MATH 221 - Differential Equations

Project 6: An Application from Chemistry - The Brusselator and Hopf Bifurcation

Fall 2020 | **Subhadip Chowdhury** | **Nov 9-18**

The **Brusselator model** is a famous model of chemical reactions with oscillations. The dynamics and chemistry of oscillating reactions has been the subject of study for the last almost 60 years, starting with the work of Boris Belousov. While studying the Krebs cycle, he witnessed a mixture of citric acid, bromate and cerium catalyst in a sulphuric acid solution undergoing periodic colour changes. These changes indicated the cycle formation and depletion of differently oxidized Ce(III) and Ce(IV) ions. This was the first reaction, where biochemical oscillations was observed in 1950. In 1961, Zhabotinsky reproduced Belousov's work and showed further oscillating reactions. The reaction mechanism is an example of an autocatalytic, oscillating chemical reaction. Autocatalytic reactions are chemical reactions in which at least one of the reactants is also a product and vice versa. The rate equations for autocatalytic reactions are fundamentally nonlinear.

Consider a Brusselator whose equations are given as follows*:

$$\begin{gathered}
\mathbf{A} \xrightarrow{k_1} \mathbf{X} \\
\mathbf{B} + \mathbf{X} \xrightarrow{k_2} \mathbf{Y} + \mathbf{D} \\
2\mathbf{X} + \mathbf{Y} \xrightarrow{k_3} 3\mathbf{X} \\
\mathbf{X} \xrightarrow{k_4} \mathbf{E}
\end{gathered}$$

where **A** and **B** are reactants (substrates), **D** and **E** are products and **X** and **Y** are the autocatalytic reactants of the set of reactions. Also k_1, k_2, k_3 and k_4 are the rate of reactions for each component reaction.

The governing equations of the Brusselator are obtained using law of mass action (the rate of a chemical reaction is directly proportional to the product of the concentration of reactant) and the set of equations for the change in concentrations of **X** and **Y** are found to be (after some scaling):

$$\begin{aligned}
\frac{dx}{dt} &= a - (1+b)x + yx^2 \\
\frac{dy}{dt} &= bx - yx^2
\end{aligned}$$

where x and y represent the concentrations of the autocatalytic reactants and $a, b > 0$. Because of obvious reasons, we are only going to be interested in the case where x and y are positive.

For the purpose of this project, you may use whatever tools you have at your disposal (excluding the internet), including our textbooks, Jupyter notebooks posted on Moodle, online apps linked from your Worksheets, and PPLANE, that best serves your purpose.

*Look here for an explanation of how the differential equations are found: https://en.wikipedia.org/wiki/Brusselator

Part I

Read the text from the introduction and watch the linked video below before you begin!

https://www.youtube.com/watch?v=wHKnZ13FslU

The video uses different compounds than the original experiment by Belousov but the theory is still the same. Note that there is no jump cuts in the video, it's happening in real time.

What's going on in the reaction? It seems that after stability is reached, the amount of each chemical in the solution oscillates periodically, which is demonstrated by the change in color. We are going to try to mathematically explain this phenomenon.

§A. Equilibrium Point Analysis

Question 1. (1+1+2 points)

Find the equation of the nullclines and the equilibrium point in terms of a and b.

Question 2. (2+1+1 points)

Find the Jacobian of the system at the equilibrium point. Show that its trace is

$$T = b - 1 - a^2$$

and determinant is

$$D = a^2$$

§B. Bifurcation

Question 3. (2+2+2 points)

Suppose we keep a fixed and vary b. Classify the type of phase portrait that occurs at the point of equilibrium in the following three cases. Use the Jacobian to justify your answer.

a) $a = 1$ and $b = 1$.
b) $a = 1$ and $b = 3$.
c) $a = 1$ and $b = 5$.

Question 4. (1+3+2 points)

Since the type of equilibrium changed twice as we changed b from 1 to 5, we conclude that there are at least two bifurcation values of b when a is fixed at 1.

(a) Check that D is always positive, so the equilibrium is source or sink based on values of T.

(b) Find the curves $T = 0$ and $T^2 = 4D$ in terms of a and b and draw them in the (a, b)-plane (with $a, b > 0$).

(c) Find all bifurcation values of b when $a = 1$. These are the points where the type of equilibrium changes.

Question 5. **(4 points)**

Find all possible type of equilibrium points for different values of the parameters a and b. In particular, identify the regions in the first quadrant of the (a, b)-plane that correspond to source, sink, spirals etc.

§C. Nullclines and Direction Field

Question 6. **(2+2 points)**

Use `Desmos` to draw the nullclines. Set sliders for a and b.

(a) Move the slider to check that the nullclines intersect only once for all values of a and b. How does changing a and b change the x and y coordinates of the point of intersection? Is this consistent with the formula of equilibrium point you obtained above?

(b) Set $a = 1, b = 2.5$ and copy the resulting graphs of the nullclines on to paper. Draw the direction field along the nullclines. You may use `PPLANE` for this.

Question 7. **(4 points)**

Find whether x' and y' are positive or negative in other regions (4 of them) and use this information to draw the direction field arrows in those regions (on your paper).

Part II

§D. Phase Portrait

Something very interesting happens in the phase portrait as the equilibrium becomes a source. Let's use PPLANE to draw the phase portrait in each of the three cases from question (3). *You may need to change the window width in each case for a comfortable viewing size.*

Question 8. (2+2+2 points)

Include a screenshot of the phase portrait with some sample solution curves in each case. Your pictures must clearly demonstrate the distinct behavior of solution curves near the equilibrium point in each case. Describe in your own words, the long term behavior of these solution curves as you see in your picture.

§E. Existence of a Limit Cycle

Let's focus on the second case $a = 1, b = 3$ for the remainder of this project. We observe that the solution curves starting near the equilibrium point go outward to a limit cycle! Could we have predicted that the existence of this limit cycle mathematically?

Recall the four possibilities for the trajectory of a solution curve of a nonlinear system as a consequence of **Poincaré–Bendixson** theorem (look in the last worksheet). Assuming all necessary requirements hold (and they do), there are only two possibilities for solution curves that start near $(a, b/a)$. Since the equilibrium point is a source, the solution curves can

- either become unbounded, or
- they spiral towards a limit cycle.

In the following questions, we would like to show that that they are not going to infinity. That will prove the existence of a limit cycle.

Consider the five dotted lines that we have drawn along with the nullclines in figure 1. We will describe and find equations for them in the next problem.

Question 9. (1+1+1+1+0 points)

(a) The red dotted line is vertical and it passes through the point of intersection of the x-nullcline and the x-axis. Find it's equation.

(b) The blue dotted line is horizontal and it passes through the point of intersection of the red line and the y-nullcline. Find it's equation.

(c) The green dotted line has slope -1 and passes through the point $(1, 12)$. Find it's equation.

(d) The orange dotted line is vertical and passes through the intersection of the green line and the y-nullcline. Find it's equation.

(e) The purple dotted line is just the $\mathbf{X}-$axis. Mark and shade the region bounded by the five dotted straight lines.

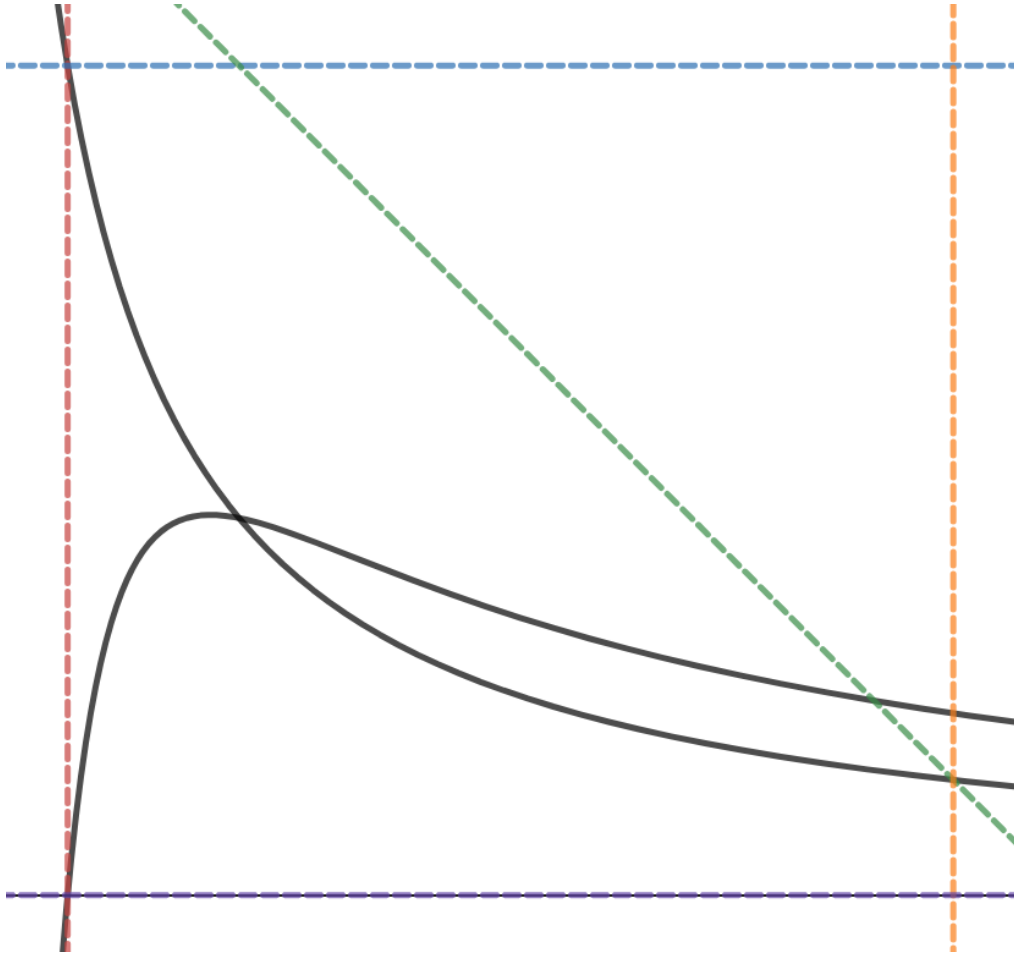

Figure 1: Trapping Region

Question 10. (2+3 points)

We are going to find the direction field arrows along the boundary of this region. Arrows along the horizontal and vertical segments are easy to find from PPLANE. So we only need to check the case of the diagonal line segment by hand.

(a) Show that $-y' > x'$ if $x > 1$. [Hint: Calculate $x' + y'$.]

(b) Explain how this inequality implies that the direction field arrows point **inward towards the shaded region** (i.e. to the left of the green line) along the diagonal green line. Note that the facts $x' < 0$ and $y' > 0$ are not enough to justify this assertion.

[Hint: What is dy/dx for $x > 1$?]

Question 11. (2 points)

Draw the arrows along the five boundary (dotted) line segments. They should all point inward towards the shaded region. With this behavior of the direction field, what can you conclude about the long-term behavior of a solution curve that either starts inside the region or crosses **into** the region from outside? Can it ever leave the region?

End of Question 11

The region we have constructed above is called a **Trapping Region**. It 'traps' the trajectories inside as all the arrows are pointing inward! On the other hand, when the equilibrium point is a spiral source, all trajectories that start near the point are going outwards. Since they can't escape the trapping region, they are doomed to converge towards a limit cycle! Note that the requirement of being a repelling equilibrium point is crucial, since otherwise all trajectories could have converged to a point.

§F. Hopf Bifurcation

The kind of bifurcation you observed above is called a **Hopf Bifurcation**. The uniqueness of such bifurcations lies in two aspects: unlike other common types of bifurcations (e.g. pitchfork, saddle-node or transcritical) Hopf bifurcation cannot occur in one dimension. The minimum dimensionality has to be two. The other aspect is that Hopf bifurcation deals with birth or death of a periodic solution or limit cycle as and when its stability changes at an equilibrium point. More accurately, it is a local bifurcation in which a equilibrium point of a dynamical system loses stability, as a pair of complex conjugate eigenvalues—of the linearization around the equilibrium point—crosses the complex plane imaginary axis. Under reasonably generic assumptions about the dynamical system, a small-amplitude limit cycle branches from the equilibrium point.

Question 12. **(3 point)**

Demonstrate the above paragraph in the context of the Brusselator model with our system of ODEs and use Hopf bifurcation to explain the periodic behavior observed in the reaction for certain concentrations of **A** and **B**.

End of Question 12

Hopf bifurcations arise in lots of real-life oscillatory processes: in Predator-Prey models, in models for Action Potential transference across neurons, in Glycolysis and Krebs Cycle etc. Recently, Hopf bifurcations of some famous chaotic systems have been investigated and it is becoming one of the most active topics in the field of chaotic systems. Check out this link

https://en.wikipedia.org/wiki/Hopf_bifurcation#/Example

for a neat gif of Hopf bifurcation in the Selkov model of Glycolysis.

§F. References

[1] Strogatz, Steven H. 1994. *Non-Linear Dynamics and Chaos*. New York: Perseus Books Group. 1994.