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Analysis of a periodically forced reaction–diffusion system: the case of exponential autocatalysis

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Abstract. An exponentially autocatalysed reaction–diffusion system has been analysed in the presence of periodically forced inlet concentrations with a view to study the instability of a homogeneous state due to diffusion. The effects of external periodic force has been analysed in the parameter space of initial concentrations, amplitudes of periodic force, entrainment parameter, and ratio of diffusivities of the reactants and in general show a decrease in the threshold value for the occurrence of instability.

1. Introduction

Linear systems are characterized by using a technique referred to as the frequency response method, where a forced oscillation in the input gives a characteristic response in the output. Nonlinear systems on the other hand cannot be so easily characterized, since the output response to a forced input may vary depending on the kind and type of nonlinearity present in the system. Thus, some systems may show subharmonic response, or exhibit quasiperiodic or even chaotic behaviour when subjected to external forcing. In addition, the system may undergo abrupt transitions or bifurcations when some parameter in the system changes showing a possibility of one or multiple response to a given forced input. The output response of the system may also depend on the initial conditions and the history of the system.

Studies on forced oscillations in nonlinear systems have acquired interdisciplinary character (McKarnin *et al* 1988) and examples such as the response of an electronic device to AC voltages of a heart to a pacemaker or the behaviour of RF plasma discharges have all benefited from such studies. In chemical systems, several studies (Hoffman and Schadlich 1986, Silveston *et al* 1986) reveal the beneficial effects of periodic forcing on the conversion and selectivity of reactors. Optimization of reactors incorporating the effects of periodic forcing have also been undertaken. Most of these studies, however, are concerned with the analysis of lumped parameter systems. Also very few studies attempting to understand the dynamic behaviour or bifurcations of nonlinear systems subject to external forcing are available (Bailey 1973, 1977). In the present investigation we analyse an exponentially autocatalysed reaction–diffusion system (Inamdar and Kulkani 1990, Inamdar *et al* 1990, 1991) in the presence of periodic forcing. The presence of diffusion itself can cause effects such as instability of the homogeneous state. We analyse the effects of periodic forcing in the neighbourhood of such an instability point and study the effects of parameters such as the amplitude

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and frequency of the forced oscillations, and the variations in diffusivity ratios of the reactant in the system. The paper begins by obtaining conditions for the concurrence of different types of instabilities due to diffusion. The instability conditions are then analysed to seek the effects of forcing function on the system behaviour.

2. Reaction–diffusion system for exponential autocatalysis

The reaction–diffusion system for the case of exponential autocatalysis (Inamdar and Kulkani 1990, Inamdar *et al* 1990) in the presence of periodic external force influencing the inlet concentrations, is given as

$$\frac{\partial x}{\partial t}=D_1\frac{\partial^2 x}{\partial r^2}+x_0-x-Da_1 x\exp(\alpha y)+\delta x_0\cos(\omega t) \tag{1}$$

$$\frac{\partial y}{\partial t}=D_2\frac{\partial^2 y}{\partial r^2}+y_0-y+Da_1 x\exp(\alpha y)-Da_2 y+\delta y_0\cos(\omega t) \tag{2}$$

where x and y are the dimensionless concentrations of species X and Y with initial concentrations x_0, y_0 and molecular diffusivities D_1, D_2 respectively. Da_1, Da_2 are Damkohler numbers for the two reaction steps (Inamdar *et al* 1991), while δx_0 and δy_0 are the amplitudes of external periodic forcing terms influencing the initial concentrations of the species X and Y respectively, with a frequency of oscillation equal to ω.

This non-autonomous system of equations can be converted into an autonomous form by applying the following transformation:

$$z=\frac{(\delta x_0\delta y_0)}{\omega}\cos(\omega t). \tag{3}$$

Using (3), the system of equations given in (1) and (2) reduces to

$$\frac{\partial x}{\partial t}=D_1\frac{\partial^2 x}{\partial r^2}+x_0-x-Da_1 x\exp(\alpha y)+\frac{\omega z}{\partial y_0} \tag{4a}$$

$$\frac{\partial y}{\partial t}=D_2\frac{\partial^2 y}{\partial r^2}+y_0-y+Da_1 x\exp(\alpha y)-Da_2 y+\frac{\omega z}{\delta x_0} \tag{4b}$$

$$\frac{\partial z}{\partial t}=-(\delta x_0\delta y_0)\left[1-\left(\frac{\omega z}{\delta x_0\delta y_0}\right)^2\right]^{1/2}. \tag{4c}$$

The homogeneous solutions (x_s, θ, z_s) to this modified autonomous system turn out to be

$$e^{(\alpha\theta)}=\frac{(x_0+\delta x_0)-x_s}{x_s Da_1} \tag{5a}$$

$$\theta=\frac{(x_0+\delta x_0)+(y_0+\delta y_0)-x_s}{1+Da_2} \tag{5b}$$

$$z_s=\frac{\delta x_0\delta y_0}{\omega}. \tag{5c}$$

Defining the deviations from homogeneous solution of the system expressed in (5) as

$$u=x-x_s \qquad v=y-\theta \qquad w=z-z_s \tag{6}$$

we can write down the evolution equations of the modified system in (4) as

$$\frac{\partial u}{\partial t}=D_1\frac{\partial^2 u}{\partial r^2}+k_1u+k_2v-\alpha k_3uv+\frac{\omega p^2}{\delta y_0} \tag{7a}$$

$$\frac{\partial v}{\partial t}=d_1\frac{\partial^2 u}{\partial r^2}+k_3u+k_4v+\alpha k_3uv+\frac{\omega p^2}{\delta x_0} \tag{7b}$$

$$\frac{\partial p}{\partial t'}=-\mathrm{i}(\delta x_0\delta y_0)\psi^{1/2}\{1+\tfrac{1}{2}\psi p^2\} \tag{7c}$$

where w is replaced as p_2 and ($4c$) has been approximated using the binomial expansion. The constants k_1, k_2, k_3, k_4 and the term ψ are defined as

$$k_1=-(1+Da_1\,\mathrm{e}^{\alpha\theta}) \tag{8a}$$

$$k_2=-(\alpha x_s Da_1\,\mathrm{e}^{\alpha\theta}) \tag{8b}$$

$$k_3=(Da_1\,\mathrm{e}^{\alpha\theta}) \tag{8c}$$

$$k_4=[\alpha x_s Da_1\,\mathrm{e}^{\alpha\theta}-(1+Da_2)] \tag{8d}$$

$$\psi=\left(\frac{\omega}{2\delta x_0\delta y_0}\right). \tag{8e}$$

Since, the objective of this work is to establish criticality conditions where instabilities set into the dynamical system, we have a relation for the deviations u, v as,

$$u,\, v\propto\exp(\mathrm{i}qr+\lambda t) \tag{9}$$

which gives us

$$D_1\frac{\partial^2 u}{\partial r^2}=-D_1q^2u \qquad D_2\frac{\partial^2 v}{\partial r^2}=-D_2q^2v. \tag{10}$$

From (7) and (10), we obtain an operator form of system equations as

$$\frac{\partial}{\partial t}\begin{pmatrix}u\\ v\\ p\end{pmatrix}=\begin{pmatrix}-D_1q^2+k_1 & k_2 & 0\\ k_3 & -D_2q^2+k_4 & 0\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}u\\ v\\ p\end{pmatrix}+\begin{pmatrix}(\omega p^2/\delta y_0)-\alpha k_3uv\\ (\omega p^2/\delta x_0)+\alpha k_3uv\\ -\mathrm{i}\phi p^2\end{pmatrix} \tag{11a}$$

where ϕ is defined as

$$\phi=(\delta x_0\delta y_0)\psi^{3/2}. \tag{11b}$$

The frequency of oscillation of the system in the absence of periodic forcing ω_0 can be obtained by putting the trace equal to zero and using the relation for evaluating the determinant, the square root of which gives the desired quantity ω_0. Setting the frequency of the external periodic oscillations to ω, we define the following relation between the two frequencies as

$$\gamma=\omega_0/\omega. \tag{12}$$

Clearly, entrainment occurs when $\gamma=1$.

The Jacobian matrix of the modified system of equations can be useful in obtaining the characteristic equation, based on which the linear stability properties of the periodically forced system can be predicted. The characteristic equation for the modified autonomous form of the system can be written using (11) as

$$\det|J_{3\times 3}-\lambda I| = \begin{pmatrix} -D_1q^2+k_1-\lambda & k_2 & 0 \\ k_3 & -D_2q^2+k_4-\lambda & 0 \\ 0 & 0 & 0 \end{pmatrix} = 0. \tag{13}$$

Imposing a condition that, the modified autonomous system goes through a Hopf bifurcation, where the critical eigenvalues are given as $\lambda_c = \pm i\omega_0$. Then, we see that, the resulting characteristic polynomial turns out to be of second order, and is given as

$$\lambda_c^2 + \{(D_1+D_2)q^2-(k_1+k_4)\}\lambda_c + \{D_1D_2q^4 - q^2(k_4D_1+k_1D_2)+(k_1k_4-k_2k_3)\} = 0. \tag{14}$$

Comparing the characteristic equations in the absence and presence of periodic external forcing, one can easily deduce an important result that the only change observed is that the initial concentrations (x_0, y_0) are replaced by $(x_0+\delta x_0, y_0+\delta y_0)$. Therefore, the equations and methods to obtain bifurcation diagrams remain the same as in the case of analysis without periodic force influencing the initial concentrations. We summarize the final results below:

Type I instability (absence of diffusion):

$$y_{0c} = (x_s - x_0 - \delta x_0 - \delta y_0) + \left(\frac{1+Da_2}{\alpha}\right)\ln\left[\frac{Da_2+2}{Da_1(\alpha x_s - 1)}\right] \tag{15}$$

subject to $x_s > (1/\alpha)$.

Type II instability (presence of diffusion):

$$q_c^2 = \frac{D_1[\alpha x_s Da_1 e^{\alpha\theta} - (1+Da_2)] - D_2(1+Da_1 e^{\alpha\theta})}{2D_1D_2} \tag{16}$$

and

$$y'_{0c} = (x_s - x_0 - \delta x_0 - \delta y_0) + \left(\frac{1+Da_2}{\alpha}\right)\ln\left[\frac{z}{Da_1}\right] \tag{17}$$

where

$$z' = Da_1 e^{\alpha\theta} = \frac{-b' \pm \sqrt{b'^2 - 4a'c'}}{2a'} \tag{19}$$

and the constants are given as

$$a' = \frac{D_1}{D_2}(\alpha x_s)^2 + \frac{D_2}{D_1} - 2\alpha x_s \tag{20a}$$

$$b' = 2\left\{\frac{D_2}{D_1} - \frac{D_1}{D_2}\alpha x_s(1+Da_2) + \alpha x_s - (1+Da_2)\right\} \tag{20b}$$

$$c' = \frac{D_1}{D_2}(1+Da_2)^2 + \frac{D_2}{D_1} - 2(1+Da_2). \tag{20c}$$

This is a subject to a condition

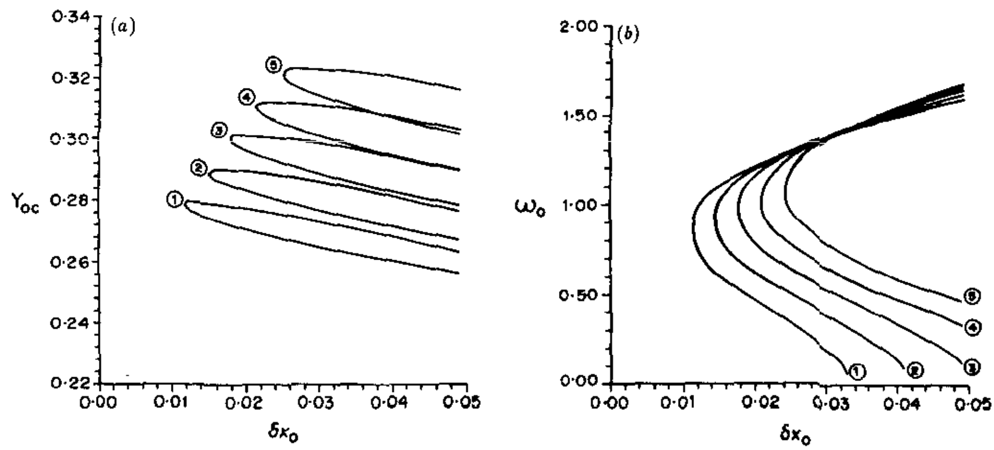
$$\frac{D_1}{D_2} < \frac{1}{\alpha x_s}. \tag{21}$$

3. Results and discussion

The homogeneous solution of the system given by (5) and the condition for instability of this solution as given by (15) have been solved using the bisection method to obtain the critical value of y_{0c}. The results have also been employed to obtain the frequency of oscillation ω_0 given by following equation

$$\omega_0 = \left\{ \frac{(1 + Da_2)^2 - \alpha x_s}{(\alpha x_s - 1)} \right\}. \tag{21}$$

The entrainment parameter γ is defined by (12) and its calculation requires an additional condition, $\phi = 1$ which is obtained during normalization of the left and right eigenvectors. Figure 1(a) shows the plots of critical concentration of y_0 versus the initial concentration x_0. For a fixed value of δy_0 (0.02) and varying δx_0 (0.02, 0.04, 0.08), it



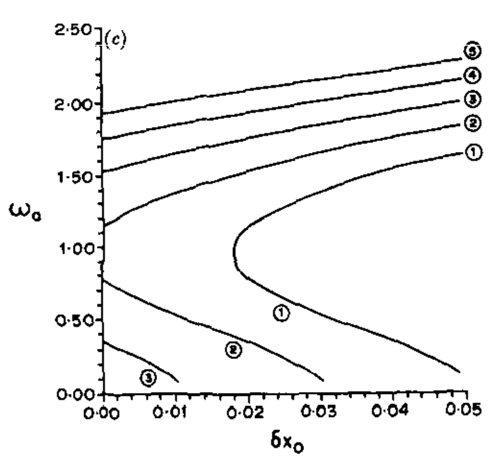
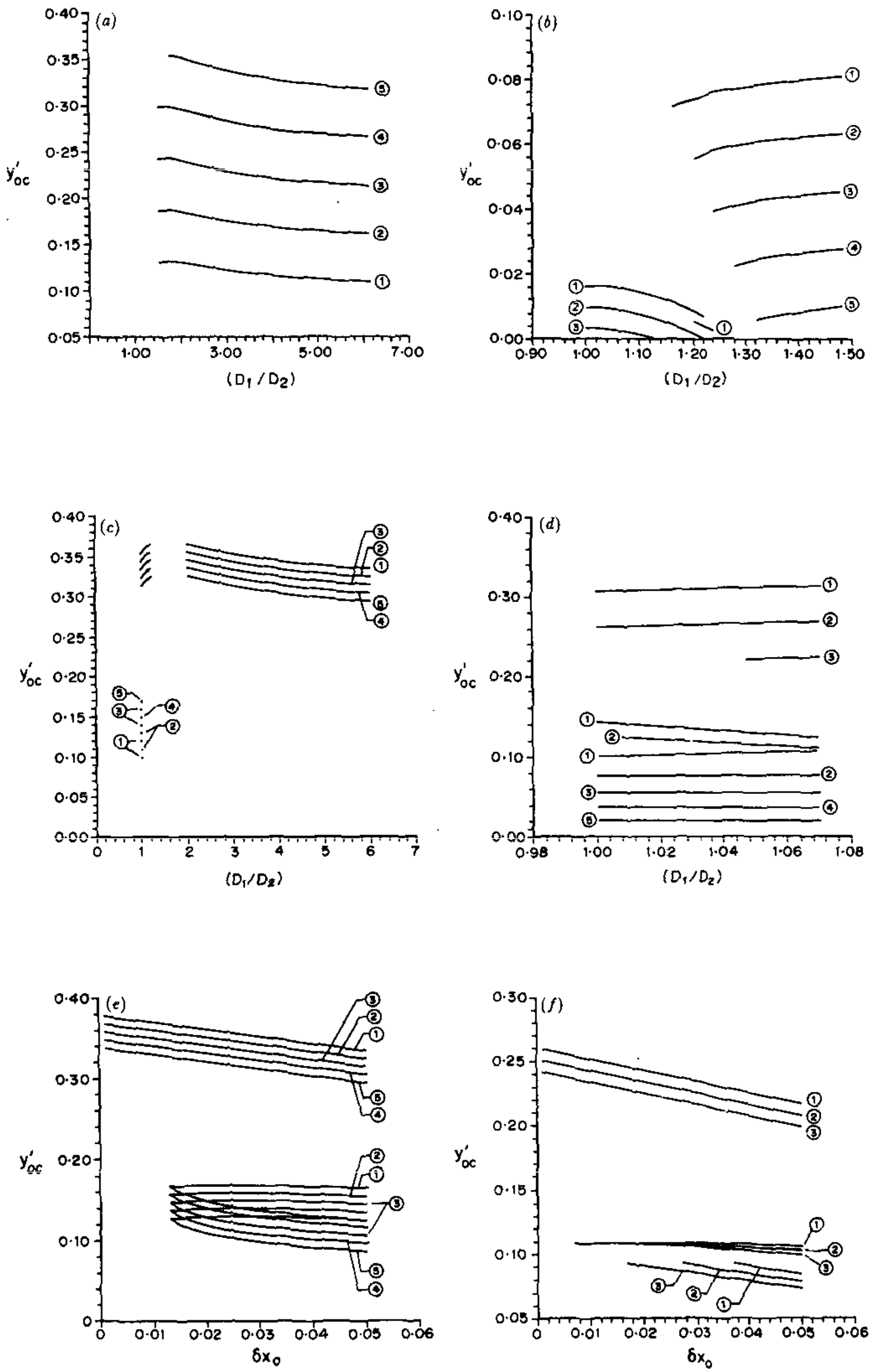


Figure 1. (a) Critical concentration $y_0(y_{0c})$ versus amplitude of periodic force (δx_0) for different values of Da_2 (1, 1.00; 2, 1.05; 3, 1.10; 4, 1.15; 5, 1.20). Other parameters are: $\alpha = 24.0$, $Da_1 = 0.004$, $x_0 = 0.3$, $\delta y_0 =$ 0.03. (b) Frequency of oscillation (ω_0) versus amplitude of periodic force (δx_0) for different values of Da_2 (1, 1.00; 2, 1.05; 3, 1.10; 4, 1.15; 5, 1.20). Other parameters are: $\alpha = 24.0$, $Da_1 = 0.004$, $x_0 = 0.3$, $\delta y_0 =$ 0.03. (c) Frequency of oscillation (ω_0) versus amplitude of periodic force (δx_0) for different values of x_0 (1, 0.30; 2, 0.32; 3, 0.34; 4, 0.36; 5, 0.38). Other parameters are: $\alpha = 24.0$, $Da_1 = 0.004$, $Da_2 = 1.1$, $\delta y_0 = 0.03$.


(a)
0·40
0·35
0·30
0·25
0·20
0·15
0·10
0·05
y'_{oc}
1·00
3·00
5·00
7·00
(D_1 / D_2)
(b)
0·10
0·08
0·06
0·04
0·02
0·00
y'_{oc}
0·90
1·00
1·10
1·20
1·30
1·40
1·50
(D_1 / D_2)
(c)
0·40
0·35
0·30
0·25
0·20
0·15
0·10
0·05
0·00
y'_{oc}
0
1
2
3
4
5
6
7
(D_1/D_2)
(d)
0·40
0·30
0·20
0·10
0·00
y'_{oc}
0·98
1·00
1·02
1·04
1·06
1·08
(D_1/D_2)
(e)
0·40
0·30
0·20
0·10
0
y'_{oc}
0
0·01
0·02
0·03
0·04
0·05
0·06
δx_o
(f)
0·30
0·25
0·20
0·15
0·10
0·05
y'_{oc}
0
0·01
0·02
0·03
0·04
0·05
0·06
δx_o

is seen clearly that the critical value of y_{0c} decreases with increase in δx_0 for a given value of x_0. Also, the figure shows a multi-valued nature, and in a certain region of the inlet concentration x_0, we may have two values of the critical concentration for the same set of parameter values. Similar trends are observed with regard to the fundamental frequency of oscillation ω_0, which decreases with increase in δx_0 and shows a multi-valued nature over certain range of x_0 (figure 1(*b*)). The entrainment parameter $\gamma = (\omega_0/\omega)$, on the other hand is seen to increase with increasing δx_0 for a given value of x_0 (figure 1(*c*)).

At the Hopf bifurcation point we have

$$Da_1 \exp(\alpha\theta_c) = \frac{Da_2 + 2}{\alpha x_s - 1}. \tag{23}$$

Equation (17) defines the condition for the occurrence of instability in the presence of diffusion and can be used along with (15) to delineate the region in parameter space where type I instability would occur earlier than type II.

Using (23) to derive the equation for demarcating the critical value of y_0 for occurrence of type I instability earlier than type II, we equate the equations for y_{0c} and y'_{0c}, to obtain an equation in final form as

$$\alpha x_s^2 + [Da_1(Da_2 + 2) - (1 + \alpha(x_0 + \delta x_0))]x_s + (x_0 + \delta x_0) = 0. \tag{24}$$

Equations (24) and (20), along with the steady-state equation are solved to obtain the desired results for the condition for the appearance of instabilities of type I and II.

Figure 2(*a*) shows a plot of $\sqrt{D_1/D_2}$ versus critical inlet concentration y'_{0c}. These plots indicate that, as periodic frequency starts operating on the system the critical value of y_0 decreases in comparison to the value under condition of no external forcing. The figure also reveals a range of diffusivity ratios, around unity, where the instability condition is single-valued. Beyond this range of diffusivity ratio the criterion acquires multi-valued nature. Figure 2(*b*) shows the values of the diffusivity ratios as a function of inlet concentration x_0 for the instability to occur. The various curves show the effect of variations of the amplitude of forcing oscillations. As shown earlier, the multi-valued nature of instability and a decrease in threshold value of x_0 for an increase in δx_0 is clearly evident.

Figure 2. (*a*) Critical concentration y_0 (y'_{0c}) in presence of diffusion versus (D_1/D_2) for different values of Da_2 (1, 2.7; 2, 2.9; 3, 3.1; 4, 3.3; 5, 3.5). Other parameters are: $\alpha = 20.5$, $Da_1 = 0.083$, $x_0 = 0.78$, $\delta x_0 = 0.03$, $\delta y_0 = 0.03$. (*b*) Critical concentration y_0 (y'_{0c}) in presence of diffusion versus (D_1/D_2) for different values of amplitude of periodic external force (δy_0) (1, 0.02; 2, 0.04; 3, 0.06; 4, 0.08; 5, 0.10). Other parameters are: $\alpha = 20.5$, $Da_1 = 0.083$, $Da_2 = 2.5$, $\delta x_0 = 0.03$. (*c*) Critical concentration y_0 (y'_{0c}) in presence of diffusion versus (D_1/D_2) for different values of amplitude of periodic external force (δy_0) (1, 0.01; 2, 0.02; 3, 0.03; 4, 0.04; 5, 0.05). Other parameters are: $\alpha = 20.5$, $Da_1 = 0.083$, $Da_2 = 3.3$, $x_0 = 0.72$, $\delta x_0 = 0.03$. (*d*) Critical concentration y_0 (y'_{0c}) in presence of diffusion versus (D_1/D_2) for different values of x_0 (1, 0.75; 2, 0.80; 3, 0.85; 4, 0.90; 5, 0.95). Other parameters are: $\alpha = 20.5$, $Da_1 = 0.083$, $Da_2 = 3.3$, $x_0 = 0.72$, $\delta x_0 = 0.03$, $\delta y_0 = 0.03$. (*e*) Critical concentration y_0 (y'_{0c}) in presence of diffusion versus amplitude of periodic external force (δx_0) for different values of amplitude δy_0 (1, 0.01; 2, 0.02; 3, 0.03; 4, 0.04; 5, 0.05). Other parameters are: $\alpha = 20.5$, $Da_1 = 0.083$, $Da_2 = 3.3$, $x_0 = 0.72$). (*f*) Critical concentration y_0 (y'_{0c}) in presence of diffusion versus amplitude of periodic external force (σx_0) for different values of x_0 (1, 0.59; 2, 0.60; 3, 0.61). Other parameters are: $\alpha = 20.5$, $Da_1 = 0.083$, $Da_2 = 2.5$, $(D_1/D_2) = 1.0$, $\delta y_0 = 0.02$.

The nature of the solution curve does not change for zero and non-zero values of the amplitudes of periodic forcing term. Figures 3(a), 3(b), 3(c), and 3(d) depict the plots for type II instability, i.e. critically caused due to diffusion, and the effect of the amplitudes of the periodic forcing term is studied. Figure 3(a) shows that for a fixed value of x_0 with δx_0 kept constant ($=0.02$), the value of y'_{0c} decreases as δy_0 increases. The behaviour holds true for zero and non-zero values of δx_0 and δy_0. Figure 3(b) is a plot of y'_{0c} versus x_0 for different values of diffusivity ratio (D_1/D_2), in the absence of periodic forcing. The abrupt transition noticed in figure 3(a) for a diffusivity ratio value of unity persists even in this case. However, for ratios greater than unity the solutions become smoother. The critical value for y'_{0c} is seen to decrease, with increase in the values of the diffusivity ratio, although the values always remain above the one corresponding to case where the ratio takes a value of unity. Figure 3(c) shows the combined effect of varying values of amplitudes of periodic external force, for two

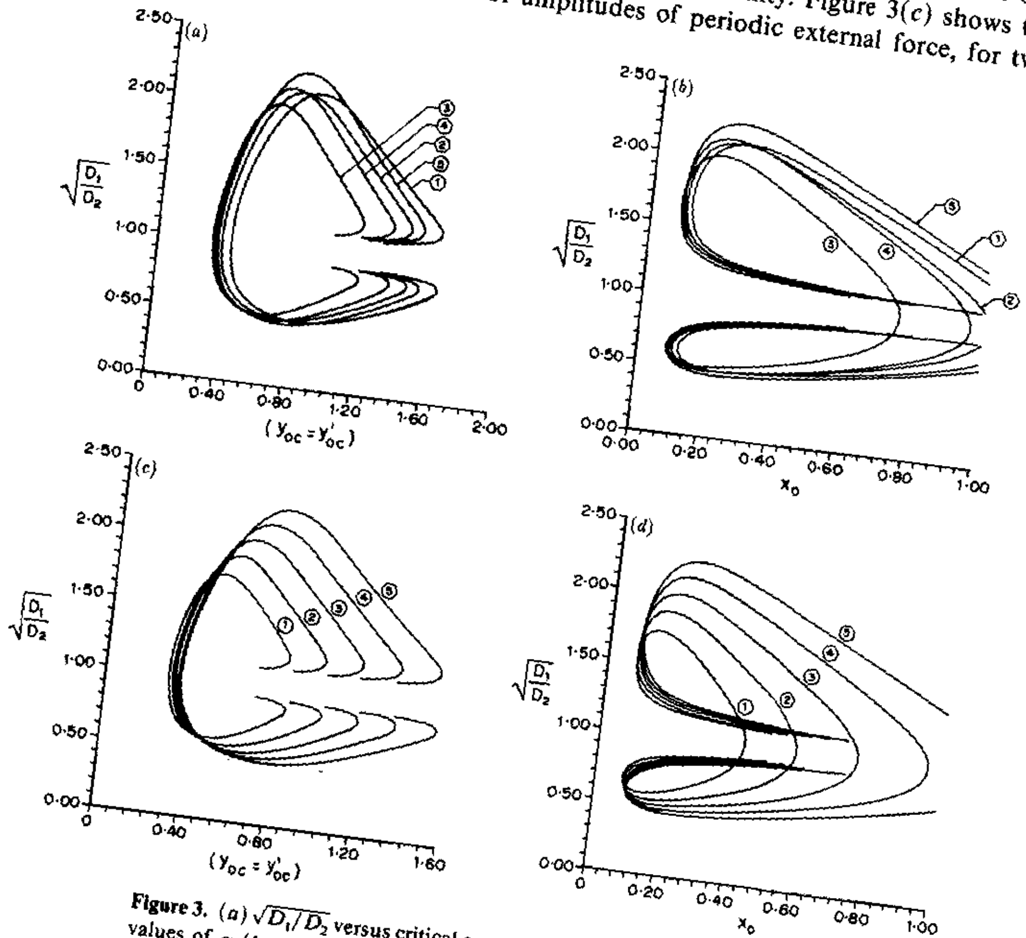


Figure 3. (a) $\sqrt{D_1/D_2}$ versus critical concentration of y_0 given by equation (22) for different values of α (1, 17; 2, 19; 3, 21; 4, 23; 5, 25). Other parameters are: $x_0=0.05$, $Da_1=0.05$, $Da_2=3.4$, $\delta x_0=0.02$, $\delta y_0=0.02$. (b) $\sqrt{D_1/D_2}$ versus initial concentration of x_0 for different values of α (1, 17; 2, 19; 3, 21; 4, 23; 5, 25). Other parameters are: $Da_1=0.05$, $Da_2=3.4$, $\delta x_0=0.02$, $\delta y_0=0.02$. (c) $\sqrt{D_1/D_2}$ versus critical concentration of y_0 given by equation (22) for different values of Da_2 (1, 2.0; 2, 2.5; 3, 3.0; 4, 3.5; 5, 4.0). Other parameters are: $\alpha=21.0$, $x_0=0.05$, $Da_1=0.05$, $Da_2=3.4$, $\delta x_0=0.02$, $\delta y_0=0.02$. (d) $\sqrt{D_1/D_2}$ versus critical concentration of x_0 for different values of Da_2 (1, 2.0; 2, 2.5; 3, 3.0; 4, 3.5; 5, 4.0). Other parameters are: $\alpha=21.0$, $Da_1=0.05$, $Da_2=3.4$, $\delta x_0=0.02$, $\delta y_0=0.02$.

different values of diffusivity ratio. As a general observation, we can infer that as the magnitude of frequency of periodic external force increases, there is a fall in the critical concentration value y'_{0c}, Similar effects arise as diffusivity ratio is increases beyond unity towards higher values, with non-zero magnitudes of δx_0 and δy_0. The case for the ratio equal to unity is however different. Figure 3(d) is a plot of y'_{0c} versus diffusivity ratio, for different values of x_0 with periodic forcing suppressed. It is observed that the critical value decreases steeply for increasing values of x_0, over a wide range of values of diffusivity ratios. No solutions are found to exist for values of ratio less than unity.

4. Conclusions

To summarize, the results of the analysis in general show that the presence of external forcing has the effect of decreasing the threshold value required for the occurrence of instability of the homogeneous state.

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