An Extended Look into the Belousov-Zhabotinsky Reaction

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I. INTRODUCTION: THE DISCOVERY OF THE BELOUSOV-ZHABOTINSKY REACTION

The Belousov-Zhabotinsky reaction (BZ reaction) is a type of chemical reaction that exhibits oscillatory behavior. Typically when we think about chemical reactions, we think about combining two chemicals together in order to get a third chemical, and that would be the end of it. The idea of that process reversing itself without any new chemical being added is not only surprising, but also a bit uncanny since that type of reaction would be violating one of the most fundamental laws of thermodynamics. This isn't the case with the BZ reaction though, since it is an example of experimenting with the least idealized conditions.

The usual chemical reaction that we are used to thinking about only happens near equilibrium, the same can be said about studying thermodynamic in general. The question that we never asks ourselves is, what happens when we move very far away from equilibrium? We might not expect anything different to happen, which was the case for B.P. Belousov, the initial discoverer of the BZ reaction.

During the 1950s, Belousov attempted to recreate a metabolic reaction known as the Krebs cycle by using citric acid and bromate dissolved in water. The surprising observation that Belousov made during his experiments was that his solution was changing between two colors over time, without him adding any extra chemicals nor changing the room temperature. This observation lead Belousov to a deeper study into the mechanics behind the reaction with a goal of publishing a paper about the reaction. He ended up failing at that goal twice and decided not to publish anything, but his recipe was circulated all throughout Russia. This brings Zhabotinsky into the story, and he fortunately had a greater success at exposing the world to this amazing chemical reaction. Zhabotinsky spent a couple of years investigating Belousov's recipe, working with both his advisor and Belousov on a manuscript which would gain recognition in the 1968 Symposium on Biological and Biochemical Oscillators. Zhabotinsky's success with Belousov's reaction resulted in the birth of a rich research field involving the modeling of the BZ reaction as well as the discovery of this reaction within nature.

II. THE DIFFERENT MODELS FOR THE BZ REACTION

The BZ reaction has been a well studied reaction both in physical chemistry and computational physics. The deep study of the BZ reaction has resulted in numerous models which are not only used in understanding the mechanics behind the BZ reaction, but are also used to understand population dynamics. The fascinating thing about these models is that you can start off at one dimension and then very easily expand them into two dimensions, which results in the simulation of some very awesome patterns.

A thing to note before further looking into the one dimension and two dimensional cases is the generalization of the models describing the BZ reaction. Every chemical reaction can be described as a reaction-diffusion system, in which chemical A and B react, and over time, their concentrations tend towards an equilibrium point. The reaction-diffusion system is very general and allows us to combine different types of models, for example, we can use the Fitzhugh-Nagumo model to describe a reaction-diffusion system, and investigate whether this system has excitable behavior or not. This plays an extremely important role when investigating the Oregonator model in the following section.

A. The One Dimensional Case

The first attempt at modeling the BZ reaction comes in the form of the Brusselator, a model proposed by Ilya Prigogine, who was based in Brussels! This model is based on the following chemical reactions[1]:

$$\begin{aligned} \bar{X}_1 &\rightarrow Y_1 \\ \bar{X}_2 + Y_1 &\rightarrow Y_2 + Z_1 \\ 2Y_1 + Y_2 &\rightarrow 3Y_1 \\ Y_1 &\rightarrow Z_2 \end{aligned} \tag{1}$$

The way the Brusselator model works is that you initially start with two chemicals $\bar{X}_1$ and $\bar{X}_2$ with an extremely high initial concentration, which allows the rate equations to treat those concentrations as constants, simplifying the equations to an extent[1].

$$\frac{dY_1}{dt} = c_1X_1 - c_2X_2Y_1 + (c_3/2)Y_1^2Y_2 - c_4Y_1$$
$$\frac{dY_2}{dt} = c_2X_2Y_1 - (c_3/2)Y_1^2Y_2 \tag{2}$$

The Brusselator is a good intial model, it exhibits oscillations in both chemical Y_1 and Y_2, and follows the actual behavior of a BZ Oscillation, which will be investigated in a later section. The main criticism of this model mostly lies on the fact that it is not a realistic model, due to the fact that it depends on every single Y_1 and Y_2 molecule having perfectly timed collisions in order to have the proposed chemical reactions.

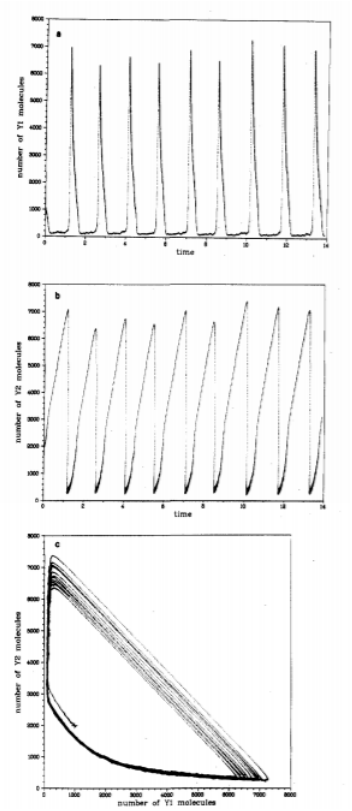

FIG. 1. Plots of Y_1 and Y_2 as well as the phase trajectory plot. These plots come from Gillespie's article

Following the Brusselator is the Oregonator model which was proposed by Field and Noyes, both researchers from Oregon. This model is a bit like the Brusselator, but with an added third chemical Y_3, which helps get around the problem that the Brusselator had[1]. This model depends on the following chemical reactions:

$$\begin{aligned} \bar{X}_1 + Y_2 &\rightarrow Y_1 \\ Y_1 + Y_2 &\rightarrow Z_1 \\ \bar{X}_2 + Y_1 &\rightarrow 2Y_1 + Y_3 \\ 2Y_1 &\rightarrow Z_2 \\ \bar{X}_3 + Y_3 &\rightarrow Y_2 \end{aligned} \tag{3}$$

The cool thing about this model is that it is an idealized model of the BZ reaction, specifically for the reaction involving malonic acid and bromate[1]. There is a highly realistic model proposed by Noyes, Fields, and Körös, which isn't idealized for one specific reaction and has actually been tested by other researchers [2]. The Gillespie paper gives a specific form for the Oregonator model, but the following equations uses the Fitzhugh-Nagumo model:

$$\begin{aligned} \epsilon \dot{U} &= U(1-U) - fV(U-q)/(U+q) \\ \dot{V} &= U - V \end{aligned} \tag{4}$$

The graphs for the Oregonator and Brusselator are extremely similar, but you will notice that the graph for one of the chemical's concentration as a function of time has a very thin size, and a sharp peak.

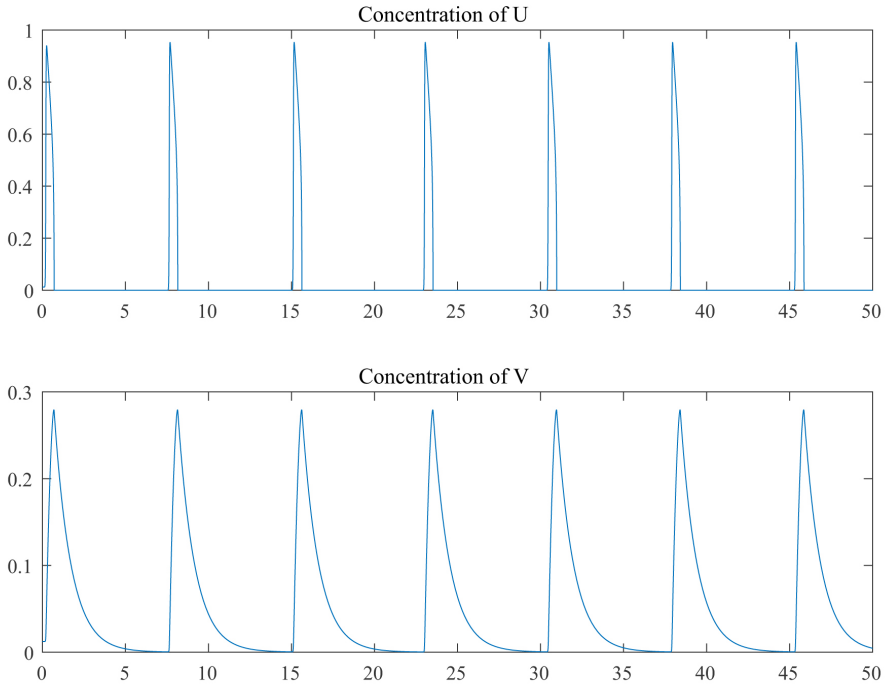

FIG. 2. A plot of the concentrations of chemical U and chemical V as a function of time. This plot was made in Matlab.

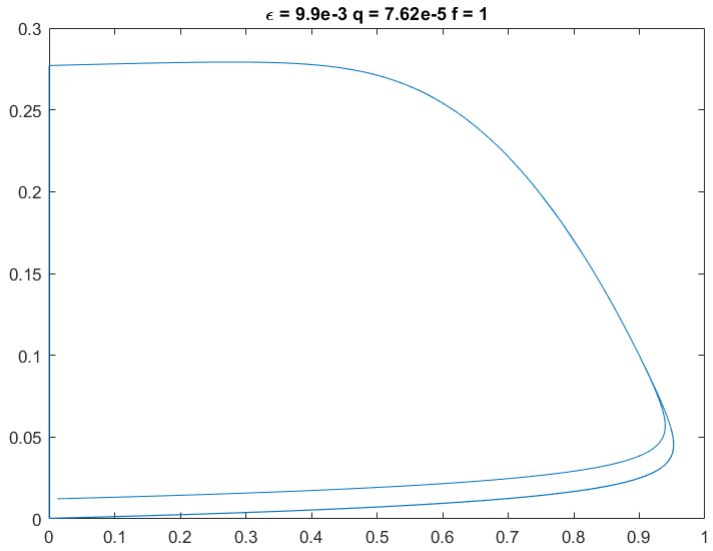

FIG. 3. Phase-space plot for the Oregonator model made in Matlab.

Another interesting and insightful plot that comes from the Oregonator model is the

phase-space plot. A phase-space plot show how our variables in our model change as a function of each other. In the case of the Oregonator model that I used, the plot will be showing the concentration of V as a function of the concentration of U. In general, these plots really just shows all the possible values that our variables can take given a specific initial. The behavior of the phase-space plot can be significantly changed by changing the parameters.

Earlier, I talked about how the Oregonator model can be described as a reaction-diffusion system, I also talked about how we're going to be using the Fitzhugh-Nagumo model to describe the reaction part of the reaction-diffusion system. The Fitzhugh-Nagumo model describes an excitable system (i.e. neurons), essentially, this means that there is a threshold that some initial condition must pass in order for it to excite the rest of the system. We can observe this behavior using a phase-space plot, which will result in some very interesting trajectories.

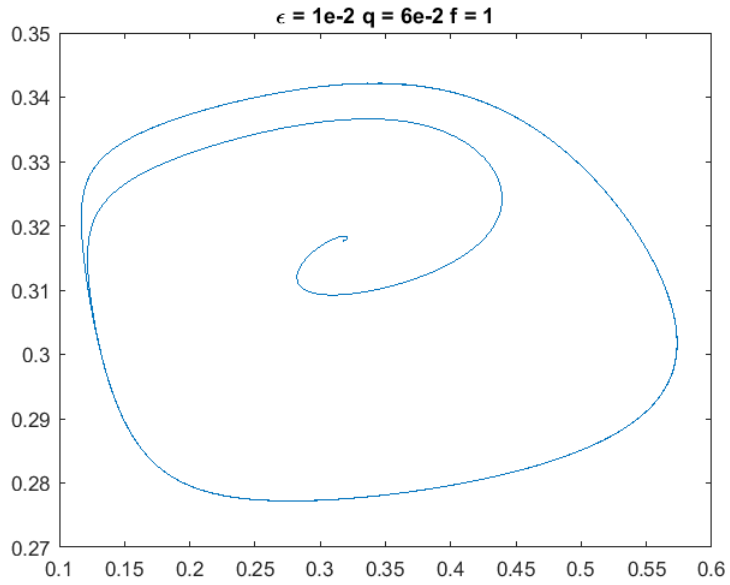

FIG. 4. Phase-space diagram showing a limit cycle for a specific parameter. This plot was made with Matlab.

The plot in 4 is not showing the same behavior an excitable system would have, but it does show that the Oregonator has a preferred state, which is known as a limit cycle. The following figure will show behavior that is expected from an excitable system in which the initial conditions, were not large enough to excite the rest of the system.

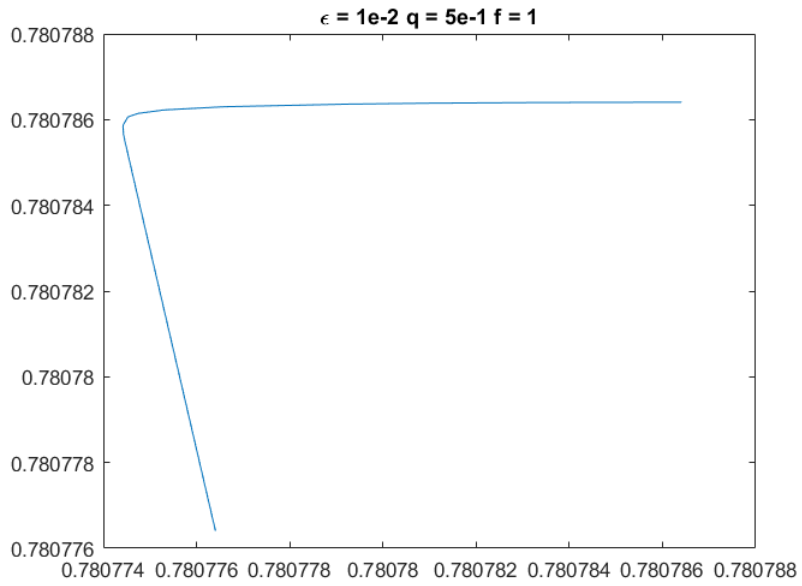

FIG. 5. Phase-space plot which exhibits excitable behavior. This plot was made in Matlab.

B. A small conversation about nullclines

In the last part of the previous section, there was a slight conversation about excitability within the Oregonator model. Although, showing that the Oregonator model is excitable with phase trajectory plots is satisfactory, one can also show that the model is excitable through mathematics, which arguable results in a more aesthetically pleasing result.

In order to begin understanding excitability through a more mathematical lens, we need to introduce some definitions and theorems. First, consider a system of differential equations with the following form:

$$\begin{aligned} \dot{X} &= Y - f(X) \\ \dot{Y} &= -X \end{aligned} \tag{5}$$

The main focus of these equations is $f(X)$. The importance of $f(X)$ has to do with something called linear nullclines, which act like guides to our phase trajectories. In more formal language, linear nullclines are boundaries in which our phase trajectories do not approach a single point [3].

The study of linear nullclines within a system of differential equations has resulted in a very useful theorem, which allows us to further analyze the ways in which the linear

nullclines interact with our phase trajectories. The theorem is known as the Poincaré-Bendixson Theorem which states that if a trajectory is bounded and doesn't approach any singular point, then it is either a closed periodic orbit or approaches a closed period orbit for $t \to \infty$ [3]. In other words, if we have a phase trajectory that is not converging to a single point, then that phase trajectory has either reached a limit cycle, or is approaching a limit cycle.

There are many different ways we can explore this theorem, including proving the existence of a limit cycle within a model, but we are only going to focus on excitability. The first thing we must consider is a form for $G(u)$, the most traditional form (following the Fitzhugh-Nagumo model), is:

$$f(X) = \frac{X^3}{3} - X \tag{6}$$

This form is known as a cubic nullcline, and the investigation of this type of nullcline can be generalized to any function that has an s-form [3]. The basic idea behind a nullcline is that we first have specific directions in which our phase trajectory can follow. For $f(X)$, we have that the direction can only be vertical with respect to the curve. If we consider $\dot{Y}$, and plot it's linear parts, then the direction that the phase trajectory can follow on the Y nullcline can only be horizontal. This results in the following plot:

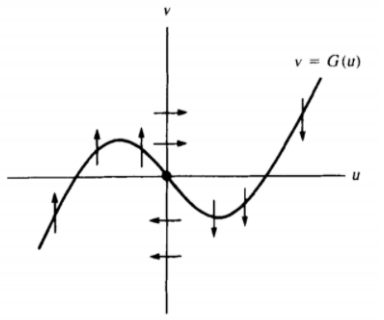

FIG. 6. X nullcline plot with directions. This figure comes from Edelstein's book Mathematical Models in Biology, chapter 8.

From this plot, we can see that there is a equilibrium point at the origin, if we begin our trajectory from the origin, we won't go anywhere, since we are at a stable point. However, if we move away from the equilibrium point, our phase trajectory would have to follow the directions set by the nullclines until it gets to the equilibrium point. If we move sufficiently away from that point, we get the following trajectory:

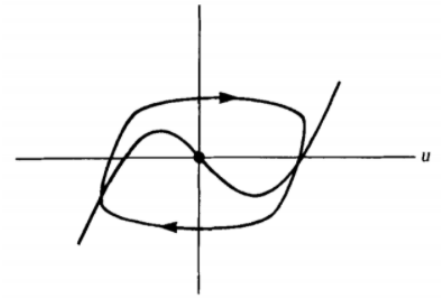

FIG. 7. Phase Trajectory and nullcline plot. This figure also comes from Mathematical Models in Biology, chapter 8.

This kind of behavior is excitable behavior. Starting off very close to an equilibrium point does not result in a limit cycle, but if we move sufficiently far away from that equilibrium point, we can have suddenly have a limit cycle appear. In the case of the Oregonator model, this means we have BZ reactions. Again, this understanding of the linear nullclines can be extened to any nullcline that has an s shape to it, meaning that we do not necessarily need to have a cubic function, which is the case for equation 4.

C. The Two Dimensional Case

The two dimensional case can be easily gotten from the previous models, this is because the two dimensional case strictly uses the different ways in which the chemicals interact with each other. The way that the two dimensional case is modeled is by using a cellular automaton, which is basically a collection of pixels that evolve over time[4]. These cells can randomly evolve however, you can specify rules for how they evolve, in this case you can use the proposed chemical reactions as a general rule for how each individual pixel interacts with other pixels.

Cellular automaton lends itself nicely to modeling the two dimensional case for BZ reactions since, it relies on the use of neighboring pixels to determine the next state for one

specific pixel. There are many algorithms for cellular automoton, but one of the most widely used algorithms is called the Moore neighborhood. Essentially, you have one center pixel and 8 surrounding pixels, each pixel is assigned specific numbers, in this case those numbers represents the concentration of chemicals A,B,C. In order to determine the next state for the center pixel, you first run the values of all 9 pixels through the following rules:

$$\begin{aligned} A_{t+1} &= A_t + A_t(\alpha B_t - \gamma C_t) \\ B_{t+1} &= B_t + B_t(\beta C_t - \alpha A_t) \\ C_{t+1} &= C_t + C_t(\gamma A_t - \beta B_t) \end{aligned} \tag{7}$$

After doing that, you average the new values from all 9 cells, and the average will be the updated value for the center cells and you move on to the next cell. A thing to note about the rules in equation (7), is that they depend on the production of other chemicals and the use of the chemical that you are currently looking at. For example, the next time step for chemical A depends on the current concentration of Chemical A, and the way it is being used to produce chemical B, as well as the rate in which chemical B is producing chemical A. In other words, the rules found in equation (7) mimic the chemical reactions happening within the BZ solution. This means that you are not limited to only using the rules in equation (7), you can actually derive rules for the Brusselator and Oregonator models and apply it to this method.

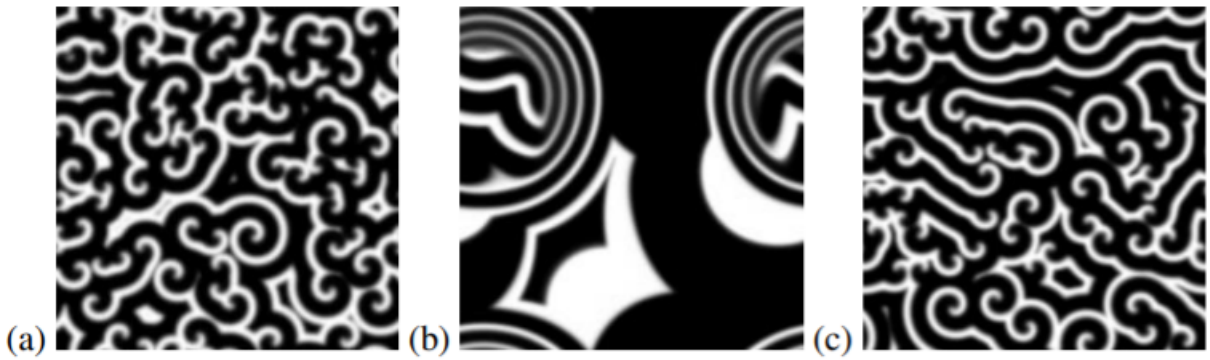

FIG. 8. Output of the BZ reaction model with cellular automaton from the Turner paper.

III. EXPERIMENTS WITH BZ SOLUTIONS

There are a lot of ways to experiment with the BZ reaction, but we are only going to focus on two experiments which gather information about the BZ reaction's oscillatory behavior and its wave behavior.

A. Oscillatory Behavior

The experiment focusing on the oscillatory behavior of the BZ reaction uses the fact that a BZ solution changes colors over time if you continuously stir it. For this specific set-up, we used a mix of 3.8 g of potassium bromate, 3.2 g of malonic acid, 14.5 mL of sulfuric acid, 1.223 g of ceric ammonium sulfate, and 100 mL of ultra-pure water. We also used 5 mL of ferroin indicator solution, a blue light, and a gray-scale camera to make the data collection easier.

There a total of 4000 images taken, with 4 images taken per second, the data from the photos were collected using Matlab and its image library, which made data collecting and processing as painless as it can get. The following plot is from the data we collected compared with the Oregonator model.

We can get a lot of information from the measured intensity vs time plot, such as frequency, but we cannot get the concentration due to how limited the set-up for the experiment was.

B. Wave Behavior

If we leave the same solution that we used in the experiment for the oscillatory behavior in a petri dish, we can observe some really nice patterns from the BZ reaction.

Apart from the use of the petri dish and the lack of stirring, the set-up for this experiment is identical to the previous one. The purpose of this experiment was to explore the wave-like behavior of the BZ oscillation, this means that we were focused on things like the distances between the wave-fronts and space-time plots for the reaction.

Gathering data for this experiment was done in the same manner, but this specific experiment required us to somehow keep the spatial information from the photo. The best

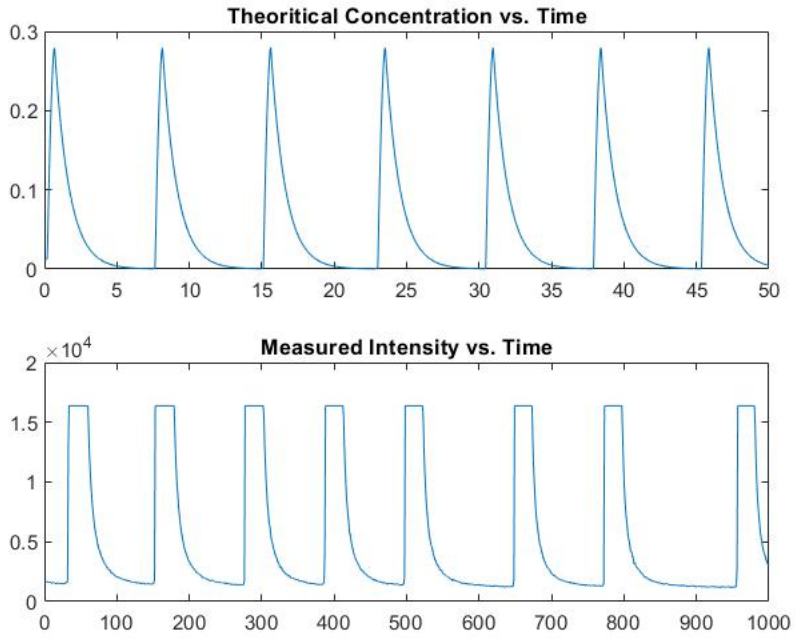

FIG. 9. Plots of intensity vs time from the photos compared with the concentration plot vs time from the Oregonator model.

way to do this was by using the imread() function from Matlab, and using the indices for the photo matrix as a marker for position.

Using the matrix's indices as markers for position allows us to make a lot of useful measurements. A measurement we can make is intensity as a function of position, which should give us a waveform when plotted. This measurement allows us to determine the separation between wave-fronts and also allow us to make a space-time plot.

The second thing we can do is make a space-time plot. This plot is very useful and it gives information about the wavelength, frequency, and also the direction in which the wave is propagating without having to animate the 1200 photos.

From these measurements we can observe a lot of interesting things about our BZ reaction. The first thing I want to focus on is the wavelength. The intensity vs. position plot gives us a waveform in which the separation between peaks is the wavelength of the wave. One can use a Fast Fourier Transform to accurately determine the wavelength or you can use the plot.

From this plot, we got that the separation was 40 pixels, which roughly converts to

FIG. 10. Petri dish set-up for the wave behavior experiment.

4.5 mm assuming the petri dish has an 89 mm diameter. The way we got the intensity vs position plot can be extended to different photos which correspond to a different time during the BZ reaction. We can make a matrix containing the intensities of different pixels and construct a matrix in which the row index gives us the position of the pixel and the column index gives us a time. Finally, we can use the imagesc() method to make a heat-map of this matrix in order to get a space-time plot.

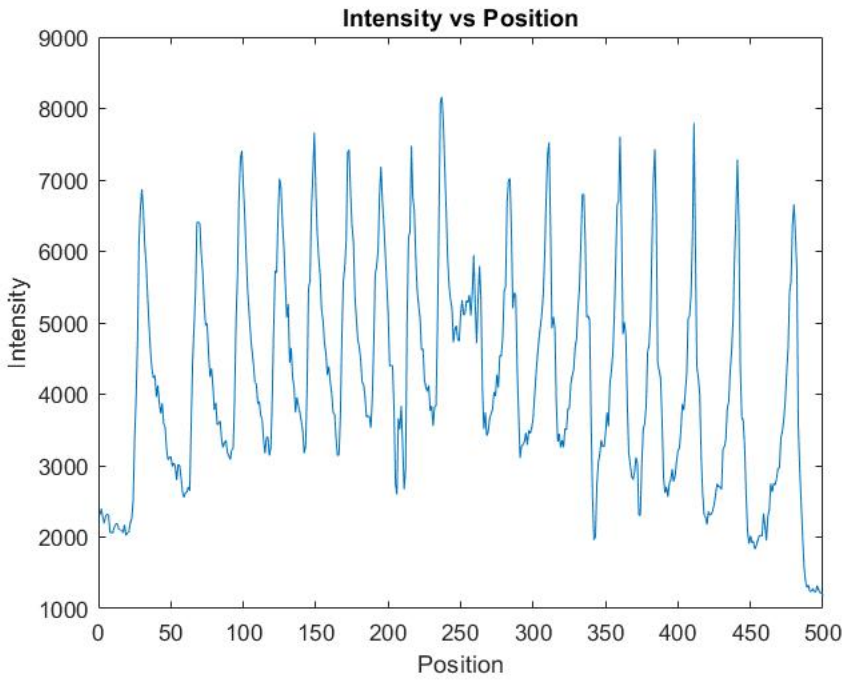

FIG. 11. Intensity as a function of position. This plot was made with Matlab.

From this plot we can determine the direction of the wave-front as well as the source of the wave. First, note the peaks and their position on the 250th pixel. This observation tells us that the waves are coming from the center of the petri dish, which corresponds to the images of the reaction. The second thing to notice is how the waves seem to be going towards the left side of the plot, since time is evolving to the right, this indicates that the each wave-front is moving away from each other as well as from the center of the petri dish, which also agrees with the photos.

IV. CONCLUDING REMARKS

BZ reactions are a very interesting and aesthetically pleasing to experiment with as well as to model. Although the one dimensional models don't offer the amazing patterns that the two dimensional models offer, we can still find beauty within the phase-space plots, especially when we begin to play around with the parameters of the model and the initial conditions. Understanding the mechanics of the BZ reaction also allows us to study what happens when a system is extremely outside of thermodynamic equilibrium and how that system evolves over time as it travels to thermodynamic equilibrium.

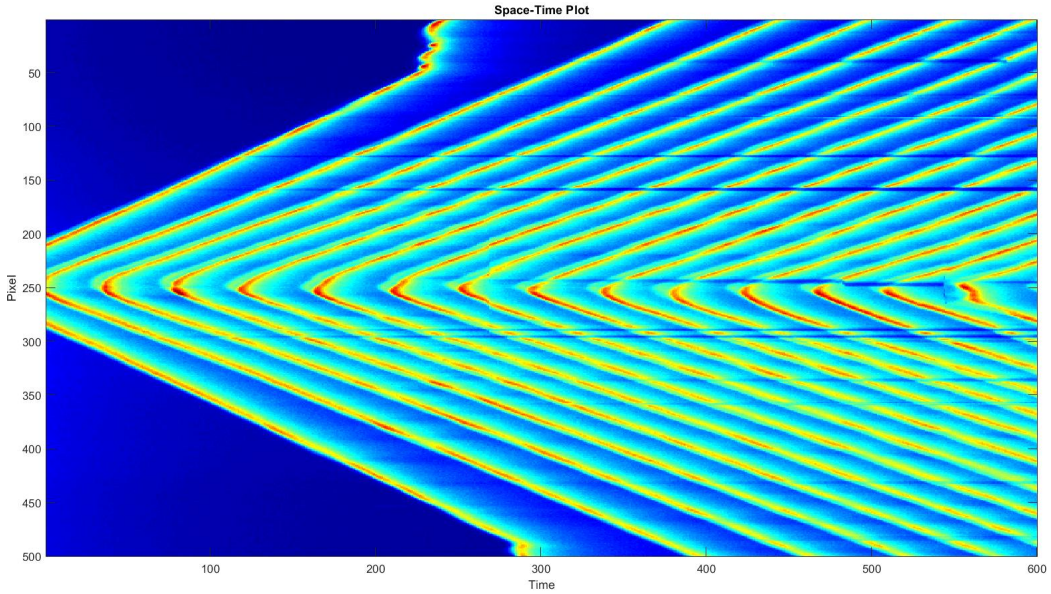

FIG. 12. Space-time plot of the wave-fronts for the BZ reaction. This plot was made with Matlab.

Apart from having one of the most aesthetically pleasing experiments, especially with the ones involving wave fronts, modeling the BZ reactions has resulted in major advancements in areas outside of physics and chemistry. One of the most notable developments has to do with ecology and population dynamics within a predator-prey environment, the most famous model is known as the Lotka-Volterra model, which can also be used to model the BZ reactions! Although the chemical and physical behaviors of the BZ reactions are interesting, one can generalize these behaviors and apply them to outside areas such as ecology and even epidemiology.

[1] D. T. Gillespie, The Journal of Physical Chemistry **81**, 2340 (1977), https://doi.org/10.1021/j100540a008.

[2] R. Noyes, R. Field, and E. Körös, Journal of the American Chemical Society **94**, 1394 (1972), https://doi.org/10.1021/ja00759a080.

[3] L. Edelstein-Keshet, *Mathematical Models in Biology* (Society for Industrial and Applied Mathematics, USA, 2005).

[4] A. Turner, Bartlett School of Graduate Studies (2009), https://discovery.ucl.ac.uk/id/eprint/17241/1/17241.pdf.