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Limit-cycle behaviour in a model chemical reaction: the cubic autocatalator

L.K. FORBES and C.A. HOLMES

Department of Mathematics, University of Queensland, St. Lucia, Queensland, 4067, Australia

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Abstract. Limit cycles are sought in a mathematical model of a simple hypothetical chemical reaction involving essentially only two reacting species. Physically, these limit cycles correspond to time-periodic oscillations in the concentrations of the two chemicals. A combination of analytical and numerical methods reveals that limit-cycle behaviour is only possible in a restricted region of the parameter space. Strong numerical evidence is presented to assert that the limit cycle is unique and stable to infinitesimal perturbations. Numerical solutions are displayed and discussed.

1. Introduction

It is usual to think of chemical reactions occuring in a monotonic fashion, so that a smooth transition is observed from reactants to products. There may be a colour change as the concentration of the reactants falls and that of the products rises, and the reaction may be accompanied by the generation or absorption of heat. It is also possible for a reaction to proceed monotonically to equilibrium if the reaction is reversible, so that, instead of a complete conversion of reactants to products, the participating chemical species attain constant non-zero concentrations.

There has, however, been a great deal of interest recently in chemical reactions which do not progress monotonically, but instead give rise to persistent oscillations in the concentrations of reactants and products. Of these reactions, perhaps the most famous is the Belousov–Zhabotinskiĭ reaction, which is actually observable in the laboratory as a sustained periodic alternation between the colours red and blue, when a suitable chemical indicator is added to the solution (see Tyson [14, page 30]). These oscillatory reactions are possibly of significance in biology, as discussed by Grasman [2, page 8], where perhaps they provide a mechanism for the processes of aging or the regular beat of the heart. Mathematical models of these reactions, such as the "oregonator" proposed by Field and Noyes [1] to describe the Belousov–Zhabotinskiĭ reaction, often assume isothermal conditions apply; however, oscillations are also theoretically possible in exothermic reactions governed by an Arrhenius rate law, as shown for example by the work of Gray, Kay and Scott [6], Kay and Scott [10] and Gray and Roberts [4].

Possibly the simplest model of a chemical reaction capable of exhibiting periodic oscillations is the cubic autocatalator, proposed by Gray and Scott [7]. It models the hypothetical reaction

$$\mathrm{P}\xrightarrow{k_0}\mathrm{A}\,,\quad \mathrm{A}+2\mathrm{B}\xrightarrow{k_1}3\mathrm{B}\,,\quad \mathrm{B}\xrightarrow{k_2}\mathrm{C}\,,\quad \mathrm{A}\xrightarrow{k_3}\mathrm{B}\,, \tag{1.1}$$

in which P, A, B and C are certain chemical species with molar concentrations p, a, b and c,

respectively, and the quantities $k_0 - k_3$ are rate constants. The reactions are assumed to take place isothermally, and for simplicity we will invoke the "pool chemical approximation", in which the precursor species P is assumed to be in such great excess as to be virtually inexhaustible. The scheme (1.1) is the subject of the present paper.

The rate equations describing the progress of reaction (1.1) are

$$\begin{aligned} \frac{da}{dt} &= k_0 p - k_1 a b^2 - k_3 a \,, \\ \frac{db}{dt} &= k_1 a b^2 - k_2 b + k_3 a \end{aligned} \tag{1.2}$$

for the concentrations a, b of the two reacting species A, B of interest. Here, t denotes time.

It is convenient to introduce non-dimensionalized concentrations x and y for the two chemical species A and B according to the relations

$$x = a(k_1/k_2)^{1/2} \quad \text{and} \quad y = b(k_1/k_2)^{1/2} \,.$$

In addition, the time t is made dimensionless by reference to the rate constant k_2. The problem is thus seen to be dependent upon the two dimensionless parameters

$$\mu = \left(\frac{k_1}{k_2}\right)^{1/2} \frac{k_0 p}{k_2} \,, \quad r = \frac{k_3}{k_2} \,, \tag{1.3}$$

and the rate equations (1.2) in non-dimensionalized form become

$$\begin{aligned} \frac{dx}{dt} &= \mu - xy^2 - rx \,, \\ \frac{dy}{dt} &= xy^2 - y + rx \,. \end{aligned} \tag{1.4}$$

The system (1.4) has been analyzed in some detail by Merkin, Needham and Scott [11], and includes an extensive discussion of the effect of the pool-chemical approximation. In a later paper [12], these authors considered equations (1.4) in the special case in which $r = 0$, presenting a complete phase-plane analysis of the possible solutions. They showed that periodic solutions are possible for values of the parameter μ in the interval $\mu_0 < \mu < 1$, with the value μ_0 determined numerically to be about $\mu_0 = 0.9003$. The periodic solutions arise at $\mu = 1$ through a Hopf bifurcation from the equilibrium steady-state, and the amplitude of the oscillations increases rapidly with decreasing μ, finally becoming infinite at $\mu = \mu_0$. An approximation to the limit cycle in the phase plane was derived using matched asymptotic expansion arguments. We summarize some of the qualitative results of these papers in the next section (Section 2).

In a recent paper, Gray and Thuraisingham [5] have "unfolded" the system (1.4) by inclusion of an extra parameter, and performed a rather complete bifurcation analysis. They showed that, for $r \neq 0$, the amplitude of the oscillations does not become infinite near $\mu = \mu_0$, but rises very sharply to some large but finite value. In the vicinity of this rapid change of amplitude, a numerical solution of equations (1.4) shows apparent chaotic behaviour, as numerical round-off error causes the solution scheme to jump almost randomly from the large- to the small-amplitude solution. Gray and Thuraisingham [5] suggest the

existence of an unstable limit cycle in this vicinity, and in addition, conjecture the existence of limit cycles in the region $\mu > 1$. It is the purpose of the present paper to examine these suggestions.

Qualitative results concerning limit-cycle behaviour for solutions of equations (1.4) are presented in Section 2. The numerical technique used for the solution of this highly non-linear problem is briefly reviewed in Section 3, where the numerical Floquet-theory stability analysis is presented. The results of extensive numerical computation are given in Section 4, and a discussion in Section 5 concludes the paper.

2. Qualitative results

It is instructive to investigate the nature of the equilibrium solutions to equations (1.4). The single equilibrium point, obtained when $\dot{x} = \dot{y} = 0$, is easily seen to be

$$(x_{eq}, y_{eq}) = \left(\frac{\mu}{\mu^2 + r}, \mu\right). \tag{2.1}$$

Merkin, Needham and Scott [12] have shown that, for $r = 0$, periodic solutions may emanate from the point $\mu = 1$ via a supercritical Hopf bifurcation. The solutions increase in amplitude as μ is decreased, until the value $\mu = \mu_0 \approx 0.9003$ is attained, at which point a heteroclinic orbit of infinite amplitude and period is produced. For $r > 0$, Merkin, Needham and Scott [11] demonstrated that two Hopf bifurcation points exist, at the values

$$\mu_{\pm} = \left[\frac{(1-2r) \pm (1-8r)^{1/2}}{2}\right]^{1/2}. \tag{2.2}$$

These values approach 0 and 1, as $r \to 0$. Periodic solutions are generated at these points via supercritical Hopf bifurcations, and for small r, the two branches of limit-cycle solutions thus produced meet abruptly at about the value $\mu = \mu_0 \approx 0.9003$. Thus, for a given value of r, limit cycles are expected in the interval $\mu_- < \mu < \mu_+$. The length of this interval decreases as r is increased, finally becoming zero at $r = 1/8$. At this value of r, the two Hopf bifurcation points given in equation (2.2) coalesce, and the branch of periodic solutions is extinguished in an $H2_1$ degeneracy of type A (adopting the language and notation of Gray and Roberts [3]). Merkin, Needham and Scott [11] argued that limit cycles are not a possibility for $r > 1/8$.

It is of interest, then, to know whether limit cycle behaviour is possible outside the interval $0 < \mu < 1$. Indeed, Gray and Thuraisingham indicate that, for $\mu > 1$, it is possible that the equilibrium point given by equation (2.1) (which is stable in this region) could in principle be surrounded by two limit cycles, one of which is unstable and the other stable. The following theorem, however, shows that this behaviour is not realized for the cubic autocatalator, and consequently, that no periodic orbits exist in this interval:

THEOREM. *The cubic autocatalator problem defined in equations* (1.4) *has no periodic solutions*

(1) *when* $\mu^2 > 1 - r$,

(2) *for all* μ *when* $r > 1/8$.

Proof: First we transform system (1.4) to a Liénard equation which may be written in the form

$$\frac{d\bar{v}}{d\tau} = -g(\bar{y}), \quad \frac{d\bar{y}}{d\tau} = \bar{v} + F(\bar{y}),$$

where

$$\bar{v} = x + y - \left(\mu + \frac{\mu}{\mu^2 + r}\right), \quad \bar{y} = y - \mu$$

and

$$\mathrm{d}\tau = ((\bar{y} + \mu)^2 + r)\,\mathrm{d}t.$$

Now by Dulac, Ye Yan-Qian [16], if there is a function $B(\bar{v}, \bar{y})$ such that

$$\left\{-\frac{\partial}{\partial \bar{v}}[B(\bar{v}, \bar{y})g(\bar{y})] + \frac{\partial}{\partial \bar{y}}[B(\bar{v}, \bar{y})(\bar{v} + F(\bar{y}))]\right\}$$

has constant sign and is not identically zero, then the system has no closed trajectory.

To show part (1), we choose a Dulac function $B(\bar{v}) = \mathrm{e}^{-2\mu\bar{v}}$ and require

$$\left\{g(\bar{y})2\mu + \frac{\partial F}{\partial \bar{y}}\right\}$$

negative. Since

$$g(\bar{y}) = \frac{\bar{y}}{(\bar{y} + \mu)^2 + r}$$

and

$$\frac{\partial F}{\partial \bar{y}} = \frac{-\bar{y}^2 - 2\bar{y}\mu - (\mu^2 + r - 1)}{(\bar{y} + \mu)^2 + r} - \frac{2r}{[(\bar{y} + \mu)^2 + r]^2},$$

this is the case if $\mu^2 > 1 - r$.

For the proof of part (2), we simply take $B = 1$ and note that

$$\frac{\partial F}{\partial \bar{y}} = \frac{P((\bar{y} + \mu)^2)}{[(\bar{y} + \mu)^2 + r]^2}$$

is negative, since the discriminant of

$$P(z) = z^2 + z(1 - 2r) + r + r^2$$

is negative for $r > 1/8$.

3. Numerical solution and stability analysis

We seek periodic solutions to the system (1.4), in which the period P is an unknown to be determined. It is natural to seek such solutions in the form of Fourier series, following Urabe [15] for example, but it is quickly observed that the stiffness of the solutions obtained is responsible for very slow convergence of the Fourier series and consequent difficulties with numerical accuracy. Re-casting the Fourier series in the form of Padé fractions to enhance convergence is possible, and a technique of this sort has been utilized by Holmes and Wood [8], but in the present problem, we find that even this refinement is insufficient to cope completely with the regions of stiffness encountered.

Consequently, the system (1.4) is solved by a shooting algorithm. A new unit of time τ is introduced via the transformation

$$\tau = \frac{2\pi t}{P}\,, \tag{3.1}$$

in which P denotes the unknown period. The system (1.4) may be written

$$\begin{aligned} \frac{\mathrm{d}x}{\mathrm{d}\tau} &= \frac{P}{2\pi}\,(\mu - xy^2 - rx)\,, \\ \frac{\mathrm{d}y}{\mathrm{d}\tau} &= \frac{P}{2\pi}\,(xy^2 - y + rx)\,, \end{aligned} \tag{3.2}$$

where the functions $x(\tau)$ and $y(\tau)$ are now 2π-periodic.

The shooting algorithm is straightforward, and need only be described briefly. With the parameters μ and r given, we are free to choose the value of x at the beginning of a cycle, and so we take $x(0) = \mu/(\mu^2 + r)$, without loss of generality. An initial guess is now made for the period P and the starting value $y(0)$, and equations (3.2) are integrated through a full cycle, $0 \leqslant \tau \leqslant 2\pi$. Newton's method is used iteratively to adjust the values of P and $y(0)$ until the final values $x(2\pi)$ and $y(2\pi)$ agree with the starting values $x(0)$ and $y(0)$ to within a pre-set numerical tolerance. At this point, a periodic solution has been obtained, and the iteration is stopped. To enhance the utility of the algorithm, *damping* is introduced into Newton's method, so that an update to P and $y(0)$ is only accepted if it reduces the overall error; otherwise, the Newton correction vector is halved and the iteration repeated.

This shooting algorithm runs extremely quickly, and generates numerical results of great accuracy. It could be further enhanced by the use of a more sophisticated routine to integrate equations (3.2), but in view of the speed of the algorithm and some minor constraints arising from the consideration of stability, we have been content to use fourth-order Runge–Kutta integration on a uniform mesh, employing a large number of numerical grid points as required. The method is capable of yielding in excess of seven significant figures of accuracy for all values of the parameters we have investigated, and typically requires about 150 seconds of execution time on the PYRAMID 9810 mini-computer in the Mathematics Department at the University of Queensland. This algorithm can be at least two orders of magnitude faster than the Fourier-series methods, for the same accuracy. We also make use of a modification to this method, in which the period P and the parameter r are assumed known, and the constant μ found as part of the solution.

The stability of the solutions is investigated using numerical Floquet theory (see Sánchez [13] and Jordan and Smith [9]). Suppose that a 2π-periodic solution $X(\tau)$ and $Y(\tau)$ has been

found to the system (3.2), along with the period P. We consider a perturbation of the form

$$x(\tau) = X(\tau) + \epsilon\xi(\tau) + \mathrm{O}(\epsilon^2)\,, \qquad (3.3)$$
$$y(\tau) = Y(\tau) + \epsilon\eta(\tau) + \mathrm{O}(\epsilon^2)\,,$$

where ϵ is some small positive real number. Equations (3.3) are inserted into the system (3.2) and only the first-order terms retained. This gives the variational equations in matrix form as

$$\dot{\mathbf{u}} = A\mathbf{u}\,, \qquad (3.4)$$

where we have defined the vector $\mathbf{u} = [\xi, \eta]^T$ and the matrix

$$A(\tau) = \frac{P}{2\pi}\begin{bmatrix} -r - Y^2(\tau) & -2X(\tau)Y(\tau) \\ r + Y^2(\tau) & 2X(\tau)Y(\tau) - 1 \end{bmatrix}.$$

This is a system of linear differential equations for the vector $\mathbf{u}$, in which coefficient matrix A is a known 2π-periodic function of τ.

Let $\Phi(\tau)$ be the fundamental matrix for the system (3.4), satisfying the equation

$$\dot{\Phi} = A\Phi\,, \quad \Phi(0) = I\,,$$

in which I denotes the identity matrix. Floquet's theorem guarantees that the fundamental matrix has the property

$$\Phi(\tau + 2\pi) = \Phi(\tau)C\,, \qquad (3.5)$$

where C is a constant matrix. The eigenvalues λ_1 and λ_2 of matrix C determine whether the perturbation $\mathbf{u}$ is stable or unstable, since equation (3.5) is equivalent to the statement that solutions to equation (3.4) must be of the form

$$\mathbf{u}(\tau + 2\pi) = \lambda_j \mathbf{u}(\tau)\,, \quad j = 1, 2\,.$$

For periodic solutions, one eigenvalue must be unity, $\lambda_1 = 1$, and so the other eigenvalue λ_2 determines the stability of the orbit. The limit cycle is stable if $|\lambda_2| < 1$, and unstable otherwise.

The matrix C is computed numerically by observing that $C = \Phi(2\pi)$ (which follows on setting $\tau = 0$ in equation (3.5)), and integrating the linear equations once around the limit cycle. Alternatively, the monodromy matrix C can be obtained by recognizing it as the Jacobian

$$C = \begin{bmatrix} \dfrac{\partial x(2\pi)}{\partial x(0)} & \dfrac{\partial x(2\pi)}{\partial y(0)} \\ \dfrac{\partial y(2\pi)}{\partial x(0)} & \dfrac{\partial y(2\pi)}{\partial y(0)} \end{bmatrix} \qquad (3.6)$$

and estimating the derivatives numerically. We use both methods to compute matrix C, which serves as a valuable check on accuracy. Although C is easier to compute in the form (3.6), we generally find superior accuracy when it is obtained by direct integration of the linearized equations.

4. Presentation of results

In this section, we present a summary of the results of several hundred separate runs using the algorithm described in Section 3, for a wide variety of values of the parameters μ and r.

In Fig. 1, the amplitude A_X of the periodic oscillations in the variable x is shown as a function of the parameter μ, for three different values of the constant r. In this figure, we display the cases $r = 0.01$, $r = 0.003$ and $r = 0.001$, and a similar graph is given by Gray and Thuraisingham [5] for the case $r = 10^{-4}$. Although we have likewise investigated other values of r, the results are not qualitatively different to those presented in Fig. 1, and therefore have not been included.

All solutions shown in Fig. 1 were found to be stable, according to the numerical Floquet method of the preceding section. In fact, we have not found unstable solutions for *any* of the many values of μ and r investigated; this point is discussed more fully in Section 5. As r is decreased, the curves in Fig. 1 develop a sharp region of rapid variation, at about $\mu = 0.9$. The curves obtained for the cases $r = 0.01$ and $r = 0.003$ are clearly continuous, although for r smaller than about 0.002, the growth in amplitude of the periodic orbit near $\mu = 0.9$ is so rapid that the numerical solution technique cannot follow the entire solution branch, even

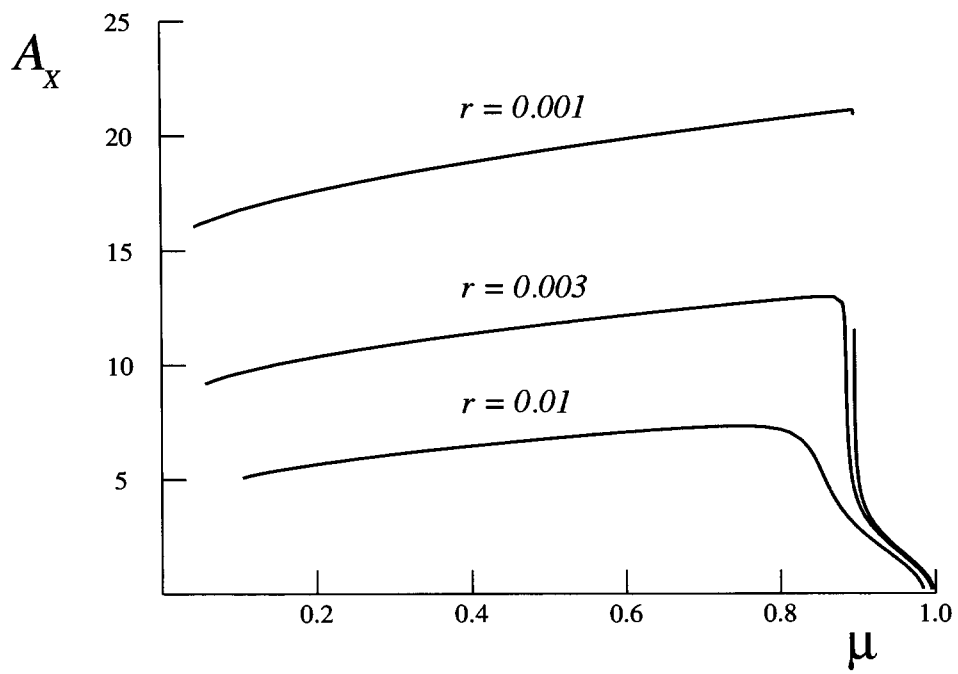

Fig. 1. Variation of the amplitude A_X of the concentration x with the parameter μ, for $r = 0.01$, $r = 0.003$ and $r = 0.001$.

when the modified algorithm is used, in which the period P is given and the parameter μ found as part of the solution. Consequently, some doubt exists as to whether the two different portions of the branch found numerically are in fact analytically connected. The two portions of the solution curve obtained by the shooting algorithm of Section 3 for the case $r = 0.001$ are displayed in Figure 1.

It has been suggested by Gray and Thuraisingham [5] that the two different portions of the solution curve for $r = 0.001$ shown in Figure 1, for example, might be connected by a family of unstable solutions. For this to be possible, the upper portion of the curve would need to overhang the lower portion, resulting in an S-shaped curve with an unstable middle section; there would thus be a small interval of μ-values in which three different solutions could exist simultaneously, for the same values of the parameters. We have investigated this intriguing possibility with great care, for a variety of different values of r, but have not detected any such unstable solutions. Indeed, if unstable solutions were possible, the numerical Floquet theory of Section 3 would indicate the point at which they were generated. Specifically, the two eigenvalues λ_1 and λ_2 of the Floquet matrix C determine the stability of the solution branch, and since $\lambda_1 = 1$ for periodic solutions, it follows that λ_2 alone indicates the stability of the solution. Thus $|\lambda_2|$ must pass through the value 1 at any point at which the solution branch changes from stable to unstable. Furthermore, this transition should occur smoothly at a simple fold in the solution branch, and thus could be anticipated from the numerical results simply by observing that $|\lambda_2|$ was nearing 1 as the critical point was approached. No such behaviour is observed in the present problem, however, and we are consequently prepared to suggest that there is thus a unique stable solution only, in the vicinity of rapid increase in amplitude A_x at about $\mu = 0.9$. The situation for small μ is somewhat less clear, although the solution branches shown in Figure 1 presumably terminate abruptly at the other Hopf-bifurcation point $\mu = \mu_-$ given in equation (2.2).

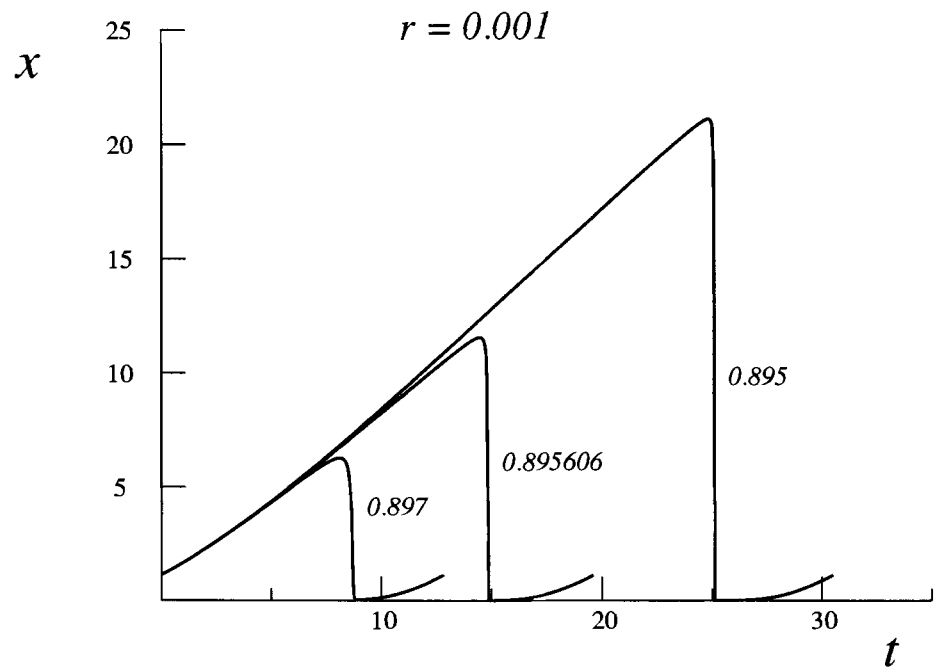

Fig. 2. Solution profiles for the concentration x as a function of time t, for $\mu = 0.895$, $P = 19.6$ ($\mu = 0.895606$) and $\mu = 0.897$. Here, $r = 0.001$, and the solution is shown over one complete period.

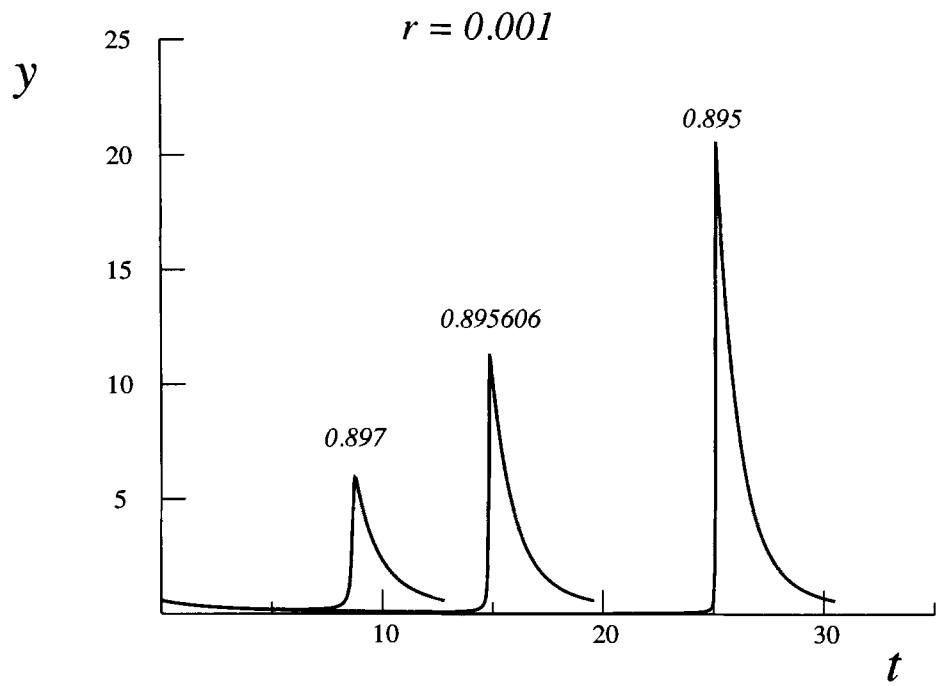

Fig. 3. Solution profiles for the concentration y as a function of time t, for $\mu = 0.895$, $P = 19.6$ ($\mu = 0.895606$) and $\mu = 0.897$. Here, $r = 0.001$, and the solution is shown over one complete period.

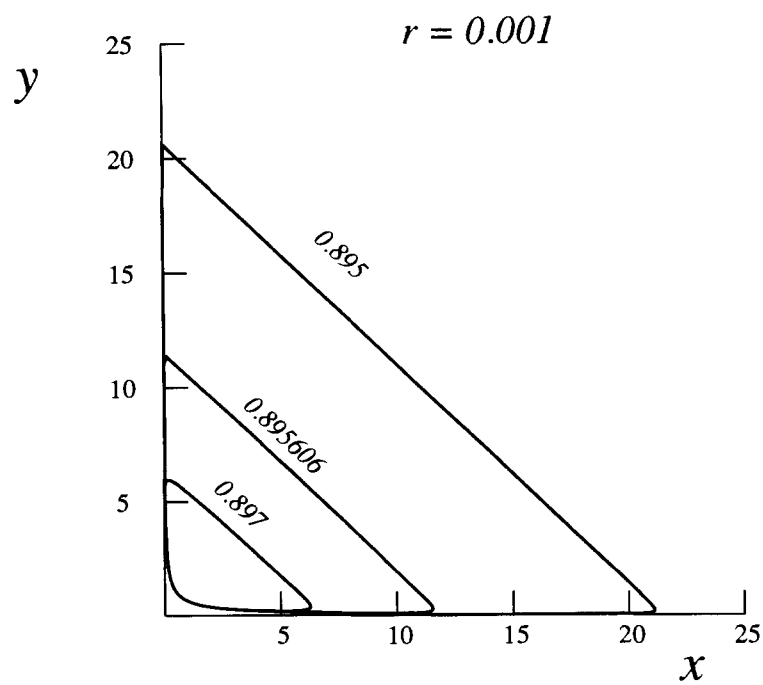

Fig. 4. Phase-plane orbits for the case $r = 0.001$, for three different solutions obtained with $\mu = 0.895$, $P = 19.6$ ($\mu = 0.895606$) and $\mu = 0.897$.

Solution profiles for the variables x and y are presented in Figs. 2 and 3, for the case $r = 0.001$. Three profiles are shown in the region of rapid increase of amplitude with decreasing μ, and correspond to values $\mu = 0.895$, $P = 19.6$ ($\mu = 0.895606$ to six significant figures) and $\mu = 0.897$. Although the difference between the greatest and least of these μ-values is only about 0.2%, there is almost a four-fold increase in solution amplitude in this interval.

Phase-plane orbits are shown in Fig. 4, for the three solutions discussed in Figs. 2 and 3. The orbits for $\mu = 0.895$ and $\mu = 0.897$ correspond approximately to solutions at the top and bottom, respectively, of the jump in amplitude A_X shown in Fig. 1 for the case $r = 0.001$. However, the portions of these orbits along the x- and y-axes and near the origin are almost indistinguishable, and consequently, a numerical solution technique which simply integrated forward in time would be expected to jump almost randomly between these solutions, as a result of numerical round-off error. This behaviour was observed by Gray and Thuraisingham [5].

5. Discussion

We have employed a combination of analytical and numerical techniques to investigate the properties of solutions to the cubic autocatalator problem, which serves as a model of an oscillating chemical reaction. Dulac's theorem has been used to prove that limit-cycle behaviour is only possible in a restricted region of the parameter space, when $r < 1/8$ and $0 < \mu^2 < 1 - r$. In fact, periodic solutions are only observed for values of μ lying between the two Hopf-bifurcation points given by equation (2.2).

Periodic solutions have been generated numerically by means of a shooting algorithm, which also incorporates a test for the stability of the solution according to Floquet's theorem. A great many solutions has been obtained over a wide variety of values of the parameters μ and r in which the theorem of Section 2 indicates the possibility of limit-cycle behaviour. However, all the solutions obtained have been stable, and the stability analysis gives no indication of any approach to an unstable portion of a solution branch. The numerical results therefore strongly suggest that the limit cycle for the cubic autocatalator may well be unique, for all values of r. In an attempt to observe the unstable solution branches and regions of multiple solutions anticipated by Gray and Thuraisingham [5], we have also included their extra "unfolding" parameter s in our numerical scheme, but remain unable to observe this more exotic behaviour.

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