001598$ , approximately  $2q$ ). Figures 5(c) and 5(d) illustrate the collision of these travelling pulses. As the waves collide, they cannot pass through each other as the region behind each wave is at first refractory to further excitation. Hence the waves of excitation slowly die out, leaving the refractory state as shown in fig. 5(a). The finite region then gradually recovers excitability for the whole process to be repeated.

Although we used a very small value for  $D$  in this case, a value for which up to six distinct waves were seen in each wavetrain for the previous (unstable) case, here we saw only one wave pulse generated at each boundary. To compute this case we required a very large number ( $n = 500$ ) of grid points across the region to represent the solution in the boundary layer properly and to maintain a reasonable overall accuracy. Also, a large number of time steps were required to allow transients to die out and to represent the full sequence shown in fig. 5. This was about the limit of the computational resources available to us, so we were unable to take much smaller values of  $D$  to see if it were possible for more than one travelling wave pulse to be generated, with a sequence of events similar to that depicted in fig. 5. We expect this to require (if it occurs at all) a value of  $D$  several orders of magnitude smaller than the one used above.

Finally, we considered the case when  $u_0 \neq u_1$ . Here we again took  $u_0 = 1$  but now put  $u_1 = 0$ , and used the same values for  $\varepsilon$ ,  $f$  and  $D$  as in the previous case. The

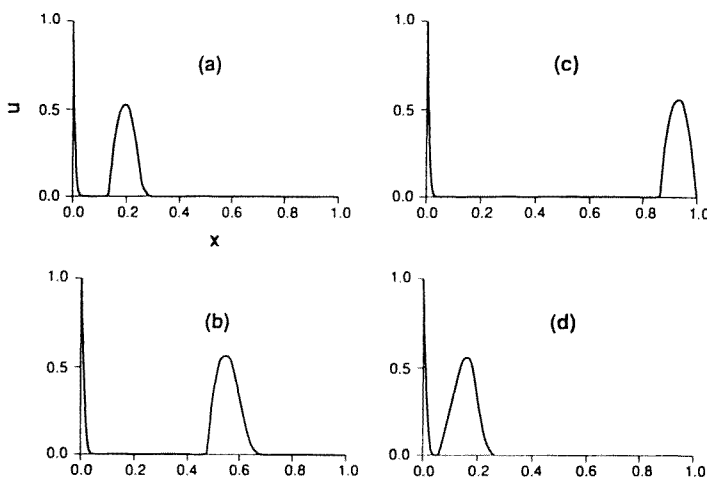


Fig. 6. Concentration profiles of  $u$  plotted against  $x$  for  $\varepsilon = 0.05$ ,  $f = 3.0$ ,  $D = 0.00001$ ,  $q = 0.0008$  and  $u_0 = 1.0$ ,  $u_1 = 0.0$ .



sequence of  $u$  concentration profiles is shown in fig. 6 (after transients had died out). In fig. 6(a) we can see that a wave has become detached from the boundary-layer region close to  $x = 0$  (there is now no equivalent structure on  $x = 1$ ). This wave now travels across the whole region, figs. 6(b) and 6(c), into a refractory region (where  $u = q$ ) and also leaving behind the system in its refractory state. This wave is dissipated on the wall at  $x = 1$  (there is no reflection of waves in this system) while at the same time another wave is being formed in the boundary-layer region on  $x = 0$ , fig. 6(d), enabling the whole sequence to be repeated.

### 3. Discussion

In this paper we have conducted an initial numerical study of a finite one-dimensional system with BZ kinetics. Initially, the system is assembled at an unstable steady state ( $u = v = 0$ ). The waves are initiated and sustained by imposing constant values for the concentration of reactant species X at the boundaries. The species Z (Ce(IV)) is assumed to be immobilized in the reaction zone and only the autocatalyst X (hypobromous acid) is allowed to diffuse. The kinetic parameters  $q$ ,  $\varepsilon$  and  $f$  have been varied so as to cover a range of cases, such that the corresponding non-zero steady state of the well-stirred system may be either stable or unstable. With an unstable non-zero steady state, the system displays a stable limit cycle in this case. For our reaction-diffusion problem, such parameters set up an essentially phase-wave behind the travelling reaction front. At any given point, the concentrations  $u$  and  $v$  undergo time-periodic variations that follow closely the corresponding oscillations for the well-stirred system.

If the steady state behind the wave front is sufficiently stable, the reaction-diffusion problem evolves to this solution, with thin transition regions close to the boundaries being required to satisfy the boundary conditions. However if the system is sufficiently excitable (i.e.  $\varepsilon$  is sufficiently small) and if the boundary conditions impose a sufficiently high concentration of the reactant X, the stable steady state is not attained after the initial passage of the reaction front. A supercritical disturbance is released before  $u$  can approach  $u_s$  and a second reaction pulse is initiated. Successive repetitions then lead to the establishment of a periodic spatiotemporal response even though the corresponding well-stirred system has a stable steady state: a periodic wavetrain has emerged in this system even though constant concentrations of reactant X are maintained at the boundaries.

One further feature worth noting is the synchronization between the collision and collapse of the waves at the centre of the region and the birth of further waves at the two boundaries. This is, perhaps, best illustrated by the results shown in fig. 4, but it applied in all the other cases. The leading waves in each wavetrain collide and then dissipate at the centre and when the concentration here has just reached its refractory state another wave is born in each boundary-layer region so as to maintain the uniformity of the wavetrains propagating towards the centre.

To complete the discussion we note, from eq. (1a) that for small  $D$  the boundary-layers have a thickness of  $O(D^{1/2})$  and thus the rescaling

$$\xi = D^{1/2}x \quad \text{or} \quad \bar{\xi} = D^{-1/2}(1-x) \quad (6)$$

is suggested. Consider the boundary-layer in  $x = 0$  (the argument for the boundary-layer on  $x = 1$  follows almost exactly). Equation (1a) becomes, using (6),

$$\varepsilon \frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial \xi^2} + u(1-u) + fv \frac{(q-u)}{(q+u)} \quad (7)$$

with eq. (1b) unaltered. The boundary condition on  $\varepsilon = 0$  is still  $u = u_0$  and the solution must match with the solution in the central part of the region as  $\xi \rightarrow \infty$ . This is most easily realised if we are in a situation in which this outer solution is the stable stationary state  $u = v = u_s$ . In this case (with time derivatives put to zero) we have, from eq. (1b),  $v = u$  and hence we have to solve the equation

$$\frac{d^2 u}{d\xi^2} + u(1-u) + fu \frac{(q-u)}{(q+u)} = 0 \quad (8a)$$

in the boundary-layer region  $0 \leq \xi < \infty$  with

$$u = u_0 \quad \text{on} \quad \xi = 0, \quad u \rightarrow u_s \quad \text{as} \quad \xi \rightarrow \infty. \quad (8b)$$

Equation (8a) can be integrated once to get

$$\begin{aligned} \left( \frac{\partial u}{\partial \xi} \right)^2 &= \frac{1}{2}(u_s^2 - u^2) + \frac{1}{3}(u^3 - u_s^3) \\ &+ \frac{f}{2} \left( u^2 - u_s^2 - 4q(u - u_s) + 4q^2 \log \left( \frac{u+q}{u_s+q} \right) \right). \end{aligned} \quad (9)$$

Equation (9) cannot be integrated further to give  $u$  directly in terms of  $\xi$ , but it does show that a solution can be obtained in this boundary-layer region which is monotone decreasing if  $u_0 > u_s$  and monotone increasing if  $u_0 < u_s$ .

The explanation of the large time behaviour of the system when the system approaches a steady state is thus complete. The large-time behaviour when a genuine spatio-temporal structure develops is far more complex to deal with and will be the subject of a subsequent paper.

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