Computational Lab Report
Project B: Oscillating chemical reactions
Graphical Methods

Report by: **Jamie Somers**

January 5, 2022

Abstract

In this report we will be using the graphical and numerical skills we have developed as physicists to describe systems of differential equations which cant be easily modelled by hand. Using our skills we will be able to analyse a real system with many different factors such as growth, fluid motion or oscillations. Using our programmes we should be able to predict how the system should behave over time for all possible solutions with varying initial conditions, this process will be done in the form of quiver plots. This specific system is known as a Brusselator model which is a theoretical model for a type of autocatalytic chemical reaction. This system exhibits oscillating behaviour as the fixed point $\{X, Y\} = \{A, \frac{B}{A}\}$ becomes unstable at $B > 1 + A^2$ causing the system to never reach a steady state and continually oscillate back and forth. This effect is represented in a physical chemical reaction by a solution continuously oscillating back and forth between two different colours representing the oscillating state. We will use python programming techniques such as vector plots and streamlines to find the initial conditions to use as our parameters to achieve a 'Brusselator model' similar to what we have described. These same graphical methods can be extrapolated to understand many real world physical system such as population / virus transmission or the relationship between magnetic field and plasma flow in the sun.

1 Introduction

The Brusselator is a theoretical physical model for a type of autocatalytic reaction which occurs in chemistry. The model was first proposed by Ilya Prigogine and his collaborators most notably René Lefever in 1968. However chemical oscillators had already been observed as far back as 1921 in the Bray-Leibhafsky reaction, which is a chemical clock wherein iodine oxidises to iodate before reducing from iodate back to iodine in the following chemical reaction:

oxidation of iodine to iodate:

$$5\ H_2O_2 + I_2 \rightarrow 2\ IO_3^- + 2\ H^+ + 4\ H_2O \tag{1}$$

reduction of iodate back to iodine:

$$5\ H_2O_2 + 2\ IO_3^- + 2\ H^+ \rightarrow I_2 + 5\ O_2 + 6\ H_2O \tag{2}$$

This was followed by other experiments such as the Belousov-Zhabotinsky reaction which mixed potassium bromate, cerium(IV) sulfate, propanedioic acid and citric acid dilute to produce an oscillating chemical reaction which creates a visibly observable oscillation between a yellow solution and a colourless solution. This is due to the cerium(IV) being reduced to cerium(III) by the propanedioic acid before being oxidised back to cerium(IV) by the bromate(V).

The goal of this experiment is to introduce methods of analysing dynamical systems that we can use to predict the behaviour of the system at different time scales given initial conditions for the system, during the report we will introduce concepts such as isoclines / nullclines, fixed points and stability of fixed points. Once we have laid the ground work we can then apply all of these techniques and concepts to the brusselator model which we have described above.
For the purpose of this report we will be using the following non-linear first order differential equation to describe the Brusselator model:

$$\frac{dx}{dt} = 1 - (b+1)x + ax^2y \tag{3}$$

$$\frac{dy}{dt} = bx - ax^2y \tag{4}$$

Where (a) and (b) are the parameters of this particular models equations (where a and b are both > 0).

This particular equation will be used in the latter part of the report when designing plots which represent the brusselator model specifically, however we will first use example of non-linear differential equations which we can use to represent the different graphical methods we will be using throughout the report, these equations will be denoted as they appear during the report.

2 Background and Theory

The first graphical method we will introduce and use is quiver plots, quiver plots graphically represents vector fields of systems using arrows which have a direction and magnitude. Quiver plots have been explained extensively in previous reports so we will not go into the background and theory behind them.

We will however explain the theory behind the techniques we will use to determine the equilibrium locations on a vector field such as fixed points.

2.1 Isoclines, Nullclines

In a situation where we have coupled, first order equations such as

$$\frac{dx}{dt} = y \text{ and } \frac{dy}{dt} = -\omega^2 x \tag{5}$$

and we stay that $f(x, y) = \frac{dx}{dt}$ and $g(x, y) = \frac{dy}{dt}$, setting both $f(x, y) = 0$ and $g(x, y) = 0$ implies that both $\frac{dx}{dt} = 0$ and $\frac{dy}{dt} = 0$ for every point that lies on the curve.

These two curves are referred to as zero growth isoclines, or nullclines of the system. Any line which connects two points with equal slopes is called an isocline. if the slope is specifically 0 then it is known as Nullclines.

Nullclines will start to play a part in this report when we want to differentiate points in time where our system begins to behave differently than it did previously, using isoclines and nullclines you can visibly see a change in behaviour of the system.

2.2 Fixed points

If we consider intersection points (the point where two nullclines intersect) $f(x^*, y^*) = 0$ and $g(x^*, y^*) = 0$ this implies:

$$\frac{dx}{dt} = 0 \text{ and } \frac{dy}{dt} = 0 \tag{6}$$

The points denoted as x^* and y^* are known as the fixed points of the solution.

We can use these newly found points as our initial values for our solutions ($\mathrm{x_0} = \mathrm{x^*}$, $\mathrm{y_0} = \mathrm{y^*}$) we get the equation:

$$\frac{dx}{dt} = f(x^*, y^*) = 0 \text{ and } \frac{dy}{dt} = g(x^*, y^*) = 0 \tag{7}$$

We integrate these equations to arrive at $x(t) = x^*$ and $y(t) = y^*$ are constants. This implies that the fixed points represent equilibrium points of our system. These fixed points can be described as being stable and unstable fixed points, we can determine the stability of a fixed point using mathematical stability theory. If we determine the stability of a fixed point to be a stable equilibrium point, then we can choose initial values close to the fixed point and expect the solution will converge to the fixed point along with the streamlines. Alternatively if the equilibrium point is an unstable fixed point then the same process should result in solutions and streamlines diverging away from he fixed point.

2.3 Stability of fixed points

In this report we will also be using the concept of a Jacobian matrix to help us better explore our physical system. Currently we have our fixed points and their behavior however in order to be able to expand our understanding of the physical system to the behaviour of the solutions near these points, we can use a jacobian to find the behaviours such as stability.

A Jacobian matrix takes the partial derivative of a bunch of variables in a matrix, an example of a Jacobian matrix is included below:

$$J = \begin{pmatrix} \frac{\partial f}{\partial x} & \frac{\partial f}{\partial y} \\ \frac{\partial g}{\partial x} & \frac{\partial g}{\partial y} \end{pmatrix} \tag{8}$$

The jacobian matrix can be determined by subbing in for the variables f and g and solving the partial differential equations individually. The jacobian matrix should have one solution for each partial derivative included in the original matrix, in the case of Eq. 8 the jacobian matrix would have 4 values in a 2x2 matrix.

Once we have our Jacobian matrix, we can evaluate it for specific fixed points by calculating the matrix determinant (det(J)) and trace (Tr(J)). Once we have these values we can compare them to a classification table which will tell us what type of fixed point we have depending on our values for determinant, trade and trace squared minus 4 times the determinant.

The classification table is as follows: These are the analytical methods we will use to analyse

Determining fixed points			
det(J)(Δ)	Tr(J)(τ)	τ^2-4Δ	Type of fixed point
$\Delta > 0$	$\tau > 0$	$\tau^2 - 4\Delta > 0$	Unstable Node (source)
$\Delta > 0$	$\tau > 0$	$\tau^2 - 4\Delta < 0$	Unstable Spiral (source)
$\Delta > 0$	$\tau < 0$	$\tau^2 - 4\Delta < 0$	Stable Spiral (sink)
$\Delta > 0$	$\tau < 0$	$\tau^2 - 4\Delta > 0$	Stable Node (sink)
$\Delta < 0$			Saddle point
$\Delta > 0$	$\tau = 0$		Centre
$\Delta = 0$	$\tau < 0$		Line of stable fixed points
$\Delta = 0$	$\tau > 0$		Line of unstable fixed points
	$\tau < 0$	$\tau^2 - 4\Delta = 0$	Degenerate sink
	$\tau > 0$	$\tau^2 - 4\Delta = 0$	Degenerate source

Table 1: Fixed point classification using the Jacobian J

our Brusselator model we have described above, we will now go into more detail about the Brusselator method itself.

2.4 Brusselator model

The Brusselator model is characterised by the following chemical reaction scheme:

$A \rightarrow X$

$2X + Y \rightarrow 3X$ (autocatalytic reaction)

$B + X \rightarrow Y + D$

$X \rightarrow E$

Where A, B, D, E, X and Y are the different reactants. The different colours correspond to the different concentration of the species in the solution (X, Y, D, E, A, B) Under conditions where A and B are present in huge quantities and thus assumed to be constant, the rate equations become:

$$f(x, y) : \frac{dx}{dt} = 1 - (1 + b)x + ax^2y \tag{9}$$

$$g(x,y): \frac{dy}{dt} = bx - ax^2y \tag{10}$$

x and y are the concentrations of the reactants X and Y while a and b , (both > 0), are the parameters of the reaction, they depend on the concentrations of A and B . The oscillating reaction only occurs for certain values of a and b .

Now that we have explored all of the theory behind the analysis we will be carrying out during this experiment we can begin applying them with examples before using them all together to analyse our particular chemical oscillator system.

3 Results

We will begin by finding the nullclines and fixed points of the following system of differential equations:

$$\frac{dx}{dt} = f(x,y) = x^2 + xy - 2x \quad \text{and} \quad \frac{dy}{dt} = g(x,y) = xy^2 + 3y$$

(a). plot the nullclines and the quiver plot for this system
(b). determine the fixed points of the system (there are 4 of them).

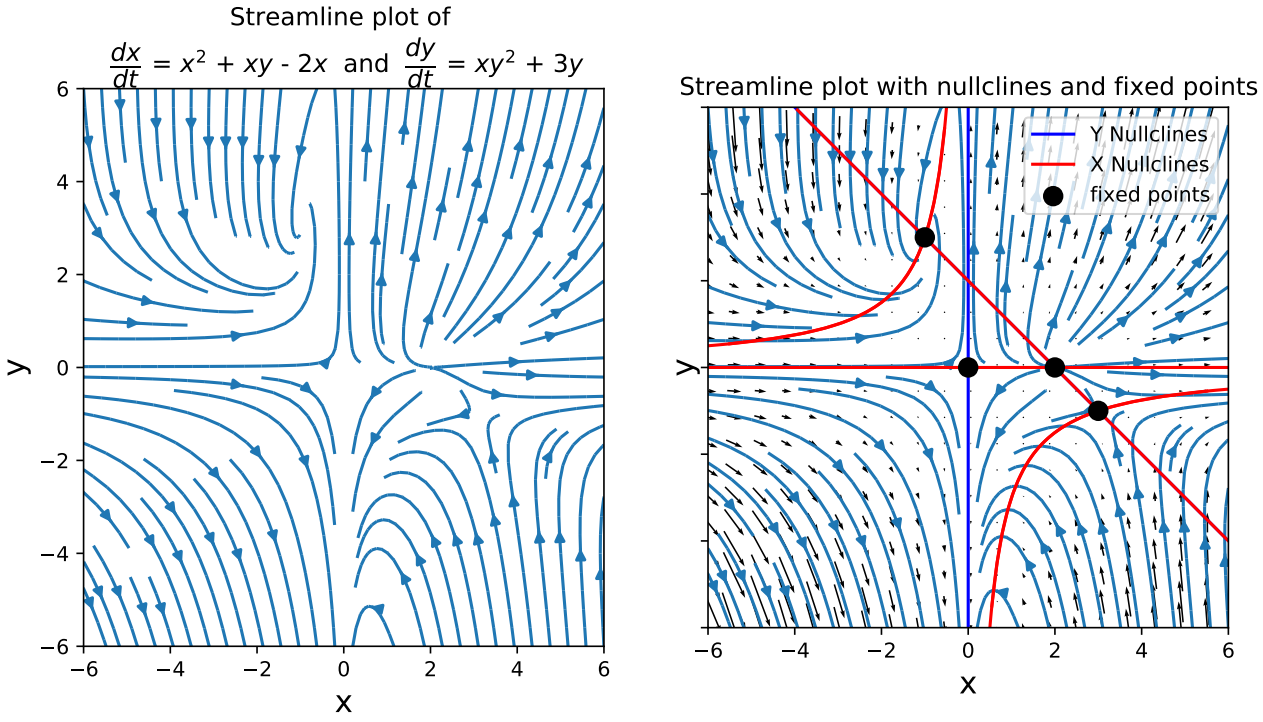

Figure 1: Streamline plot before and after nullclines and fixed points found

The streamline plots shows us the many solutions to the equations visually. In the graphs above we have used the python function for graphing a streamline plot to generate the multiple possible solutions for our questions.

We have also included the nullclines and fixed points (where the nullclines intersect) on the streamline plots. This is done using the process discussed in Eq. 6 where the black dots represent the equilibrium points of the system. The nullclines and fixed points clearly show a change of behaviour within the streamline plot. Fixed points can be used to find nearby points with interesting and different behaviour.

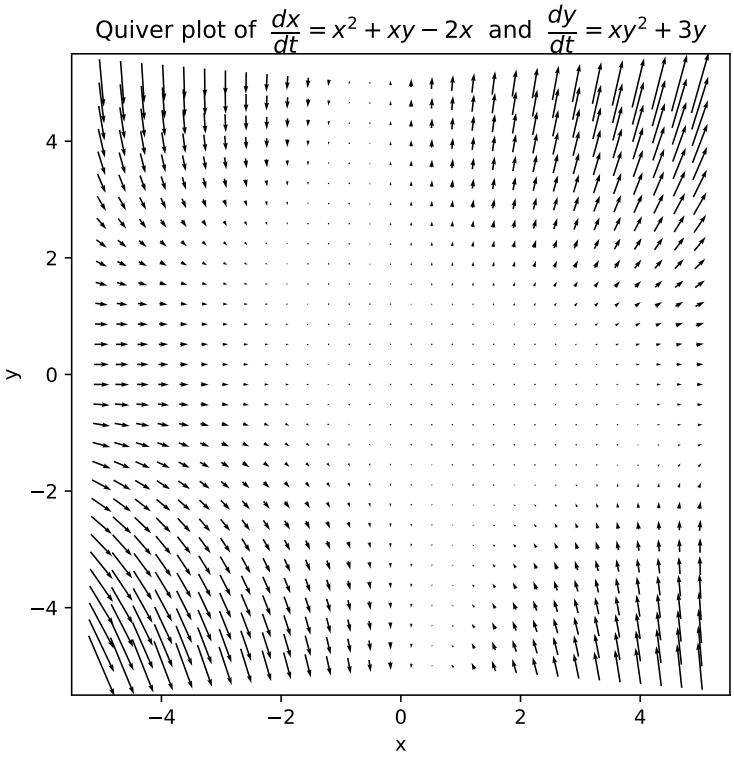

Figure 2: Quiver plot

This quiver plot is useful for giving us a general sense of the direction and magnitude for each point in a certain x and y position. This will be useful when creating a quiver plot for our chemical oscillator as it will give us an idea how the system will behave given the initial conditions. Compared to the streamline plots the quiver plot gives very limited information about the physical system it is graphically describing.

(c). Determine the Jacobian matrix.

In order for us to use a Jacobian matrix to determine the behaviour of the system we need to have fixed points which we have just found, now we can determine wether or not these points are stable or unstable.

Once we find the Jacobian matrix we can use the table (Table 1) included in the background and theory section to determine the classification of the fixed points. We will start by using Eq. 8 for our particular equations:

$$J = \begin{pmatrix} \frac{\partial f}{\partial x} & \frac{\partial f}{\partial y} \\ \frac{\partial g}{\partial x} & \frac{\partial g}{\partial y} \end{pmatrix}$$

We will solve this matrix one derivative at a time as follows:

$$\frac{\partial f}{\partial x} = \frac{\partial (x^2 + xy - 2x)}{\partial x} = 2x + y - 2 \qquad \frac{\partial f}{\partial y} = \frac{\partial (x^2 + xy - 2x)}{\partial y} = x$$

$$\frac{\partial g}{\partial x} = \frac{\partial (xy^2 + 3y)}{\partial x} = y^2 \qquad \frac{\partial g}{\partial y} = \frac{\partial (xy^2 + 3y)}{\partial y} = 2xy + 3$$

Therefore the Jacobian is:

$$J = \begin{pmatrix} 2x + y - 2 & x \\ y^2 & 2xy + 3 \end{pmatrix}$$

(d). Evaluate the Jacobian matrix at all of the fixed points, and from this find the determinant and trace of the Jacobian at the fixed points.

We can now begin exploring the determinant and the trace of the Jacobian matrix, both of which we will need to use the characteristic table above and find the characteristics of the data points. We will find the determinant and trace for each of the points as follows:

(0,0),

$$J = \begin{pmatrix} -2 & 0 \\ 0 & 3 \end{pmatrix} \quad det(J_{(0,0)}) = (-2 \times 3) - (0 \times 0) = -6 \quad Tr(J_{(0,0)}) = -2 + 3 = 1$$

(2,0),

$$J = \begin{pmatrix} 2 & 2 \\ 0 & 3 \end{pmatrix} \quad det(J_{(2,0)}) = (2 \times 3) - (2 \times 0) = 6 \quad Tr(J_{(2,0)}) = 2 + 3 = 5$$

(3,-1),

$$J = \begin{pmatrix} 3 & 3 \\ 1 & -3 \end{pmatrix} \quad det(J_{(3,-1)}) = (3 \times -3) - (3 \times 1) = -12 \quad Tr(J_{(3,-1)}) = 3 - 3 = 0$$

(-1,3),

$$J = \begin{pmatrix} -1 & -1 \\ 9 & -3 \end{pmatrix} \quad det(J_{(-1,3)}) = (-1 \times -3) - (-1 \times 9) = 12 \quad Tr(J_{(-1,3)}) = -1 - 3 = -4$$

(e). Use the chart and/or table to determine the stability and behaviour of the solution close to the fixed points.

Now that we have the determinant and trace for each of the fixed points in the jacobian matrix we can begin to use Table 1 to determine the stability of the points as follows:

Determining fixed points			
det(J)(Δ)	Tr(J)(τ)	τ^2-4Δ	Type of fixed point
-6 $<$ 0	1 $>$ 0	$1^2 - 4(-6) > 0$	Saddle point
6 $>$ 0	5 $>$ 0	$5^2 - 4(6) > 0$	Unstable Node (source)
-12 $<$ 0	0 = 0	$0^2 - 4(-12) > 0$	Saddle point
12 $>$ 0	-4 $<$ 0	$-4^2 - 4(12) < 0$	Stable Spiral (sink)

Table 2: Fixed point classification using the Jacobian J

(f). Choose an initial point close to each of the four fixed points (i.e. choose 4 initial points) and solve the equations at these points (i.e. you should produce 4 separate plots of x and y versus t , one for each initial point).
(g). comment on your solutions.

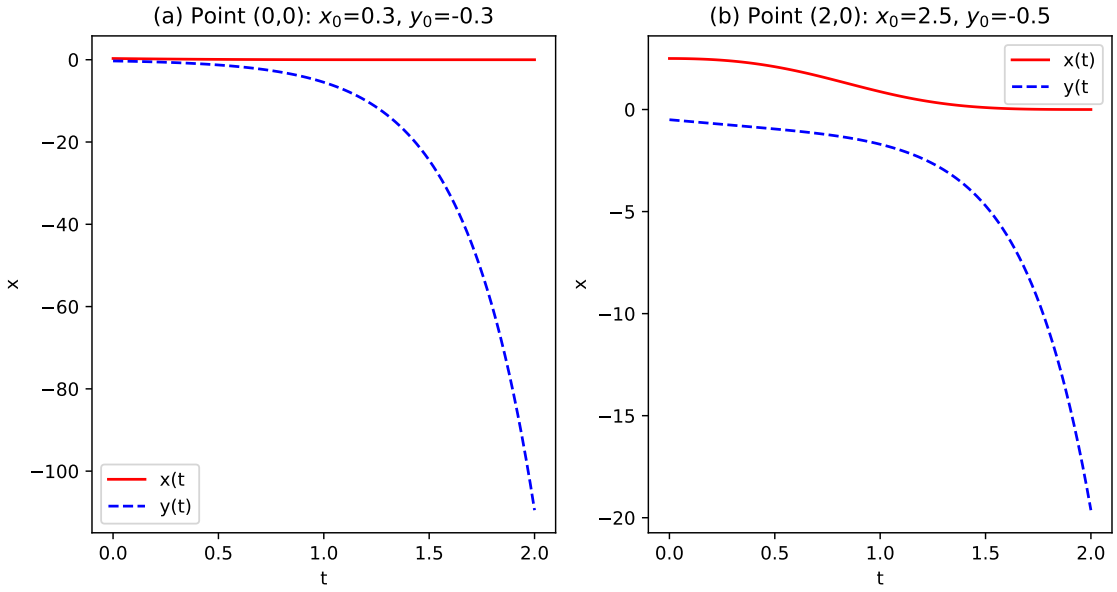

Figure 3: Plots of x and y versus t for point near (0,0) and (2,0)

We can see from our graphs that both of the points near their respective fixed point is diverging away from the fixed state which implies that both of these points would be considered unstable points.

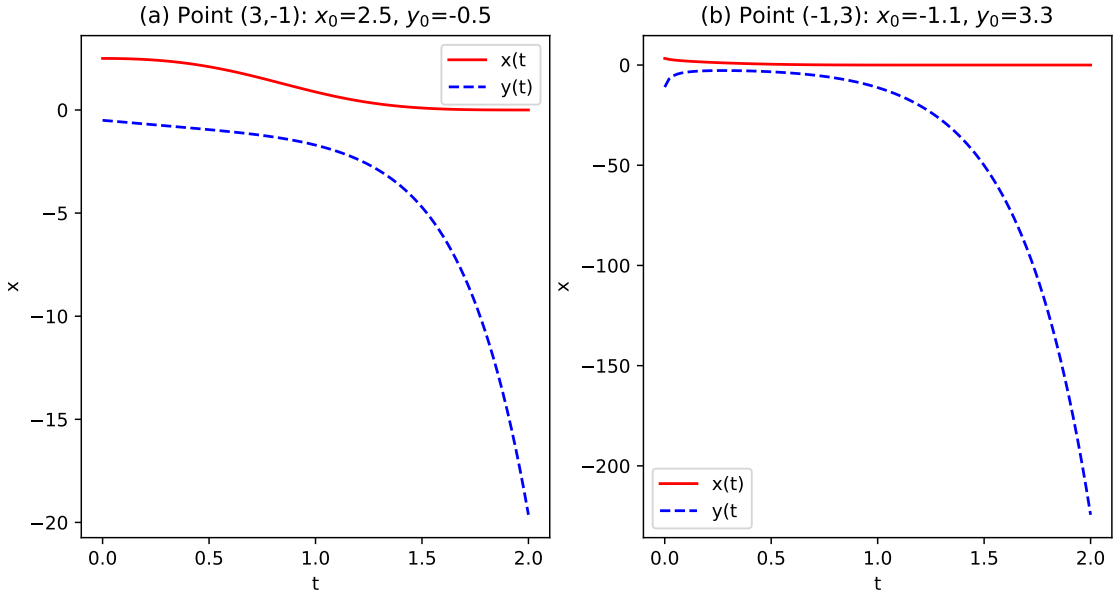

Figure 4: Plots of x and y versus t for point near (3,-1) and (-1,3)

Once again we see our graphs diverge implying that the chosen initial values and the point chosen near the fixed points are considered unstable points.

3.1 Brusselator model

We will start exploring the Brusselator model by finding the fixed points of the model using the equations provided in Eq. 9 and Eq. 10 as follows:

$$\frac{dx}{dt} = 1 - (b+1)x + ax^2y$$

$$\frac{dy}{dt} = bx - ax^2y$$

Where x and y are the concentration of two reactants used in a chemical reaction and a and b are constants which are > 0. In this section of the report we will be repeating the process we completed earlier on the exame differential equation, this time instead subbing in the real equation which governs these oscillating chemical reactions. The first thing we do is create our streamline plots and our nullclines so that we can find our fixed points.

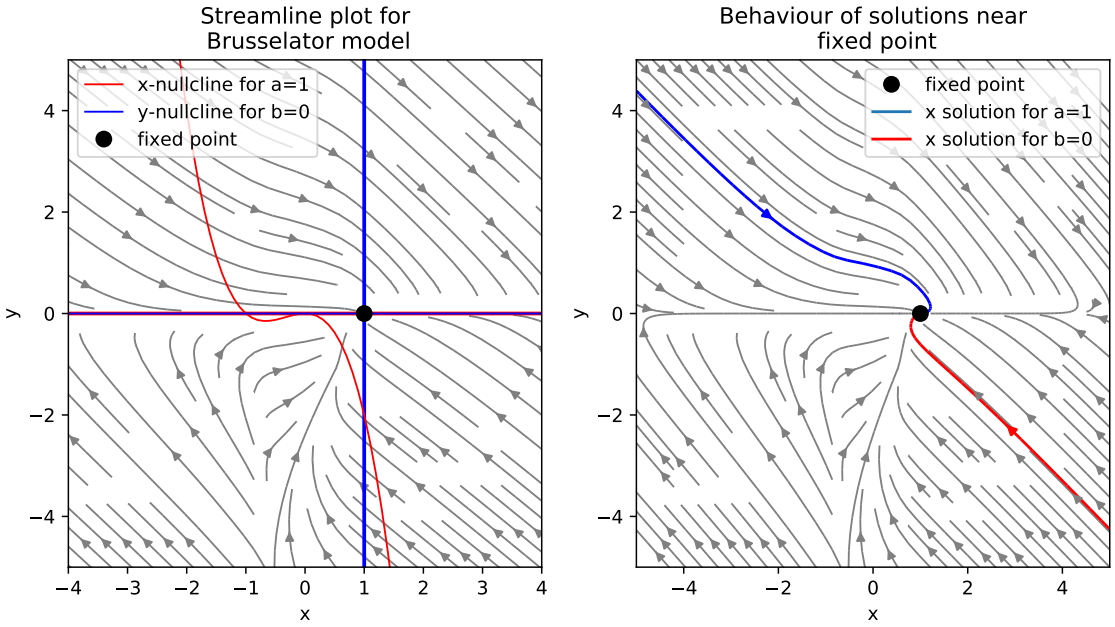

Figure 5: streamline plots for parameters of (a) and (b) and its fixed points

In this example we have set one of our constants to 1 and the other constant to not affect the system by setting b equal to 0. These initial values for our constants gives us a fixed data point which is stable which we can extrapolate to the real world physical system of a chemical reaction where no oscillation is taking place. We can start from this point and find a situation where the system will move from a stable state to begin oscillating, we can start this process by finding the nullclines of the system.

Taking Eq.9 we can solve for y as follows:

$$1 - (b+1)x + ax^2y$$

$$ax^2y = -(1 - (b+1)x)$$

$$ax^2y = -1 + bx + x$$

$$y = \frac{-1 + bx + x}{ax^2}$$

From this point we can also set $\frac{dy}{dt} = 0$ and find the nullcline for Eq.10:

$$bx - ax^2y = 0$$

$$x(b - axy) = 0$$

$$x(b - axy) = 0$$

$$x(b - axy) = 0 \text{ if } x = 0 \quad \text{or} \quad \text{if } y = \frac{b}{ax}$$

In both of these cases, once we have solved for y, we notice that our equations still contain both our a and b concentration constants, so this means that our nullclines are dependent on these values of constants in the initial equations. From out graph Fig. 5 we can see that our graph contains a cubic component which is independent of the y component. This cubic equations shape will once again depend on the initial values given for the constant a and b. We can also find the relationship which exists between our constants and the fixed point.

To find out fixed point for this system, we equate the two differential functions which both equal to zero in this situation as follows:
Equation 1:

$$1 - (b + 1)x + ax^2y = 0$$

Equation 2:

$$bx - ax^2y = 0$$

Equating these two equations:

$$1 - (b + 1)x + ax^2y = bx - ax^2y$$

$$1 - x = 0$$

$$x = 1$$

Plugging in x = 1 to our Equation 2 we can solve for y:

$$bx - ax^2y = 0$$

$$b(1) - a(1)^2y = 0$$

$$b - ay = 0$$

$$b = ay$$

$$\frac{b}{a} = y$$

We have determined that the fixed point will be located at $(1, \frac{b}{a})$, this verifies that the fixed points location is dependent on the initial constant values of a and b. We have found the fixed point of our chemical oscillator and we can now move on to categorising the fixed point by finding the determinate and trace of the Jacobian matrix and using Table 1. This will be slightly tricky to do as the stability of our fixed point is most likely also dependent on the values given for our concentrations a and b.

$$J = \begin{pmatrix} \frac{\partial f}{\partial x} & \frac{\partial f}{\partial y} \\ \frac{\partial g}{\partial x} & \frac{\partial g}{\partial y} \end{pmatrix}$$

$$\frac{\partial f}{\partial x} = \frac{\partial(-b-1+2axy)}{\partial x} = b-1 \qquad \frac{\partial f}{\partial y} = \frac{\partial(ax^2)}{\partial y} = a$$

$$\frac{\partial g}{\partial x} = \frac{\partial(b-2axy)}{\partial x} = -b \qquad \frac{\partial g}{\partial y} = \frac{\partial(-ax^2)}{\partial y} = -a$$

Jacobian:

$$J = \begin{pmatrix} b-1 & a \\ -b & -a \end{pmatrix}$$

We can determine the determinant and the trace of the Jacobian

$$det(J_{1,\frac{b}{a}}) = b - a - 1; \qquad Tr(J_{1.\frac{b}{a}}) = a$$

Assuming

$$a, b > 1 \text{ and } b > a$$

the fixed point will be greater than zero and the fixed point $(1, \frac{b}{a})$ is not a saddle point. If

$$b < a + 1$$

then the trace will be equal to zero, meaning the fixed point is stable. If

$$b > a + 1$$

the trace will be > 0 and the fixed point would be unstable.

We can now generate $x(t)$ and $y(t)$ solutions with phase plane graphs to test our claims about the stability of the fixed points for given values of a and b.

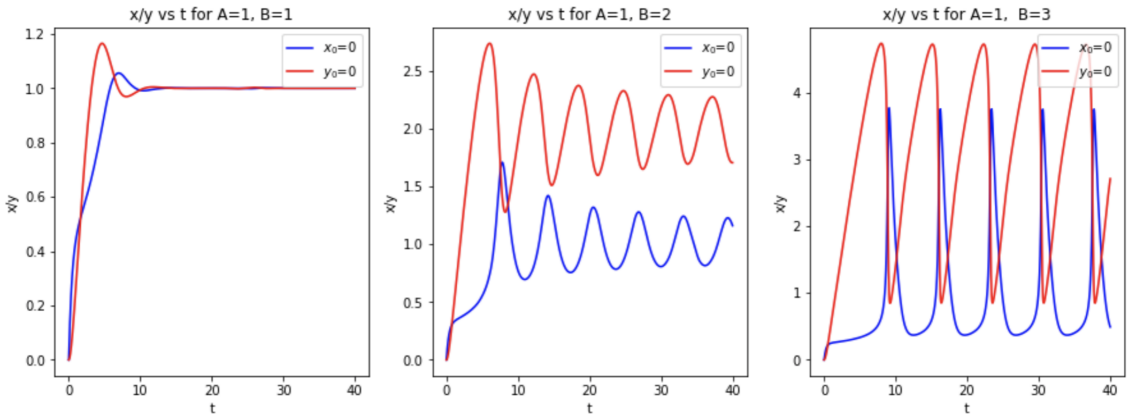

Figure 6: Solution curves at A=1,B=1 , A=1,B=2 and A=1,B=3

We see a pattern emerge from our solution curves which are consistent with what one would expect to see from an oscillating system, the values follow a pattern of low and high values and we can see that the values of A and B strongly impact the pattern that emerges.

The reason the first graph does not have a continous pattern is because $a + 1 > b$ which we explained earlier would cause the system to reach a steady state, after a slight oscillation the system goes into equilibrium and remains there.

In the second figure B = A we get the oscillating pattern we expect to observe in a Brusselator system. The third figure shows us that the greater the value of B the more noticeable this oscillating behaviour becomes, there also doesn't appear to be any damping on the system at this point and the pattern remains constant for the full 40 seconds. We can use phase diagrams to explore these three distinct situations more closely like so:

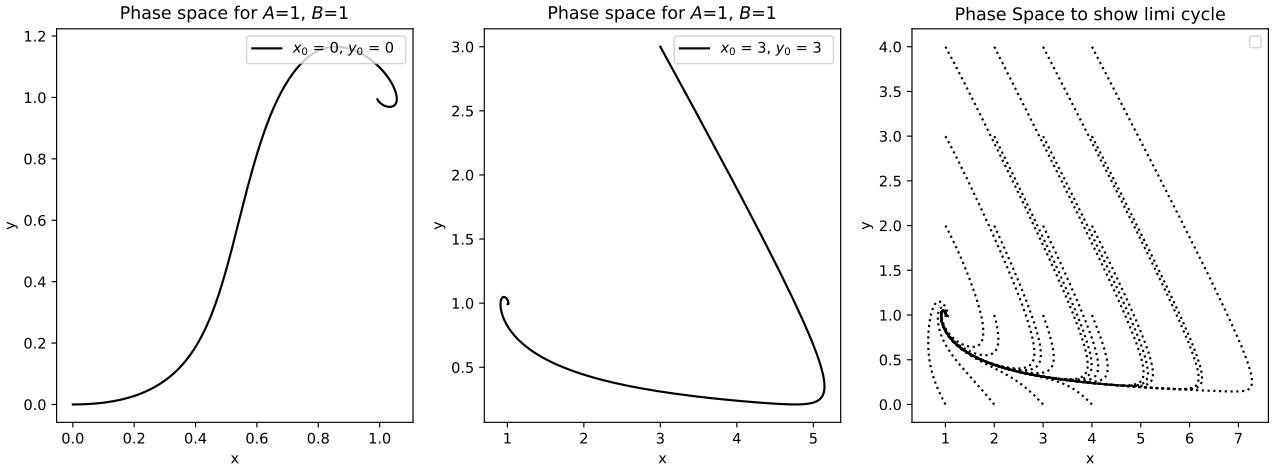

Figure 7: Phase plot when $b < a + 1$

We can see from this graph that when $b < a+1$ the phase plot does not show circular oscillating behaviour but instead shows the phase of a system which is reaching an equilibrium point that becomes stable and remains there this verifies our belief that a b value smaller than a + 1 will eventually reach a steady state.

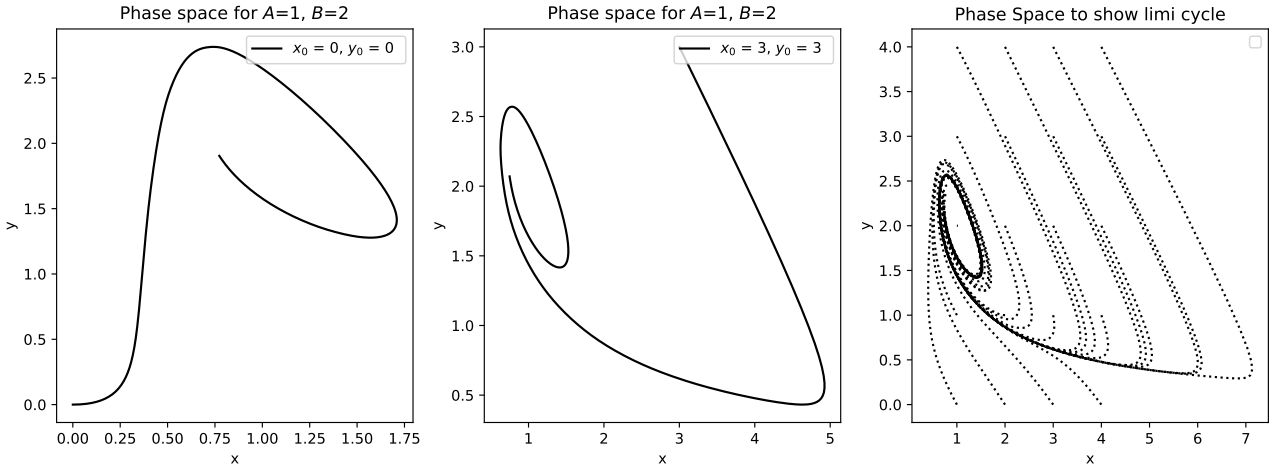

Figure 8: Phase plot when $b = a + 1$

In this graph when $b = a + 1$ the cyclical oscillating behaviour begins to show however the decaying nature is also present as the phase plots do not produce a perfect loop. We can also see from the phase space plot that regardless of the initial values of x_0 and y_0 the solution will always converge to the same cycle.

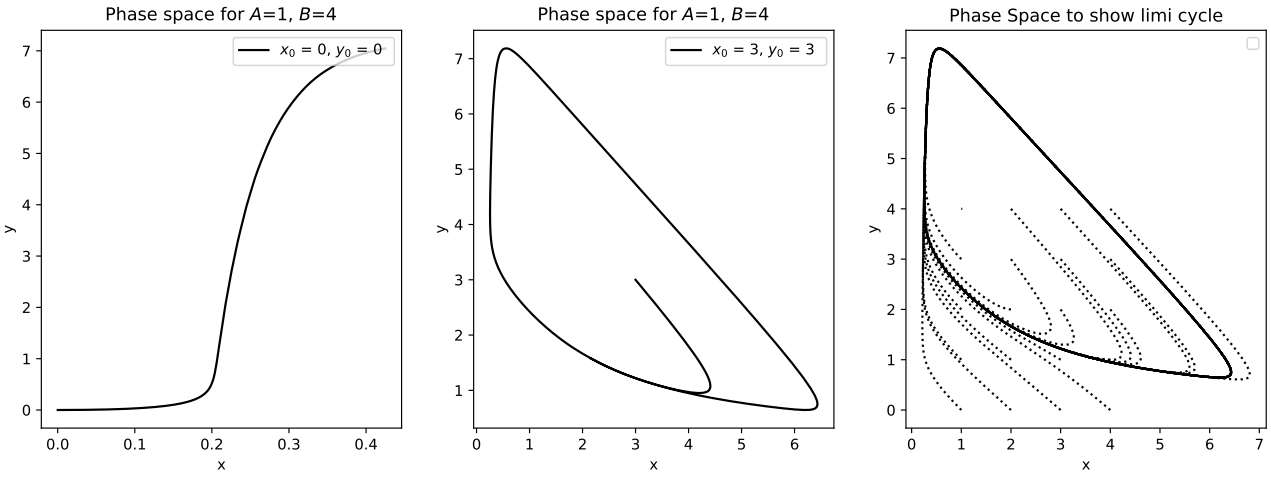

Figure 9: Phase plot when $b > a + 1$

Finally we can observe what happens when $b > a + 1$. In this phase plot the oscillation is extremely apparent with no decay and the cycle continues to occur regardless of the initial values of x_0 and y_0. This means that our phase plots verify what we concluded earlier mathematically.

4 Discussion and Conclusion

We have successfully introduced and utilised multiple methods of analysing physical systems. We successfully used these methods to draw conclusions about the role concentrations play in the behaviour of an oscillating chemical reaction as well as the initial values for x_0 and y_0. Specifically we found that a chemical reaction where the concentration of b was less than $a + 1$ resulted in the reaction reaching a steady equilibrium and the oscillation did not occur, a chemical reaction where the concentration of b was equal to $a + 1$ resulted in a reaction that would oscillate back and forth but would decay over time and a chemical reaction where b was greater than $a + 1$ resulted in a reaction that would oscillate without decaying regardless of the initial values of x_0 and y_0.

This report has shown the benefit of being able to solve differential equations within python and the techniques which can be used to analyse physical systems which are governed by differential equations. We have covered characteristics of physical systems such as fixed points, nullclines and stability which all contribute to a better understanding of a particular physical system such as an oscillating chemical reaction. These methods of analysing real world systems using python is carried out everyday by physicists, engineers and data scientists where a solid understanding of how a physical system works and its constraints and variables can be used to achieve some desirable outcome such as better efficiency or new applications in the future. As an example the brusselator model which was modelled after oscillating chemical reactions is the foundation for clock signals in electrical circuits such as computers.