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Multi-timescale approach to analysis of exponential autocatalysis: limit cycle and global non-uniform steady patterns

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Abstract. Limit cycle and non-uniform global steady patterns that appear in an exponentially autocatalysed reaction-diffusion system have been constructed using a two-timescale approach. The stability of these nonlinear structures is also examined.

1. Introduction

The present paper considers an alternate form of autocatalysis (Inamdar *et al* 1990) given as,

$$X \overset{k}{\rightarrow} Y \rightarrow Z$$

where the product Y systemically autocatalyses its own rate of formation by affecting the rate constant k. Ravi Kumar *et al* (1984) showed that this rate form has wide applications in several biochemical systems as also in explaining the phenomena in diverse chemical and combustion type of reactions. The exponential autocatalysis has received acceptance as a general model for class of reaction–diffusion systems (Bar-Eli 1984) and results obtained by using the conventional autocatalysis such as the one used in Brusselator type of models compare well with this model system. As shown by Ravi Kumar *et al* (1984) the exponential autocatalysis has revealed the existence of multiplicity and oscillatory behaviour under homogeneous conditions. More recently the scheme in presence of diffusion was analysed with a view to establish bounds on the steady state solutions (Inamdar and Kulkarni 1990). The conditions for the existence of nonuniform solutions in the form of dissipative structures have also been analysed analytically (Inamdar 1990) and the behaviour near the Hopf bifurcation point has been derived using the reductive perturbation to obtain the description in terms of Ginzburg–Landau equation (Inamdar 1990). In the present work we employ the two-time scales (singular perturbation) method to construct the limit cycle and global non-uniform steady patterns that appear in this reaction–diffusion system for a defined set of initial and boundary conditions. The stability of these nonlinear structures is also analysed.

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2. The exponential autocatalysis model

The reaction–diffusion system is represented by the following coupled nonlinear partial differential equations:

$$\frac{\partial X}{\partial t} = D_1 \Delta X + x_0 - X - Da_1 X \exp(\alpha Y) \tag{1a}$$

$$\frac{\partial Y}{\partial t} = D_2 \Delta Y + y_0 - Y + Da_1 X \exp(\alpha Y) - Da_2 Y \tag{1b}$$

where the operator $\Delta = \partial^2/\partial r^2$. Here, X and Y are the concentrations of species, and D_1, D_2 are the diffusivities. It is assumed that Fick's law holds. The initial reactant concentrations are given by x_0 and y_0. Other parameters of the system are Da_1, Da_2 giving Damkohler numbers for the two species, and α is the exponential autocatalytic parameter.

The steady state homogeneous solution to system in equation (1) is given as,

$$\exp(\alpha\theta) = \frac{(x_0 - x_s)}{x_s Da_1} \qquad \theta = \frac{x_0 + y_0 - x_s}{1 + Da_2} \tag{2}$$

where x_s and θ are the steady state values of X, Y respectively.

The existence of this solution in equation (2) depends upon the boundary conditions. In the present case, we assume the concentrations to be fixed at the boundaries i.e. Dirichlet condition. This boundary condition is given as,

$$\begin{aligned} &X(0, t) = X(1, t) = x_s \\ &Y(0, t) = Y(1, t) = \theta \qquad \text{for } t > 0. \end{aligned} \tag{3}$$

All the calculations have been carried out for a one-dimensional system. To make this a well-posed problem, we add the following initial conditions,

$$X(r, 0) = X_{\text{in}}(r) = x_0 \tag{4a}$$

$$Y(r, 0) = Y_{\text{in}}(r) = y_0. \tag{4b}$$

Assuming the initial conditions x_0 and y_0 to be non-negative, there exists a non-negative pair $(X(r, t), Y(r, t))$ of solutions of the system defined for $0 \leqslant r \leqslant 1$ and $0 \leqslant t < \infty$. These solutions are infinitely differentiable functions of both r and t on $(0, 1)X(0, \infty)$.

Defining deviations from steady state as $u = \binom{x}{y}$,

$$X = x + x_s \qquad Y = y + \theta$$

which obey homogeneous boundary conditions, and linearization of the exponential term

$$\exp(\alpha y) = 1 + \alpha y$$

results in the following evolution equations,

$$\frac{\partial x}{\partial t} = D_1 \Delta x - (1 + Da_1\, e^{\alpha\theta})x - (\alpha Da_1 x_s\, e^{\alpha\theta})y - \alpha Da_1\, e^{\alpha\theta} xy \tag{5a}$$

$$\frac{\partial y}{\partial t} = D_2 \Delta y + Da_1\, e^{\alpha\theta} x + (\alpha x_s Da_1\, e^{\alpha\theta} - Da_2 - 1)y + \alpha Da_1\, e^{\alpha\theta} xy. \tag{5b}$$

The boundary and initial conditions, in terms of the deviation variables, are,

$$x(0, t) = x(1, t) = y(0, t) = y(1, t) = 0 \qquad t \geqslant 0 \tag{6}$$

and,

$$x(r, 0) = X_{in}(r) - x_s \tag{7}$$

$$y(r, 0) = Y_{in}(r) - \theta \qquad 0 \leqslant r \leqslant 1. \tag{8}$$

Introducing $\eta = D_1/D_2$, and $D = D_2$ for any parameter $\gamma = (\alpha, x_0, y_0, Da_1, Da_2, D, \eta)$, the linear differential operator can be written as,

$$L(\gamma) = \begin{pmatrix} \eta D\Delta - (1 + Da_1\, e^{\alpha\theta}) & -\alpha x_s Da_1\, e^{\alpha\theta} \\ Da_1\, e^{\alpha\theta} & D\Delta + \alpha x_s Da_1\, e^{\alpha\theta} - (1 + Da_2) \end{pmatrix}. \tag{9}$$

The nonlinear function is represented as

$$N(\gamma, u) = \begin{pmatrix} -\alpha Da_1\, e^{\alpha\theta} xy \\ \alpha Da_1\, e^{\alpha\theta} xy \end{pmatrix}. \tag{10}$$

So, the original equation (5) becomes,

$$u_t = L(\gamma)u + N(\gamma, u). \tag{11}$$

We are now interested in finding out the asymptotic solutions of equation (11) for $t \to \infty$ which are non-trivial solutions $u \neq 0$ with a boundary condition described in equation (6).

The sufficient condition for instability with respect to boundary condition (6) is that the solution $u = 0$ be unstable to small disturbances. Hence, the linearized form of equation (11),

$$\left[\frac{\partial}{\partial t} - L(\gamma)\right] u = 0 \tag{12}$$

would have a non-trivial solution for the specified boundary condition.

The solution to equation (12) can be given as,

$$u(r, t) = \Xi(r)\, e^{\lambda t} \tag{13}$$

where $\Xi(r) = (\xi(r), \kappa(r))^T$ corresponds to a solution to the space-dependent part, and λ is the eigenvalue for the time-dependent part. Then the eigenvalue problem to steady state version of equation (11) can be written as,

$$[L(\gamma) - \lambda I]\Xi(r) = 0. \tag{14}$$

The solution to equation (12) then becomes,

$$u(r, t) = \sum_{n=1}^{\infty} c_n\, e^{\lambda_n t}\, \Xi_n(r). \tag{15}$$

The eigenfunctions for any wavenumber n, can be written for the Dirichlet problem as, $\Xi(r) = \binom{\xi_n(r)}{\kappa_n(r)}$, where,

$$\xi_n(r) = \sin n\pi r \qquad \kappa_n(r) = M_n \sin n\pi r. \tag{16}$$

Using equations (9) and (14), we can write the characteristic equation in terms of trace $\mathrm{Tr}(\gamma, n)$ and determinant $\mathrm{Det}(\gamma, n)$ as,

$$\lambda_n^2 - \mathrm{Tr}(\gamma, n)\lambda_n + \mathrm{Det}(\gamma, n) = 0. \tag{17}$$

The trace and determinant expressions are given as,

$$\mathrm{Tr}(\gamma, n) = (\alpha x_s Da_1\, e^{\alpha\theta} - Da_2 - 1) + (1 + Da_1\, e^{\alpha\theta}) - n^2\pi^2 D(1+\eta) \tag{18}$$

$$\mathrm{Det}(\gamma, n) = (n^2\pi^2 D)^2\eta - n^2\pi^2 D[\eta(\alpha x_s Da_1\, e^{\alpha\theta} - Da_2 - 1) - (1 + Da_1\, e^{\alpha\theta})] - [\alpha x_s Da_1\, e^{\alpha\theta} - Da_2 - 1](1 + Da_1\, e^{\alpha\theta}) + \alpha x_s (Da_1\, e^{\alpha\theta})^2. \tag{19}$$

The eigenvalues are then obtained from equation (17) as,

$$2\lambda_n^{\pm} = [[Da_1\, e^{\alpha\theta}(\alpha x_s - 1) - (Da_2 + 2)] - n^2\pi^2 D(1+\eta)] \pm \{(n^2\pi^2 D)^2(1-\eta)^2 + 2(1-\eta)n^2\pi^2 D[Da_2 - Da_1\, e^{\alpha\theta}(\alpha x_s + 1)] + Da_2^2 + Da_1\, e^{\alpha\theta}[(\alpha x_s - 1)^2 Da_1\, e^{\alpha\theta} - 2Da_2(\alpha x_s + 1)]\}^{1/2} \tag{20}$$

and, the eigenfunctions can be obtained in terms of the eigenvalues as,

$$\lambda_n^{\pm} + (1 + Da_1\, e^{\alpha\theta}) + n^2\pi^2\eta D + \alpha x_s Da_1\, e^{\alpha\theta} M_n^{\pm} = 0. \tag{21}$$

Note that, the eigenvalues have negative real part if and only if $\mathrm{Tr}(L(\gamma)) < 0$ and $\mathrm{Det}(L(\gamma)) > 0$, in which case the solution is linearly stable. If either $\mathrm{Tr}(L(\gamma)) > 0$ or $\mathrm{Det}(L(\gamma)) < 0$, then the solution is linearly unstable. If $\mathrm{Det}(L(\gamma))$ changes sign, an exchange of stability takes place as one eigenvalue of $L(\gamma)$ changes sign. This results in bifurcation of steady state solution branches. If $\mathrm{Det}(L(\gamma)) > 0$ and $\mathrm{Tr}(L(\gamma))$ changes sign, exchange of stability occurs as the real part of the eigenpair of $L(\gamma)$ changes sign. This corresponds to Hopf bifurcation, which generates a non-trivial branch of periodic solutions. However, if $\mathrm{Det}(L(\gamma)) < 0$ when $\mathrm{Tr}(L(\gamma))$ changes sign, no bifurcation occurs, and hence there is no exchange of stability. This is depicted in figure 1.

In this present study, we are interested in analysing the possible modes through which instability sets in ending up with Hopf bifurcation. This can happen in two ways.

(i) At some $\gamma = \gamma_c$, an eigenvalue $\lambda_{n_c}^{\pm}$ crosses the imaginary axis with non-vanishing imaginary part. This case is in accordance with the conditions, that for critical value of parameter γ_c, and for any wavenumber n if trace is negative and determinant is non-negative, the solution is stable. For the critical value of wavenumber n, we may have a vanishing trace condition, leading to Hopf bifurcation which is the onset of instability. To find the critical value n_c we then put the trace derivative $\mathrm{d}\,\mathrm{Tr}(\gamma, n)/\mathrm{d}n|_{n=n_c}$ equal to zero. This yields the result $n_c = 1$. Substituting for the critical value of n we

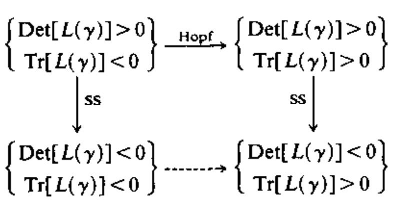

Figure 1. Stability exchange diagram; If $\mathrm{Det}(L(\gamma)) > 0$ when $\mathrm{Tr}(L(\gamma))$ changes sign Hopf bifurcation occurs; However if $\mathrm{Det}(L(\gamma)) < 0$ when $\mathrm{Tr}(L(\gamma))$ changes sign, there is no exchange of stability and no bifurcation, which is depicted by the broken line; ss denotes bifurcation from one steady state to another.

obtain the locus of points corresponding to neutral stability ($\mathrm{Re}\,\lambda_{n_c}^{\pm}=0$) in the plane Da_1, Da_2 as,

$$Da_1\,\mathrm{e}^{\alpha\theta}(\alpha x_s-1)-(Da_2+2)=\pi^2 D(1+\eta). \tag{22}$$

(ii) At $\gamma=\gamma_c$, the only value of n_c that crosses the imaginary axis from negative to positive has vanishing imaginary part. This means that at critical value of wavenumber n_c trace is negative and determinant is zero, while for other values of n the solution is stable as trace is again negative and determinant is non-negative. Then the critical value of wavenumber is obtained by putting determinant derivative $\mathrm{d}\,\mathrm{Det}(\gamma, n)/\mathrm{d}n|_{n=n_c}$ equal to zero. This gives,

$$n_c=\|\pi^{-1}D^{-1/2}\eta^{-1/4}\{(1+Da_2)+Da_1\,\mathrm{e}^{\alpha\theta}[(1+Da_2)-\alpha x_s]\}^{1/4}\|. \tag{23}$$

Also, the locus of neutrally stable states is given by the following equation,

$$\{\eta[(1+Da_2)+Da_1\,\mathrm{e}^{\alpha\theta}[(1+Da_2)-\alpha x_s]]\}^{1/2} = \frac{\eta[\alpha x_s Da_1\,\mathrm{e}^{\alpha\theta}-(1+Da_2)]-(1+Da_1\,\mathrm{e}^{\alpha\theta})}{2}. \tag{24}$$

Inserting equation (24) into the condition $\mathrm{Tr}(L(\gamma_c, n_c))<0$, we obtain an inequality as,

$$(1-\eta)[\eta[\alpha x_s Da_1\,\mathrm{e}^{\alpha\theta}-(1+Da_2)]+(1+Da_1\,\mathrm{e}^{\alpha\theta})]<0 \tag{25}$$

and from the sufficiency condition of minimum $\mathrm{Det}(\gamma, n)$ one obtains,

$$1<\eta \qquad \text{or} \qquad D_1>D_2. \tag{26}$$

Figure 2 depicts for some specific values of Da_1 the linear stability diagram in the

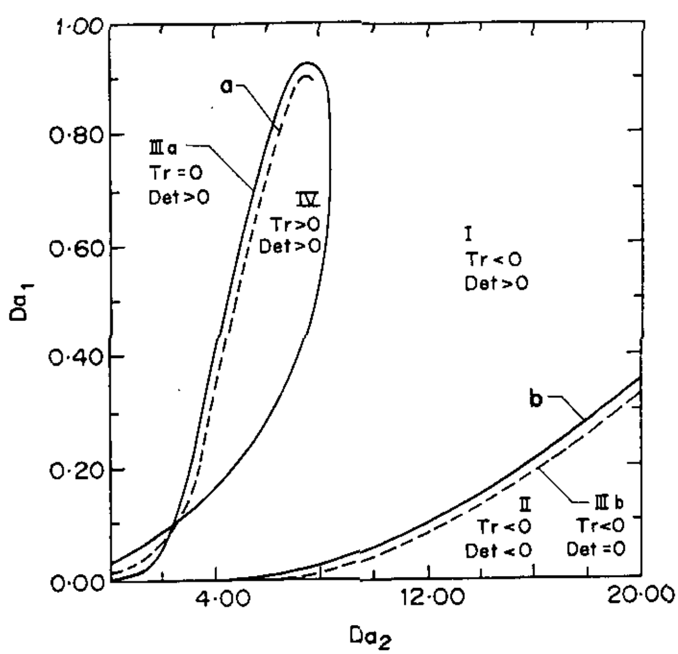

Figure 2. Stability diagram in the neighbourhood of the homogeneous steady state [equation (2)]. Region I is of stability. Region IIIa [equation (22)] and IIIb [equation (24)] contains the unstable zone between the solid line and dotted line. In region IIIa along ***a*** there is bifurcation to limit cycle behaviour. In region IIIb, along ***b*** spatial dissipative structures can occur. In region IV limit cycle behaviour is expected.

neighbourhood of $u = 0$. It should be noted that in this work the diffusion plays the destabilizing role, where the mixing in a stirred vessel is very poor.

3. Multiple timescale analysis

In this section, we would apply the technique of multiple time scale to obtain the global non-uniform steady patterns. The multiple time scale analysis takes advantage of the existence of slow and fast time scales, inherent in the system to construct an asymptotic solution. The method has been extensively employed and illustrated in the literature (Newell and Whitehead 1969, Nayfeh 1973, Ortelova and Ross 1974, Bender and Orszag 1978, Bonilla and Velarde 1979, Keener 1982, Ramakrishna and Amundson 1985, van Kampen 1985).

To construct the non-uniform steady solution that branches at $Da_1 = Da_{1c}$, in region IIIb of figure 2, we see that in terms of a small expansion parameter ε the perturbations upon the trivial fixed point $x = y = 0$ can be arbitrarily written as,

$$x(r, 0) = h(r, \varepsilon) \qquad h_\varepsilon(r, 0) = \left(\frac{\partial h(r, \varepsilon)}{\partial \varepsilon}\right)_{\varepsilon=0} \tag{27a}$$

$$y(r, 0) = g(r, \varepsilon) \qquad g_\varepsilon(r, 0) = \left(\frac{\partial g}{\partial \varepsilon}\right)_{\varepsilon=0} \tag{27b}$$

$$h(r, 0) = g(r, 0) = 0. \tag{27c}$$

The two time scales used in the asymptotic analysis are defined as, a fast time scale $\bar{t} = t$, and a slow scale $\tau = [Da_1(\varepsilon) - Da_{1c}]t$. Now we define following expansions for the variables x and y,

$$x(r, t, \tau) \approx \sum_{i=1}^{\infty} \varepsilon^i x_i(r, t, \tau) \qquad y(r, t, \tau) \approx \sum_{i=1}^{\infty} \varepsilon^i y_i(r, t, \tau). \tag{28}$$

Note that the equation is exact as the series expands to all powers of ε and the corresponding expansions for initial and boundary conditions as,

initial condition:

$$x_j(r, 0, 0) = \frac{1}{j!}\frac{\partial^j h(r, 0)}{\partial \varepsilon^j} \tag{29a}$$

$$y_j(r, 0, 0) = \frac{1}{j!}\frac{\partial^j g(r, 0)}{\partial \varepsilon^j} \tag{29b}$$

boundary condition:

$$x_j(0, t, \tau) = x_j(1, t, \tau) = y_j(0, t, \tau) = y_j(1, t, \tau) = 0. \tag{29c}$$

Also the expansion for the bifurcation parameter Da_1, assuming it to be analytic in ε neighbourhood of Da_{1c} can be written as,

$$Da_1(\varepsilon) = Da_{1c} + Da_1'(0)\varepsilon + \tfrac{1}{2}Da_1''(0)\varepsilon^2 + O(\varepsilon^3). \tag{30}$$

In terms of these expansions, $L(\gamma)$ and $N(\gamma, u)$ become,

$$L(Da_1)=\begin{pmatrix}\eta D\Delta-(1+Da_{1c}\,e^{\alpha\theta}) & -\alpha x_s Da_{1c}\,e^{\alpha\theta}\\ Da_{1c}\,e^{\alpha\theta} & D\Delta+\alpha x_s Da_{1c}\,e^{\alpha\theta}-Da_2-1\end{pmatrix}$$
$$+\varepsilon\begin{pmatrix}-Da_1'(0)\,e^{\alpha\theta} & -\alpha x_s Da_1'(0)\,e^{\alpha\theta}\\ Da_1'(0)\,e^{\alpha\theta} & \alpha x_s Da_1'(0)\,e^{\alpha\theta}\end{pmatrix}$$
$$+\tfrac{1}{2}\varepsilon^2\begin{pmatrix}-Da_1''(0)\,e^{\alpha\theta} & -\alpha x_s Da_1''(0)\,e^{\alpha\theta}\\ Da_1''(0)\,e^{\alpha\theta} & \alpha x_s Da_1''(0)\,e^{\alpha\theta}\end{pmatrix} \tag{31}$$

and,

$$N(Da_1, u)=\varepsilon^2\begin{pmatrix}-\alpha\,e^{\alpha\theta}Da_{1c}x_1y_1\\ \alpha\,e^{\alpha\theta}Da_{1c}x_1y_1\end{pmatrix}$$
$$+\varepsilon^3\begin{pmatrix}-\alpha\,e^{\alpha\theta}[Da_{1c}(x_1y_2+x_2y_1)+Da_1'(0)x_1y_1]\\ \alpha\,e^{\alpha\theta}[Da_{1c}(x_1y_2+x_2y_1)+Da_1'(0)x_1y_1]\end{pmatrix} \tag{32}$$

and the derivative term becomes,

$$\frac{\partial}{\partial t}=\frac{\partial}{\partial \tilde{t}}+[Da_1'(0)\varepsilon+\tfrac{1}{2}Da_1''(0)\varepsilon^2+O(\varepsilon^3)]\frac{\partial}{\partial\tau}. \tag{33}$$

Here onwards, the tilde ˜ on t will be dropped.

From equations (12) and (31), collecting terms of equal powers of ε we obtain the following linear equations,

$$L\begin{pmatrix}x_1\\ y_1\end{pmatrix}\equiv\begin{pmatrix}\dfrac{\partial}{\partial t}-[\eta D\Delta-(1+Da_{1c}\,e^{\alpha\theta})] & \alpha x_s Da_{1c}\,e^{\alpha\theta}\\ -Da_{1c}\,e^{\alpha\theta} & \dfrac{\partial}{\partial t}-[D\Delta+\alpha x_s Da_{1c}\,e^{\alpha\theta}-(1+Da_2)]\end{pmatrix}\begin{pmatrix}x_1\\ y_1\end{pmatrix}=0 \tag{34}$$

$$L\begin{pmatrix}x_2\\ y_2\end{pmatrix}=\begin{pmatrix}-Da_1'(0)\dfrac{\partial x_1}{\partial\tau}+x_1(-Da_1'(0)\,e^{\alpha\theta})+y_1(-\alpha x_s Da_1'(0)\,e^{\alpha\theta})-x_1y_1\alpha\,e^{\alpha\theta}Da_{1c}\\ -Da_1'(0)\dfrac{\partial y_1}{\partial\tau}+x_1(Da_1'(0)\,e^{\alpha\theta})+y_1(\alpha x_s Da_1'(0)\,e^{\alpha\theta})+x_1y_1\alpha\,e^{\alpha\theta}Da_{1c}\end{pmatrix} \tag{35}$$

$$L\begin{pmatrix}x_3\\ y_3\end{pmatrix}=\begin{pmatrix}-Da_1'(0)\dfrac{\partial x_2}{\partial\tau}-\tfrac{1}{2}Da_1''(0)\dfrac{\partial x_1}{\partial\tau}+x_2(-Da_1'(0)\,e^{\alpha\theta})+y_2(-\alpha x_s Da_1'(0)\,e^{\alpha\theta})\\ \quad+\tfrac{1}{2}x_1(-Da_1''(0)\,e^{\alpha\theta})+\tfrac{1}{2}y_1(-\alpha x_s Da_1''(0)\,e^{\alpha\theta})\\ \quad-\alpha\,e^{\alpha\theta}[Da_{1c}(x_1y_2+x_2y_1)+Da_1'(0)x_1y_1]\\ -Da_1'(0)\dfrac{\partial y_2}{\partial\tau}-\tfrac{1}{2}Da_1''(0)\dfrac{\partial y_1}{\partial\tau}+x_2(Da_1'(0)\,e^{\alpha\theta})+y_2(\alpha x_s Da_1'(0)\,e^{\alpha\theta})\\ \quad+\tfrac{1}{2}x_1(Da_1''(0)\,e^{\alpha\theta})+\tfrac{1}{2}y_1(\alpha x_s Da_1''(0)\,e^{\alpha\theta})\\ \quad+\alpha\,e^{\alpha\theta}[Da_{1c}(x_1y_2+x_2y_1)+Da_1'(0)x_1y_1]\end{pmatrix}. \tag{36}$$

The solution of equation (34) is,

$$\begin{pmatrix}x_1(r,t,\tau)\\ y_1(r,t,\tau)\end{pmatrix}=\mathrm{Re}\sum_{n=1}^{\infty}\{c_n^+(\tau)\,e^{\lambda_n^+t}\Xi_n^+(r)+c_n^-(\tau)\,e^{\lambda_n^-t}\Xi_n^-(r)\}. \tag{37}$$

Here the dominant eigenvalue is $\lambda_{n_c}^{+}=0$, while the eigenmodes corresponding to all other eigenvalues decay exponentially with t. Equation (37) therefore reduces to,

$$\begin{pmatrix} x_1(r, t, \tau) \\ y_1(r, t, \tau) \end{pmatrix} = c_{n_c}^{+}(\tau)\Xi_{n_c}^{+}(r) + (\text{EDT}) \tag{38}$$

where (EDT) denotes exponentially decaying terms.

The coefficients $c_{n_c}^{+}(0)$ can be obtained using equations (27), (28) and (A7) as,

$$c_n^{\pm}(0) = \frac{\left\langle \hat{\Xi}_n^{\pm} \middle| \begin{pmatrix} h_\varepsilon(r,0) \\ g_\varepsilon(r,0) \end{pmatrix} \right\rangle}{\langle \hat{\Xi}_n^{\pm} | \Xi_n^{\pm} \rangle}$$

$$= 2\int_0^1 \{\sin n\pi r(h_\varepsilon(r,0) - \alpha x_s M n^{\pm} g_\varepsilon(r,0))\, dr\}. \tag{39}$$

Thus, constants $c_n^{\pm}$ are directly expressed in terms of the initial condition (27). Using the definition of Fredholm alternative the coefficient $c_{n_c}^{\pm}(\tau)$ can be obtained from the ε^2 equation in the set of equations (34)–(36). It is convenient to introduce the following average which is useful when we take the limit $t \to \infty$.

$$\langle\langle \hat{\Xi}_{n_c}^{+} | f \rangle\rangle = \lim_{T\to\infty} \frac{1}{T} \int_0^T \langle \hat{\Xi}_{n_c}^{+} | f \rangle\, dt \tag{40}$$

where f is some arbitrary function in this equation. All products of $\hat{\Xi}_{n_c}^{+}$ with EDT then vanish according to this definition.

From equations (35), (40) and (A9) we obtain,

$$\tfrac{1}{2} Da_1'(0) \frac{dc_{n_c}^{+}(\tau)}{d\tau}(1-\eta)$$

$$= \frac{Da_1'(0)}{4} e^{\alpha\theta} c_{n_c}^{+}(\tau)$$

$$\times \left\{ \frac{2[\eta(\alpha x_s Da_1 e^{\alpha\theta} - (1+Da_2)) + (1 + Da_1 e^{\alpha\theta})] - 2Da_1 e^{\alpha\theta}(1+\alpha x_s \eta)}{Da_1 e^{\alpha\theta}} \right\}$$

$$+ c_{n_c}^{+^2} \left\langle \hat{\Xi}_{n_c}^{+} \middle| \left[\frac{1}{2} \frac{\partial^2}{\partial\varepsilon^2} N(\gamma, u) \right]_{\varepsilon=0} \right\rangle \tag{41}$$

where

$$\left\langle \hat{\Xi}_{n_c}^{+} \middle| \left[\frac{1}{2} \frac{\partial^2}{\partial\varepsilon^2} N(\gamma, u) \right]_{\varepsilon=0} \right\rangle$$

$$= \left\{ \frac{\alpha e^{\alpha\theta} Da_{1c}[\eta(\alpha x_s Da_1 e^{\alpha\theta} - (1+Da_2)) + (1 + Da_1 e^{\alpha\theta}) - 2\alpha x_s \eta Da_1 e^{\alpha\theta}]}{2\alpha x_s Da_1 e^{\alpha\theta} \frac{3}{4} n_c \pi} \right\}$$

when n_c is odd

$= 0$ when n_c is even. (42)

When n_c is odd and

$$\left\langle \hat{\Xi}_{n_c}^{+} \middle| \left[\frac{1}{2} \frac{\partial^2}{\partial\varepsilon^2} N(\gamma, u) \right]_{\varepsilon=0} \right\rangle \neq 0$$

then we have

$$\frac{dc^+_{n_c}(\tau)}{d\tau} = \nu\left[1 - \frac{c^+_{n_c}(\tau)}{c^+_{n_c}(\infty)}\right]c^+_{n_c}(\tau) \tag{43a}$$

where,

$$\nu = \frac{1-\eta(1+Da_2)}{Da_1(1-\eta)} \tag{43b}$$

$$c^+_{n_c}(\infty) = -\frac{3n_c\pi Da_1'(0)x_s}{4}\,\frac{1-\eta(1+Da_2)}{Da_{1c}[1+Da_1\,e^{\alpha\theta}(1-\alpha x_s\eta)-\eta(1+Da_2)]}. \tag{44}$$

Integrating equation (43a) we obtain,

$$c^+_{n_c}(\tau) = \frac{c^+_{n_c}(0)c^+_{n_c}(\infty)\,e^{\nu\tau}}{c^+_{n_c}(\infty) - c^+_{n_c}(0)(1-e^{\nu\tau})}. \tag{45}$$

From equations (37) and (45) and after substituting for, $M^+_{n_c}$ from equation (A8), we obtain to first order in ε.

$$\begin{aligned}\varepsilon\begin{pmatrix}x\\y\end{pmatrix} \simeq{}& \varepsilon c^+_{n_c}(\infty)c^+_{n_c}(0)\exp\left[\frac{-xy(Da_{1c}-Da_1)t}{c^+_{n_c}(\infty)-c^+_{n_c}(0)\left[1-\exp[-\nu(Da_{1c}-Da_1)t]\begin{pmatrix}1\\M^+_{n_c}\end{pmatrix}\sin n_c\pi r\right]}\right]\\ &+\varepsilon c^-_{n_c}(0)\,e^{\lambda^-_{n_c}t}\begin{pmatrix}1\\M^-_{n_c}\end{pmatrix}\sin n_c\pi r\\ &+\varepsilon\,\mathrm{Re}\sum_{n\neq n_c}^{\infty} c^\pm_n(0)\,e^{\lambda^\pm_n t}\begin{pmatrix}1\\M^\pm_n\end{pmatrix}\sin n\pi r + O(\varepsilon^2)\end{aligned} \tag{46}$$

if the trivial solution is to be asymptotically stable for $Da_1 > Da_{1c}$. To have such a case $c^+_{n_c}(\tau)=0$ for $t\to\infty$. This is obtained by imposing a condition,

$$\nu\tau = \nu(Da_1 - Da_{1c})t < 0 \qquad \text{as} \qquad t\to\infty. \tag{47}$$

It follows from above that,

$$\nu = \frac{1-\eta(1+Da_2)}{Da_1(1-\eta)} < 0. \tag{48}$$

Since $\eta > 1$, we have, $\eta(1+Da_2) < 1$.

Equation (48) can also be stated as follows:

$$\frac{\partial L(\gamma_c)}{\partial\varepsilon} = \begin{pmatrix}-Da_1'(0)\,e^{\alpha\theta} & -\alpha x_s Da_1'(0)\,e^{\alpha\theta}\\ Da_1'(0)\,e^{\alpha\theta} & \alpha x_s Da_1'(0)\,e^{\alpha\theta}\end{pmatrix}. \tag{49a}$$

Then, using equation (31), it can be shown that,

$$\left\langle \hat{\Xi}^+_{n_c}\middle|\left[\frac{\partial L(\gamma_c)}{\partial\varepsilon}\right]_{\varepsilon=0}\Xi^+_{n_c}\right\rangle = \frac{(1-\eta)\nu}{2}. \tag{49b}$$

Hence, equivalently equation (48) can be stated as

$$\left\langle \hat{\Xi}^+_{n_c}\middle|\left[\frac{\partial L(\gamma_c)}{\partial\varepsilon}\right]_{\varepsilon=0}\Xi^+_{n_c}\right\rangle < 0. \tag{50}$$

In equations (49*b*) and (50) we have on the left-hand side, an inner product between $\hat{\Xi}_{n_c}^+$ and the vector obtained by the operation of $[\partial L(\gamma_c)/\partial\varepsilon]_{\varepsilon=0}$ over $\Xi_{n_c}^+$.

For the sake of simplicity, we choose $Da_1'(0)=1$ in equation (30). This gives,

$$Da_1 - Da_{1c} = \varepsilon + O(\varepsilon^2). \tag{51a}$$

To first order in ε, we then have the solutions x and y as,

$$\begin{aligned} x &\simeq c_{n_c}^+(\tau)(Da_1 - Da_{1c}) \sin n_c\pi r \\ y &\simeq c_{n_c}^+(\tau)M_{n_c}^+(Da_1 - Da_{1c}) \sin n_c\pi r. \end{aligned} \tag{51b}$$

If $c_{n_c}^+(0)$ and $c_{n_c}^+(\infty)$ have the same sign, with $Da_1 < Da_{1c}$, then as $t\to\infty$, the following asymptotic state will be reached.

$$\begin{pmatrix} x(r) \\ y(r) \end{pmatrix} \sim \begin{pmatrix} x_s \\ \theta \end{pmatrix} + c_{n_c}^+(\infty)\begin{pmatrix} 1 \\ M_{n_c}^+ \end{pmatrix}(Da_{1c} - Da_1) \sin n_c\pi r + \mathrm{O}[(Da_{1c} - Da_1)^2]. \tag{52}$$

In more explicit terms, this becomes,

$$\begin{pmatrix} x(r) \\ y(r) \end{pmatrix} \sim \begin{pmatrix} x_s \\ \theta \end{pmatrix} + \left\{ \frac{3n_c\pi Da_1'(0)x_s}{4} \times \frac{1-\eta(1+Da_2)}{Da_1[1+Da_1\,\mathrm{e}^{\alpha\theta}(1-\alpha x_s\eta) - \eta(1+Da_2)]} \right\} \times \begin{pmatrix} 1 \\ M_{n_c}^+ \end{pmatrix}(Da_{1c} - Da_1) \sin n_c\pi r + \mathrm{O}[(Da_{1c} - Da_1)^2]. \tag{53}$$

The derivation assumes that the signs of $c_n^\pm(0)$ and $c_n^\pm(\infty)$ are similar. In the instance the signs of these differ, the denominator in equation (45) vanishes for a time interval of the order of $[\nu(Da_{1c} - Da_1)]^{-1}$. The solution after this time goes out of the ε region. Also, when Da_1 is slightly larger than Da_{1c} we would obtain the same equation for x and y; however, the solution is now unstable and the neighbouring concentration profiles diverge with time. The initial perturbation for this case with the signs of $c_{n_c}^\pm(0)$ and $c_{n_c}^\pm(\infty)$ different, will decay and the solution will culminate into the trivial asymptotically stable point.

The calculation of $c_n^\pm(\tau)$ for the case when n_c is even requires us to consider the next higher order equation (36). After some algebraic manipulations we then have

$$\left[\frac{\partial}{\partial t} - L(\gamma_c)\right]\begin{pmatrix} x_2 \\ y_2 \end{pmatrix} = \begin{pmatrix} -\alpha\,\mathrm{e}^{\alpha\theta}Da_{1c}M_{n_c}^+ \\ \alpha\,\mathrm{e}^{\alpha\theta}Da_{1c}M_{n_c}^+ \end{pmatrix} c_{n_c}^{+2} \sin^2 n_c\pi r + (\mathrm{EDT}). \tag{54}$$

The particular solution to equation (54) is written as

$$u_2^{\mathrm{ps}} = \sum_{n\neq n_c} \beta_n^\pm(\tau)\Xi_n^\pm(r). \tag{55}$$

Knowing that,

$$L(\gamma_c)\Xi_n^\pm(r) = \lambda_n^\pm(r) \tag{56}$$

the equations (54) and (56) give

$$\sum_{n\neq n_c} \beta_n^\pm(\tau)\lambda_n^\pm\Xi_n^\pm(r) = \begin{pmatrix} 1 \\ -1 \end{pmatrix} M_{n_c}^+\alpha\,\mathrm{e}^{\alpha\theta}Da_{1c}c_{n_c}^{+2} \sin^2 n_c\pi r + (\mathrm{EDT}). \tag{57}$$

Using equation (A7), we get the result

$$\beta_n^\pm(\tau) = \begin{Bmatrix} \rho_n^\pm c_{n_c}^{+2}(\tau) & \text{for odd } n \\ 0 & \text{for even } n \end{Bmatrix} \tag{58}$$

where

$$\rho_n^{\pm}=\frac{8n_c^2}{n(n^2-4n_c^2)\pi\delta_n^{\pm}}\,\frac{Da_{1c}(1+\alpha x_s M_n^{\pm})\{\eta[\alpha x_s Da_1\,e^{\alpha\theta}-(1+Da_2)]+(1+Da_1\,e^{\alpha\theta})\}}{2x_s Da_1(1-\alpha x_s M_n^{\pm 2})}. \tag{59}$$

The general solution of equation (54) then reduces to

$$u_2=b_{n_c}^{+}(\tau)\Xi_{n_c}^{+}(r)+c_{n_c}^{+2}(\tau)\Omega(r)+(\text{EDT}) \tag{60}$$

where

$$\Omega(r)=\begin{pmatrix}\omega(r)\\ \xi(r)\end{pmatrix}=\sum_{\substack{n\neq n_c\\ n\text{ is odd}}}\rho^{\pm}\Xi_n^{\pm}(r). \tag{61}$$

Substituting equations (60) and (61) into equation (36) we obtain

$$\left[\frac{\partial}{\partial t}-L(\gamma_c)\right]u_3=-\tfrac{1}{2}Da_1''(0)\frac{\partial u_1}{\partial\tau}+L_{11}(\gamma_c)u_1+N_{\text{III}}(\gamma_c,u_1,u_2) \tag{62}$$

where

$$L_{11}=\left[\frac{1}{2}\frac{\partial^2 L(\gamma_c)}{\partial\varepsilon^2}\right]_{\varepsilon=0}=\begin{pmatrix}-1 & -\alpha x_s\\ 1 & \alpha x_s\end{pmatrix}\frac{Da_1''(0)}{2}\,e^{\alpha\theta} \tag{63a}$$

and

$$N_{\text{III}}(\gamma_c,u_1,u_2)=\begin{pmatrix}-1\\ 1\end{pmatrix}\alpha\,e^{\alpha\theta}Da_{1c}(x_1y_2+x_2y_1). \tag{63b}$$

Multiplying equation (62) with $\hat{\Xi}_{n_c}^{+}(r)$ and applying Fredholm alternative with equation (40), the result is

$$\frac{Da_1''(0)}{2}\frac{dc_{n_c}^{+}}{d\tau}=\frac{Da_1''(0)}{2}\nu c_{n_c}^{+}-\beta\nu c_{n_c}^{+3} \tag{64}$$

where

$$\nu=\frac{1-\eta(1+Da_2)}{Da_1(1-\eta)} \tag{65}$$

and

$$\beta=\frac{-Da_{1c}\{\alpha x_s\xi(r)[Da_1\,e^{\alpha\theta}(\alpha x_s\eta-1)-\eta(1+Da_2)+1]\}}{2(1-\eta(1+Da_2))}+\frac{-Da_{1c}\{\omega(r)[1+Da_1\,e^{\alpha\theta}-\eta[(1+Da_2)+\alpha x_s Da_1\,e^{\alpha\theta}]]\}}{2(1-\eta(1+Da_2))}. \tag{66}$$

In the limit $\tau\to\infty$ one notices that

$$c_{n_c}^{+}(\infty)=\pm[Da_1''(0)/2\beta]^{1/2}. \tag{67}$$

Therefore equation (64) using equation (67) becomes

$$\frac{dc_{n_c}^{+}}{d\tau}=\nu c_{n_c}^{+}\left[1-\frac{c_{n_c}^{+2}(\tau)}{c_{n_c}^{+2}(\infty)}\right] \tag{68}$$

Integrating equation (68) we obtain

$$c_{n_c}^{+}(\tau)=|c_{n_c}^{+}(\infty)|c_{n_c}^{+}(0)\,e^{\nu\tau}[c_{n_c}^{+2}(0)(e^{2\nu\tau}-1)+c_{n_c}^{+2}(\infty)]^{-1/2}. \tag{69}$$

It is interesting to note that depending on the positive or negative sign of $c_n^+(0)$, the solution $c_n^+(\tau)$ goes to $|c_n^+(\infty)|$ or $-|c_n^+(\infty)|$. The dissipative structure at $t\to\infty$ therefore depends only on the sign of the initial conditions. The asymptotic expansion of the solution in this case gives,

$$\begin{pmatrix} x(r,t,\varepsilon) \\ y(r,t,\varepsilon)\end{pmatrix} = \begin{pmatrix} x_s \\ \theta \end{pmatrix} + \varepsilon \begin{pmatrix} 1 \\ M_{n_c}^+ \end{pmatrix} c_{n_c}^+(\tau)\sin n_c\pi r + \varepsilon c_{n_c}^-(0)\begin{pmatrix} 1 \\ M_{n_c}^+ \end{pmatrix} e^{\lambda_n^{\pm} t}\sin n_c\pi r + \varepsilon \sum_{n\neq n_c}^{\infty} c_n^{\pm}\, e^{\lambda_n^{\pm} t}\begin{pmatrix} 1 \\ M_n^{\pm} \end{pmatrix}\sin n\pi r. \tag{70}$$

As $t\to\infty$,

$$\begin{pmatrix} x(r) \\ y(r)\end{pmatrix} \simeq \begin{pmatrix} x_s \\ \theta \end{pmatrix} \pm \left(\frac{Da_1 - Da_{1c}}{\beta}\right)\times\begin{pmatrix} 1 \\ M_{n_c}^+ \end{pmatrix}\sin n_c\pi r + \mathrm{O}(|Da_1 - Da_{1c}|). \tag{71}$$

Conclusively, we can say in the end that, when $Da_1 > Da_{1c}$, then the trivial solution is asymptotically stable, and vice-versa in the case of odd n_c.

4. Stability analysis of limit cycle

We shall begin with the neutral stability curve given by equation (22)

$$Da_1\, e^{\alpha\theta}(\alpha x_s - 1) - (Da_2 + 2) = \pi^2 D(1+\eta) \tag{72}$$

and note that the critical eigenvalue from equation (20) is

$$\lambda_1^{\pm} = \pm \mathrm{i}\{(Da_1\, e^{\alpha\theta})^2 \alpha x_s - (\pi^2 D\eta + 1)^2\}^{1/2}. \tag{73}$$

From equation (21), we have

$$M_1^+ = \frac{-[\pm \mathrm{i}\omega + (1 + Da_1\, e^{\alpha\theta}) + \pi^2 D\eta]}{\alpha x_s Da_1\, e^{\alpha\theta}}. \tag{74}$$

We assume the solution to equation (34) with $n_c = 1$, as

$$u_1(r,t,\tau) = \mathrm{Re}\{c_1^+(\tau)\, e^{\mathrm{i}\omega t}\Xi_1^+(r) + c_1^-(\tau)\, e^{-\mathrm{i}\omega t}\Xi_1^-(r)\} + (\mathrm{EDT}). \tag{75}$$

The above equation contains two coefficients, which are unknown. It would be appropriate to define a new coefficient as follows,

$$c_1(\tau) \equiv \tfrac{1}{2}[c_1^+(\tau) + c_1^{-*}(\tau)]. \tag{76}$$

In addition, we have, $M_1^- = M_1^{+*}$ and $e^{-\mathrm{i}\omega t}\Xi_1^-(r) = [e^{\mathrm{i}\omega t}\Xi_1^+(r)]^*$ we can then write

$$u_1(r,t,\tau) = c_1(\tau)\, e^{\mathrm{i}\omega t}\Xi_1^+(r) + \mathrm{CC} + (\mathrm{EDT}) \tag{77}$$

where CC stands for complex conjugate

The initial condition for $c_1(\tau)$ is given by,

$$c_1(0) = \frac{2\int_0^1 \{h_\varepsilon(r,0) - \alpha x_s M_1^+ g_\varepsilon(r,0)\}\sin \pi r\, \mathrm{d}r}{(1 - \alpha x_s M_1^{+2})}. \tag{78}$$

Substitution of equation (75) into equation (35) gives,

$$\begin{aligned}\left[\frac{\partial}{\partial t} + (1 + Da_1\, e^{\alpha\theta}) - \eta D\Delta\right]x_2 - \alpha x_s Da_{1c}\, e^{\alpha\theta} y_2 \\ = \{-Da_1'(0)\sin \pi r(c_1'\, e^{\mathrm{i}\omega t} + \mathrm{CC}) + (c_1\, e^{\mathrm{i}\omega t} + \mathrm{CC})\sin \pi r[-Da_1'(0)\, e^{\alpha\theta}] \\ + (c_1\, e^{\mathrm{i}\omega t} M_1^+ + \mathrm{CC})\sin \pi r(-\alpha x_s Da_1'(0)\, e^{\alpha\theta}) + \sin^2 \pi r[(M_1^+ + M_1^{+*})|c_1|^2 \\ + c_1^2\, e^{2\mathrm{i}\omega t} M_1^+ + \mathrm{CC}](-\alpha\, e^{\alpha\theta} Da_{1c})\} + (\mathrm{EDT})\end{aligned} \tag{79}$$

and

$$\left[\frac{\partial}{\partial t}-[\alpha x_s Da_{1c}\,\mathrm{e}^{\alpha\theta}-(1+Da_2)]-D\Delta\right]y_2+Da_{1c}\,\mathrm{e}^{\alpha\theta}x_2$$
$$=\{-Da_1'(0)\sin\pi r(c_1'M_1^+\,\mathrm{e}^{\mathrm{i}\omega t}+\mathrm{cc})+(c_1\,\mathrm{e}^{\mathrm{i}\omega t}+\mathrm{cc})\sin\pi r(Da_1'(0)\,\mathrm{e}^{\alpha\theta})$$
$$\times(c_1\,\mathrm{e}^{\mathrm{i}\omega t}M_1^++\mathrm{cc})\sin\pi r(\alpha x_s Da_1'(0)\,\mathrm{e}^{\alpha\theta})$$
$$+\sin^2\pi r[(M_1^++M_1^{+*})|c_1|^2+c_1^2\,\mathrm{e}^{2\mathrm{i}\omega t}M_1^++\mathrm{cc}](\alpha\,\mathrm{e}^{\alpha\theta}Da_{1c})\}+(\mathrm{EDT}). \tag{80}$$

Now, defining an average

$$\langle\!\langle[\hat{\Xi}_1^+]|f\rangle\!\rangle=\lim_{T\to\infty}\frac{1}{T}\int_0^T\langle\hat{\Xi}_1^+|f\rangle\,\mathrm{e}^{\mathrm{i}\omega t}\,\mathrm{d}t \tag{81}$$

and using Fredholm alternative one sees that $Da_1'(0)=0$, if c_1 is non-vanishing. Now, *for the eigenvalue problem for the operator* $L(u_2)$ we have,

$$\sum_{n\neq n_c}\beta_n^\pm(\tau)\lambda_n^\pm\Xi_n^\pm(r)$$
$$=\begin{pmatrix}\alpha\,\mathrm{e}^{\alpha\theta}Da_{1c}[(M_1^++M_1^{+*})|c_1|^2+c_1^2\,\mathrm{e}^{2\mathrm{i}\omega t}M_1^++\mathrm{cc}]\\-\alpha\,\mathrm{e}^{\alpha\theta}Da_{1c}[(M_1^++M_1^{+*})|c_1|^2+c_1^2\,\mathrm{e}^{2\mathrm{i}\omega t}M_1^++\mathrm{cc}]\end{pmatrix}\sin^2\pi r+(\mathrm{EDT}). \tag{82}$$

Applying equation (A7) we obtain,

$$\beta_n^\pm=\frac{\langle\hat{\Xi}_n^\pm|f(r)\rangle}{\langle\hat{\Xi}_n^\pm|\Xi_n^\pm\rangle}$$
$$=\frac{2\left\langle\begin{pmatrix}\sin\pi r\\-\alpha x_s M_n^{\pm*}\sin n\pi r\end{pmatrix}\middle|\begin{pmatrix}\alpha\,\mathrm{e}^{\alpha\theta}Da_{1c}[(M_1^++M_1^{+*})|c_1|^2+c_1^2\,\mathrm{e}^{2\mathrm{i}\omega t}M_1^++\mathrm{cc}]\\-\alpha\,\mathrm{e}^{\alpha\theta}Da_{1c}[(M_1^++M_1^{+*})|c_1|^2+c_1^2\,\mathrm{e}^{2\mathrm{i}\omega t}M_1^++\mathrm{cc}]\end{pmatrix}\sin^2\pi r\right\rangle}{(1-\alpha x_s M_n^{\pm 2})}. \tag{83}$$

Integration of the system in equation (79) and (80) yields

$$u_2(r,t,\tau)=b_1(\tau)\,\mathrm{e}^{\mathrm{i}\omega t}\Xi_1^+(r)+\mathrm{cc}+c_1^2(\tau)\,\mathrm{e}^{2\mathrm{i}\omega t}\Omega(r)+\mathrm{cc}$$
$$+|c_1(\tau)|^2[\Omega(r)+\mathrm{cc}]_{\omega=0}+(\mathrm{EDT}) \tag{84}$$

where,

$$\Omega(r)=\begin{pmatrix}\omega(r)\\\xi(r)\end{pmatrix}=\sum_{\substack{n=3\\n\text{ is odd}}}^{\infty}\frac{\rho_n^\pm}{2\mathrm{i}\omega-\lambda_n^\pm}\{M_1^+(1+\alpha x_s M_n^\pm)\}\Xi_n^\pm(r) \tag{85}$$

and,

$$\rho_n^\pm=\frac{-8}{n(n^2-4)}[1-\alpha x_s M_n^{\pm 2}] \tag{86}$$

$$[\Omega(r)]_{\omega=0}=\sum_{\substack{n=3\\n\text{ is odd}}}^{\infty}-\frac{\rho_n^\pm}{\lambda_n^\pm}\{M_1^+(1+\alpha x_s M_n^\pm)\}\Xi_n^\pm(r). \tag{87}$$

To obtain $c_1(\tau)$, we substitute for u_1 and u_2 from equation (77) and (84) respectively into equation (36), with $Da_1'(0)=0$. Multiplication of the result with $\hat{\Xi}_1^+(r)$ and using the identity in equation (81) as before, yields following differential equation,

$$\frac{Da_1''(0)}{2}\frac{\partial c_1^*}{\partial\tau}=\frac{Da_1''(0)}{2}\nu c_1^*+|c_1|^2c_1^*\kappa \tag{88}$$

where

$$\nu = \frac{-e^{\alpha\theta}(1+\alpha x_s M_1^{+*})^2}{(1-\alpha x_s M_1^{+*2})} \tag{89}$$

and,

$$\kappa = \frac{-2\int_0^1 \sin^2 \pi r \, dr \, \alpha \, e^{\alpha\theta} Da_{1c}[\xi^*(r)+[\xi(r)+\mathrm{cc}]_{\omega=0}+M_1^+\omega^*(r) + M_1^{+*}[\omega(r)+\mathrm{cc}]_{\omega=0}]\{1+\alpha x_s M_1^{+*}\}}{(1-\alpha x_s M_1^{+*2})}. \tag{90}$$

Writing, $c_1(\tau)=c(\tau)\,e^{-i\beta(\tau)}$ where $c(\tau)$ and $\beta(\tau)$ are yet to be specified, and then separating the real and imaginary parts in equation (88) gives us,

$$\frac{Da_1''(0)}{2}\frac{dc}{d\tau}=\frac{Da_1''}{2}\,c\,\mathrm{Re}\,\nu + c^3\,\mathrm{Re}\,\kappa \tag{91a}$$

$$\frac{Da_1''(0)}{2}\frac{d\beta}{d\tau}=\frac{Da_1''(0)}{2}\,\mathrm{Im}\,\nu + c^2\,\mathrm{Im}\,\kappa. \tag{91b}$$

From equation (91*a*), as $\tau\to\infty$ we can write,

$$c(\infty)=\left[-\frac{Da_1''(0)}{2}\frac{\mathrm{Re}\,\nu}{\mathrm{Re}\,\kappa}\right]^{1/2}. \tag{92}$$

Using equation (92), equation (91*b*) can be rewritten as

$$\frac{dc}{d\tau}=\mathrm{Re}\,\nu\left[1-\frac{c^2}{c(\infty)^2}\right]c. \tag{93}$$

The solution to this equation is

$$c(\tau)=\frac{c(0)c(\infty)\,e^{\mathrm{Re}\,\nu\tau}}{\{c(\infty)^2+c(0)^2[e^{2\mathrm{Re}\,\nu\tau}-1]\}^{1/2}}. \tag{94}$$

The solution to unknown phase can be written using equations (91*b*) and (94),

$$\beta(\tau)=\beta(0)+\tau\,\mathrm{Im}\,\nu+\frac{2\,\mathrm{Im}\,\kappa}{Da_1''(0)}\int_0^\tau c^2(s)\,ds \tag{95}$$

which for large values of time becomes

$$\beta(\tau)\simeq\tau\left\{\mathrm{Im}\,\nu-\frac{\mathrm{Im}\,\kappa\,\mathrm{Re}\,\nu}{\mathrm{Re}\,\kappa}\right\}. \tag{96}$$

Finally, to first order in ε, the following result is obtained:

$$u(r,t,\varepsilon)\simeq\varepsilon\frac{2c(0)c(\infty)\exp[-(Da_{1c}-Da_1)\,\mathrm{Re}\,\nu t]}{\{c(\infty)^2+c(0)^2\{\exp[-2(Da_{1c}-Da_1)\,\mathrm{Re}\,\nu t]-1\}\}^{1/2}} \times\left(\frac{1}{-\dfrac{2[1+Da_1\,e^{\alpha\theta}+\pi^2 D\eta]}{\alpha x_s Da_1\,e^{\alpha\theta}}}\right)\cos[\omega t-\beta(Da_1-Da_{1c})t] + \varepsilon\,\mathrm{Re}\sum_{n=2}^{\infty}c_n^{\pm}(0)\,e^{\lambda_n^{\pm}t}\,\Xi_n^{\pm}(r)+O(\varepsilon^2). \tag{97}$$

Equation (97) reduces to following form as $t \to \infty$:

$$\begin{pmatrix} x(r,t) \\ y(r,t) \end{pmatrix} \simeq \begin{pmatrix} x_s \\ \theta \end{pmatrix} + 2\left[\frac{\operatorname{Re} \nu}{\operatorname{Re} \kappa}(Da_{1c} - Da_1)\right]^{1/2} \begin{pmatrix} 1 \\ -\dfrac{2[1 + Da_1 e^{\alpha\theta} + \pi^2 D\eta]}{\alpha x_s Da_1 e^{\alpha\theta}} \end{pmatrix} \sin \pi r$$

$$\times \cos\left[\omega + (Da_{1c} - Da_1)\left(\operatorname{Im} \nu - \frac{\operatorname{Im} \kappa \operatorname{Re} \nu}{\operatorname{Re} \kappa}\right)\right] t + O(|Da_1 - Da_{1c}|). \quad (98)$$

5. Conclusions

The paper employs the two-time scale method to obtain the limit cycle and global non-uniform solutions for an exponentially autocatalyzed reaction-diffusion system. Sufficient condition for the steady uniform distribution of reactants in the presence of diffusion is established and stability of such states are examined. Global non-uniform solutions depending on whether n_c, the critical wavenumber, is even or odd, are then constructed and given respectively by equations (46) and (70). Conditions under which the dissipative structures are asymptotically stable or when the inhomogeneous steady state solutions lose their stability are also identified. In a similar fashion equation (97) describes the limit cycle solution, the stability of which depends on whether Da_1 exceeds Da_{1c} or not. In addition, we observe that, for sufficiently large values of diffusion parameters the limit cycle may not exist.

The important feature of the method of multiple time scales is that in addition to allowing us to construct the non-uniform and limit cycle solutions, it affords information on their stability. The detailed account of the evolution of initial disturbances upon the trivial steady state of the system is thus possible.

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Appendix. Linear operator properties

In this section, we will describe some of the important properties of the linear operator $L(\gamma)$ defined in equation (9), which are relevant to the analysis presented in this paper (Bonilla and Velarde 1979, Ramakrishna and Amundson 1985).

(1) If the eigenvalues $\lambda_n^{\pm}$ are complex, then the eigenvector $M_n^- = M_n^{+*}$, where $*$ denotes complex conjugation.

(2) Let F be the space of analytic functions $u(r) = \binom{x(r)}{y(r)}$ such that $u(0) = u(1) = 0$, then, the inner product is defined as

$$\langle u | \bar{u} \rangle = \int_0^1 \{x^*(r)\bar{x}(r) + y^*(r)\bar{y}(r)\}\, dr. \quad (A1)$$

(3) From the definition of the eigenfunctions, we can write that,

$$M_n^+ M_n^- = \frac{1}{\alpha x_s}. \quad (A2)$$

(4) Let $\hat{L}(\gamma)$ be the adjoint operator of $L(\gamma)$ and

$$\hat{\Xi}_n^{\pm}(r) = \begin{pmatrix} \sin n\pi r \\ N_n^{\pm} \sin n\pi r \end{pmatrix}$$

the eigenfunctions of the adjoint operator with same BC. Then, we have a relation,

$$N_n^{\pm} = -\alpha x_s M_n^{\pm *}. \tag{A3}$$

(5) Also, we have following inner products

$$\langle \hat{\Xi}_m^{\pm} | \Xi_n^{\pm} \rangle = \tfrac{1}{2}(1 - \alpha x_s M_m^{\pm} M_n^{\pm})\delta_{n,m} \tag{A4}$$

and

$$\langle \hat{\Xi}_n^{\mp} | \Xi_n^{\pm} \rangle = 0. \tag{A5}$$

Thus, the orthogonal set of $\Xi_n^{\pm}(r)$ in F is defined, and for any arbitrary function $f(r)$ belonging to F we have an expansion

$$f(r) = \sum_{n=1}^{\infty} (\beta_n^{+} \Xi_n^{+}(r) + \beta_n^{-} \Xi_n^{-}(r)) \tag{A6}$$

where

$$\beta_n^{\pm} = \frac{2\langle \hat{\Xi}_n^{\pm} | f \rangle}{(1 - \alpha x_s M_n^{\pm 2})}. \tag{A7}$$

(6) At the critical point, $Da_1 = Da_{1c}$ if the eigenvalue with vanishing real part is real (i.e. simple zero eigenvalue), then,

$$M_{n_c}^{+} = -\frac{1}{2\alpha x_s Da_1 \, e^{\alpha\theta}} \{\eta[\alpha x_s Da_1 \, e^{\alpha\theta} - (1 + Da_2)] + (1 + Da_1 \, e^{\alpha\theta})\}. \tag{A8}$$

(7) Using equations (23) and (A8), we obtain,

$$\eta = \alpha x_s M_{n_c}^{+*}. \tag{A9}$$

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The existence of a kinetic roughening transition in $d' = 2$ for models belonging to the KPZ-class is somewhat controversial. Since dimension $d' = 2$ is the marginal dimension, no analytical prediction is known for this case. The results of some numerical simulations of discrete models [22, 19, 20] have been interpreted as evidence of the transition. However, other papers [21, 24, 37] show that there is a crossover rather than a sharp transition; a direct numerical solution of the KPZ equation [38] does not indicate any transition either.

We have observed crossover behaviour in two cases: either with increasing disequilibrium for temperature above the roughening temperature $T = 2T_R$ (figure 4(*a*)) or with increasing temperature for sufficiently large disequilibrium ($\Delta\tilde{\mu} = 10$) (figure 5). In the former case the crossover occurs for $1 < \Delta\tilde{\mu} < 8$ and in the latter for a temperature around $T = 1.5T_R$. A similar crossover with increasing temperature as in figure 5 is also seen for lower constant disequilibrium $\Delta\tilde{\mu} = 5$ (not shown). On the other hand for a temperature below T_R ($T = 0.7T_R$) we do not observe any crossover: the roughness remains logarithmic even for very large disequilibrium (figure 4(*b*)).

For large disequilibrium and at temperatures of the order of T_R, the exponent extracted from our data is lower than that measured by Meakin *et al* [7] and by Liu and Plischke [36]. For example for $T = 2T_R$, $\tilde{\Delta\mu} = 50$ and $N = 128$ we get $\zeta = 0.225$. This value is close to a value $\zeta = 0.25$ obtained by Amar and Family [17] in the case of the restricted SOS model (for the low-temperature phase). To allow a comparison with the results of Meakin *et al* and of Liu and Plischke we also ran our program for the case of probabilities independent of the surroundings (infinite temperature limit) and $\beta\Delta\mu = 25$, i.e. the same $\beta\Delta\mu$ as in the case $T = 2T_R$ and

(*a*)