

Dynamics of Methylene Blue-Glucose-O₂ System

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Abstract. The *blue bottle reaction* is a very well known first year chemistry experiment that exhibits some very interesting dynamics. This paper begins with the kinetic reactions for the system and attempts to discover the mathematics behind the oscillations between a colorless and blue liquid that have been observed in practice. Extensions such as pumping oxygen into the system to drive the oscillation through perturbation functions are explored.

Keywords: Methylene Blue, chemical oscillations

1 Introduction

I first learned of the Methylene Blue-Glucose-O₂ System while in a graduate level math course (M540: Dynamical Systems) at Colorado State University. Professor Steve Thompson of the Chemistry Department allowed us to perform some basic experiments to get a hands on look at dynamical systems in the real world.

In the Methylene Blue-Glucose-O₂ experiment, one combines a starch such as glucose with an aqueous solution of NaOH and adds a small amount of Methylene Blue (or a similar dye). After a short period of time, many interesting phenomena may be observed: oscillations in the color of the liquid (blue-clear), small ‘tornados’ emerging from the air-liquid interface, and interesting spatial patterns emerging and disappearing. I found the experiment very interesting and enjoyable.

This paper explores some of the many interesting dynamics exhibited in the Methylene Blue-Glucose-O₂ System and is organized as follows. In Section 2, we discuss the idea of oscillations in chemical systems. In Section 3, we introduce and analyze the Methylene Blue-Glucose-O₂ System. Finally, Section 4 draws together the ideas presented.

2 Oscillations in Chemical Systems

When studying the dynamics in chemical reactions, one begins by writing down the kinetic equations that explain how the substances combine to create other substances and at what rate the reactions occur. After this has been accomplished, one then applies the very well-known *Law of Mass Action* that states that the rate of a given chemical reaction is proportional to the product of the activities (or concentrations) of the reactants.

2.1 The Belousov-Zhabotinsky Reaction

According to [8, 254-255], the Belousov-Zhabotinsky Reaction was discovered in the mid-twentieth century by the Russian biochemist Boris Belousov when he “mixed citric acid and bromate ions in a solution of sulfuric acid” [8]. He observed that, in the presence of a cerium catalyst, the solution turned yellow, then a minute later colorless again. He found that these oscillations continued for around an hour at which time the system reached equilibrium.

At the time his discovery, the idea that a chemical system that could oscillate sporadically was radical. It was not until the 1960’s, when a graduate student named Anatol Zhabotinsky confirmed Belousov’s findings, that the Belousov-Zhabotinsky Reaction was presented at an international conference in Prague. In 1980 Belousov and Zhabotinsky received the Lenin Prize for their ground breaking work on oscillating chemical reactions.

2.2 Hopf Bifurcations and the Poincaré-Bendixson Theorem

Suppose that a given system of ordinary differential equations has a stable fixed point. A *Hopf Bifurcation*; occurs “when an equilibrium has a pair of eigenvalues that cross the imaginary axis and corresponds to the creation or destruction of a periodic orbit” [5, 296]. In the Methylene Blue-Glucose-O₂ System we will hope to find a limit cycle that describes the oscillations in color observed in practice, if we cannot find such a limit cycle, we will try varying parameters to see if we can find a Hopf Bifurcation.

Another useful theorem from the study of dynamical systems found in [8, 203] is

Theorem 1 (Poincaré-Bendixson Theorem) *Suppose that:*

1. R is a closed, bounded subset of the plane;
2. $\dot{x} = f(x)$ is a continuously differentiable vector field on an open set containing R ;
3. R does not contain any fixed points;
4. There exists a trajectory C that is “confined” in R , in the sense that it starts in R and stays in R for all future time.

Then either C is a closed orbit, or it spirals toward a closed orbit as $t \rightarrow \infty$. In either case, R contains a closed orbit.

In the Methylene Blue-Glucose-O₂ System we will look to see if the trajectories are contained in a trapping region with no stable fixed point which would indicate the existence of a limit cycle.

3 The Methylene Blue-Glucose-O₂ System

In the Methylene Blue-Glucose-O₂ System, or the more commonly known *blue bottle reaction*, one combines glucose with an aqueous solution of NaOH and then adds a small amount of Methylene Blue (or a similar dye). Depending on the surface area to volume ratio, many different patterns can be observed. The most common version of the experiment consists of a test tube half filled with the colorless liquid. Upon shaking (or agitation of any kind) the liquid turns blue (or whatever color your dye is) due to the oxygenation of the methylene blue by the atmospheric oxygen. After leaving the solution stationary for a sufficient period of time, the solution returns to its colorless state indicating “that the methylene blue has been reduced by the glucose” [1]. The experiment can be repeated multiple times and is very fun!

The Methylene Blue-Glucose-O₂ System is a very interesting to study as it, like the Belousov-Zhabotinsky Reaction, is an example of a chemical system that can oscillate sporadically in color over time. There are many interesting papers on the Methylene Blue-Glucose-O₂ System that investigate how slight adjustments in the experiment affect the dynamics of the Methylene Blue-Glucose-O₂ System [1], [2], [6], [7], [3],[4].

3.1 Model Development

Let W represent the clear/white (i.e. non-oxygenated) form of Methylene Blue, B the blue/oxygenated form of Methylene Blue, g represent the gaseous phase of the substance, a the aqueous form, and X represent the glucose. We make the simplifying assumption that many of the reactions in the Methylene Blue-Glucose-O₂ System occur very very slowly so we approximate the concentrations of the slow reacts as constants. Then, the essential kinetics of the Methylene Blue-Glucose-O₂ System can be represented by



where Table 1 shows the notation used in this paper.

Table 1: Notation for Concentration of Important Substances

Notation	Concentration of Substance	Constant/Variable
m	$[\text{O}_2(\text{g})]$	\approx constant
n	$[\text{O}_2(\text{a})]$	variable
w	$[W]$	variable
b	$[B]$	variable
\bar{m}	$[B] + [W]$	\approx constant
x	$[X]$	\approx constant

From the kinetics, we use the Law of Mass Action to obtain the following system of differential equations,

$$\dot{n} = k_1 m - k_{-1} n - k_2 n w \quad (4)$$

$$\dot{w} = -k_2 n w + k_3 x b \quad (5)$$

$$\dot{b} = k_2 n w - k_3 x b \quad (6)$$

Using the fact that $\bar{m} = b + w$ we replace w by $\bar{m} - b$ and Equation (5) becomes,

$$\dot{w} = \frac{d}{dt} (\bar{m} - b) = -\dot{b}$$

thus, Equation (5) is actually just a linearly dependent combination of Equation (6) so we learn no new information by including it in the system. Now replacing w by $\bar{m} - b$ in Equations (4) and (6) we have,

$$\begin{cases} \dot{n} = k_1 m - k_{-1} n - k_2 n (\bar{m} - b) \\ \dot{b} = k_2 n (\bar{m} - b) - k_3 x b \end{cases} \quad (7)$$

3.2 Nondimensionalization

As the system in (7) has 6 parameters and 2 variables, we can non-dimensionalize the system to reduce the number of parameters.

By analyzing the equations in (7) we determine what the dimensions of the parameters must be (see Table 2). Now let $t = t^*\tau$, $n = n^*\tilde{n}$, and $b = b^*\tilde{b}$ where t^* is the dimensionless time

Table 2: Dimensions of variables and parameters

Variable/Parameter	Dimensions	Variable/Parameter	Dimensions
n	$\frac{\text{mol}}{\text{vol}}$	k_1	$\frac{1}{\text{vol}}$
b	$\frac{\text{mol}}{\text{vol}}$	k_{-1}	$\frac{1}{\text{vol}}$
m	$\frac{\text{mol}}{\text{vol}}$	k_2	$\frac{\text{vol}}{\text{mol}\cdot\text{time}}$
\bar{m}	$\frac{\text{mol}}{\text{vol}}$	k_3	$\frac{\text{vol}}{\text{mol}\cdot\text{time}}$
x	$\frac{\text{mol}}{\text{vol}}$		

variable, n^* the dimensionless aqueous oxygen variable, b^* the dimensionless oxygenated Methylene Blue variable and τ , \tilde{n} , and \tilde{b} carry the dimensions of t , n , and b respectively. Then after much manipulation we have,

$$\begin{cases} \frac{dn^*}{dt^*} = 1 - \alpha n^* + \beta (n^* b^* - n^*) \\ \frac{db^*}{dt^*} = \gamma (n^* - n^* b^*) - \delta b^*, \end{cases} \quad (8)$$

where

$$\alpha = \frac{k_{-1}}{k_1}, \quad \beta = \frac{k_2 \bar{m}}{k_1}, \quad \gamma = \frac{k_2 m}{k_1}, \quad \delta = \frac{k_3 x}{k_1} \quad (9)$$

are the dimensionless parameters. We have therefore reduced the system in (7) with 2 variables and 6 parameters to a dimensionless system of 2 variables and 4 parameters!

The Jacobian of the system is given by

$$J(n, b) = \begin{pmatrix} -\alpha + \beta(-1 + b) & \beta n \\ \gamma(1 - b) & -\gamma n - \delta \end{pmatrix}.$$

The intersection of the nullclines gives us the equilibria for the system. Unfortunately, their general form is extremely messy

$$\left(n = \text{RootOf}[f(z)], b = \frac{-1 + (\alpha + \beta)\text{RootOf}[f(z)]}{\beta \text{RootOf}[f(z)]} \right) \quad (10)$$

where,

$$f(z) = \gamma \alpha z^2 + (-\gamma + \delta \alpha + \delta \beta) z - \delta$$

and

$$\text{RootOf}[f(z)] = \begin{cases} \frac{-\gamma + \delta\alpha + \delta\beta - \sqrt{\gamma^2 + 2\gamma\alpha\delta - 2\gamma\delta\beta + \delta^2\alpha^2 + 2\delta^2\alpha\beta + \delta^2\beta^2}}{-2\gamma\alpha}, \\ \frac{-\gamma + \delta\alpha + \delta\beta + \sqrt{\gamma^2 + 2\gamma\alpha\delta - 2\gamma\delta\beta + \delta^2\alpha^2 + 2\delta^2\alpha\beta + \delta^2\beta^2}}{-2\gamma\alpha} \end{cases}$$

3.3 Analysis

The complicated nature of the general form of the equilibria makes stability analysis very difficult without using at least a few experimentally determined parameter values. Thus, we now incorporate the following parameter values known from the literature [1] (see Table 3). In Section 3.4 we will

Table 3: Parameter Values from [1]

Parameter	Value
k_1	$k_1 > k_2$
k_{-1}	small
k_2	$10 \leq k_2 \leq 100$
k_3	≈ 0.5
m	0.0005
x	0.08
\bar{m}	0.01

modify the flow of oxygen at the air-liquid interface, therefore we now abandon the dimensionless system and work with the system in Equation (7) with the parameter values from Table 2 and create some plots using Maple.

For $k_1 = 1000$, $k_{-1} = 1$, and $k_2 = 10$ the equilibria (found in Maple) are

$$(n_1, b_1) = (0.4996031771, 0.009920572384), \quad (n_2, b_2) = (-0.004003177105, 12.60007943),$$

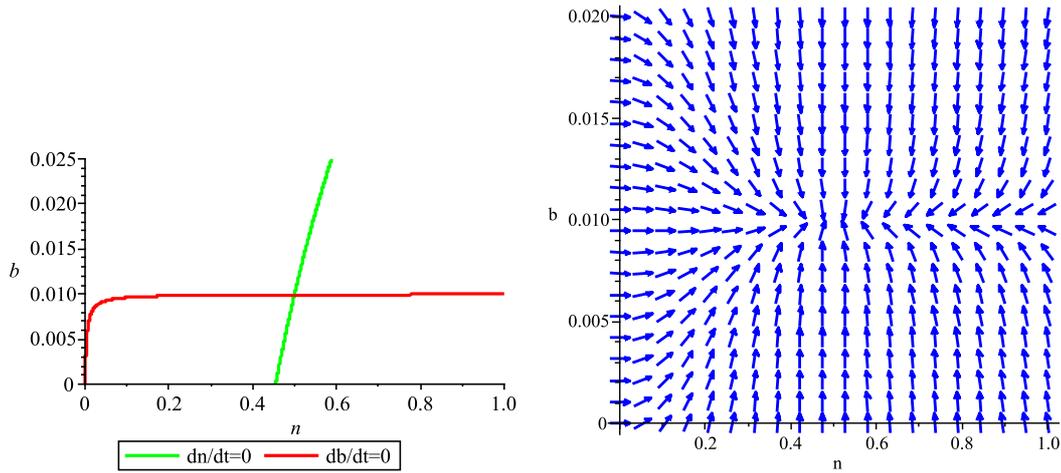
the Jacobian evaluated at the positive equilibrium (n_1, b_1) is

$$J(n_1, b_1) = \begin{pmatrix} -1.000794276 & 4.996031771 \\ 0.00079427616 & -5.036031771 \end{pmatrix},$$

with eigenvalues $\lambda_1 = -.999811121392063740$ and $\lambda_2 = -5.03701492560793618$. From the plots you can see that the equilibrium (n_1, b_1) is a stable node so we do not get the interesting oscillatory behavior we were looking for (see Figure 1).

Notice that even if we increase the value of x (which represents the concentration of glucose in the system) to a gigantic number such as 10^{30} , the equilibria remain in the same quadrants of the (n, b) plot and are $(.4545454545, 9.090909091 \cdot 10^{-32})$, and $(-5.500 \cdot 10^{28}, .110)$. The value of b in the positive equilibrium point decreases to zero in the limiting case. Therefore, if we hope to find oscillatory behavior, we need to try to do something else.

Perhaps we should vary m (the concentration of gaseous oxygen in the system). If we increase m to 500, the equilibria become $(4.999999996 \cdot 10^5, 0.009999999920)$, and $(-0.004, 1.250 \cdot 10^7)$. Through more calculation and experimentation we find that as we increase m , the equilibrium moves further and further out the n axis so we need more and more aqueous oxygen for the equilibrium to exist. Unfortunately, this is not going to change of the dynamics of the positive equilibrium. Similarly varying both x and m simultaneously does not affect the dynamics of the positive equilibria. I am very doubtful that with the system described in (7) we will be able to find the oscillatory behavior (in the color) that we observed during the actual experiments.

Figure 1: Plots for $k_1 = 1000$, $k_{-1} = 1$, and $k_2 = 10$.

3.4 Modifications such as Pumping Oxygen

We now explore two modifications to (7) where we change how the oxygen enters the system. In [1], Adamčíková et al. describe a situation where oxygen is added to the system in pulses. We will explore modifying the rate at which O₂(g) enters the system through the surface by using a ‘hill function’, then by using a trigonometric function.

3.4.1 Hill function

Note that as b (the concentration of the oxygenated form of Methylene Blue) increases, it modifies the air-liquid interface so that it is more difficult for oxygen to cross the barrier into the liquid. This is incorporated into the system by allowing the source term $k_1 m$ to decrease with b so that it behaves like the hill function $\frac{k_1 m}{1+b}$. Our modified system is

$$\begin{cases} \dot{n} = \frac{k_1 m}{1+b} - k_{-1} n - k_2 n (\bar{m} - b) \\ \dot{b} = k_2 n (\bar{m} - b) - k_3 x b. \end{cases} \quad (11)$$

Using the values of the parameters given in Table 3, the Jacobian of this new system is

$$J(n, b) = \begin{pmatrix} -1.10 + 10b & -\frac{0.5000}{(1+b)^2} + 10n \\ 0.10 - 10b & -10n - 0.04 \end{pmatrix}.$$

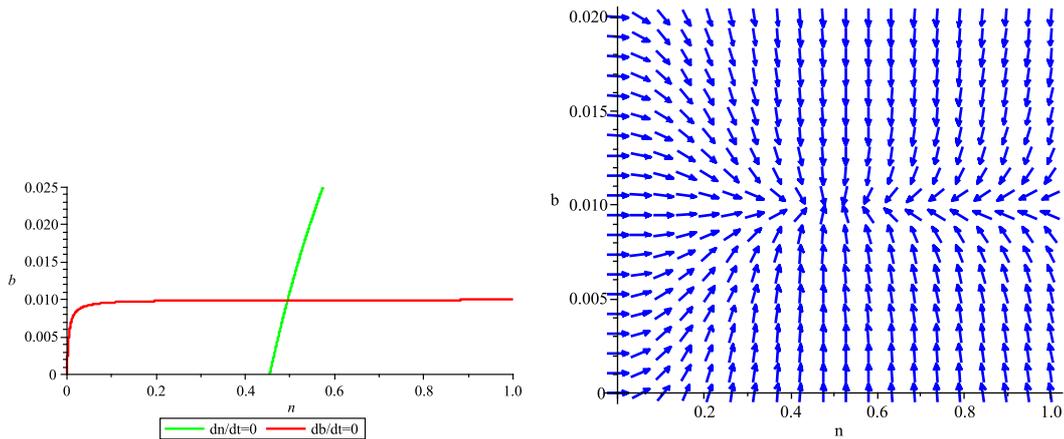
This new system now has three equilibria, but still only one positive equilibrium which is almost the same as the original system,

$$(.4946920312, 0.00991979018), \quad (-0.003990094506, -4.028162921), \quad (-0.004012827736, 3.128243130),$$

and the Jacobian evaluated at the positive equilibrium is

$$J(.4946920312, 0.00991979018) = \begin{pmatrix} -1.000802098 & 4.456694427 \\ 0.00080209820 & -4.986920312 \end{pmatrix},$$

with eigenvalues -0.999905510764673266 and -4.98781689923532756 which again give us a stable node which can be seen in Figure (2).

Figure 2: Plots for $k_1 = 1000$, $k_{-1} = 1$, and $k_2 = 10$.

3.4.2 Trig function

We now try modifying the source term by adjusting the rate at which the O₂ crosses the barrier from the constant term $k_1 m$ to one that oscillates in time $k_1 m + A \sin(pt)$. With this modification, we have the following non-autonomous system of ODEs

$$\begin{cases} \dot{n} = k_1 m + A \sin(pt) - k_{-1} n - k_2 n (\bar{m} - b) \\ \dot{b} = k_2 n (\bar{m} - b) - k_3 x b. \end{cases} \quad (12)$$

Or equivalently,

$$\begin{cases} \dot{n} = k_1 m + A \sin(py) - k_{-1} n - k_2 n (\bar{m} - b) \\ \dot{b} = k_2 n (\bar{m} - b) - k_3 x b \\ \dot{y} = 1. \end{cases} \quad (13)$$

We now explore the existence of limit cycles in the new system. Figure 3 shows the system in (13) for $k_1 = 1000$, $k_{-1} = 1$, $k_2 = 10$, $A = 2$, and $p = 3$ with the initial condition $(n(0) = 0.4, b(0) = .01, y(0) = 1)$ for $t = 0..10$ and $t = 0..40$. Another view of the n vs. b plane can be seen in Figure 4. Figure 5 shows the the system with a larger amplitude $A = 20$ of the pumping term. From these plots, it appears that we do get oscillatory behavior! As the amplitude of the sine function is increased to $A = 200$, the oscillatory behavior remains as can be seen in Figure 6.

As the trajectories for solutions to (12) appear to be contained within a trapping region with no stable fixed point which suggests the existence of a limit cycle or more complicated behavior such as chaos.

4 Conclusions

In this paper we have shown that for the original system described by (7) there were no limit cycles (in the positive n vs. b plane), rather we had a stable node. In (11), we adjusted the rate at which oxygen entered the system and found that merely adjusting by a hill function did not significantly change the dynamics enough to develop a limit cycle. Next, in (12), we tried adjusting the rate at which oxygen entered the system by adding a sine function. Here we changed the system from an autonomous to a non-autonomous system of ODEs and saw the creation of a limit cycle! All

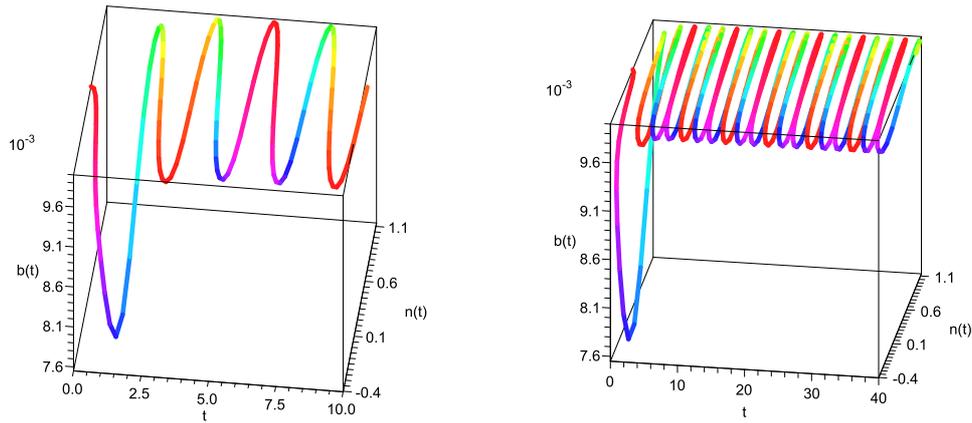


Figure 3: Plots for $k_1 = 1000$, $k_{-1} = 1$, $k_2 = 10$, $A = 2$, and $p = 3$

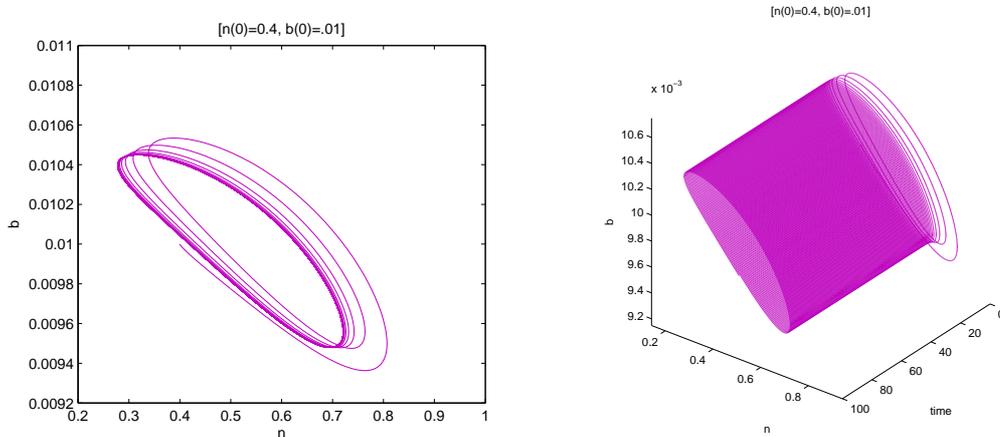


Figure 4: Plots for $k_1 = 1000$, $k_{-1} = 1$, $k_2 = 10$, $A = 2$, $t = 100$ and $p = 3$ and initial condition $(n(0) = 0.4, b(0) = .01, y(0) = 1)$

of this suggests that the original system in (7) does not really represent the full dynamics of the Methylene Blue-Glucose-O₂ System.

While in the lab, with Dr. Steven Thompson and Dr. Patrick Shipman, I was able to observe the solution in a variety of containers. We found that varying the surface area to volume ratio had profound effects on the dynamics of the system as well as the patterns that arose. When using the tiny test tubes we saw tiny ‘tornadoes’ form after a small induction period. The reaction showed a swirl of color travel down from the air/liquid interface to the bottom of the tube.

Another very interesting situation is when we pour a very small layer of liquid into a petri dish. Leaving the system to sit we saw the color of the liquid oscillate from blue to colorless and back. The color distribution was not uniform across the dish, rather very intricate spatial patterns such as ripples and spirals formed over time. From what I have seen of the Belousov-Zhabotinsky Reaction experiment, the pictures of the patterns formed appear to be similar.

We also noticed that temperature played a role in how fast the reaction took place. When we removed the cover to the petri dish, the reaction slowed noticeably. These results are not new, [4] and [2] both found that heat accelerates the decomposition process of the oxidized methylene blue.

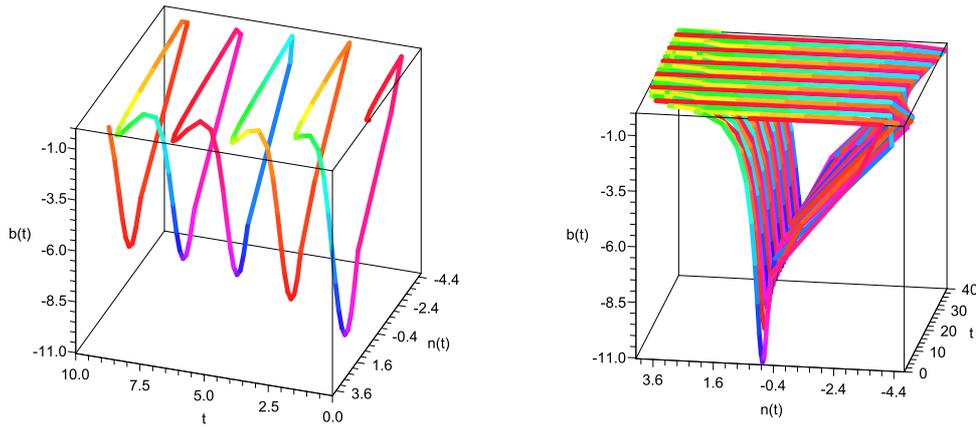


Figure 5: Plots for $k_1 = 1000$, $k_{-1} = 1$, $k_2 = 10$, $A = 20$, and $p = 3$

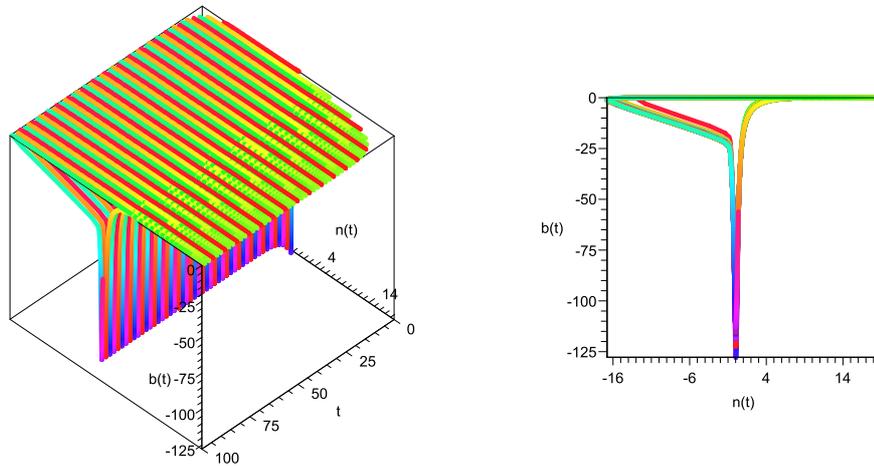


Figure 6: Plots for $k_1 = 1000$, $k_{-1} = 1$, $k_2 = 10$, $A = 200$, $t=100$ and $p = 3$

Other interesting discoveries are that the concentration of glucose affects the rate of the reaction [2] and that light does not play any role in the Methylene Blue-Glucose-O₂ System[1]. Dr. Lynch claims to have observed oscillations in color on a filter paper dipped in the solution but I have not been able to observe these first hand.

In closing, there are many interesting dynamics in both time and space that occur in the Methylene Blue-Glucose-O₂ System that are not represented in the system (7) shown in this paper. In the future, I would be interested in re-deriving the kinetics of the system to see if we could find something we missed the first time. Also, I would be very interested in taking some videos of the tornadoes and spatial patterns produced by the reaction.

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