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Math 053: Chaos!

Chaos in the Belousov-Zhabotinsky Reaction

Introduction:

For this project, we have chosen to examine the Belousov-Zhabotinsky reaction. The main purpose of this project is to analyze the dynamics involved in the Belousov-Zhabotinsky (B-Z) reaction and determine if the reaction class can be called chaotic. This reaction is a very unique reaction which self-oscillates and generates propagating waves (Lu and Teulilo 2). Throughout this course, we have learned a steady amount of definitions and theorems that will enable us to study this reaction in greater depth in terms of mathematics, and in particular the most important portions of chaos theory: lyapunov exponents and asymptotic periodicity. In order to make the reaction tractable, two simplified models of the B-Z reaction will be considered: the “Oregonator” and “Oregonator” with an external periodic force. With these two models in hand, we will have a complete view of the simplified model of the B-Z reaction. Also, these models will allow for a careful balance between understanding the mathematics of non-linear dynamics and understanding the chemistry and its role in the oscillation. By using the necessary definitions and theorems for chaos in deterministic systems, we will explore Belousov-Zhabotinsky reaction and discover, if it is indeed chaotic.

Background:

The B-Z reaction is remarkable in a sense that its oscillations and cyclical nature can relate to others such as the heartbeat and circadian rhythm (Lu and Teulilo 8). The analysis of this reaction compares to others by its chaotic properties. Chaos can also occur in other instances where “the analysis of these equations permitted the demonstration of a universal route for the appearance of the phenomenon: a cascade of period-doubling bifurcations often characterizes the oscillations before the latter become aperiodic” (Goldbeter 12). Chaos can be observed through the construction of many different graphs, such as in the B-Z reaction, note how the graphs illustrate oscillatory behavior which opens the door the possibility of chaos. From looking at the comparison of the graphs between other oscillatory occurrences and the B-Z reaction demonstrates the potential for chaos through “the appearance of aperiodic oscillations beyond a point of accumulation of a cascade of period-doubling bifurcations is one of the best-known scenarios for the emergence of chaos” (Goldbeter 126).

The comparisons of graphs and relations to the listed definitions above help provide a better understanding of the B-Z reaction as “this reaction conflicts with the Second Law of Thermodynamics” (Lu and Teulilo 3). In other words this reaction is an example of non-equilibrium thermodynamics. However, the importance of the chemistry involved in the B-Z reaction that causes its chaotic properties will deliver more concrete evidence which fulfills the conditions stated in the definition of chaos. As we will discover, the oscillations of the B-Z reaction are caused by the instability of the chemical compounds within the reaction which can be described as *autocatalytic*.

The B-Z reaction is a very complex reaction that oscillates caused by the reduction of cerous (IV) ions (back to the oxidization of cerous (III) ions (). Here are the chemicals involved in this reaction:

1. Dilute Sulfuric Acid 1 M
2. Malonic Acid (Propanedioic Acid) 0.3 M
3. Cerium (IV) Sulfate 0.02 M
4. Bromous Acid 0.25 M

Before going further with the examinations, it is important to note the discovery of this phenomenon. Boris Belousov founded this reaction in the year 1951 but was unable to publish his discovery due to the contradiction involving the second law of thermodynamics, “which states that mass is conserved and cannot be created or destroyed” (Lu and Teulilo 3). Even though Belousov was unsuccessful, his work was later picked up by Anatol Zhabotinsky. Zhabotinsky was able to prove the reaction was true by researching Belousov’s reaction in greater detail (Lu and Teulilo 3). This reaction was finalized as the Belousov-Zhabotinsky reaction. After further study of this reaction by Richard M. Noyes, Endre Kovos and Richard J. Field (1972), they were able to construct a differential (rate) equations for which they created a model known as the *Oregonator* (Peterson 1). The *Oregonator* model provides a table to better see the reaction steps and rate equations (Peterson 2).

 3





 (catalyst)



“where *B* represents all oxidizable organic species present and *f* is stoichiometric factor that encapsulates the organic chemistry involved” (Peterson 2). The term Z is used to denote the cerous (IV) ion.

 3

 These tables shown above represent the *Oregonator* model constructed by Field, Koros, and Noyes. “However, despite its relative simplicity, it nonetheless demonstrates the qualitative behavior of the Belousov-Zhabotinsky Reaction” (Peterson 2). Chaos cannot be produced from the simple *Oregonator* model. However, chaos can ultimately be produced from other models which show aperiodicity and transitions between periodicity and chaos (Gyorgi and Field 1). The table below is the differential equations used for this reaction.

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In order to determine if the B-Z reaction is chaotic, we will need to analyze the necessary definitions with regards to chaos that will help this proof. Before further examination of this reaction, it is important to understand the definition for chaotic properties:

 1

 **Definition 5.2** Let be a map of , and let be a bounded orbit of . The orbit is **chaotic** if

1. It is not asymptotically periodic,
2. No Lyapunov exponent is exactly zero, and

In order to determine if the B-Z reaction is chaotic it will need to follow the conditions stated in **Definition 5.2**. The main component for following these conditions is the knowledge and understanding of the lyapunov exponent.

 2

 **Definition 3.1** Let f be a smooth map of the real line R. The **Lyapunov number** of the orbit is defined as

,

if this limit exists. The **Lyapunov exponent** is defined as

if this limit exists. Notice that h exists if and only if L exists and is nonzero, and .

Methods:

 In this examination, a numerical approach was taken in order to analyze the qualitative and quantitative attributes of the simplified version of the B-Z reaction, known as the *Oregonator*. The programming language of Matlab was chosen for this investigation because of its apparent ease in handling non-linear ordinary differential equations, plotting capabilities, and function creation. In order to solve the non-linear differential equations, ODE45 was employed almost to exhaustion along with a host of other functions. Once the equations were solved, they were plotted and interpreted for their qualitative (periodicity and general function expression) and quantitative attributes (lyapunov exponent).

Results:

First, we examined the *Oregonator* Model without the driving function. With IC’s of [.2,.2,.2] for concentration and time span of fifty steps, Matlab produced these plots:

1(a) 1(b)

 



1( c ) Poincare map of the *Oregonator* (x3 increasing, x1 = x-axis, x2 = y-axis)

Next step to compute the lyapunov exponent, two very close IC: [.2,.2,.2] and [.2001,.2001,.2001] then taking the difference. For [.2,.2,.2] we have:

H1 = M= 3

 8.9685

 7.1285

 0.4727

H2 =

8.9681

7.1282

 0.4728

Log(abs(H2-H1))/M = (-1.92, -2.7039, -3.0701)

(Checking for sensitive dependence)

Next, we examined the *Oregonator* with a driving function (driving function represented by Acos(wt)):

w = pi, A = [-40, -40,-40] IC = [.2,.2,.2] t= 100

2(a)  2(b)



2( c.) Poincare Map



Finally, to compute the lyapunov exponent for IC = [.2 .2 .2] and IC = [.21, .21, .21]

(Identical IC in all other categories as above)

1)

H1:

 22.1184

 19.4596

 -0.8055

H2:

 22.1281

 19.4585

 -0.8054

M= 5

Log(abs(H2-H1))/M = (-.9271, -1.3625, -1.8421)

Discussion:

In the general *Oregonator* Model, both the phase plane and the concentration vs. time plot show behavior characteristic of periodicity. For the example IC’s (and all others), the system of equations “bounces” around for a while before finding a periodic orbit to fall into. Also, it appears ICs drain into a sink after so many iterations, indicating that the system is stable. The Poincare map appears to just be a line which supports the claim that it is not chaotic and that it is stable. The Lyapunov exponents are all negative, which is a clear indicator that the system of equations is not chaotic. This allows us to pair a quantitative measurement with the qualitative observation that the *Oregonator* reaction is not chaotic.

However, the *Oregonator* Model with driving function acts a little different. Instantly, by looking at the phase plot, it looks like the orbit may have chaotic potential. Also, the concentration vs. time plot does have periods of “wild” oscillation. However, after further examination both the phase plot and concentration plots settle to values and the plots do look relatively stable. The Poincare map is a bit disappointing because it only showcases one crossing, however that could be do to programming error. Even with the driving function, all the lyapunov functions continue to be negative. One possible reason for this is that the driving function: A\*cos(wt) is not dependent on the concentration of any species so when computing the jacobian of the differential equation it completely falls out. This effectively makes the equation the original *Oregonator* model which, as we know, does not exhibit chaos by having a positive lyapunov exponent.

Conclusion:

 After examining the Belousov-Zhabotinsky reaction, we have determined that it is a complex function that can produce and chaos and periodicity depending on the differential equations used. The *Oregonator* model calculated by Field, Koros, and Noyes is the simplest model with regards to the B-Z reaction. As shown, the *Oregonator* model doesn’t produce chaos. After several calculations with this reaction, we have ultimately determined the reaction is not chaotic since the lyapunov exponents are less than zero.

 After further review with this reaction and other works with the B-Z reaction, there have been studies to show the chaotic properties. With the differential equations we used, our data analysis described periodic behavior.

References:

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Appendix: (see attached documents and attachments in emails)