Chaos in the Belousov-Zhabotinsky Reaction

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Abstract

In this project, we investigate two different models of the Belousov-Zhabotinsky Reaction, the Oregonator (1973) and a model found in a 1992 paper by Györgyi and Field. We discuss the original literature and then numerically investigate both models. We find the the Oregonator is not chaotic, and that the Györgyi-Field model is for certain values of a variable parameter. For each model, we solve its system of ordinary first order differential equations, plot the 3-dimensional attractor, find its correlation dimension, calculate the Lyapunov exponents, and construct time-delay plots. For the Györgyi-Field model, we also produce a bifurcation plot, which shows what values of a certain parameter cause chaos in the system.

1 Introduction

Since its discovery 60 years ago, the Belousov-Zhabotinsky (BZ) Reaction has been the subject of intensive investigation as an example of a chemical oscillator. The reaction was discovered by Boris Pavlovitch Belousov around 1950 while he was trying to model the Krebs cycle using a metallic catalyst instead of proteins.[1] He noticed that a solution of aqueous malonic acid with acidified bromate with a catalyst would oscillate between clear and colored for up to an hour. The original reaction used a cerium catalyst, which was later replaced by iron phenanthroline. However, Belousov's efforts to publish were frustrated by the disbelief of those who thought that the reaction was impossible, as it seemingly violated the second law of thermodynamics by reversing its state. This problem was later resolved by concluding that the oscillations are due to fluctuations in intermediate concentrations that occur when the reaction starts far from equilibrium.[2] After the recipe for the reaction circulated through Moscow State University, and the Biophysics Institute of the USSR Academy of Sciences at Puschino, Belousov was eventually identified as the discoverer, and was persuaded to write an abstract which appeared in a Soviet radiology journal in 1959.[1] In 1961, while a graduate student at Moscow State University, Anatol M. Zhabotinsky was assigned by his advisor to investigate the reaction, which resulted in publication of a manuscript which was the first serious investigation describing the reaction. In the 1970s, chaotic limit cycles of the BZ reaction were observed, but whether the chaos was the result of the chemical mechanism or uncontrolled fluctuations in experimental parameters was debated.[3] By using a Continuous Flow Stirred Tank Reactor (CSTR), in which reactants are pumped into a system at a constant rate to keep the system far from equilibrium to control these possible fluctuations. The system was shown to be chaotic in the early 1980s by using the time delay reconstruction technique on experimental data from a CSTR reactor.[3]

2 The Oregonator

In 1969, Richard Field and Richard Noyes began investigation on the oscillatory behavior of the BZ reaction at the University of Oregon. Over the next few years, they were determined to find the reaction mechanism for this behavior. Along with visiting professor Endre Körös from Eötvös University in Budapest, they were able to explain the qualitative behavior of the BZ reaction using the same laws that govern all chemical reactions. Most importantly, they were able to simplify this complex reaction, which has around twenty elementary steps and chemical species, into a mechanism with only three variable concentrations that had all the essential features of the complete mechanism. The key to this simplification is to identify the rate-limiting steps in the mechanism, and assume that all other steps occur arbitrarily quickly. They named their simplified model the Oregonator.[4]

The equations used in the Oregonator are:

$$\begin{aligned}
\mathrm{A} + \mathrm{Y} &\longrightarrow \mathrm{X} \\
\mathrm{X} + \mathrm{Y} &\longrightarrow \mathrm{P} \\
\mathrm{B} + \mathrm{X} &\longrightarrow 2\,\mathrm{X} + \mathrm{Z} \\
2\,\mathrm{X} &\longrightarrow \mathrm{Q} \\
\mathrm{Z} &\longrightarrow \mathrm{fY}
\end{aligned}$$

Where X=$HBrO_2$, Y=Br^-, Z=Ce^{4+}, A=B=BrO_3^-, and P and Q are products. The variable stoichiometric factor f is just 1 in the model presented in the literature.[5]

A system of three ordinary first order differential equation can be found by assuming that all chemical species other than X, Y, and Z are held relatively constant, and non-dimensionalizing the system. The equations are:

$$\begin{aligned}
d\alpha/d\tau &= s(\eta - \eta\alpha - q\alpha - q\alpha^2) \\
d\eta/d\tau &= s^{-1}(-\eta - \eta\alpha + f\rho) \\
d\rho/d\tau &= w(\alpha - \rho)
\end{aligned}$$

Where α, η, and ρ are dimensionless variables corresponding to X, Y, and Z respectively. A complete description of the non-dimensionalization of the model, and appropriate values for the constants can be found in the literature.[5]

The Oregonator is a great model for understanding the basic oscillations in the concentrations of different compounds in the BZ reaction. However, it does not result in chaos with the conditions presented in the model. We confirm its non-chaotic behavior through our analysis. If we want to show chaos in the reaction, we need a different model.

3 The Györgyi-Field Model

The second model we investigate is the 1992 model presented by Györgyi and Field.[6] The model describes the BZ reaction in a CSTR, which has a variable residence time, k_f^{-1}. This model is slightly more complex than the Oregonator, which makes it a better representation of the BZ reaction, and k_f can give rise to chaos at certain values. Despite the added complexity, this model can be reduced to three variable concentrations, so it is a reasonable model for mathematical analysis.

The equations used are:

$$\begin{aligned}
\mathrm{Y + X + H} &\longrightarrow \mathrm{2\,V} \\
\mathrm{Y + A + 2\,H} &\longrightarrow \mathrm{V + X} \\
\mathrm{2\,X} &\longrightarrow \mathrm{V} \\
\tfrac{1}{2}X + \mathrm{A + H} &\longrightarrow \mathrm{X + Z} \\
\mathrm{X + Z} &\longrightarrow \tfrac{1}{2}X \\
\mathrm{V + Z} &\longrightarrow \mathrm{Y} \\
\mathrm{Z + M} &\longrightarrow \mathrm{?}
\end{aligned}$$

Where Y=Br^-, X=$HBrO_2$, Z=Ce^{4+}, V=$BrCH(COOH)_2$, A=BrO_3^-, H=H^+, and M=$CH_2(COOH)_2$. Again, certain chemical species are assumed to be held constant to give the dimensionless equations:

$$
\begin{aligned}
dx/d\tau &= T_0(-k_1HY_0x\overline{y} + k_2AH^2Y_0X_0^{-1}\overline{y} - 2k_3X_0x^2 \\
&\quad +\tfrac{1}{2}k_4A^{1/2}H^{3/2}X_0^{-1/2}(C - Z_0z)x^{1/2} - \tfrac{1}{2}k_5Z_0xz - k_tx) \\
dz/d\tau &= T_0(k_4A^{1/2}H^{3/2}X_0^{1/2}(C/Z_0 - z)x^{1/2} - k_5X_0xz \\
&\quad -\alpha k_6V_0zv - \beta k_7Mz - k_fz) \\
dv/d\tau &= T_0(2k_1HX_0Y_0V_0^{-1}x\overline{y} + k_2AH^2Y_0V_0^{-1}\overline{y} \\
&\quad +k_3X_0^2V_0^{-1}x^2 - \alpha k_6Z_0zv - k_fv) \\
where & \\
\overline{y} &= (\alpha k_6Z_0V_0zv/(k_1HX_0x + k_2AH^2 + k_f))/Y_0
\end{aligned}
$$

Where x, z, and v are dimensionless forms of X, Z, and V. Again, a more thorough description of the non-dimensionalization of the model, as well as appropriate values for constants can be found in the literature.[6]

4 Results

To investigate each model, we used Matlab to generate data, using initial values suggested in the literature.[5,6] We solved the system of differential equations using the $ode23s$ function on Matlab and plotted the resulting concentration oscillations and 3-dimensional attractors. We then created time delay reconstructions and computed the correlation dimensions. Finally, we computed the Lyapunov exponents. The goal of these tests was to show that chaos does not exist in the Oregonator and that chaos does exist in the Györgyi-Field Model.

4.1 The Oregonator

We originally attempted to solve the Oregonator using Matlab's $ode45$, but it is an extremely inefficient method because the Oregonator is a 'stiff' system. This means that the criteria for stability is more strict than the criteria for accuracy. Solvers such as $ode45$, which are not equipped to handle stiff systems, are forced to take extremely small step sizes in order to prevent the solution from becoming unstable, and, thus, inaccurate. Luckily, Matlab has other built-in ODE solvers, including $ode23s$, which are able to handle 'stiff' systems.

Using $ode23s$, we were able to efficiently solve the Oregonator and plot the concentrations of the three variable reacting species over time and the 3-dimensional attractor. We used an absolute tolerance of 1×10^{-6} because we noticed that setting a lower tolerance did not affect the accuracy of the calculations significantly. This allowed our code to run much faster and compute more data.

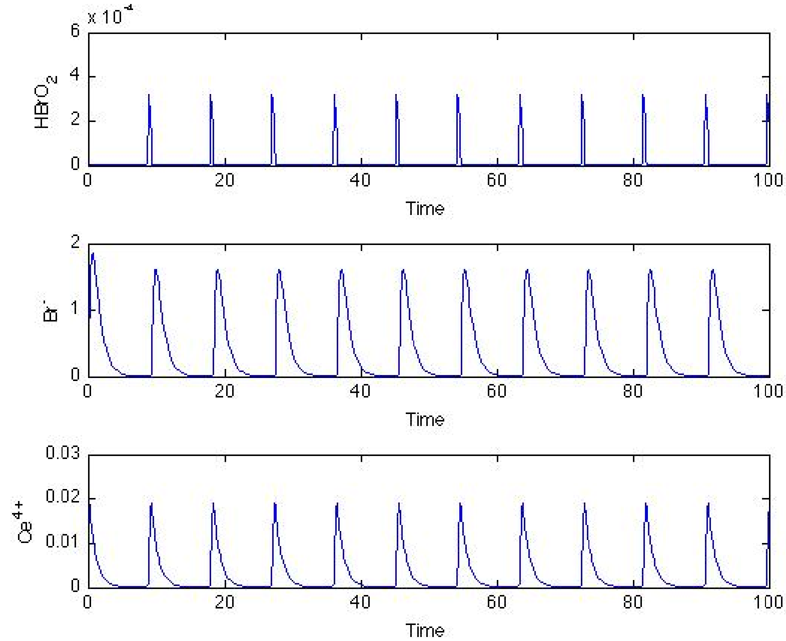

Figure 1: Concentrations of α, η, and ρ for $t = 0$ to 100

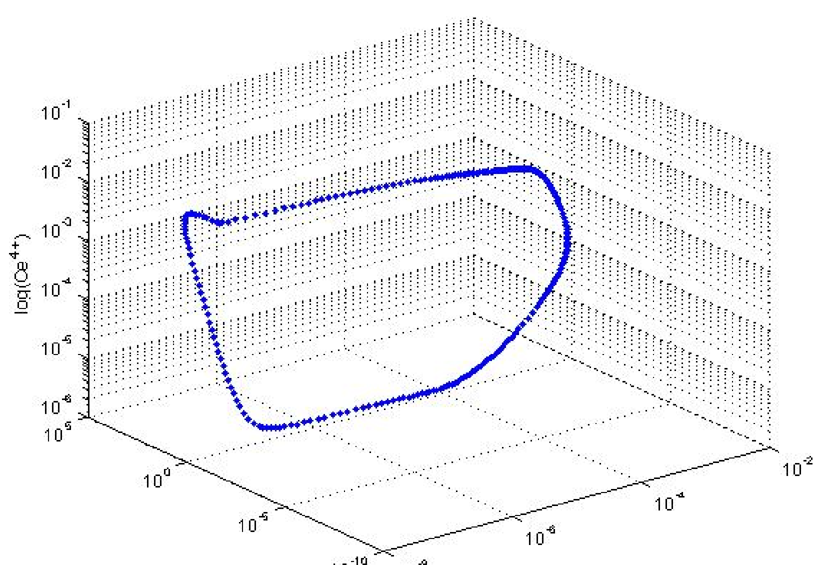

Figure 2: Attractor for Oregonator model

To solve for our time delay, we solved the Oregonator for 100,000 evenly spaced points from $t = 0$ to 200 using *ode*23*s* and the *deval* function, which samples the points such that they are evenly spaced. We plotted $x(t+1)$ vs. $x(t)$ to show the limit cycle behavior.

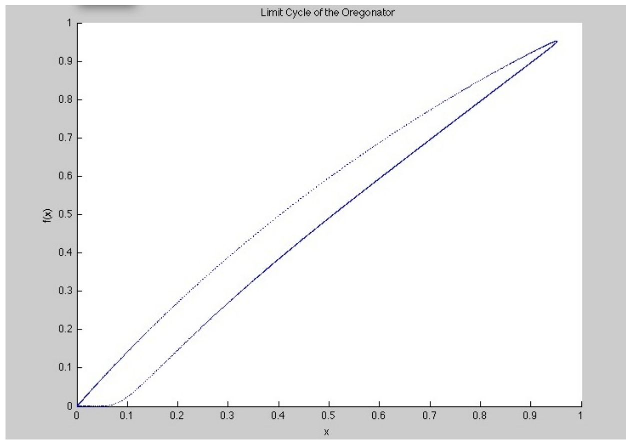

Figure 3: Time Delay for the Oregonator, time step of $\tau/500$

For the Oregonator, we found the correlation dimension of the 3-dimensional attractor. We plotted $C(r)$ vs. r, and the slope of the resulting line is the correlation dimension. Our calculation of the correlation dimension was .9678.

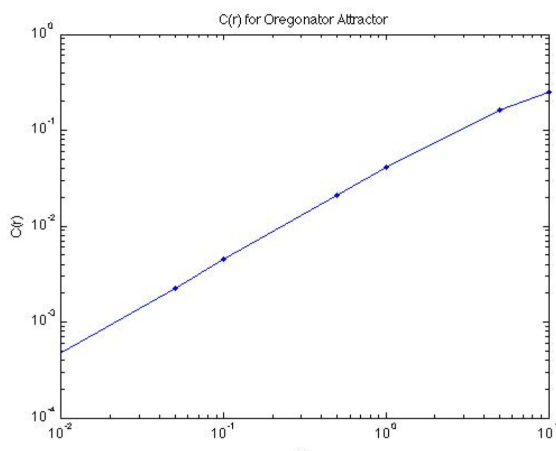

Figure 4: C(r) for the Oregonator

We found the Lyapunov exponents of the Oregonator as a final test for chaos. We used the re-orthogonalizing version for finding Lyapunov exponents with averaging over long trajectories and a time-1 map. We calculated the following values:

$$
\begin{aligned}
h_1 &= 0.0700 \\
h_2 &= -5.0436 \\
h_3 &= -29.9433
\end{aligned}
$$

4.2 The Györgyi-Field Model

We solved the GF model using the same Matlab functions as the Oregonator, *deval* and *ode*23*s* with an absolute tolerance of 1×10^{-6}. The GF model is also 'stiff,' and using a smaller tolerance does not significantly alter the results.

Using these Matlab functions, we produced plots of the concentrations of x, z, and v over τ = 0 to 2. These are the dimensionless values of the concentration, so the particular concentration values do not match well with the concentrations plotted with the Oregonator model. The second plot shows the 3-dimensional attractor.

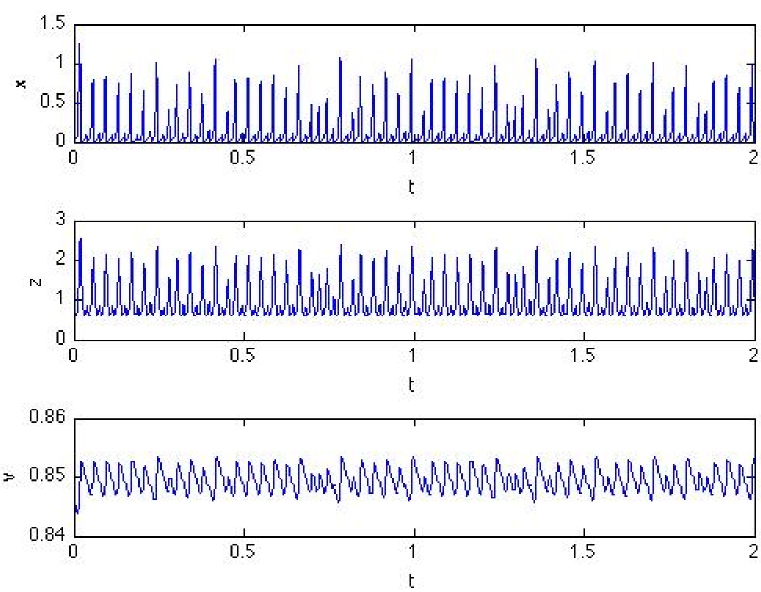

Figure 5: Concentrations of x, z, and v for $\tau = 0$ to 2

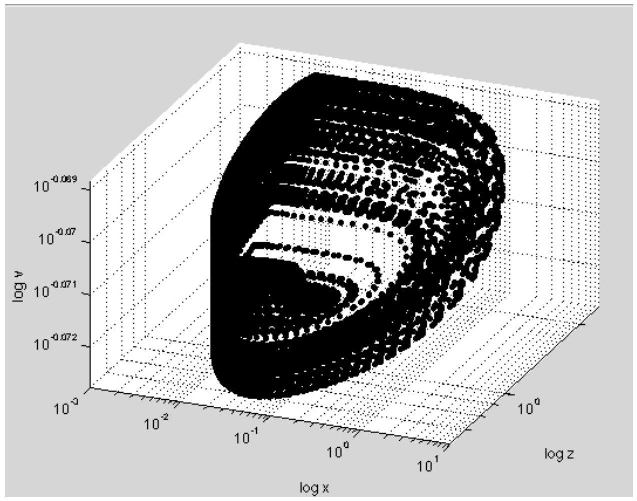

Figure 6: Attractor for GF model, $k_f = 3.9 \times 10^{-4} s^{-1}$

By varying a parameter k_f, the flow rate into the CSTR, the GF model can change from non-chaotic to chaotic and vice versa. We reproduced a bifurcation diagram for the GF model that shows where z intersects a Poincare plane as k_f changes. The Poincare plane is perpendicular to the x-axis and containing the point ($x = 0.0468627, z = 0.89870, v = 0.846515$) when x is decreasing.[6]

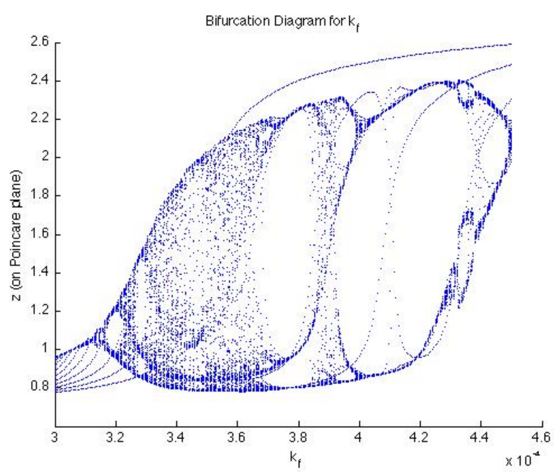

Figure 7: Bifurcation Plot for GF Model, $k_f = 3 \times 10^{-4}$ to 4.5×10^{-4}

We also created a time delay plot for the GF model. We solved it for 100,000 evenly spaced points from $\tau = 0$ to 100 using *ode*23*s* and the *deval* function. We plotted $x(t)$ vs. $x(t+1)$ to show the limit cycle behavior.

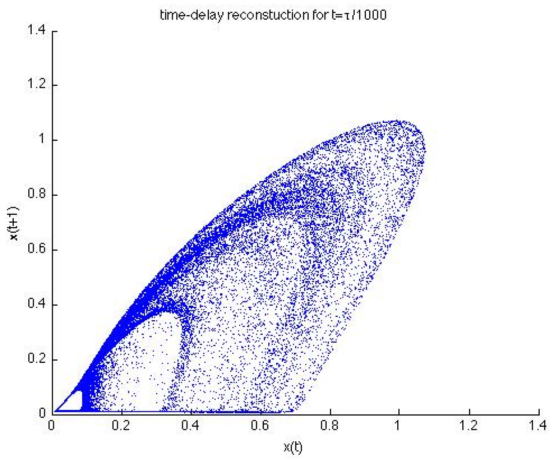

Figure 8: Time Delay for GF model, $k_f = 3.9 \times 10^{-4} s^{-1}$. Time step of $\tau/1000$.

We calculated the correlation dimension of the 3-dimensional attractor and of the attractor from the reconstruction of the time series for the GF model. For each, we plotted $C(r)$ vs. r, and the slope of the resulting line is the correlation dimension. Our calculation of the correlation dimension was 1.2903 for the 3-dimensional attractor and 1.1600 for the attractor from the reconstruction of the time series.

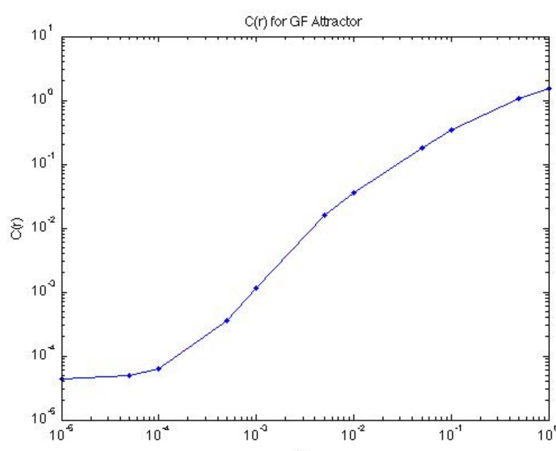

Figure 9: Correlation Dimension for 3-dimensional attractor of GF model, $k_f = 3.9 \times 10^{-4} s^{-1}$

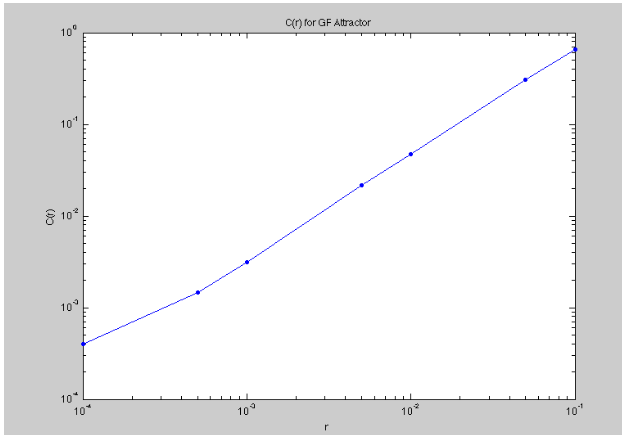

Figure 10: Correlation Dimension for attractor from time series reconstruction of GF model, $k_f = 3.9 \times 10^{-4} s^{-1}$

We found the Lyapunov exponents for the GF model using the same process that we used for the Oregonator, except we were forced to make our calculations with a time-0.001 map by the computational limits of our computers. If we used a time-1 map, our Lyapunov exponent values would be 'NaN's (Not a Number). Therefore, we used a time-0.001 map and multiplied the result by 1000 to approximate the calculation with a time-1 map. Unfortunately, the exponents are not very accurate as a result, but they still give us data that is adequate for qualitative analysis. We calculated the following Lyapunov exponent values:

$$\begin{aligned} h_1 &= 2668.0 \\ h_2 &= -47.5 \\ h_3 &= -7912.6 \end{aligned}$$

5 Conclusions

The goal of our project was to show that chaos *does not* exist in the Oregonator and that chaos *does* exist in the Györgi-Field Model, and we achieved it through numerical simulations and calculations in Matlab.

5.1 Conclusions on the Oregonator

All of our tests confirmed previous investigations by finding that the Oregonator is not chaotic.

First, we saw that the oscillations of the concentrations of the three variable reacting species were periodic over time and the 3-dimensional attractor was a 1-dimensional loop.

Our time delay reconstruction was also a 1-dimensional loop. If it was plotted in 3 dimensions, we would see that we could predict exactly what the next concentration would be.

We found the correlation dimension of the 3-dimensional attractor to be equal to approximately one.

Our Lyapunov exponents were all non-positive. The first one was zero, which is expected for a flow, and the other two were negative.

These are all characteristics of a non-chaotic system. All of our tests agreed with each other, so we can be confident that chaos *does not* exist in the Oregonator.

5.2 Conclusions on the Györgyi-Field Model

All of our tests confirmed Györgyi and Field's analysis that their model is chaotic.

The oscillations of the concentrations of the three variable reacting species appeared to not be periodic over time and the 3-dimensional attractor never fell into a 1-dimensional loop. It instead created a large swirl.

The bifurcation diagram has a period-doubling cascade at lower values of k_f and the z concentration passes through the Poincare plane seemingly at random (definitely not periodic) at higher values of k_f. Note that at $k_f = 3.9 \times 10^{-4}$ (for our simulations), there appears to be chaos.

The time delay reconstruction appears as an elliptical cloud-like blur of points. Even in 3 dimensions, we would not be able to predict what the concentration will be next.

We found the correlation dimension of the 3-dimensional attractor to be 1.2903, proving that the attractor is a fractal with greater than 1 dimension. The correlation dimension of the attractor from the reconstruction of the time series was 1.1600, confirming a dimension greater than one.

Our first Lyapunov exponent was positive. The second was approximately zero (when you consider its size compared to the other two exponents and the inaccuracy of this calculation), which is expected for a flow. The third Lyapunov exponent is negative and larger in magnitude than the first. When we add the three exponents together, we get a negative number, meaning that the 3-dimensional attractor is not volume-preserving as we see in the plot of the attractor.

These are all characteristics of a chaotic system. All of our tests agreed with each other, so we can be confident that chaos *does* exist in the GF model.

5.3 Conclusions on the BZ Reaction

The most detailed models of the BZ Reaction show that it is indeed a chaotic system under certain circumstances. In our investigation, the GF model was more computationally accurate than the Oregonator, and it was able to reproduce the chaotic behavior of the full reaction. The BZ Reaction is an extremely fascinating and complicated system, and it was very satisfying to demonstrate chaos with the knowledge that we have built throughout the term.

6 Acknowledgements

In developing code and in investigating this topic, we borrowed and modified much from Professor Alexander Barnett's Math 53 course, *Chaos!* taught at Dartmouth College.

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