ON A MATHEMATICAL MODEL FOR THE BELOUSOV-ZHABOTINSKII (BZ) REACTION

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ABSTRACT

Many real world problems can be modeled using ordinary differential equations (ODEs). An example is the Belousov-Zhabotinskii (BZ) reaction, where malonic acid is oxidized by acid bromate in the presence of ferroin. Many researchers have studied the BZ reaction and its ability to generate nonlinear waves. In this paper, we analyze a mathematical model that describes the BZ reaction in order to understand the nonlinear phenomena associated with it.

INTRODUCTION

Many real world problems can be modeled and analyzed using ordinary differential equations (ODEs). An example is the Belousov-Zhabotinskii (BZ) chemical reaction, in which malonic acid is oxidized by acid bromate in the presence of ferroin.

The Belousov-Zhabotinskii reaction was first noted when Belousov discovered the oscillation of a chemical reaction (Belousov, 1958). However, his study was not proven or published until it was rediscovered by Zhabotinskii (1964). When Zhabotinskii published his finding, Belousov was given credit for his original discovery.

Tyson (1976) discusses the BZ reaction in great detail. The chemical reactions that are part of the BZ reaction can be described as:

$$\begin{aligned} BrO_3^- + Br^- + 2H^+ &\rightarrow HBrO_2 + HOBr \\ HBrO_2 + Br^- + H^+ &\rightarrow 2HOBr \\ 2Ce^{+3} + BrO_3^- + HBrO_2 + 3H^+ &\rightarrow 2Ce^{+4} + 2HBrO_2 + H_2O \\ 2HBrO_2 &\rightarrow BrO_3^- + HOBr + H^+ \\ 4Ce^{+4} + BrCH(COOH)_2 + 2H_2O &\rightarrow 4Ce^{+3} + Br^- + HCOOH + 2CO_2 + 5H^+. \end{aligned} \tag{1}$$

Now equations (1) can be simplified into

$$\begin{aligned} A + Y &\rightarrow X + P \\ X + Y &\rightarrow 2P \\ A + X &\rightarrow 2X + 2Z \\ 2X &\rightarrow A + P \\ Z &\rightarrow hY. \end{aligned} \tag{2}$$

by replacing A with [BrO_3^-], P with [$HOBr$], X with [$HBrO_2$], Y with [Br^-], and Z with [Ce^{+4}]. Tyson re-formulates equations (2) into a mathematical form as given below.

$$\begin{aligned}
\frac{dX}{dt} &= k_{M1}AY - k_{M2}XY + k_{M3}AX + -2k_{M4}X^2 \\
\frac{dY}{dt} &= -k_{M1}AY - k_{M2}XY + hk_{M5}Z \\
\frac{dZ}{dt} &= 2k_{M3}AX - k_{M5}Z.
\end{aligned} \tag{3}$$

This system is described only with respect to X= [$HBrO_2$], Y = [Br^-], and Z= [Ce^{+4}], and the left hand sides of the equations express the rates of change of the chemical substances in the system. One can seen the terms on the right hand side of the equations (3) are nonlinear. Therefore, these equations represent a specific example of a nonlinear phenomenon in chemical studies.

The work presented here focuses on a non-dimensioned variation of the mathematical model given by (3). As noted above, a detailed background on the BZ reaction and on the various mathematical concepts used in this study can be obtained from Tyson (1976; see also, Field and Noyes, 1974).

PROBLEM

The BZ reaction model as examined here is as follows:

$$\frac{du}{dt} = u(1-u) - ruv + \varepsilon_1 v \tag{4}$$

$$\frac{dv}{dt} = -\varepsilon_2 v - buv$$

where u and v represent the concentrations as [$HBrO_2$], *and* [Br^-], *b, r,* ε_1, and ε_2 are positive constants. Here u and v are unknown variables and they need to be solved and interpreted.

The above model is a nonlinear system of ODEs and the independent variable of the system is t, the time. It is also a coupled system with the coupling coming via the interaction terms *ruv* and *buv*. Therefore, when solving, both nonlinear ODEs should be solved simultaneously.

ANALYSIS

To analyze the mathematical model in (4), let us first find the fixed points of this system of equations. Fixed points (or equilibrium points) can be found by equating the rates of change to zero.

$$i.e., \ \frac{du}{dt} = \dot{u} = 0 \ \text{and} \ \frac{dv}{dt} = \dot{v} = 0 \tag{5}$$

Here, the dots above u and v represent the first order in differentiation with respect to t. Therefore, we obtain

$$\text{and} \qquad \begin{aligned} &u(1-u) - ruv + \varepsilon_1 v = 0 \\ &-\varepsilon_2 v - buv = 0 \end{aligned} \tag{6}$$

Solving (6) gives the equilibrium points as $u^* = 0$ or $u^* = 1$ and $v^* = 0$, where the stars represent the variables' equilibrium values. Also, there is another equilibrium point at $u^* = -\frac{\varepsilon_2}{b}$. However, since ε_2 and b are positive and the fixed point u* (which is a chemical concentration value) cannot be negative in the BZ reaction, this equilibrium point is not considered viable.

The next step after finding the two fixed points $(u^*, v^*) = (0, 0)$ and $(u^*, v^*) = (1, 0)$ is to classify these points. The classification relates to the stability of an equilibrium point and we use the idea of the Jacobian matrix for the linearized system. The corresponding Jacobian matrices for the respective equilibrium points are as follows:

$$A_{(0,0)} \Rightarrow \begin{pmatrix} \frac{\partial \dot{u}}{\partial u} & \frac{\partial \dot{u}}{\partial v} \\ \frac{\partial \dot{v}}{\partial u} & \frac{\partial \dot{v}}{\partial v} \end{pmatrix}_{(0,0)} \Rightarrow \begin{pmatrix} 1-2u-rv & -ru+\varepsilon_1 \\ -bv & -\varepsilon_2 - bu \end{pmatrix}_{(0,0)} \Rightarrow \begin{pmatrix} 1 & \varepsilon_1 \\ 0 & -\varepsilon_2 \end{pmatrix} \tag{7}$$

$$A_{(1,0)} \Rightarrow \begin{pmatrix} \frac{\partial \dot{u}}{\partial u} & \frac{\partial \dot{u}}{\partial v} \\ \frac{\partial \dot{v}}{\partial u} & \frac{\partial \dot{v}}{\partial v} \end{pmatrix}_{(1,0)} \Rightarrow \begin{pmatrix} 1-2u-rv & -ru+\varepsilon_1 \\ -bv & -\varepsilon_2 - bu \end{pmatrix}_{(1,0)} \Rightarrow \begin{pmatrix} -1 & -r+\varepsilon_1 \\ 0 & -\varepsilon_2 - b \end{pmatrix} \tag{8}$$

Now, we can analyze the eigenvalues of these matrices. For the matrix (7),

$$\begin{aligned} &det\,|\,A_{(0,0)} - \lambda I\,| = \lambda^2 - (1-\varepsilon_2)\lambda - \varepsilon_{2,} = 0 \\ &i.e., \lambda_1 = 1 > 0, \lambda_2 = -\varepsilon_2 < 0, \end{aligned} \tag{9}$$

Therefore, the equilibrium point (0, 0) is called a saddle point; since both $\lambda_{1,}$ and λ_2 are real numbers with one being positive and the other negative. This means that near the equilibrium point (0,0) a portion of the solution for the system grows while the other portion of the solution decays in time. Hence, this is an unstable equilibrium point. For the other Jacobian matrix A, the solution is:

$$det\,|\,A_{(1,0)} - \lambda I\,| = \lambda^2 - (-b-\varepsilon_2-1)\lambda + (b+\varepsilon_2) = 0 \tag{10}$$

In (10) the product of the eigenvalues $\lambda_1\lambda_2 = b + \varepsilon_2 > 0$. Therefore, either both eigenvalues are either positive or negative. However, because $Trace(A) = \lambda_1 + \lambda_2$ we can conclude that both eigenvalues are negative. Therefore, the equilibrium point (1, 0) is a stable node. Thus, we have shown that our BZ system has a stable equilibrium point at (1, 0) and an unstable equilibrium point at (0, 0).

METHOD

Computational calculations are necessary to confirm the findings made from the linearized analysis. Thus, we used various software packages such as *MatLab Mathematica*, and *Maple* to calculate the complicated and tedious calculations throughout this work. Other software such as *Excel*, and *Origin* are also used to produce multiple calculations and important graphs. Using *Excel*, we calculated the solutions to the finite difference analog of the BZ model in order to confirm the results from the linear analysis. *Origin* was used to produce the necessary graphs.

RESULTS

To validate the results from the linear analysis, we compared the solutions from the computational work with the analytical work. By using *MatLab* we were able to create the vector field for the nonlinear BZ reaction.

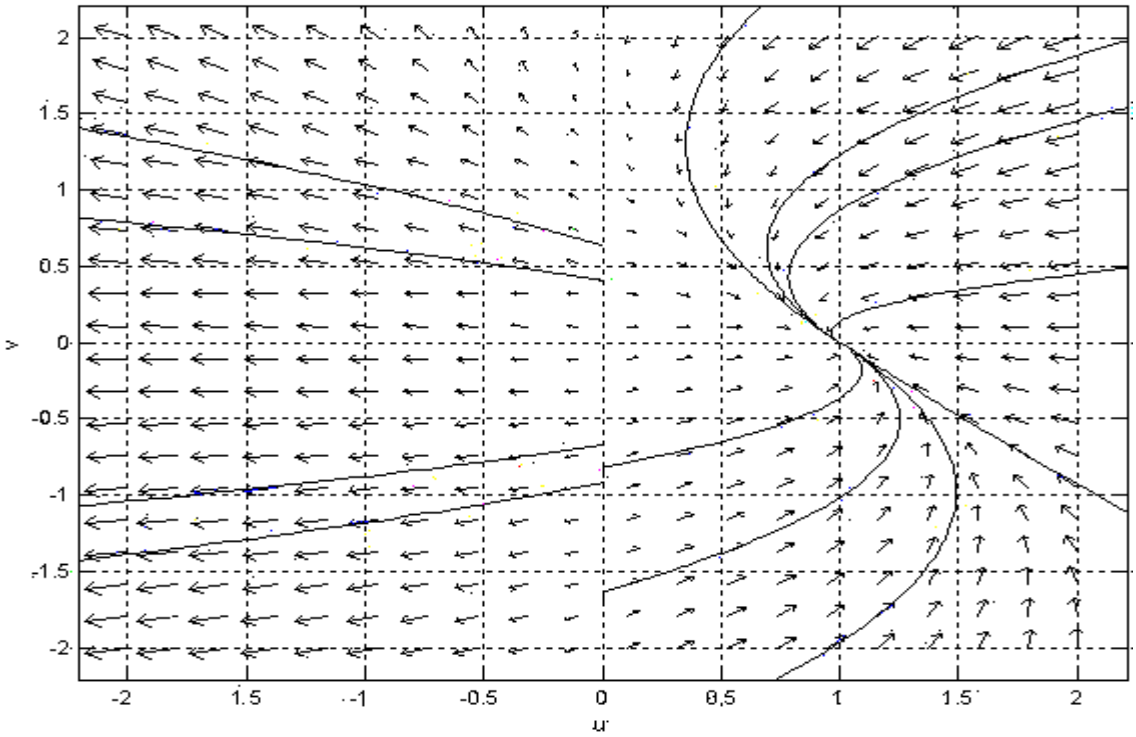

Figure 1.

As shown in Figure 1, the arrows are pointing towards (1, 0) and pointing away from (0, 0). The lines created by connecting the arrows reach (1, 0), but they never reach (0, 0). Figure 2 was created using *Maple*. As can be seen, both the *MatLab* and *Maple* graphs appear to be the same.

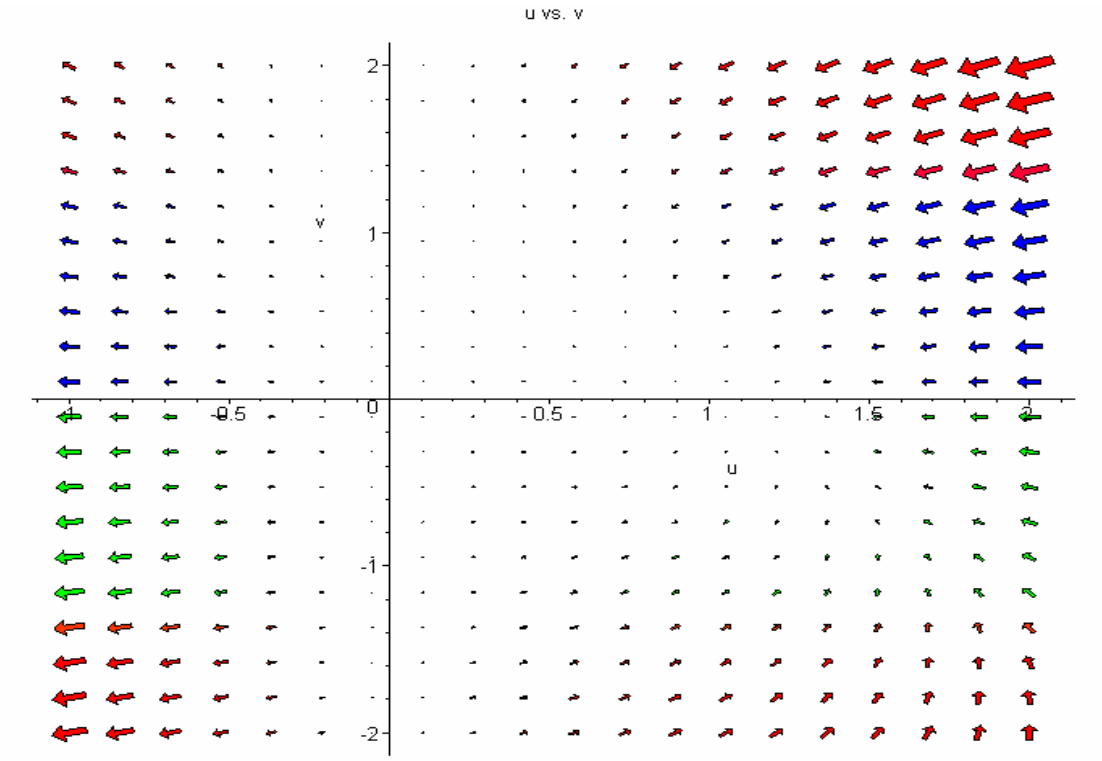

Figure 2.

Figure 2 illustrates that when (*u,v)* approaches (1, 0), the arrows move towards (1, 0). On the other hand, the arrows are pointing away from the origin (0, 0). This confirms the existence of two equilibrium points where one, (0, 0), is unstable and the other, (1,0), is stable.

The concept of nullclines can also be used to confirm our results. In Figure 3 (obtained using *MatLab*), the nullclines show that when *v* is zero the arrows are pointing towards the intersections of the two dashed lines as *u* approaches 1. On the other hand, when *u* and *v* approach zero, the arrows are pointing away from the point. This also confirms the stability behavior of the equilibrium points (1, 0) and (0, 0).

To find the solutions of the nonlinear BZ system, we used a finite difference method and the Runge-Kutta method. For the sake of simplicity, for the rest of the study we assume that $\varepsilon_1 = \varepsilon_2 = 0$. Therefore, the mathematical model reduces to:

$$\begin{aligned} u_t &= u(1-u) - ruv \\ v_t &= -buv. \end{aligned} \tag{11}$$

By setting $nk = t$ where k is time, step size and n, an integer system (11) can be discredited into:

$$\begin{aligned} \frac{U^{n+1} - U^n}{k} &= U^n(1-U^n) - rU^nV^n \\ \frac{V^{n+1} - V^n}{k} &= -bU^nV^n \end{aligned} \tag{12}$$

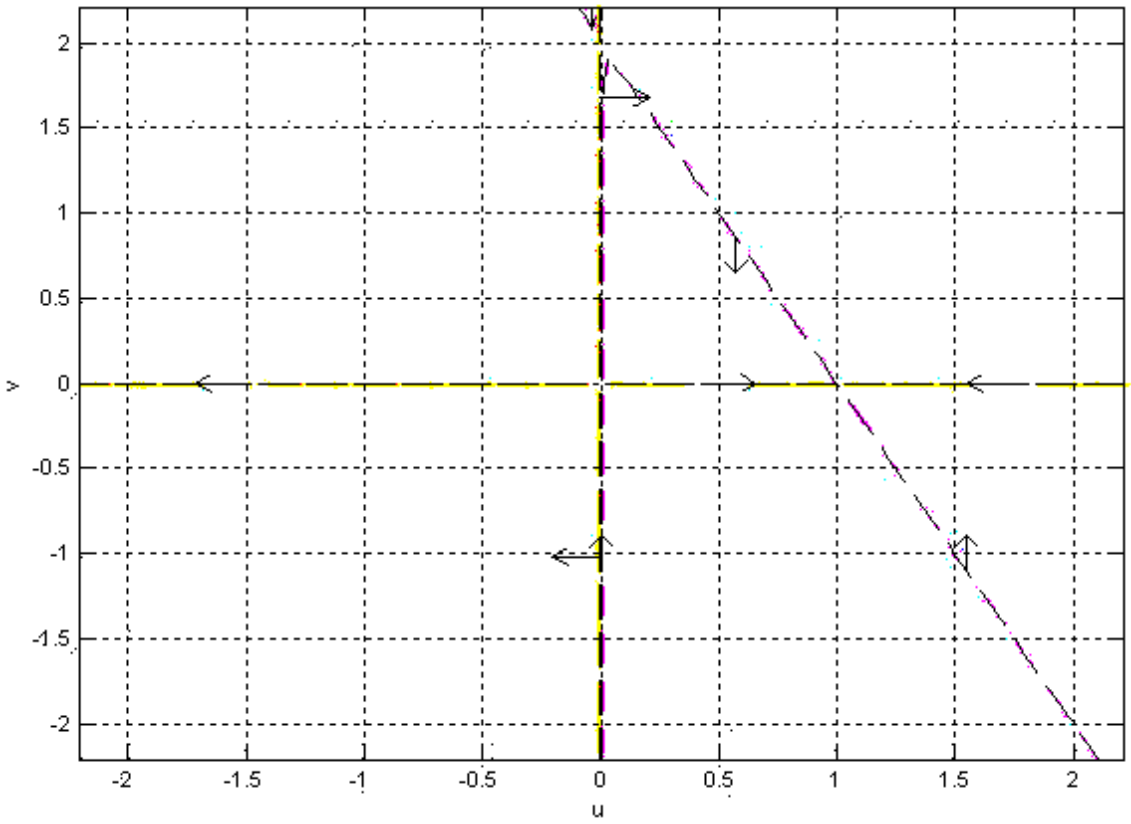

Figure 3.

Equations (12) can be re-written as,

$$
\begin{aligned}
U^{n+1} &= U^n + kU^n(1-U^n) - rkU^nV \\
&= (1+k)U^n[1 - \frac{k}{(1+k)}U^n] - rkU^nV^n \\
\frac{k}{1+k}U^{n+1} &= \frac{k}{1+k}U^n(1+k)[1 - \frac{k}{1+k}U^n] - rkU^nV^n\frac{k}{1+k} \\
i.e., \quad W^{n+1} &= (1+k)W^n[1-W^n] - rkW^nV^n \qquad (13) \\
V^{n+1} &= V^n - (1+k)bW^nV^n
\end{aligned}
$$

where $W^n = \frac{k}{1+k}U^n$.

The discrete system (13) was solved for certain parameter values under appropriate initial conditions. Figure 4 shows three different solution curves near the equilibrium point (u^*, v^*) = (1, 0). Each of these curves has different values for the initial condition, r, b, and k (step size). Of the three curves, one curve begins at a different point due to a different initial value. However, all three curves approach the same point (1, 0). This shows that the equilibrium point at (1, 0) is stable because all three curves are coming towards this point.

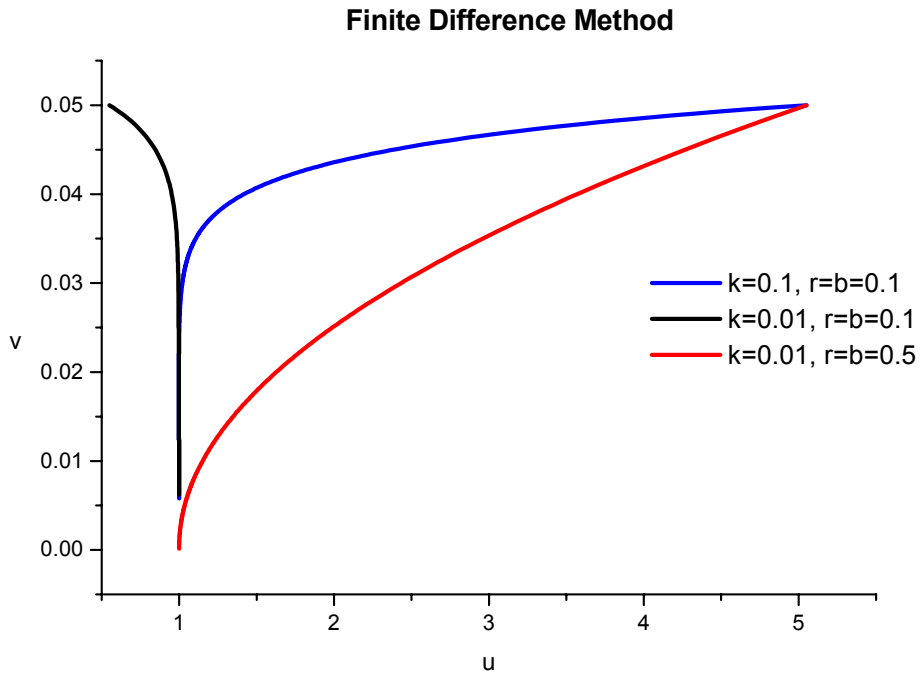

Figure 4.

Figure 5 shows the solution curves obtained using the Runge Kutta Method for the same initial conditions and parameter values that were used for the finite difference method.

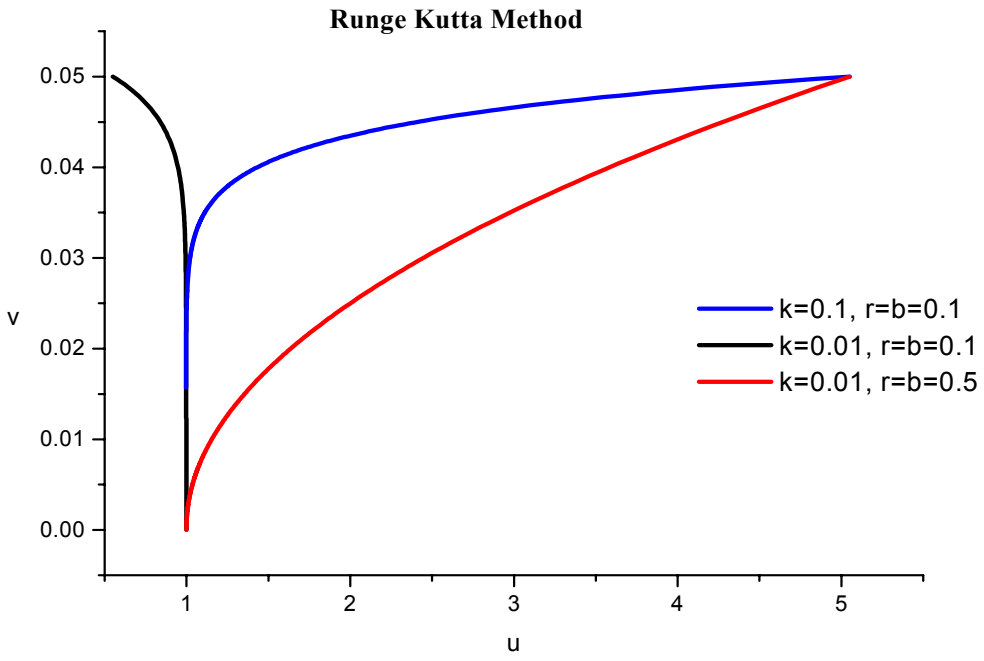

Figure 5.

As one can see, Figures 4 and 5 are qualitatively very similar. To solidify the observation further, we present Figures 6, 7, and 8 to describe the solution behavior of the nonlinear BZ system.

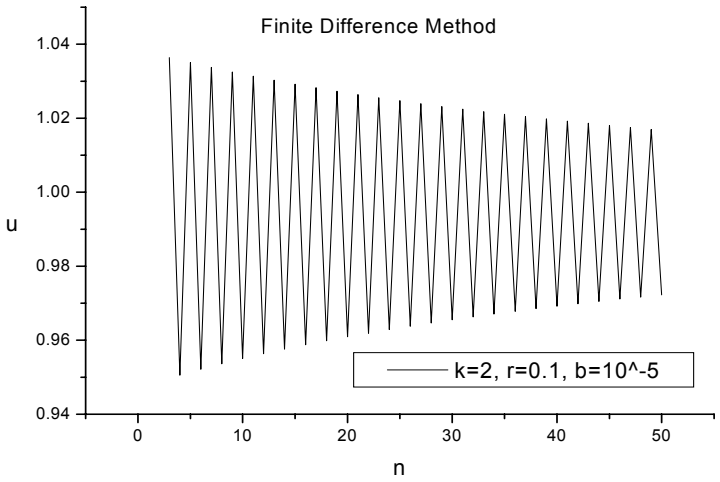

Figure 6.

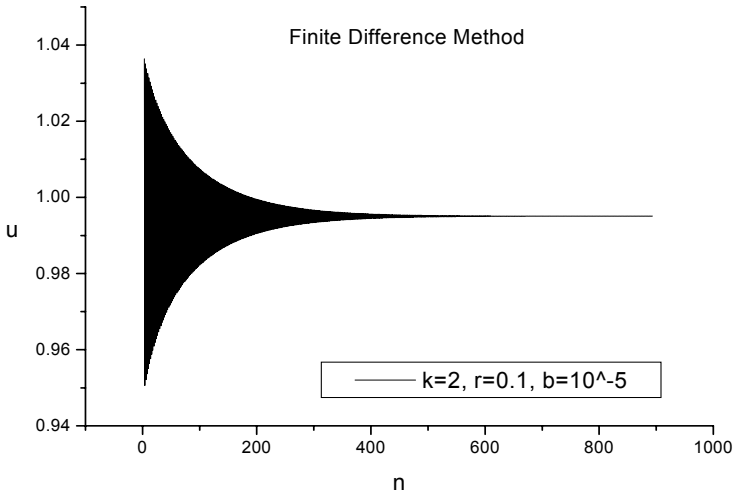

Figure 7.

After carrying out several computer calculations we are able to conclude that as *n* increases *u* always approaches 1 irrespective of the parameter values *r* and *b* or the initial conditions. However, as *k*, step size, increases, *u* approaches 1 very quickly. When *k* gets bigger than 1, such as *k=2,* the *u* value begins to oscillate and eventually reaches 1 when *n* is greater than approximately 300. But, employing the Runge-Kutta Method, while keeping all the conditions the same as the finite difference method, we find solutions with no oscillation.

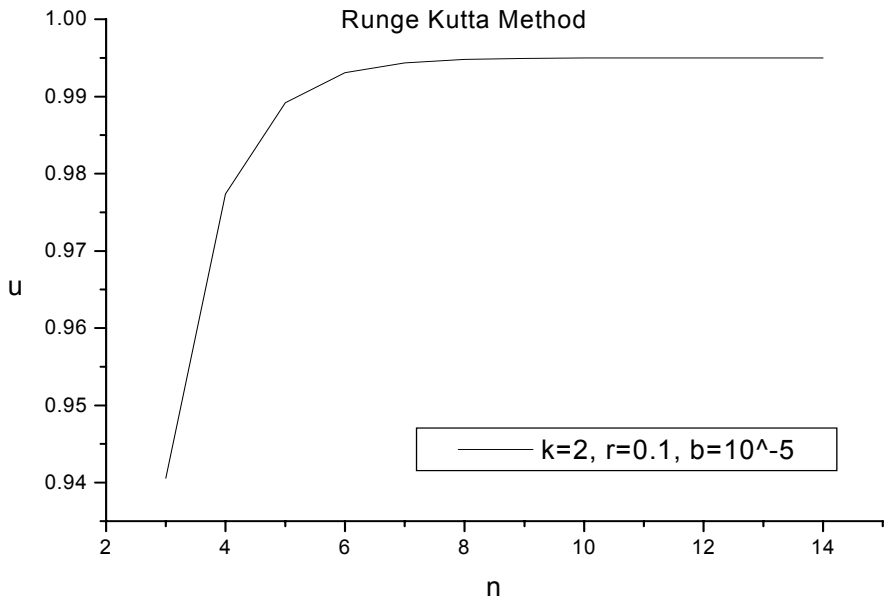

Figure 8.

Now, if *k* was chosen to be 3, then we find that the solution oscillates and never reaches equilibrium point of the system. Therefore, we can conclude that as *k*, the step, becomes very much larger than l, the nonlinear BZ system may not reach its equilibrium state (see Figure 9).

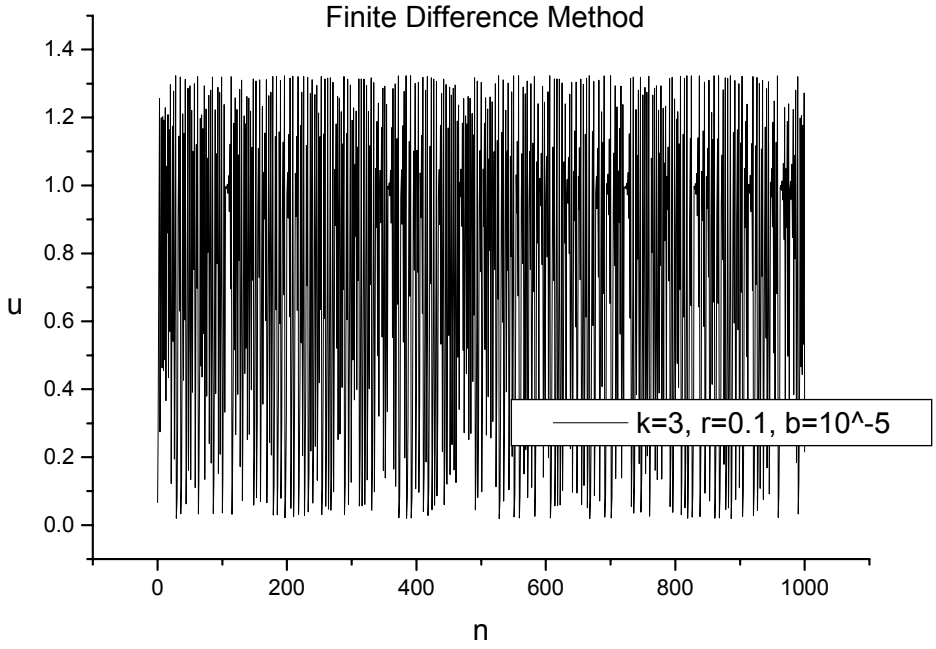

Figure 9.

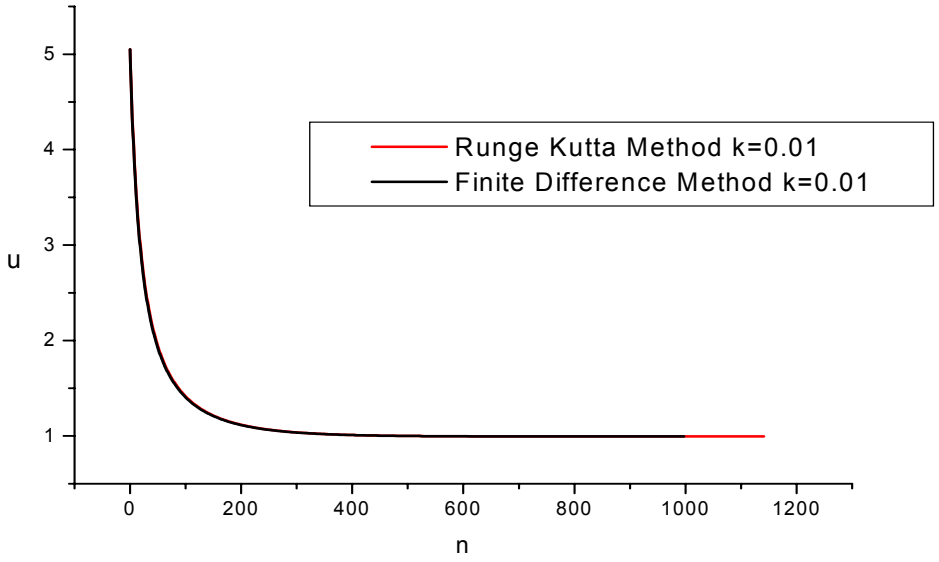

Figure 10.

Figure 10 shows that the solution behavior is exactly the same when using the Runge-Kutta Method or the finite difference method provided k is much smaller than 1 (here k=0.01). In this case, the solution reaches the equilibrium state without any oscillations.

CONCLUSION

In this paper, we have shown that two equilibrium states exist for the nonlinear BZ system, one of which is stable and the other unstable. We are able to show this by doing linearized stability analysis and carrying out computer simulations. Although our model focused on the BZ chemical reaction, it should be pointed out that the mathematical concepts presented here could be easily employed to analyze other nonlinear systems of practical interest. For instance, given an appropriate choice of parameter values, the mathematical model given in (4) can be viewed as a model for two interacting species such as a predator-prey system.

An interesting observation is the effect of increased time step on the solution behavior. The solution seems to oscillate and does appear to go towards the equilibrium state. Further investigation is needed to understand this phenomenon and determine whether it is a system behavior or some numerical artifact.

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