The Belousov-Zhabotinsky Reaction in a CSTR Using Python

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Abstract

A simulation of the Belousov-Zhabotinsky (BZ) reaction in a Continuous-flow Stirred-Tank Reactor (CSTR) has been built and investigated. The model for the system is from a paper by Gyorgyi & Field (1992). Using mainly packages from the Enthought Python Distribution (EPD), the governing ODEs have been numerically integrated and visualized. The simulator was calibrated by solving a similar by simpler (non-chaotic) system of ODEs known as the Oregonator- a task performed successfully. The chaotic system was then investigated under two sets of conditions: a 'High' flowrate and a 'Low' flowrate, where the flowrate is associated with a set of parameters and with a particular range of the bifurcation parameter k_f, which is defined as an inverse residence time (s^{-1}) of a particle of fluid in the reactor. All the constants used were from the literature. Although there were some discrepancies in the results with the literature under the Low flowrate conditions, there seemed to be better agreement under the High flowrate conditions. Under the Low flowrate conditions, a period-doubling transition to chaos was observed. The corresponding strange attractor was virtually 2D. Under the High flowrate conditions, an intermittency route to chaos was observed, and a 3D attractor was found.

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Introduction

The motivation for this topic was interest due to the famous designs produced by the Belousov-Zhabotinsky reaction in small Petri dishes. Such images have permeated texts on nonlinear dynamics, chemistry, catalysis, and related fields, due to their fascinating and appealing designs. The complexity becomes even more interesting in a Continuous-flow Stirred Tank Reactor (CSTR), where the system is thermodynamically "open," and equilibrium can be avoided(Epstein and Pojman, 1998). Dropping our concerns about the 2nd law (with respect to oscillatory behavior), more interesting behavior becomes possible, and with modern visualization tools, it is relatively easy to visualize. In a sense, the artistic merit of the spiral designs of the Petri dish can be replaced by the artistic merit of the strange attractors built by a computer simulation. In this project, a chaotic three-variable model for the BZ reaction in a CSTR has been simulated in Python, and its behavior investigated. It was found that, as predicted, interesting and even chaotic behavior occurs when the value of the bifurcation parameter, which is related to the flow rate through the reactor, is varied appropriately. At very high values of k_f, a steady-state is reached because the high k_f corresponds to a high flow rate through the reactor and a lack of time for the chemicals to react. Similarly, at very low values of k_f, steady states are reached, but due to equilibrium being reached in the reactor. The very low k_f case can be compared to the case of the Batch reactor (thermodynamically closed), or simple beaker, for which equilibrium is eventually reached. There is, however, a region of k_f wherein the value of the flowrate parameter k_f is conducive to more interesting periodic behavior and chaos, meaning that at least some portion of the simulation was successfully replicated from the literature. Both periodic and intermittency routes to chaos have been observed, and the concentration dynamics have been visualized in 2D and 3D using open-source packages from the Enthought Python Distribution (EPD).

Background

By far, the most famous chemical oscillator is the so-called Belousov-Zhabosinsky reaction, which is naturally named after its two central founders. Sometime in the late 1950's, Boris Pavlovich Belousov (1893-1970) discovered the reaction when he was looking for an inorganic analog of the Krebs cycle, a metabolic process with a citric acid intermediate (Epstein and Pojman, 1998). He made a solution of bromate ($BrO3^-$), citric acid ($C_6H_8O_7$), and cerium ions (Ce_4^+), expecting to see the yellow Ce_4^+ solution become clear Ce_3^+, but he found that solution oscillated between yellow and clear (Epstein and Pojman, 1998). The skeptical scientific establishment was less than eager to believe Belousov's claims- in fact, he was unable to publish his work, even after attempting to do so for about six years. Except for the case of one small abstract in a random conference on Radiation Biology, where he was able to publish a small mention of the oscillating reaction. In general, the objection to the chemical oscillation was that it appeared to violate the Second Law of Thermodynamics (Epstein and Pojman, 1998). Finally, in 1961, Anatol Markovich Zhabotinsky (1938-2008) began more work on the reaction, and was able to publish what he found. An important modification he made to the reaction was to use Ferroin, which is visibly red in reduced form and blue in the oxidized form. Such a substance is known as a Redox Indicator. Using the Ferroin, the oscillation was much clearer to see than in the pale yellow and clear solution that Belousov originally used. As the BZ reaction became better known, experimentalists around the

globe began to investigate it theoretically and experimentally. In practice, the concentrations of various species in solution can be monitored using special electrodes designed for specific ions such as the Br- ion (Li, Song et al. 2001). Computer simulations have also proved to be extremely useful for understanding the reactions, due to their practical nature.

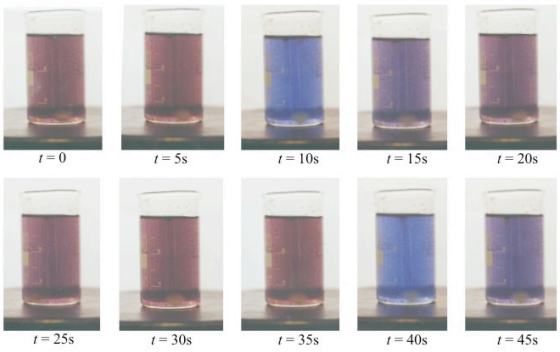


Figure 1: Simple Oscillation in the BZ reaction, indicated by the changes in the Ferroin oxidation state (GNU open-source licensed photo)

Dynamical System

One of the earliest models for the BZ reaction, proposed by Prigogine and Lefever in 1968, was known as the "Brusselator." The Brusselator became perhaps the most widely used model for chemical oscillations in general (Scott, 1992). For the BZ reaction, however, the most widely used model is known as the "Oregonator." The Oregonator, which is based on the Field-Körös-Noyes (FKN) chemical reaction mechanism put fourth in 1972, has now been thoroughly analyzed both theoretically and experimentally and is considered to be the most successful simple BZ model (Scott, 1992). The FKN mechanism is shown in Equations 1-5. The simulated results of the Oregonator agree very well with experimental data (Ren et al. 2008).

$A + Y \rightarrow X + P$	$r = k_3AY$	$A \equiv BrO_3^-$	(1)
$Z + Y \rightarrow 2P$	$r = k_2XY$	B ≡ all oxidizable organic species	(2)
$A + X \rightarrow 2X + 2Z$	$r = k_5AX$	$X \equiv HBrO_2$	(3)
$2X \rightarrow A + P$	$r = k_4AX^2$	$Y \equiv Br^-$	(4)
$B + Z \rightarrow (1/2)\ f\ Y$	$r = k_oBZ$	$Z \equiv Ce_4^+$	(5)

$$dx/dt = k_3AY - k_2XY + k_5BX - 2k_4X^2 \quad (6)$$

$$dy/dt = -k_3AY - k_2XY + fk_jZ \quad (7)$$

$$dZ/dt = 2k_5BX - k_jZ \quad (8)$$

The differential equations (rate expressions) for systems of chemical equations are typically formulated using the so-called Law of Mass Action, and are given by Equations 6-8. In 1979, John J. Tyson showed that the rate expressions could be reduced to a convenient dimensionless form, shown by Equations 9-11.

$$dx/d\tau = (qy - xy + x(1-x)/\varepsilon_1 \quad (9)$$

$$dy/d\tau = (-qy - xy + fz)/\varepsilon_2 \quad (10)$$

$$dz/d\tau = x - z \quad (11)$$

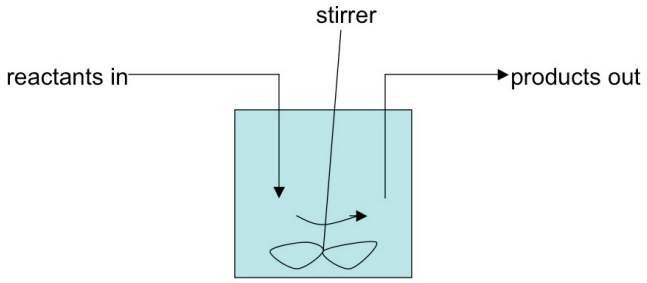


Figure 2: Operation of a Continuous-flow Stirred Tank Reactor (CSTR).

Once it had been accepted that the oscillations were genuine, people naturally began to wonder whether or not any chaotic behavior might be found in the reaction. However, the simple beakers and dishes would no longer suffice, since inside them there could only be simple oscillations until equilibrium was reached. So researchers began to investigate the behavior of the reaction in a CSTR, where, as an open system, equilibrium could be avoided and therefore more interesting behavior could be found. Complex periodicity, multistability hysteresis, and chaos have now been observed both experimentally and in various simulations of the BZ reaction (Swathi and Kulkarni, 2009). But it was long before any simple equations were found that could account for complex behavior.

In 1992, Gyorgyi and Field published the first three-variable chaotic model for the BZ reaction in a CSTR. The three-variable model was reduced from an eleven-variable model that had been published in a paper in 1991.The scaled differential equations for the chaotic model are given by Equations 12-14. As with the equations by Tyson, the species variables in Equations 12-14 are scaled, and the $\log_{10}$ of the values is taken before plotting.

$$dx/d\tau = T_o\{-k_1HY_oxy + k_2AH^2Y_o/X_oy - 2k_3X_ox^2 + 0.5k_4A^{0.5}H^{1.5}X_o - 0.5(C-Z_oz)x^{0.5} - 0.5k_5Z_oxz - k_fx\} \quad (12)$$

$$dz/d\tau = T_o\{k_4A^{0.5}H^{1.5}X^{0.5}(C/Z_o - z)x^{0.5} - k_5X_oxz - \alpha k_6V_ozv - \beta k_7Mz - k_fz \quad (13)$$

$$dv/d\tau = T_o\{2k_1HX_oY_o/V_oxy + k_2AH^2Y_o/V_oy + k_3X_o^2/V_ox^2 - \alpha k_6Z_ozv - k_fz \quad (14)$$

Methods

In order to investigate and understand the behavior of the BZ reaction in a CSTR, a Python (Version 2.5.2) simulation was constructed. ActiveState ® Komodo IDE 5.1.3 was used for the editing. In general, most of the Python packages were installed with the open-source Enthought Python Distribution (EPD). Before simulating the more complicated chaotic model given by Equations 7-9, the simpler model given by Equations 4-6 was simulated as a baseline check on the overall methodology. Although Equations 4-6 are relatively simple, they are still known to be stiff ODEs and therefore they require more elaborate integration schemes than, for example, a standard Runge-Kutta scheme (Epstein and Pojman, 1998). So an ODE integration package from SciPy, which incorporates variable step-sizes for stiff ODEs, was used. After Equations 4-6 were successfully integrated and plotted using SciPy's odeint module, it was assumed that the methodology was sound and then the same procedure was applied to the chaotic CSTR model, given by Equations 7-9. The ODE solving routines in odeint are based on popular set of Fortran ODE solvers called odepack. The vector solution is returned as an array object, and the solutions for each variable can then be plotted in 2D using matplotlib or in 3D using MayaVi.

There were two categories of flowrate examined for interesting behavior: a 'Hi' flow rate and a 'Low' flowrate, each corresponding to a particular set of constants, initial conditions, and range of kf values. For the 'Low' flowrate conditions, A = 0.1M, M = 0.25M, H = 0.26M, C = 0.000833M, α = 666.7, β = 0.3478. For the 'High' flowrate conditions, A = 0.14M, M = 0.3M, H = 0.26M, C = 0.001M, α = 333.3, β = 0.2609. The initial conditions were typically based on the points contained by the Poincaré plane from Gyorgyi and Field (1992).

Results

As expected, the only behavior of the simple Oregonator is a limit cycle, as shown in Figures 3a and 3b. In general, the $\log_{10}$ is taken of each concentration before plotting so that they can all be easily seen on the same image. Otherwise, the differences between the values are very large and so the plots are difficult to see. It was not the actual values of the concentrations that were of primary interest, as much as the general trends and behaviors. In the case of the simple Tyson-scaled Oregonator, the behavior is a periodic oscillation, the characteristics of which can be changed by varying any of the three parameters (ε_1, ε_2,q) (Ren et al. 2008). In Figure 3a, an example of a typical limit cycle is shown. All of the values for the constants were taken from Field (2007).

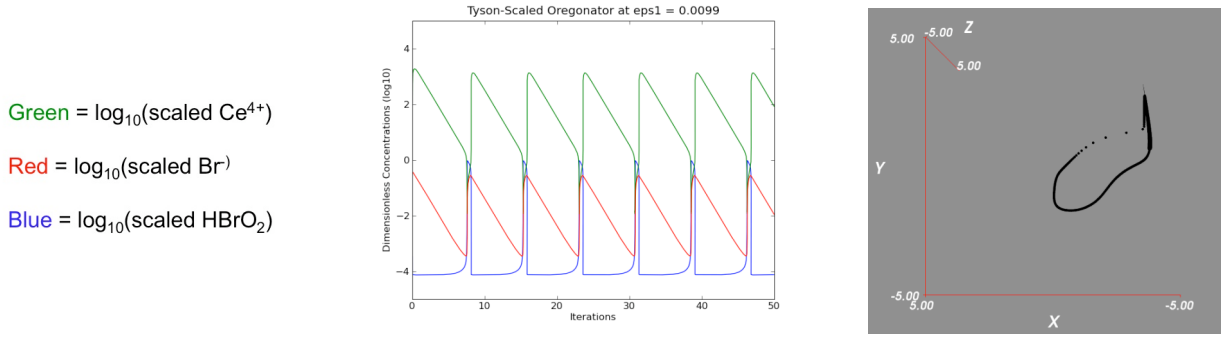


Figure 3. (a) The limit cycle of the dimensionless concentrations ($\log_{10}$) of species from Eqs. 1-3. (b) corresponding 3D attractor

Unlike the behavior from the simpler model, the behavior from the chaotic model was, as expected, rich with complexity. Although various routes to chaos have been found for the BZ reaction, period-doubling and intermittency were frequent phenomena found in this simulation. A typical example of period doubling for the 'Low' conditions is shown in Figures 4a- 4f, wherein the value of k_f decreases from $k_f = 0.05$ in Figure 4a to $k_f = 0.0003902$ in Figure 4f. In Figure 4a, the relatively high value of k_f corresponds to a very fast flow through the reactor, and so the lack of behavior is likely corresponds to a lack of reaction time. As a result of the lack of reaction time, a steady-state is quickly reached. As the value of k_f decreases further to $k_f = 0.00291$ in Figure 2b, the flow through the reactor has slowed sufficiently to allow for periodic oscillations. A period-doubling bifurcation occurs at $k_f = 0.0029$, as shown in Figure 4c. By the time k_f has reached $k_f = 0.00285$, as shown in Figure 4d, the behavior began to show a hint of complexity, as evidenced by the more subtle periodic patterns. The trend continued as k_f was decreased to $k_f = 0.0028$, as shown in Figure 4e, wherein the period had continued to double and the periodic behavior continued to subtly evolve. By the time k_f had decreased by another order of magnitude, to $k_f = 0.0003902$, it was clear that chaotic behavior was present. A 3D attractor for $k_f = 0.0003902$ is shown in Figure 5, but the attractor is virtually 2D, which agrees with the steady state reached by one of the variables in Figs. 4a-4f.

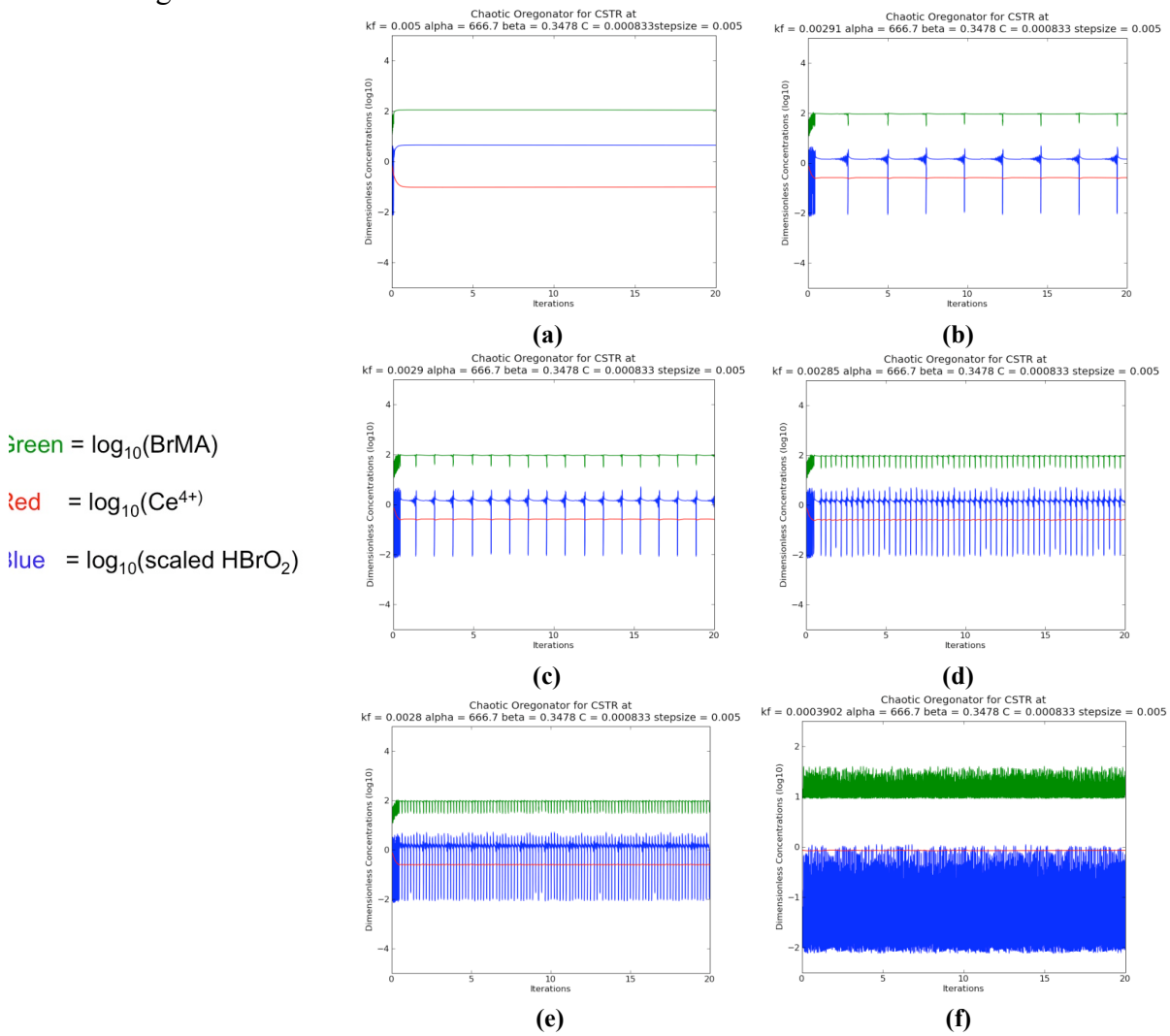


Figure 4. Low flowrate conditions. Period-doubling in Figs. 4a – 4e. Chaos in Fig. 4f at $k_f = 0.0003902$.

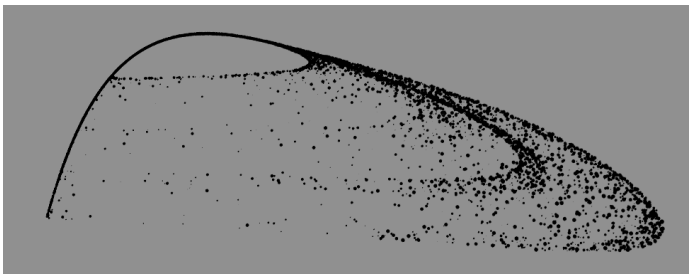


Figure 5. Low flowrate attractor for $k_f = 0.0003902$, virtually 2D

An example of the behavior at the 'High' flowrate conditions is shown in Figs. 6 a-d. Under the High flowrate conditions, chaotic windows were found near $k_f = 0.00208$ and $k_f = 0.00216$. The latter value was consistent with the literature. In Figures 6a – 6b, the value for k_f is decreased from $k_f = 0.00220999$ to $k_f = 0.00213$ in varying increments. The chaotic behavior at $k_f = 0.00216$ is illustrated in Figure 6d and in Figure 8. Both above and below that particular value, simple periodic behavior appears.

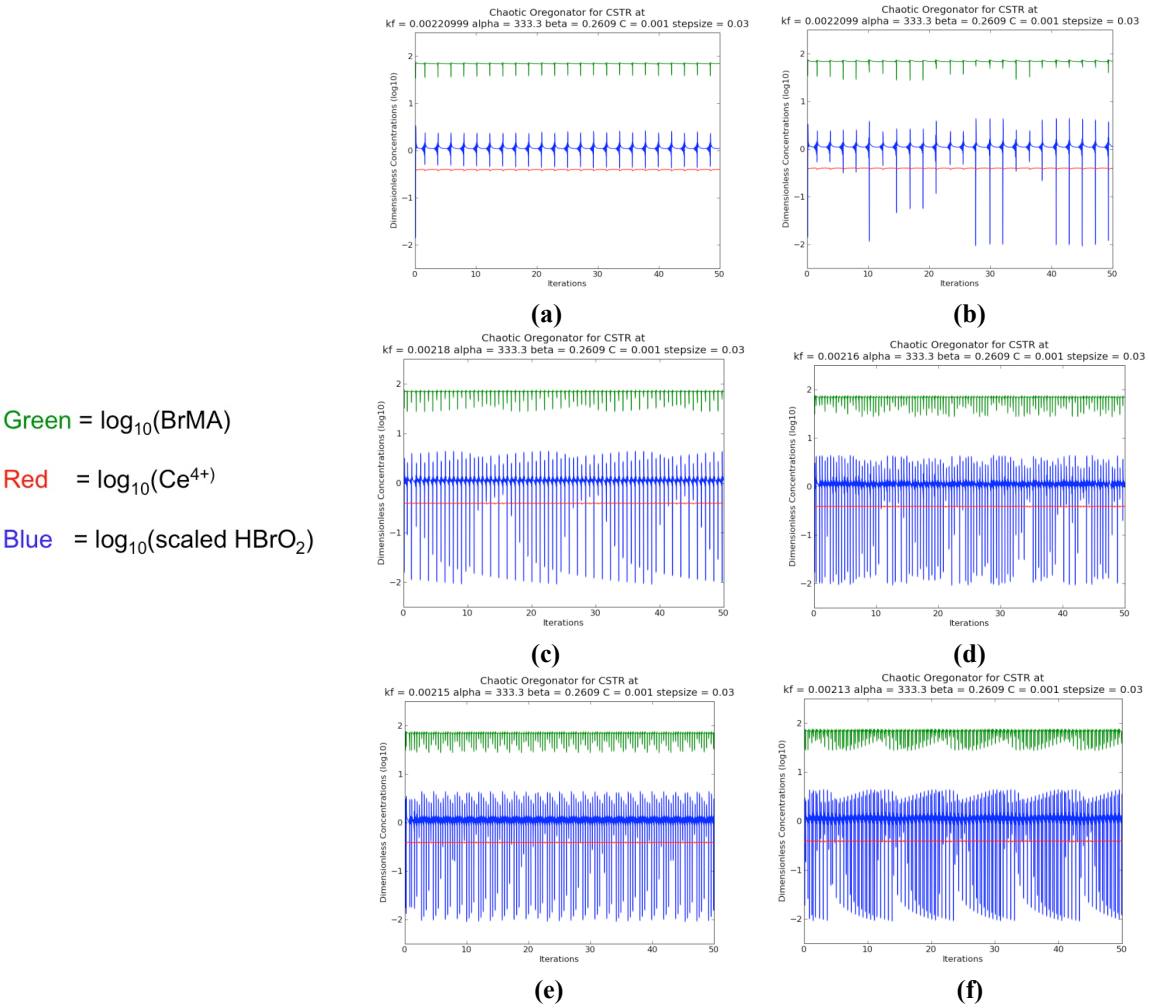
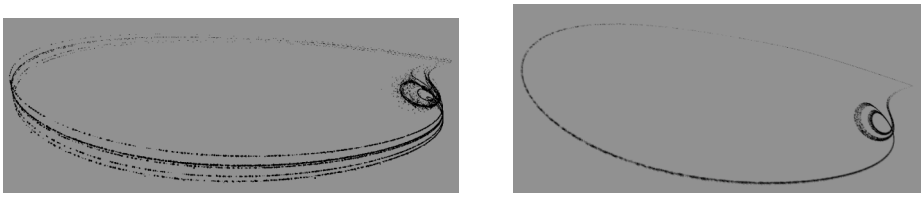


Figure 6. High flowrate conditions; intermittent chaos at kf = 0.00216 (Figure 6d)



(a) **(b)**

Figure 7. Low flowrate region. (a) a burst of chaos at $k_f = 0.0020800$ (b) the onset of ordered periodicity at $k_f = 0.0020812$

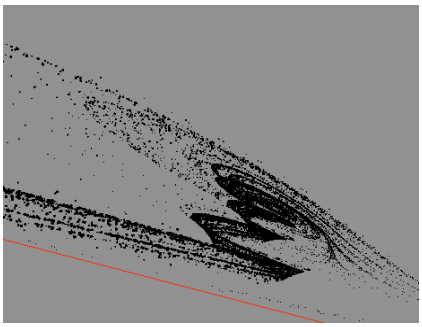


Figure 8. High flowrate region**.** Chaos at $k_f = .0021600$ (see Fig. 6d)

Conclusion

Using open-source Python software and the Enthought Python Distribution, a simulation of a chaotic three-variable BZ model was created and used to better understand the BZ reaction in a CSTR and to attempt a replication of a simulation from literature. Before the chaotic model was examined, the simpler, Tyson-scaled Oregonator was tested as a baseline check on the overall method. Since the results from the simpler model agreed well with literature, it was assumed thereon that the general method was valid. For two sets of conditions, values of k_f were manipulated and the behavior was analyzed. The set of ODEs was integrated using the SciPy integrate package, and the solutions sets were plotted using matplotlib and MayaVi. It was found that at the Low flowrate conditions, chaos appeared as a result of a period-doubling sequence as k_f was decreased. The attractor was essentially 2D, due to a lack of activity of the Cerium ions. Under the High flowrate conditions, the intermittency route to chaos occurred over certain windows of k_f values. The appearance of chaos at $k_f = 0.00216$ under the High flowrate conditions is consistent with the literature, and another chaotic window near $k_f = 0.00208$ was found.

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