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Numerical Bifurcation and Stability Analysis of the Nicolis-Puhl Reaction as an Application of Class of Integro Partial Differential Equation

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Abstract

Numerical bifurcation and stability analysis techniques is applied to the specific class of integro-partial differential equations (IPDE). This class of IPDE can be used to study many physical and chemical reaction systems as a dynamical system. The Nicolis-Puhl(NP) reaction an isothermal two-component, autocatalytic reaction exhibiting bistability, perfectly micromixed continuous-flow stirred tank reactor (CSTR) has been shown to be sensitive to the degree of micromixing under non-premixed feed conditions. These properties make it an intersting model to be study as an application of this class of IPDE. The numerical simulation methods studied here has shown excellent numerical stability and the results are similar to those are found by Fox, Villermaux (1990), Fox, Curtis and Halasi (1990), and Fax (1990) for NP reaction. These results also has been verified through numerical simulations of time dpendent solution model.

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1. Introduction

The theory of dynamical systems is a vast and vibrant area. This theory is playing an ever important role in the sciences and engineering, provoking a blurring of boundaries between scientific disciplines and a resurgence of interest in the modern as well as the classical techniques of applied mathematics. Concerning this subject the bifurcation and stability analysis of the chemical reaction systems is an old and much-honored chapter in dynamical systems, one that is experimentaly may insightful get devoid of extensive formalism and study. It is the aim of this work to introduce a class of nonlinear Integro Partial Differential Equations (IPDE) and imploy this system as a model towards a contribution and understanding the dynamical behavior of the chemical reactions such as Nicolis-Puhl (NP) reaction in the Continuous-flow Stirred Tank Reactor (CSTR). The well known CSTR, in chemical engineering, is a stirred pot into which chemicals of a certain recipe flow continuously and are stirred and heated or cooled while undergoing chemical reaction. These reactors often occur in connected multiples which can have ever increasing static and dynamic complexity. The bifurcation behavior of the CSTR has been studies for more than 30 years [13], [14] and yet qualitatively new results seem to continually appear [2], [3], [4].

The two-component reaction scheme proposed by Puhl and Nicolis in 1987 [12]. In the perfect-micromixing limit, this reaction exhibits bistability and oscillatory behavior. The rate constants for the three steps in the NP reaction are all of the same order of magnitude, hence, its numerical investigation does not require the special considerations for stiff equations nor the long computing times needed for this reaction [8]. In addition, since the NP reaction in a perfectly micromixed flow reactor is two-dimensional, any increase in the dynamical dimension observed for finite micromixing rates can be unambiguously linked to micromixing effects [6].

As we will see in next section the simplest models which can described the isotermal reaction scheme of NP in the perfect micromixing CSTR model for a flow reactor with equal concentrations of two species, is in the form of the system consists of two ordinary differential equations. Puhl and Nicolis have used this model [12] for analyzing the effect of micromining on the NP reaction. Although, expansive work has been done in their work, yet in order to invastigate more detail of dynamical behavior of this reaction another model has been imployed. This model which is known as Interaction-by-Exchange-with-the Mean (IEM) model is an IPDE with one-parameter micromixing model derived from the one-point joint probability density function by Pope in 1985 [11]. The alternative derivation of the IEM model equations along with a more detailed comparison of the model to other simple micromixing models can be found elsewhere [17], [9] and [2]. Nevertheless, due to the difficulty of solving IEM system, and further investigation and study of its time-dependent solution, it will be useful to introduce a transformation technique, to transfer this system to a simpler ordinary differential equations (ODE) system [3]. One of the main objectives of this work is to use this ODE system to analyze the behavior of the NP reaction under poorly micromixed conditions. So the remainder of this work has been arranged as follows.

In section 2, the NP reaction is briefly introduced and formulated in two deferent model equations. One is in the case of perfect-micromixing which consists of two ODEs, and another is in the form of IEM model under nonpremixed feed conditions. Among of existence derivations of IEM model outhor has attempted to illustrate an easire method of derivation in [2]. In section 3 the transformed IEM model to a simpler ODE system and the numerical simulation of this system is briefly reviewed [3], [5]. The main contributions of this work appear in section 4 where the results of the numerical bifurcation and stability analysis are presented. In order to test the results found in section 4 we have imployed transformed IEM model to find the time dependent solution using ODE solver LSODES [10]. So time dependent solutions for different types of fixed points are presented in section 5. The closing remark and conclusion is given in section 6.

2. Modeling of the Nicolis-Puhl Reaction

The NP reaction is expressed in terms of the isothermal reaction scheme [12] as follows:

$$2A + B \xrightarrow{k_1} 3A$$

$$A \xrightarrow{k_2} R$$

$$C + A \xrightarrow{k_3} A + B.$$

Here, C is held constant and when $k_2 = k_3$, the last two reaction become

$$C + A \xrightarrow{k_2} B + R.$$

This bistable reaction studied previously by Puhl and Nicolis [12], Villermaux [16] and Fox [7], [6].

Puhl and Nicolis have studied a normal mode analysis for the above reaction scheme by varying k_2 and k_3 independently so that the resultant dynamical system can have Takens-Bogdanov (TB) points in addition to multiple steady stats [12]. Their analysis of the perfect-micromixing case will be usful when analyzing our results in section 4 found from the transformed IEM model.

From the kinetic scheme above, the dimensionless, perfect-micromixing CSTR model for a flow reactor with equal concentrations of A and B in the feed stream can be found as follows:

$$\frac{dC_A}{d\theta} = \tau k_1 C_A^2 C_B - \tau k_2 C_A + 1 - C_A$$
$$\frac{dC_B}{d\theta} = -\tau k_1 C_A^2 C_B + \tau k_3 C_A + 1 - C_B. \qquad (1)$$

Here, the mean residence time, τ, has been employed to make the time variable dimensionless. This will be convenient when formulating the IEM model [6] and our transformed IEM model [3]. The parameter σ appearing in Puhl and Nicolis work [12] corresponds to $(\tau k_1)^{-1}$ in Fox studies [6], [5] and [7]. Hence if we let k_1 be unity, then this paramer σ will be equal to τ^{-1} in over study. Based on the bifurcation analysis presented in [12] Puhl and Nicolis have generated bifurcation sets from constant k_2-cross sections in (k_2, k_3, τ^{-1}) parameter space. The resultant bifucation sets incloding Hoph bifurcations and TB points (for $k_2 = \frac{52}{75}$) can be found in [12] and [6], so they are not presented here. But in order to compare our bifurcation results to these found by Puhl-Nicolis and Fox we will use some of the Fox's results using the IEM model. In section 4 we shall follow the lead of these results and fix k_2 and k_3 so that, in the perfect micromixing limit, the TB point can be attained by varing τ^{-1}.

Now we shall restrict our attention to the IEM model formulated for the NP reaction with non premixed feed and equal inlet flow rates for both components A and B. For this case, the model equations can be written in dimensionless form [6] as

$$\frac{\partial C_A^j}{\partial \alpha}(\alpha,\theta)+\frac{\partial C_A^j}{\partial \theta}(\alpha,\theta) = \tau (C_A^j)^2 C_B^j - \tau k_2 C_A^j + b[< C_A(\theta) > - C_B^j],$$

$$\frac{\partial C_B^j}{\partial \alpha}(\alpha,\theta)+\frac{\partial C_B^j}{\partial \theta}(\alpha,\theta) = -\tau (C_A^j)^2 C_B^j + \tau k_3 C_A^j + b[< C_B(\theta) > - C_B^j] \tag{2}$$

for $j = 1, 2$ with

$$C_A^1(0,\theta) = 2, C_A^2(0,\theta) = 0, C_B^1(0,\theta) = 0, C_B^2(0,\theta) = 2$$

where

$$< C_A(\theta) > = \frac{1}{2}\int_0^{+\infty} [C_A^1(\alpha,\theta) + C_A^2(\alpha,\theta)] e^{-\alpha} d\alpha$$

$$< C_B(\theta) > = \frac{1}{2}\int_0^{+\infty} [C_B^1(\alpha,\theta) + C_B^2(\alpha,\theta)] e^{-\alpha} d\alpha. \tag{3}$$

In this IPDE system $C_A^j(\alpha,\theta)$ is the dimensionless concentration of component A in fluid particles with dimensionless age α at dimensionless time θ that entered the reactor from stream j, and $< C_A >$ is the dimensionless, volume-averaged concentration of component A in the reactor. Analogous notation is employed for component B. The inlet concentrations have been chosen so that the dimensionless, flow averaged inlet concentrations of both A and B are unity [6]. The dimensionless micromixing parameter appears as b in equation [13] and, theoretically, may take on values between 0 (complete segregation) and $+\infty$ (prefect-micromixing). All other parameters are the same as those appearing in above Puhl and Nicolis model.

The above IEM model gives a mean field description of the system where chemical reactions occur locally and mass is exchanged globally, equation (2). The mean concentration is found by weighting the local concentrations according to their age in the reactor, equation (3). So the nonlinear integral equation (2), for the mean concentration, mathematically involve non-Markovian or history-dependent behavior and are known, in many cases, to exhibit dynamical behavior absent from the ordinary differential equation, such as model (1), found in the history-independent limit. Moreover, as discussed in [6] it can be shown that if b becomes very large, then $C_A^j \to < C_A >$ $, C_B^j \to < C_B >$ for $\alpha > 0$ and the IEM model, in terms of θ alone, is clearly reminiscent of the perfect micromixing model (1). Therefore, using IEM model enable us not only to study the dynamical behavior of NP reaction under perfectly micromixed conditions, but also in the region of incomplete micromixing.

Due to the presence of the integral terms in IEM model it is not possible to find an analytical solution. Nevertheless, extensive work has been done by Fox et. al., [5], [6], [7], [9], [16] and [17], to find the numerical analysis methods for bifurcation and stability analysis of this model. However, their analysis for the unsteady-state IEM model would be considerably less straightforward than the one which we will discuss here. Indeed, the method which we have use here is transformed IEM model as an ordinary differential equations system in infinite dimensional space. The detial technique of this transformation is discussed by author in [3], noting that, slightly modification have been applied here because of its application to the NP reaction (section 3). The assertion of this transformed IEM model, in addition to its simplicity, is availability of the softwares to find the solution and the dynamical behavior of the model in general, and the behavior of time dependent solutions, in particular.

3. IEM Model Transformation for NP Reaction and its Numerical Simulation

Although the general unsteady-state IEM model is given by equations (2) and (3), for the purpose of our transformation technique it is not difficult to see that a straightforward computation leads to the integro-differential equations for the volume-averaged concentrations. To see this, averaging equation (2) over α and j, as implied by equation (3), and employing integration by parts yields

$$\begin{aligned} \frac{d < C_A >}{d\theta} &= \frac{1}{2}\tau \int_0^{+\infty} [(C_A^1(\alpha,\theta))^2 C_B^1(\alpha,\theta) + (C_A^2(\alpha,\theta))^2 C_B^2(\alpha,\theta)] e^{-\alpha} d\alpha \\ &\quad -\tau k_2 < C_A(\theta) > +1- < C_A(\theta) >, \\ \frac{d < C_B >}{d\theta} &= -\frac{1}{2}\tau \int_0^{+\infty} [(C_A^1(\alpha,\theta))^2 C_B^1(\alpha,\theta) + (C_A^2(\alpha,\theta))^2 C_B^2(\alpha,\theta)] e^{-\alpha} d\alpha \\ &\quad +\tau k_3 < C_A(\theta) > +1- < C_B(\theta) > . \end{aligned} \tag{4}$$

So the IEM model for NP reaction in component notation can be written as:

$$\begin{aligned} \frac{\partial C_i^j}{\partial \alpha}(\alpha,\theta) + \frac{\partial C_i^j}{\partial \theta}(\alpha,\theta) &= \lambda\tau (C_1^j)^2 C_2^j - \lambda\tau k_{i+1} C_1^j \\ &\quad + b[< C_i > - C_i^j], \end{aligned} \tag{5}$$

$$\begin{aligned} \frac{d < C_i^j >}{d\theta} &= \lambda\tau \int_0^{+\infty} [(C_1^j)^2 C_2^j - k_{i+1} C_1^j] e^{-\alpha} d\alpha \\ &\quad + C_i^j(0,\theta) - < C_i^j > + b[< C_i > - < C_i^j >] \end{aligned} \tag{6}$$

for $i, j = 1, 2 (i \equiv A, B)$ with $C_1^1(0,\theta) = 2, C_1^2(0,\theta) = 0, C_2^1(0,\theta) = 0, C_2^2(0,\theta) = 2$ and $\lambda = \begin{cases} +1 & \text{if} \quad i = 1 \\ -1 & \text{if} \quad i = 2. \end{cases}$

Now suppose $L_n(\alpha)$ be the Laguerre polynomial of degree n and define

$$C_i^j(\alpha,\theta) = \sum_{n=0}^{\infty} F_{i,n}^j(\theta) L_n(\alpha). \tag{7}$$

Then

$$\frac{\partial C_i^j(\alpha,\theta)}{\partial \alpha} = \sum_{n=1}^{\infty} F_{i,n}^j(\theta) L_n'(\alpha). \tag{8}$$

Note that $L_0'(\alpha) = 0$, and

$$\frac{\partial C_i^j(\alpha,\theta)}{\partial \theta} = \sum_{n=0}^{\infty} \frac{dF_{i,n}^j(\theta)}{d\theta} L_n(\alpha). \tag{9}$$

On the other hand, using Rodrigue's formula [1], the orthonormality of the Leguerre polynomials and our definition for $C_i^j(\alpha,\theta)$ (equation 7) we have the following relations:

$$L_n(\alpha) = \frac{e^\alpha}{n!} \frac{d^n}{d\alpha^n}(\alpha^n e^{-\alpha}),$$

$$L_n'(\alpha) = \frac{e^\alpha}{(n-2)!} \frac{d^{n-1}}{d\alpha^{n-1}}(\alpha^{n-2} e^{-\alpha}) - L_{n-1},$$

or

$$L_n'(\alpha) = -L_{n-1} - L_{n-2} - \cdots - L_1 - L_0,$$

so

$$\int_0^\infty L_n(\alpha) L_m'(\alpha) e^{-\alpha} d\alpha = \begin{cases} 0 & \text{if} \quad n \leq m \\ -1 & \text{if} \quad n > m, \end{cases} \tag{10}$$

and

$$\int_0^\infty \sum_{n=1}^{\infty} F_{i,n}^j(\theta) L_n'(\alpha) L_m(\alpha) e^{-\alpha} d\alpha = \lambda \sum_{n=1}^{\infty} F_{i,n}^j(\theta), \tag{11}$$

where $\lambda = \begin{cases} 0 & \text{if } \ n \leq m \\ -1 & \text{if } \ n > m. \end{cases}$ Also, knowing that

$$< C_i(\theta) >= \sum_{j=1}^{2} 1/2 \int_0^\infty C_i^j(\alpha,\theta) e^{-\alpha} d\alpha, \text{ for } \ i = 1, 2,$$

or

$$< C_i(\theta) >= \sum_{j=1}^{2} 1/2 \int_0^\infty \sum_{n=0}^{\infty} F_{i,n}^j(\theta) L_n(\theta) e^{-\alpha} d\alpha,$$

we have

$$< C_i(\theta) >= \sum_{j=1}^{2} 1/2 F_{i,0}^j(\theta) = F_{i,0}^j(\theta). \tag{12}$$

Now, substituting equations (7), (8) and (9) into the equation (5), multiplying both sides of the resultant eqation by $L_m(\alpha)e^{-\alpha}d\alpha$, integrating from 0 to ∞ with respect to α and using the relations (10), (11) and (12) together with equation (6) by some calculation and simplification we obtain our transformed IEM model for NP reaction as follows (for more detail refer to [3]).

$$\frac{dF_{i,k}^j(\theta)}{d\theta} = \lambda\tau \sum_{n=0}^{\infty} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} F_{1,n}^j(\theta) F_{1,n}^j(\theta) F_{2,m}^j(\theta)$$

$$\int_0^\infty L_n(\alpha) L_n(\alpha) L_m(\alpha) L_k(\alpha) e^{-\alpha} d\alpha - \lambda\tau k_{i+1} F_{1,k}^j(\theta)$$

$$+ C_{0,i}^j - \sum_{n=0}^{k} F_{i,n}^j(\theta) + b[F_{i,0}^j(\theta)\lambda_k - F_{i,k}^j(\theta)]. \tag{13}$$

In above equation (13), $i, j = 1, 2, k = 0, 1, 2, \cdots,\ \ \lambda_k = \begin{cases} 0 & \text{if } \ k \neq 0 \\ 1 & \text{if } \ k = 0, \end{cases}$ $C_{0,1}^1 = 2, C_{0,2}^1 = 0, C_{0,1}^2 = 0$ and $C_{0,2}^2 = 2$.

Equation (13), which we refer to as transformed IEM model for NP reaction, is in the form of ordinary differential equations system and it can be solve much easier than the original IEM model (2) and (3). Indeed, with initial values and special care for computation of non-linear part we can use the continuation sofiware BIFPACK [15] and ODE solver LSODES [10] to find bifurcation, stability analysis and time dependent solutions of this transformed system.

So to find the initial values $F^j_{i,n}(0)$, from equation (7) we notice that

$$C^j_i(\alpha, 0) = \sum_{n=0}^{\infty} F^j_{i,n}(0) L_n(\alpha). \tag{14}$$

Multiplying both sides of equation (14) by $L_m(\alpha)e^{-\alpha}$ and taking integral from 0 to ∞, due to the orthonormality of the Laguerre polynomial we get

$$F^j_{i,n}(0) = \int_0^{\infty} C^j_i(\alpha, 0) L_n(\alpha) e^{-\alpha} d\alpha. \tag{15}$$

Now define

$$G^j_{i,n}(\alpha) = \int_0^{\alpha} C^j_i(\alpha, 0) L_n(\alpha) e^{-\alpha} d\alpha. \tag{16}$$

Then

$$\frac{dG^j_{i,n}(\alpha)}{d\alpha} = C^j_i(\alpha, 0) L_n(\alpha) e^{-\alpha}. \tag{17}$$

So $G^j_{i,n}(\alpha) \to F^j_{i,n}(0)$ as $\alpha \to \infty$, (numericaly as $\alpha \to 60$). Therefore, equation (17) together with steady-state of equation (5) yields the intial values for (13).

$$\frac{dC^j_i(\alpha)}{d\alpha} = \lambda\tau (C^j_1)^2 C^j_2 - \lambda\tau k_{i+1} + b[< C_i > - C^j_i]$$

$$\frac{dG^j_{i,n}(\alpha)}{d\alpha} = C^j_i L_n(\alpha) e^{-\alpha}. \tag{18}$$

Here, $i, j = 1, 2$ and $C_i^j(\alpha, 0)$ are the some as before. Note that, as we have said before, since we are going to compare our results to those on [12] and [6], here we have used the same values for $< C_i >, k_2$ and k_3 as in these studies.

Next, during our computation we should compute the integration of non-linear part

$$[\sum_{n=0}^{\infty} F_{1,n}^j(\theta) L_n(\alpha)]^2 \sum_{m=0}^{\infty} F_{2,m}^j(\theta) L_m(\alpha) L_k(\alpha) e^{-\alpha}. \tag{19}$$

The pseudo-spectral Gauss-Lagurre Integration method [1] gives us the best result. To do this first we define $h_{1,2}(\alpha) = (C_1^j)^2 C_2^j$; from

$$C_i^j(\alpha_p) = \sum_{n=0}^{\infty} F_{i,n}^j(\theta) L_n(\alpha_p),$$

for any $\alpha_p, p = 0, 1, \cdots, P$, we can compute

$$h_{1,2}(\alpha_0), h_{1,2}(\alpha_1), \cdots, h_{1,2}(\alpha_P).$$

Hence, the integration of (19) will be

$$\int_0^{\infty} h_{1,2}(\alpha) L_k(\alpha) e^{-\alpha} d\alpha. \tag{20}$$

Now, using Gauss-Laguerre Integration method the above integration (20) can be approximated by

$$\sum_{p=1}^{P} A_p h_{1,2}(\alpha_p) L_k(\alpha_p),$$

where

$$A_p = \frac{(P!)^2 \alpha_p}{(P+1)^2 [L_{P+1}(\alpha_p)]^2}.$$

Here, if we choose α_p to be the zero of the Laguerre polynomial of degree P, the integration will be exact for the function $h_{1,2}(\alpha) L_k(\alpha)$ being the polynomial of degree at most 2P-1.

We should notic that the only error in solving the transformed IEM model is the trancation error. Here for NP reaction, we have used 6 terms of the polynomial expansion and the results are very similar to those found by Puhl, Nicolis [12] and Fox [6] for steady-state case.

4. Bifurcation and Stability Analysis

Based on the techniques discussed in the previous section and knowing that

$$C_i^j(\alpha,\theta) \simeq \sum_{n=0}^{N} F_{i,n}^j(0)L_n(\alpha),$$

bifurcation and stability analysis of the NP reaction has been computed using continuation software BIFPACK [15] and ODE solver LSODES [10]. The results of these computations are summarized in Figures 1 and 2. First we compute (b, τ^{-1}) bifurcation sets, since these are the two operating parameters which can be varied in an actual experiment [6]. Indeed the computations were pereformed by fixing k_2 and k_3 so that a TB point existed in the perfect micromixing limit. The possible values for these parameters are given in [12] where the TB point has been parameterized by η, the value of the steady-state concentration of first component ($< C_1 >$) at the TB point. By this parametrization, it is convenient to refor to the parameter pair (k_2, k_3) by its corresponding η-value, denoted by $< \eta >_{TB}$. The values of $< \eta >_{TB}, k_2$ and k_3 used in the first series of computations are the same as Fox's values [6] and are given by (0.3, 0.615, 0.54609), (0.35, 0.65779, 0.58616), (0.375, 0.67634, 0.60459), (0.4, 0.69333, 0.62222), (0.425, 0.709, 0.63921), (0.46, 0.7291, 0.66215), (0.475, 0.73716, 0.67175), (0.5, 0.75, 0.6875), (0.55, 0.77393, 0.71837) and (0.6, 0.79636, 0.74876).

The results of the computations for each of the above-mentioned parameter sets are shown in Figure 1. Hopf and saddle-node bifurcation curves are plotted as dash and solid curves labled H and S, respectively. These two curves were located using BIFPACK with the steady-state system of equations (13) (for $i, j = 1, 2$ and $k = 0, 1, 2, \cdots, 6$). For all values of the parameters used in this section, only the real part of two eigenvalues were changed their signs (saddle-node bifurcation) or only two of them were purely imaginary (Hopf bifurcation). This implies that the dynamical dimension of the transformed IEM model is two for the NP reaction for all values of b.

The existence of periodic solutions to the unsteady-state transformed IEM model for parameter values near the H-curve has been confirmed by solving numerically the time-dependent model equations (13) and the results are shown in next section.

The parameter values used in Figure 1(a)-(c) result in a bifurcation set like the one shown in [12] and [6]. For example as occurs when moving from Figure 1(a) to 1(b), the S-curve above the TB point in Figure 1(a)-(c) becomes smaller and smaller, until the cusp and TB points concide. (Figure 1(d)). The same qualitaive changes can be seen in [12] and [6] for the parameter space (k_3, τ^{-1}). Thus, qualitatively, the parameters b and k_3 have the same effect in the NP reaction: decreasing either parameter while varying τ^{-1} results in an unfolding of the Hopf and saddle-node bifurcations.

It is imporfant to note, however, that for a real reaction the rate constants would be fixed, leaving only manipulatable parameters such as the residence time and the stirring rate as possible bifurcation parameters. Hence, Figure 1 can be viewed as a representation of the observable bifurcation sets in a real reactor

[6]. From this figure, it can be seen that the sensitivity of the NP reaction to micromixing depends strongly on the value of the kinetic rate parameters. In Figure 1(a), the H-curve is relatively insensitive to the value of b in the rang $[100, 1000]$, while the S-curve exhibits a slightly greater dependence. In Figure 1(c), the S-curve exists only near $b = 1000$ and disappears altogether in Figure 1(d). In these figures, the H-curve is seen to move towards larger τ^{-1}-values as b decreases, suggesting that Hopf bifurcations can be induced from a steady state by lowering the stirring rate with the flow rate held constant. In Figure 1(e)-(g) the H-curve moves out of the top of the figure making Hopf bifurcations more and more dependent of the micromixing rate. Finally, in Figure 1(h), the H-curve has disappeared, leaving only the S-curve in the remaining figures. The greatest amount of sensitivity to the micromixing rates occurs, approximatly, in Figure 1(f) where the parameter values correspond to those used in Puhl and Nicolis [12] and Fox [6]. In this figure, the Hopf and saddle-node bifurcation curves both lie above $b = 100$ (thus, in the rangs of validity of the both IEM and fransformed IEM models); hence, for these rate constants, the reaction is very sensitiue to micromixing effects [9].

5. Time Dependent, Periodic Solutions and Chaoc

In addition to the relative simplicity of transormed IEM model to find the solution and bifurcation analysis of NP reaction, it has the interest of finding the time dependent solution of this reaction. Indeed we have employed the same technique outlined in section 3 to investigate time dependent solution to the transformed IEM model for NP reaction. Example solutions for several types of fixed points will be presented here: unstable, periodic after the potential Hopf bifurcation point and even unexpected chaotic point.

We have began time-dependent solution of fixed saddle points in Figure 1. As an example consider the point 1 in Figure 1(a) for values $< \eta >_{TB} = (< C_1 >) = 0.30, \tau^{-1} = 0.078736$ and $b = 750$. We find the result shown in Figure 2(a). As we can see starting from this point as expected the time-dependent solution will change. This is because in finding this bifurcation point, using BIFPACK, in section 4 the corresponding two eighenvalues of this point had different sign of real parts. The similar results to this in Figure 1 have shown that the saddle points found in steady-state case are indeed unstable solutions of the unsteady-state transformed IEM model.

Also of interest is the periodic solution to the transformed IEM model for different parameter b at Hopf bifurcation. In this case if we choose a point along the H-curve in Figure 1 as an initial condition, the periodic solution can be observed by solving the unsteady-state transformed IEM model. Thus, taking point 3 from Figure 1(b) corresponding to $< \eta >_{TB} = (< C_1 >) = 0.35, \tau^{-1} = 0.0981315$ and we find the result presented in Figure 2(c). Similar result can be found for other points along the H-curves in Figure 1. Figure 2(d) is another example of a periodic solution to the transformed IEM model corresponding to the point 4 of Figure 1(b) for $< \eta >_{TB} = (< C_1 >) = 0.35, \tau^{-1} = 0.0935228$ and $b = 200$. The results illustrated in Figures 2(c)-(d) have shown that periodic solutions along the H-curves can be checked by using unsteady-state trunsformed IEM model. Nevertheless, due to the relatively long compoting times required to find the periodic solution by solving the unsteady-state transformed model, only a limited number of parameter values, could actually be investigated by directly solving the time dependent transformed IEM model equations.

Another solution that we have found by sloving the unsteady-state model is unexpectated chaodic solution which we absorved by choosing a few points such as point 5 in Figure 1(a) correspond to $<\eta>_{TB}=(<C_1>)=0.30$, $\tau^{-1}=0.07874$ and $b=450$. This solution illustrated in Figure 2(e). As we can see starting from this point we never know when we return to the same point. Of course this kind of the solution was to rare during our investigation.

6. Conclusions

The class of IPDE introduced here and elsewhere [2], [3], [6] and [8] can be used to steady the dynamical behavior of many systems [5], [6] and [8]. An unsteady-state version of the IEM model, as the resultant system of this IPDE, however can rarely be solved analytically. So we have derived a polynomial expansion of this model that could be used to investigate the dynamical behavior of the system in general, and the behavior of unsteady-state solutions, in particular.

The numerical simulation procedure, for transformed IEM model, employed in this work represents a direct, albeit time-consuming method for constructing the bifurcation set and time-dependent solutions for imperfectly-micromixed reactions such as NP reaction. Other application of this model can also be developed [5].

As we have seen the steady-state dynamical behavior of the NP reaction can be very sensitive to the degree of micromixing. Using the transformed IEM model, bifurcation sets have been constructed wherein Hopf and saddle-node bifurcation curves in micromixing rate (b) and the mean residence time (τ^{-1}) parameters space. These results are agree with those are found by others [6], [7] and [12].

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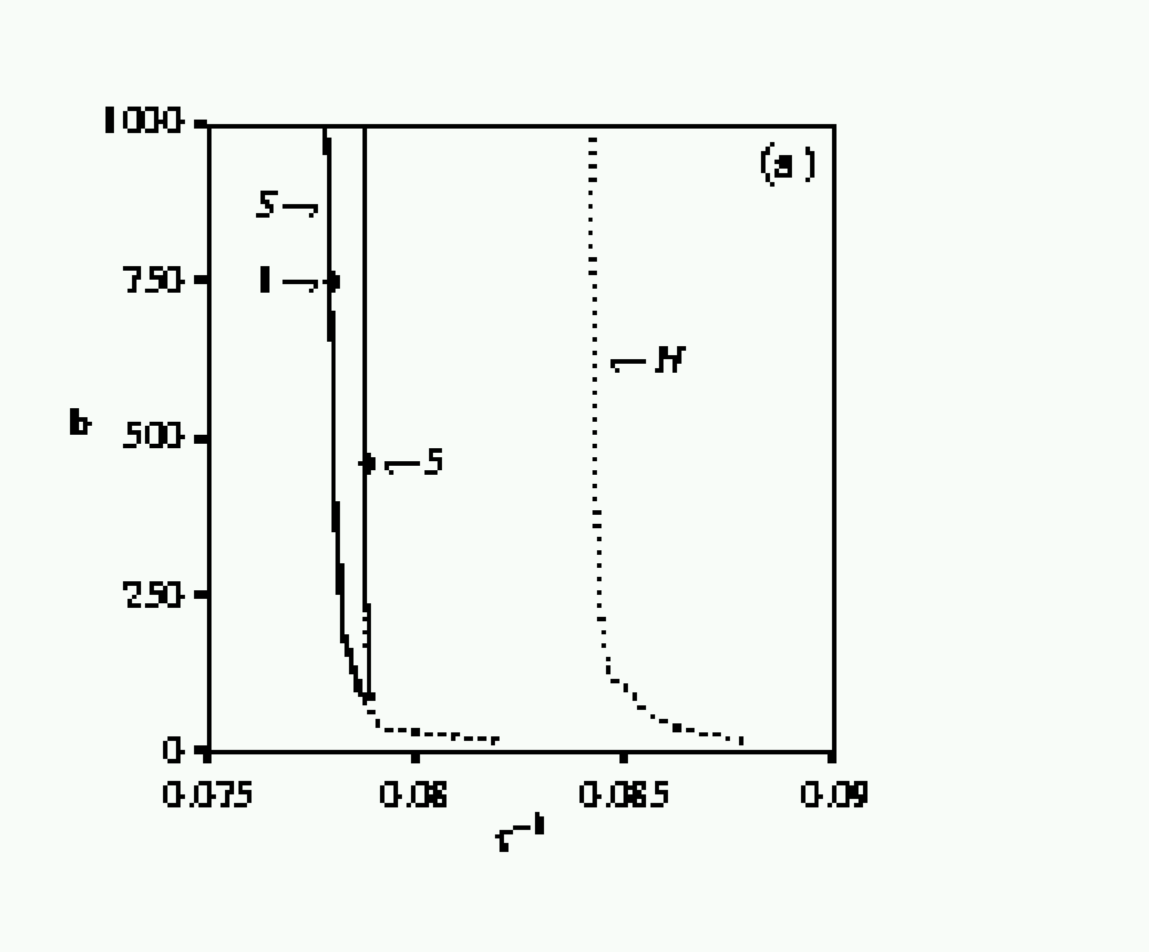
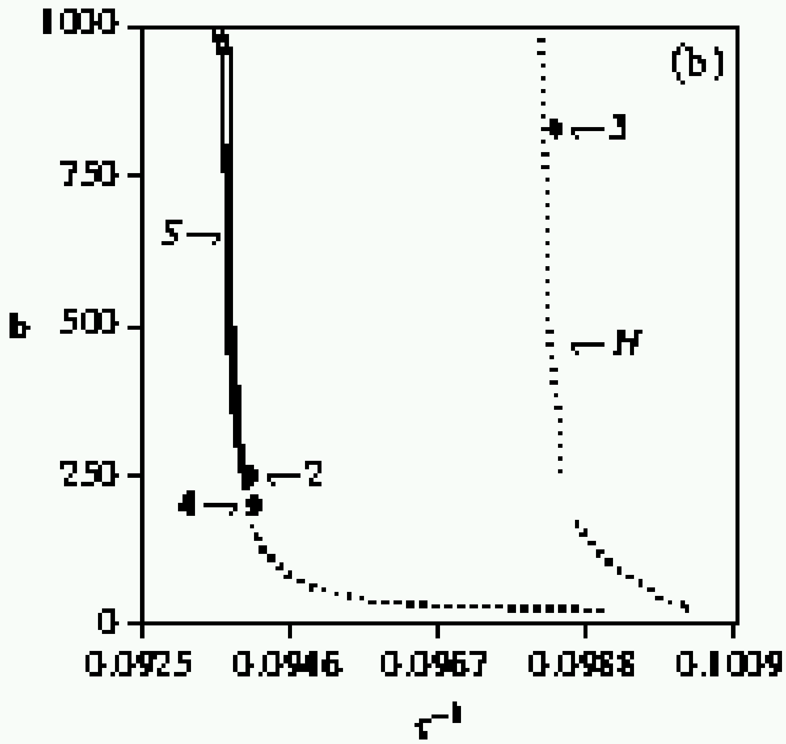
List of Figures

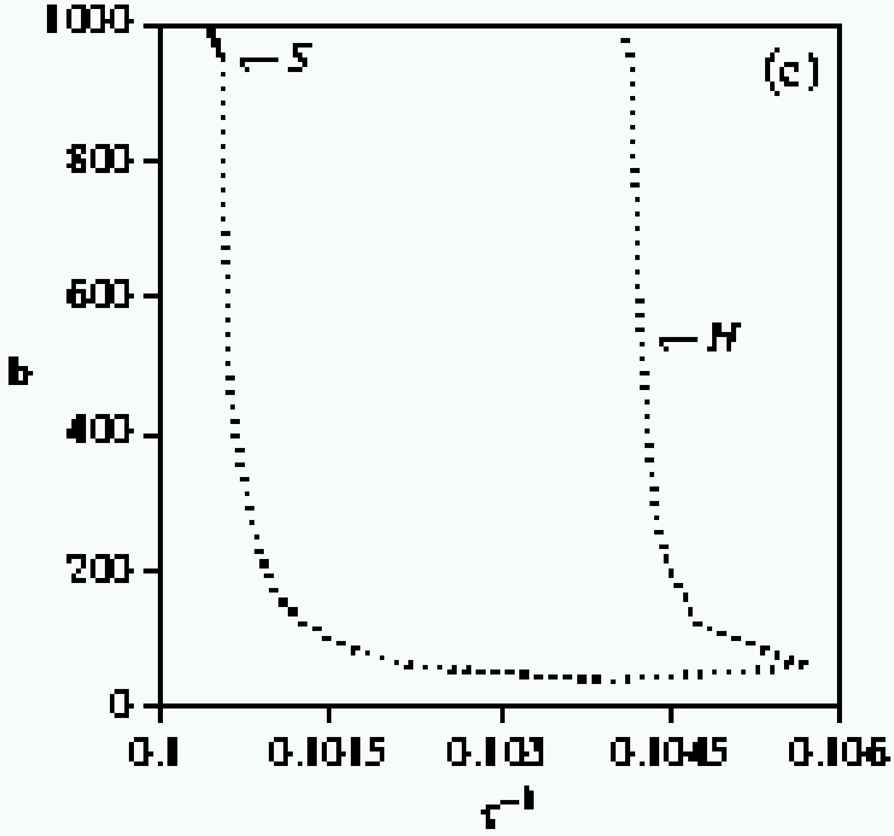
Figure 1. Bifurcation sets in (b, τ^{-1}) parameter space for the NP reaction using transformed IEM model. The kinetic rate constants k_2 and k_3 are given in the text for all figures. 1(a) to 1(j).

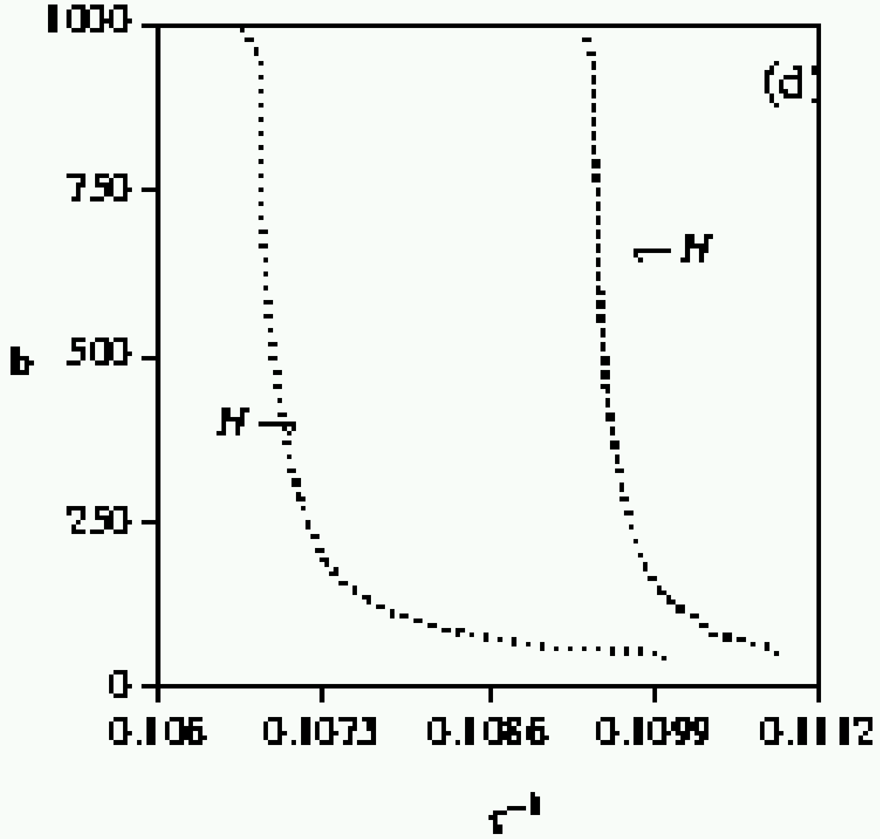
Figure 2. Unsteady-state solution for NP reaction using transformed IEM model: (a), (b) unstable solutions, (c), (d) periodic solutions with relatively small and large periods and (e) chaodic solution.

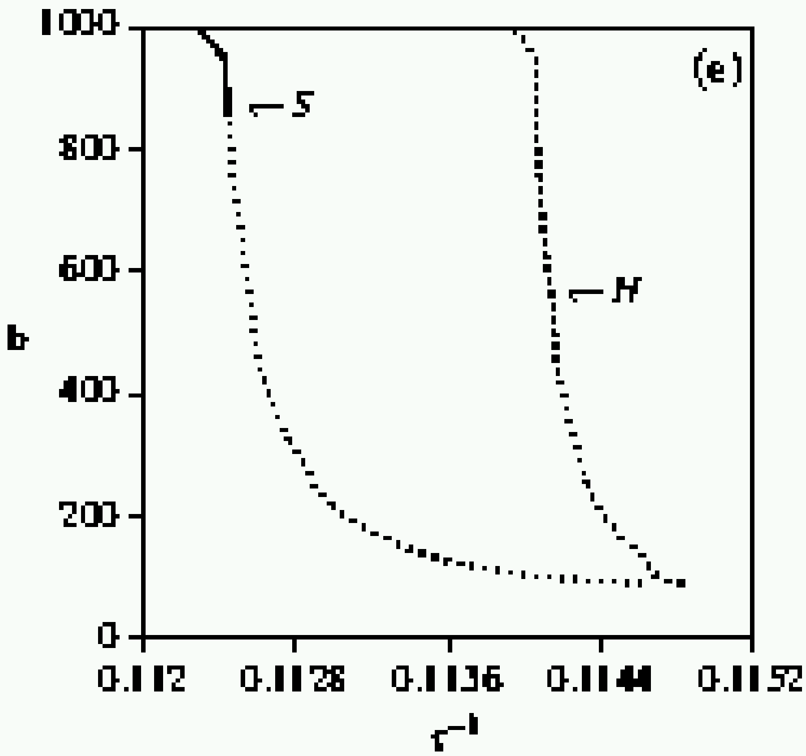


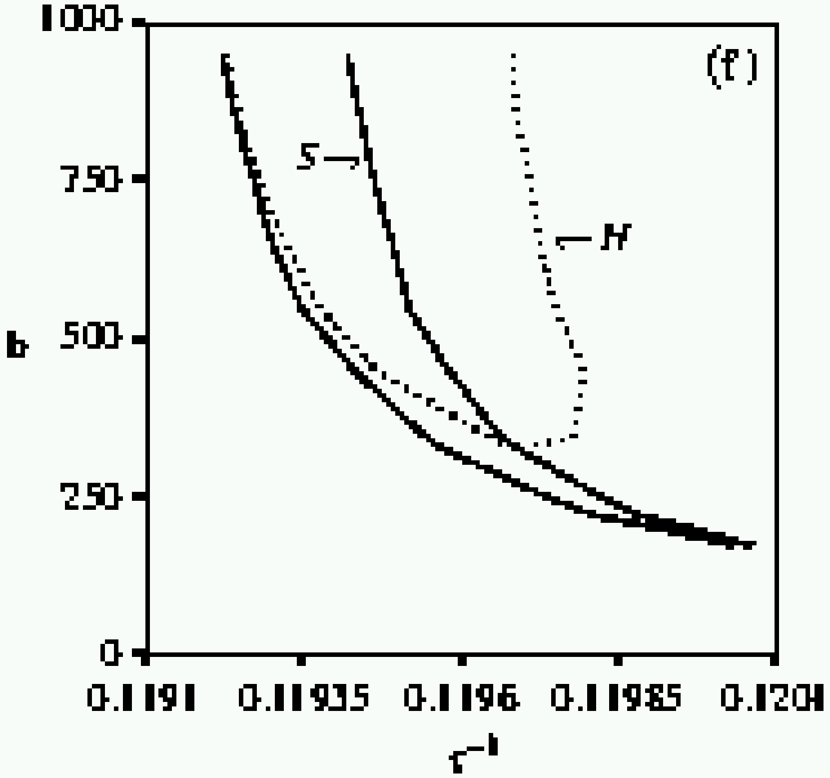
1000
750
500
250
0
b
(a)
5
1
5
H
0.075
0.08
0.085
0.09
r⁻¹


(b)
1000
750
500
250
0
b
0.0925
0.0946
0.0967
0.0988
0.1009
c^{-1}
5
2
4
3
H

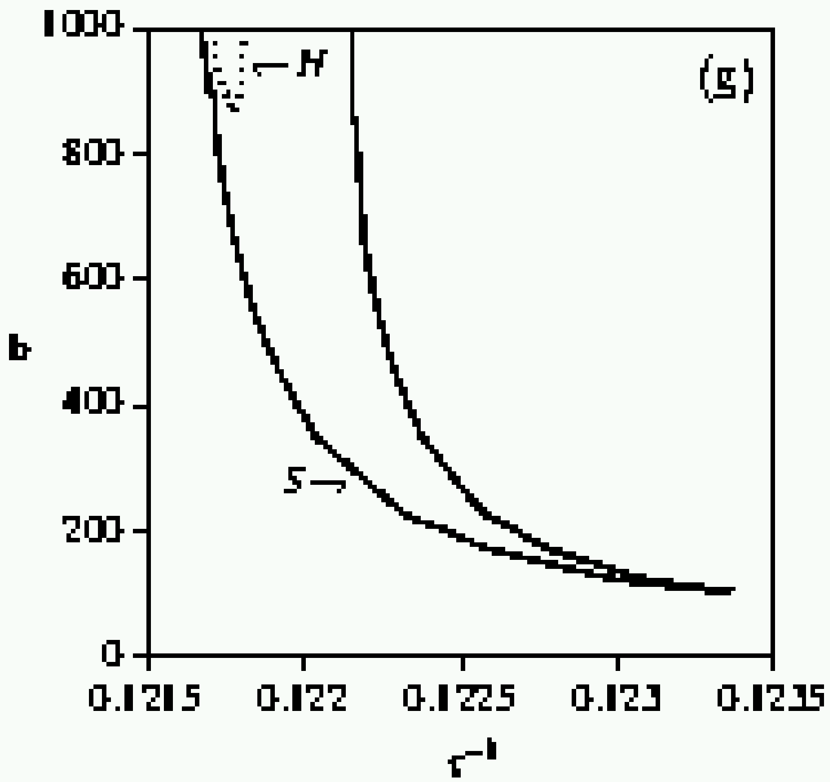

1000
800
600
400
200
0
b
0.1
0.1015
0.103
0.1045
0.106
τ⁻¹
S
H
(c)


1000
750
500
250
0
b
(d)
H
H
0.106
0.1073
0.1086
0.1099
0.1112
ϵ^{-1}

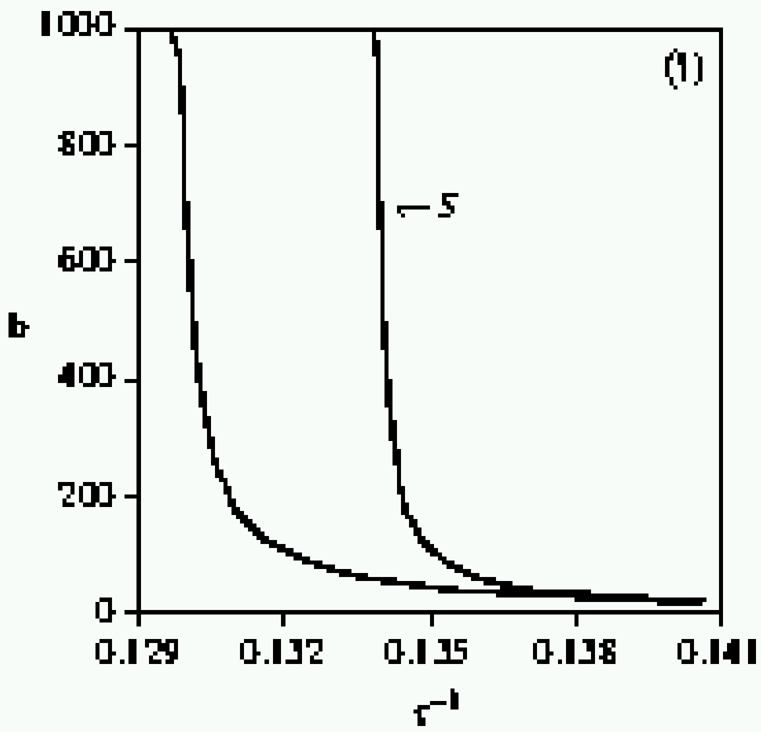

1000
800
600
400
200
0
b
(e)
S
H
0.112
0.1128
0.1136
0.1144
0.1152
ε^{-1}

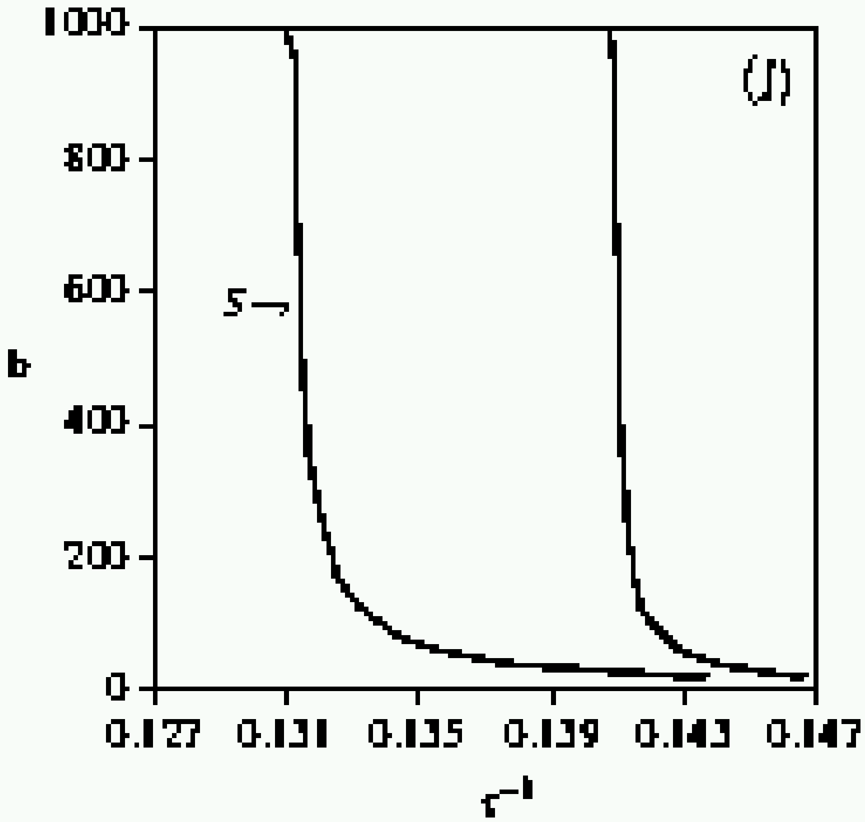


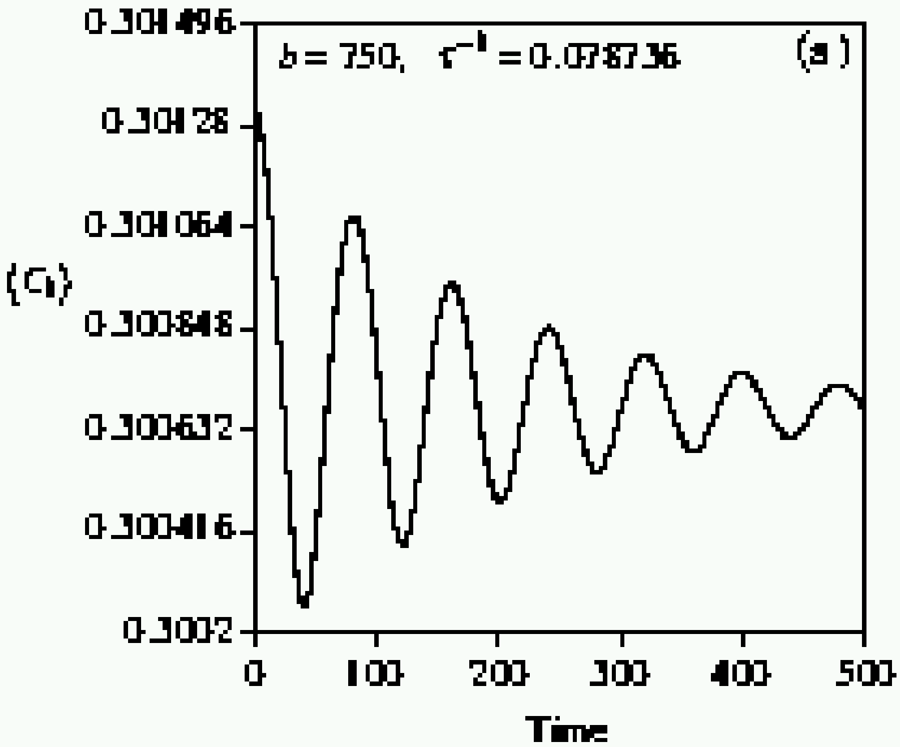
1000
750
500
250
0
b
0.1191
0.11935
0.1196
0.11985
0.1201
r^{-1}
(f)
S
H



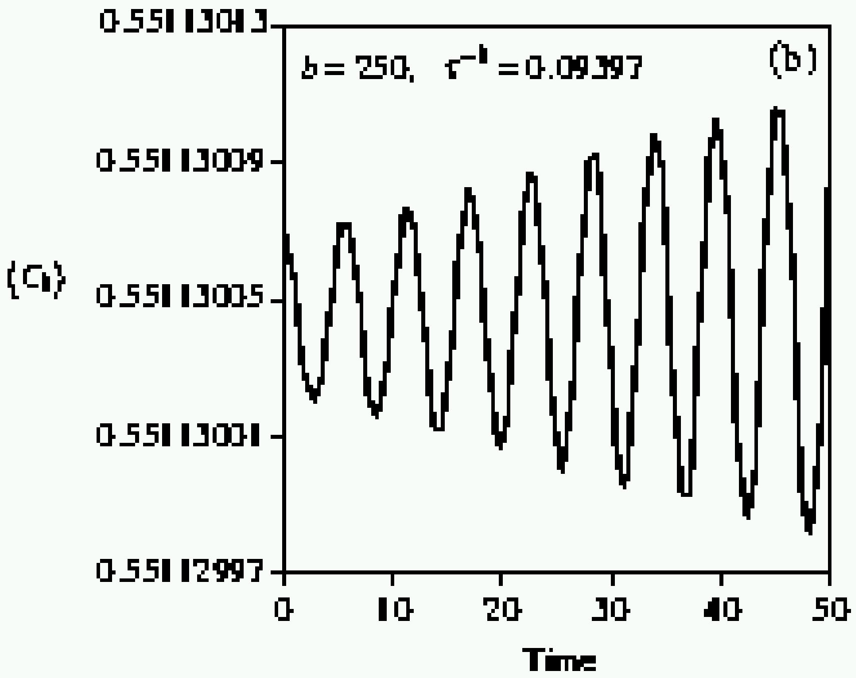
1000
800
600
400
200
0
b
0.1215
0.122
0.1225
0.123
0.1235
ε^{-1}
(g)
H
S

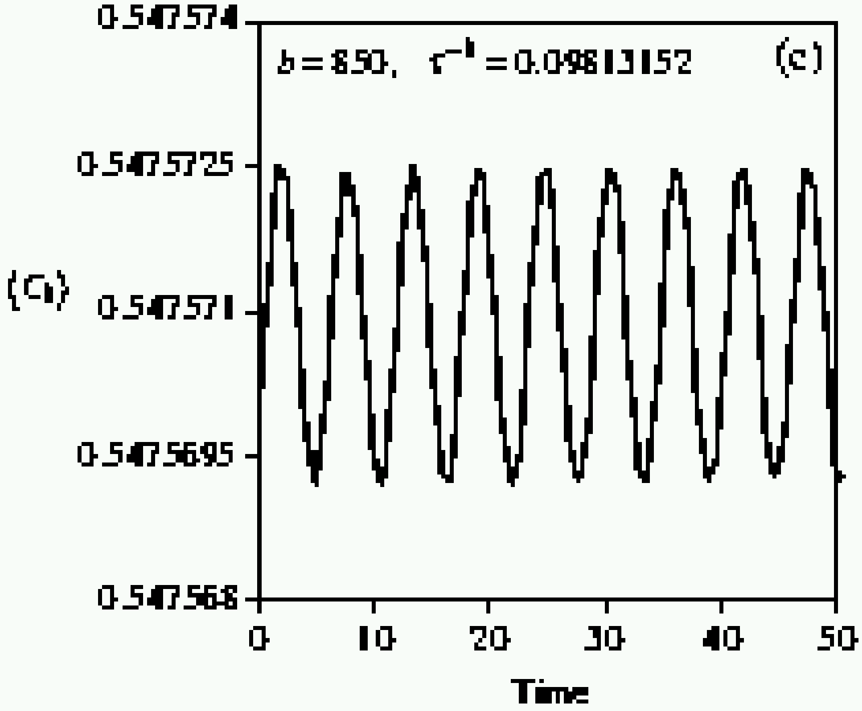

1000
800
600
400
200
0
b
0.129
0.132
0.135
0.138
0.141
τ^{-1}
(1)
5


1000
800
600
400
200
0
b
5
(J)
0.127
0.131
0.135
0.139
0.143
0.147
ε^{-1}

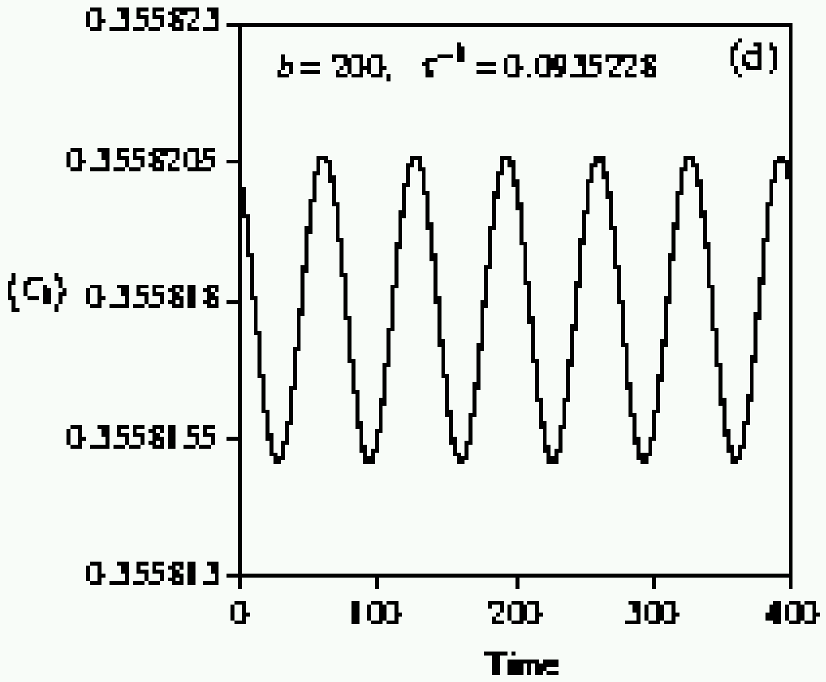


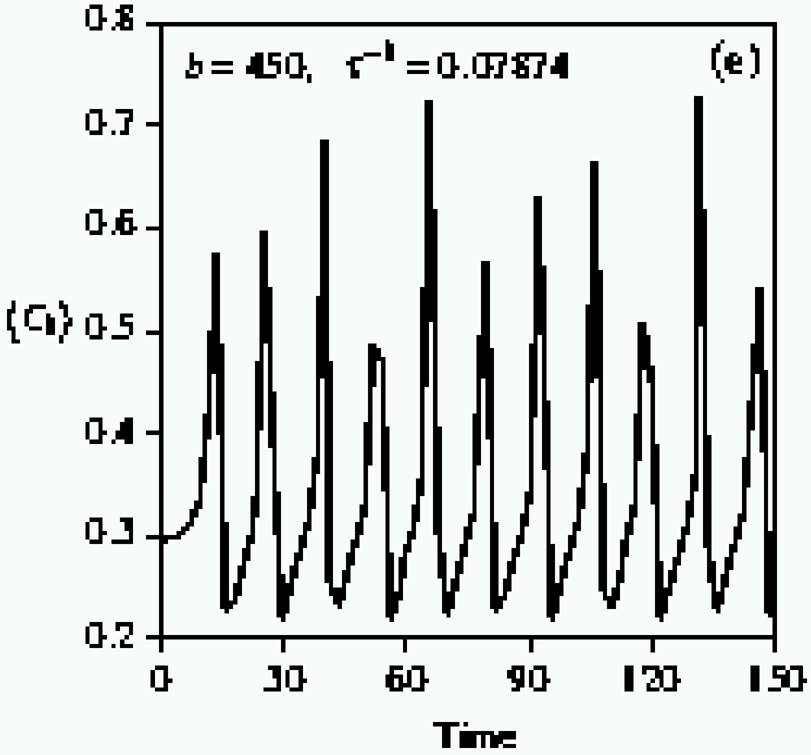
$b = 750, \quad \tau^{-1} = 0.078736$
(a)
0.301496
0.30128
0.301064
0.300848
0.300632
0.300416
0.3002
$\langle C_1 \rangle$
0
100
200
300
400
500
Time


0.55113013
0.55113009
0.55113005
0.55113001
0.55112997
⟨C₁⟩
b = 250, τ⁻¹ = 0.09397
(b)
0
10
20
30
40
50
Time



0.547574
0.5475725
0.547571
0.5475695
0.547568
$\langle C_1 \rangle$
$b = 850, \quad \tau^{-1} = 0.09813152$
(c)
0
10
20
30
40
50
Time


0.355823
0.3558205
0.355818
0.3558155
0.355813
$\langle C_1 \rangle$
$b = 200,\quad \tau^{-1} = 0.0935228$
(d)
0
100
200
300
400
Time


b = 450, τ⁻¹ = 0.07874
(e)
⟨Ci⟩
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0
30
60
90
120
150
Time