The Belousov-Zhabotinsky Oscillator:
An Overview

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A Brief History of Chemical Oscillators

- Have only been recognized as mainstream science since the 1960s.
- Prior belief was that all chemical reactions progressed in one direction (monotonically) to equilibrium.

A Brief History of Chemical Oscillators

- First oscillating reaction discovered around 1950 by Boris Pavlovich Belousov.

- Solution of citric acid in water with acidified bromate and ceric ions oscillated from colorless to yellow for up to an hour.

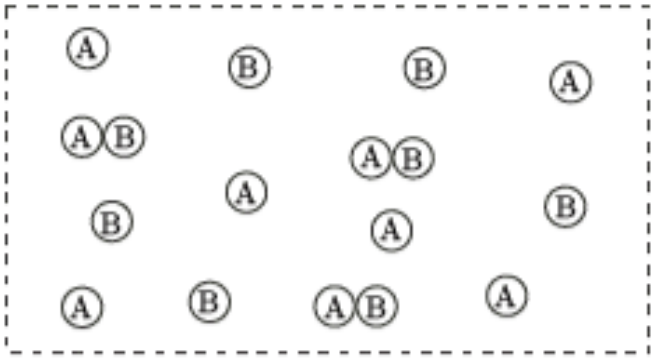
A Brief History of Chemical Oscillators

- Belousov's work ill-received by scientific community.
- Was only recognized posthumously for his contributions.
- Work was continued by Anatol Zhabotinsky in 1961.
- Zhabotinsky succeeded in awakening the scientific community to the validity of chemical oscillators.
- The cerium-bromate reaction became known as the Belousov-Zhabotinsky (BZ) Reaction.

A Brief History of Chemical Oscillators

- Today, many chemical systems are known to oscillate.
- Various mathematical models have been developed to describe the BZ reaction.
  - Brusselator
  - Oregonator
- To date, however, the actual reaction mechanism remains a mystery.

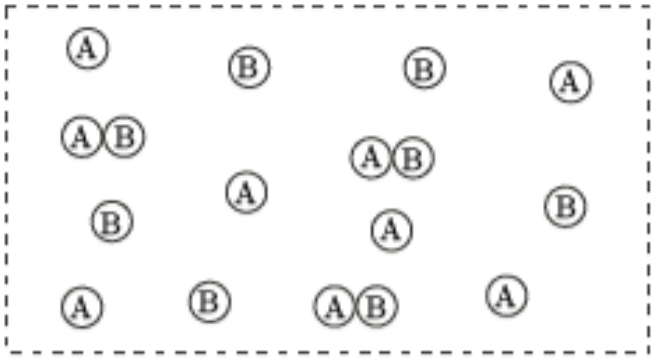
Background: Chemical Kinetics



- Suppose 2 species, A and B, are distributed throughout a domain and are in motion.
- When they come in contact, they form a new species C.
- We can represent this by the chemical equation

$$A + B \rightarrow C.$$

Background: Chemical Kinetics



- Over time, concentrations of A and B will decrease at the same rate, and the rate of change of C will be the negative of this rate.

Background: Chemical Kinetics

- We can express the rate of change of concentrations of A, B, and C as a dynamical system:

$$\dot{A} = -r$$

$$\dot{B} = -r$$

$$\dot{C} = r$$

- Intuitively, the reaction rate r depends on the concentrations of A and B.

Background: Chemical Kinetics

- In this simple example, it can be shown that

$$r = kAB$$

where the rate constant k must be determined experimentally.

Background: Chemical Kinetics

- We will now extend this idea to more complicated reactions. Consider

$$\alpha A + \beta B \rightarrow \gamma C + \delta D.$$

The constants $\alpha, \beta, \gamma, \delta \geq 0$ are called the *stoichiometric coefficients* of the reaction.

A and B are the *reactants*, C and D are the *products*.

Background: Chemical Kinetics

- We can derive a dynamical system for this reaction using the Law of Mass Action.

- The Law of Mass Action states:
  1) The reaction rate *r* is proportional to the product of the reactant concentrations, with each concentration raised to the power equal to its respective stoichiometric coefficient.

$$r = kA^{\alpha}B^{\beta}$$

Background: Chemical Kinetics

2) The rate of change of the concentration of each species in the reaction is the product of its stoichiometric coefficient with the rate of the reaction, adjusted for sign (+ if product, - if reactant)

$$\dot{A} = -\alpha r$$

$$\dot{B} = -\beta r$$

$$\dot{C} = \gamma r$$

$$\dot{D} = \delta r$$

Background: Chemical Kinetics

- Thus we arrive at the dynamical system

$$\dot{A} = -\alpha k A^{\alpha} B^{\beta}$$

$$\dot{B} = -\beta k A^{\alpha} B^{\beta}$$

$$\dot{C} = \gamma k A^{\alpha} B^{\beta}$$

$$\dot{D} = \delta k A^{\alpha} B^{\beta}.$$

With known initial concentrations

$$A(0) = A_0, \quad B(0) = B_0, \quad C(0) = C_0, \quad D(0) = D_0.$$

Modeling The BZ Reaction

- There are many variations on the BZ reaction recipe.
- The recipe that we will demonstrate later contains the following:

Solution	Composition
Solution A	0.23M Potassium bromate
Solution B	0.31M Malonic acid, 0.059M Potassium bromide
Solution C	0.019M Cerium(IV) ammonium nitrate, 2.7M Sulfuric acid
Ferroin Indicator Solution	

Modeling The BZ Reaction

- However, our analysis will concern the Oregonator, which is based on a slightly different recipe.
- The Oregonator is considered the simplest model of the BZ Reaction.
- The actual reaction mechanism is extremely complicated; some models have as many as 80 steps and 26 variable species concentrations.

Modeling The BZ Reaction

- Let $X = [\mathrm{HBrO_2}]$ (hypobromous acid)
  $Y = [\mathrm{Br^-}]$ (bromide)
  $Z = [\mathrm{Ce(IV)}]$ (cerium-4)
  $A = [\mathrm{BrO_3^-}]$ (bromate)
  $B = [\mathrm{Org}]$ (organic species)
  $P = [\mathrm{HOBr}]$.

- The Oregonator Scheme is then given by the series of 5 reactions:

$\mathrm{A+Y} \rightarrow \mathrm{X+P}$	$r = k_3 AY$
$\mathrm{X+Y} \rightarrow \mathrm{2P}$	$r = k_2 XY$
$\mathrm{A+X} \rightarrow \mathrm{2X+2Z}$	$r = k_5 AX$
$\mathrm{2X} \rightarrow \mathrm{A+P}$	$r = k_4 X^2$
$\mathrm{B+Z} \rightarrow \frac{1}{2} f\,\mathrm{Y}$	$r = k_o BZ$

(Note that the rate constants can be determined empirically).

Modeling The BZ Reaction

- Using the Law of Mass Action, we can derive the following dynamical system:

$$\frac{dX}{dt} = k_3 AY - k_2 XY + k_5 AX - 2k_4 X^2$$

$$\frac{dY}{dt} = -k_3 AY - k_2 XY + \frac{1}{2} f k_0 BZ$$

$$\frac{dZ}{dt} = 2k_5 AX - k_0 BZ$$

- We assume that initial concentrations are known.

Modeling The BZ Reaction

- Using nondimensionalization and some simplifying assumptions, we can reduce the system to:

$$\varepsilon \frac{dx}{d\tau} = x(1-x) + \frac{f(q-x)}{q+x} z$$

$$\frac{dz}{d\tau} = x - z$$

- Note that $\varepsilon = \dfrac{k_0 B}{k_5 A}$, $q = \dfrac{2k_3 k_4}{k_2 k_5}$.

Mathematical Analysis

- Taking $f = \frac{2}{3}, \quad q = 8\times10^{-4}, \quad \varepsilon = 4\times10^{-2}$ (based on empirical data using typical initial concentrations) yields

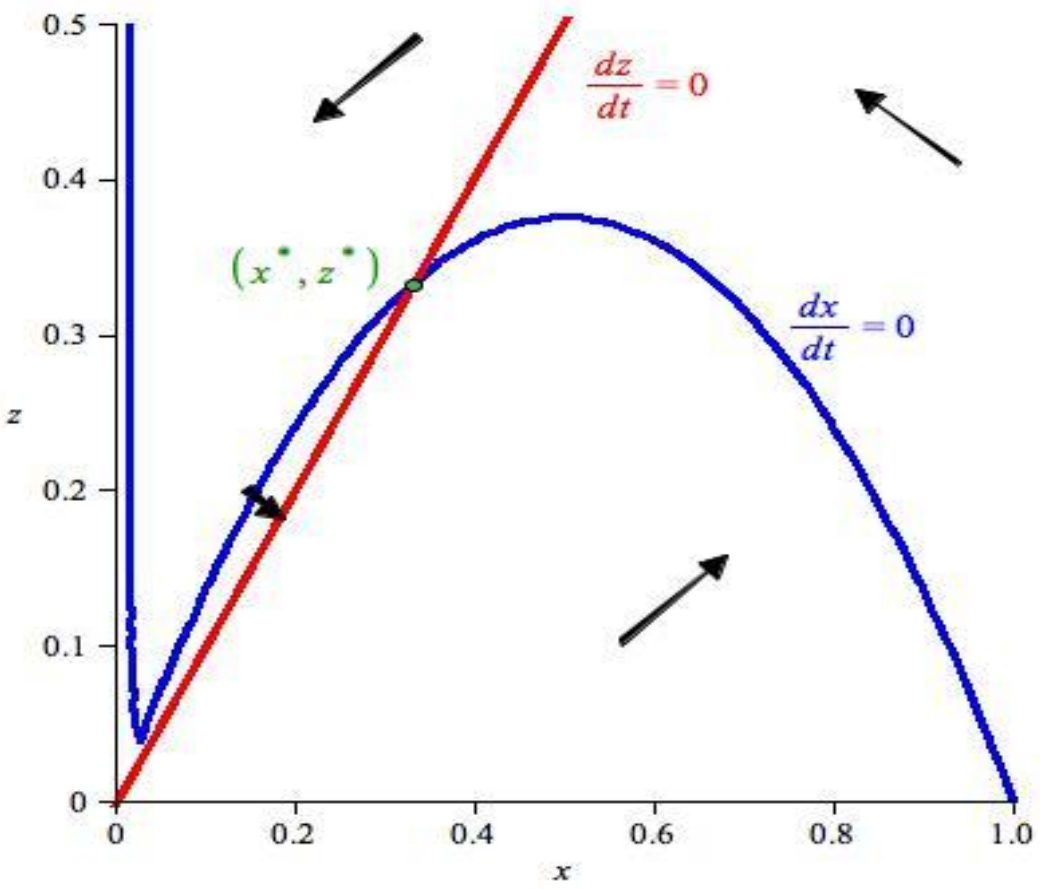
$$\frac{dx}{d\tau} = 25x(1-x) + \frac{50}{3}\left(\frac{1-1250x}{1+1250x}\right)z$$

$$\frac{dz}{d\tau} = x - z.$$

- As always, the nullclines for this system will be given by

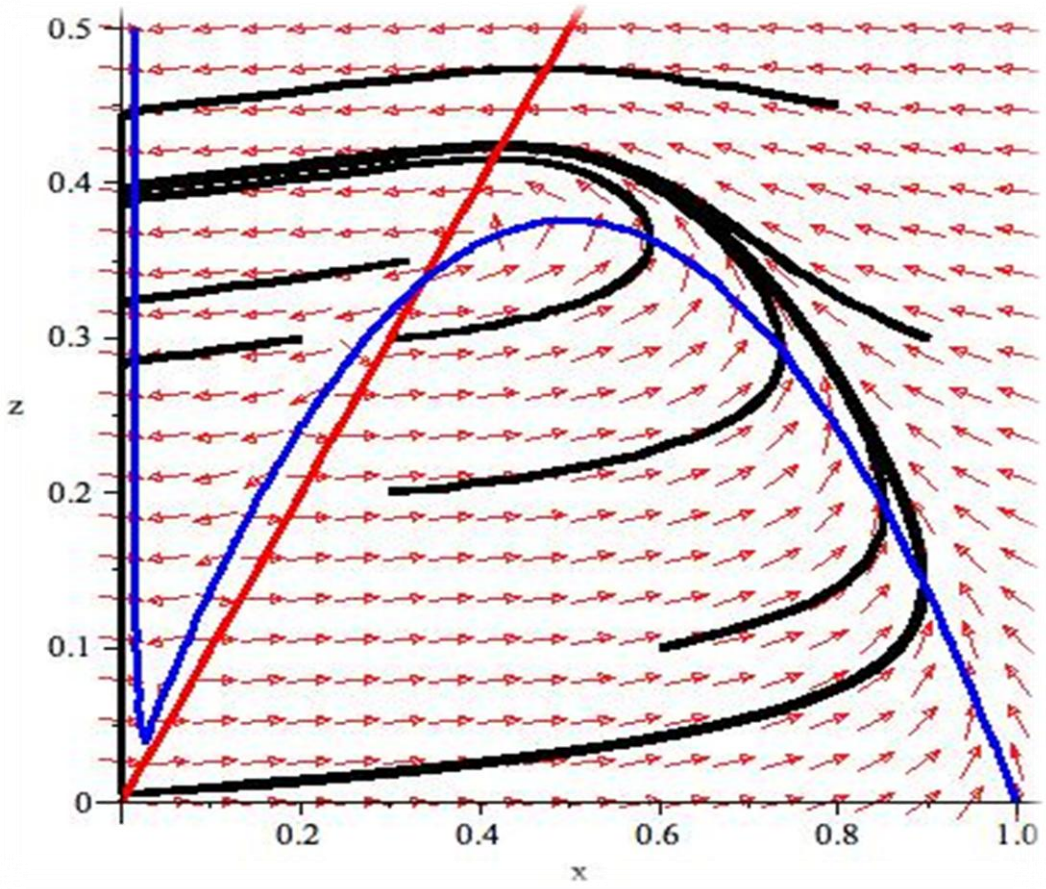
$$\frac{dx}{d\tau} = 0, \quad \frac{dz}{d\tau} = 0.$$

Mathematical Analysis



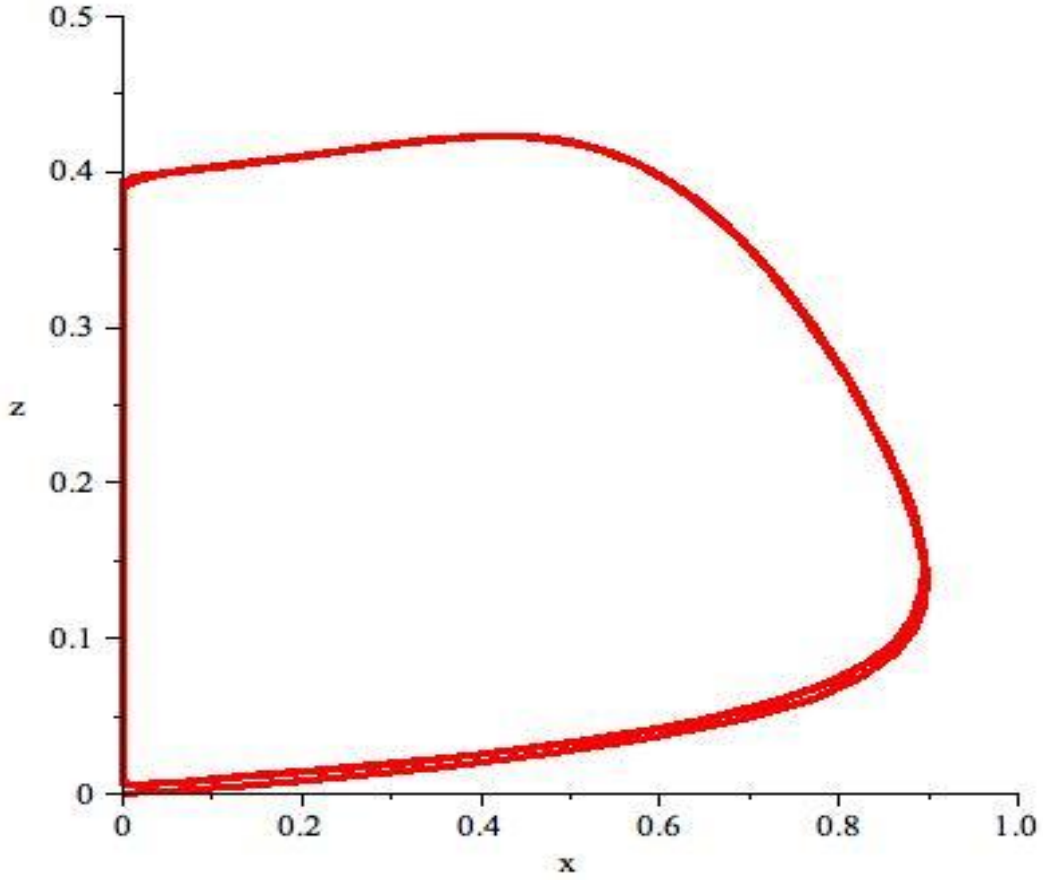
- We can graph the nullclines and use test points to find flow directions.
- Clearly, there is one positive fixed point (x^*, z^*).
- It can be shown this fixed point will exist for any $f, q > 0$

Mathematical Analysis



- Plotting a few trajectories reveals a stable limit cycle.
- Note that the fixed point is clearly unstable.

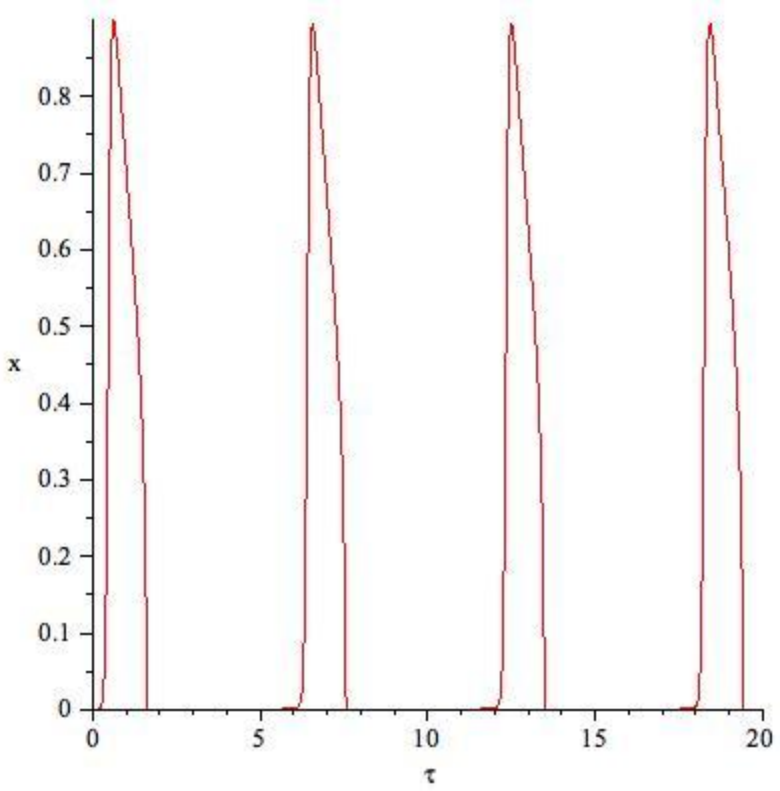
Mathematical Analysis

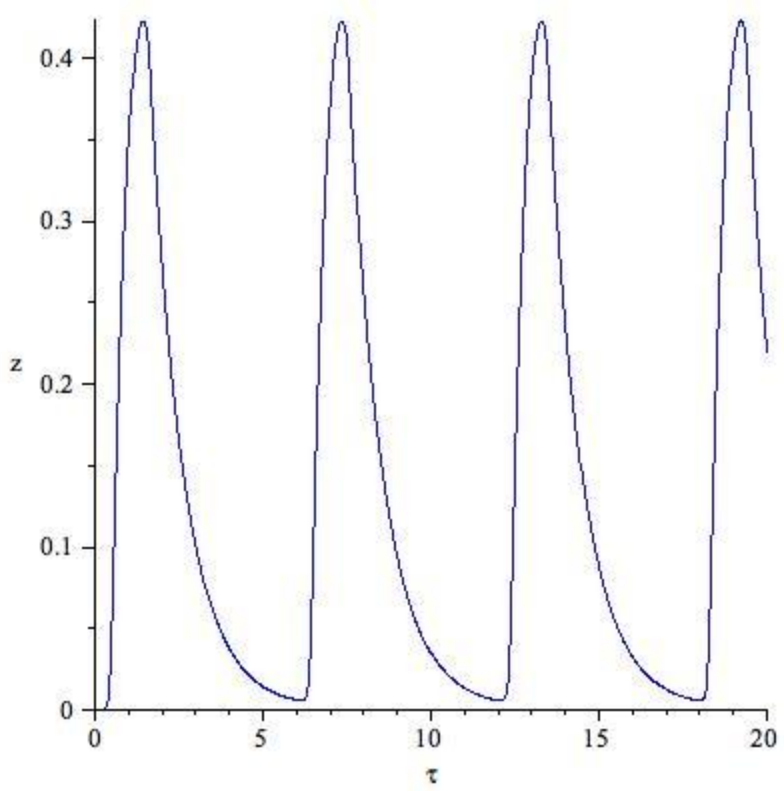


- A view of one trajectory with initial conditions close to (0,0).

Mathematical Analysis

- In fact, this system exhibits relaxation oscillations.

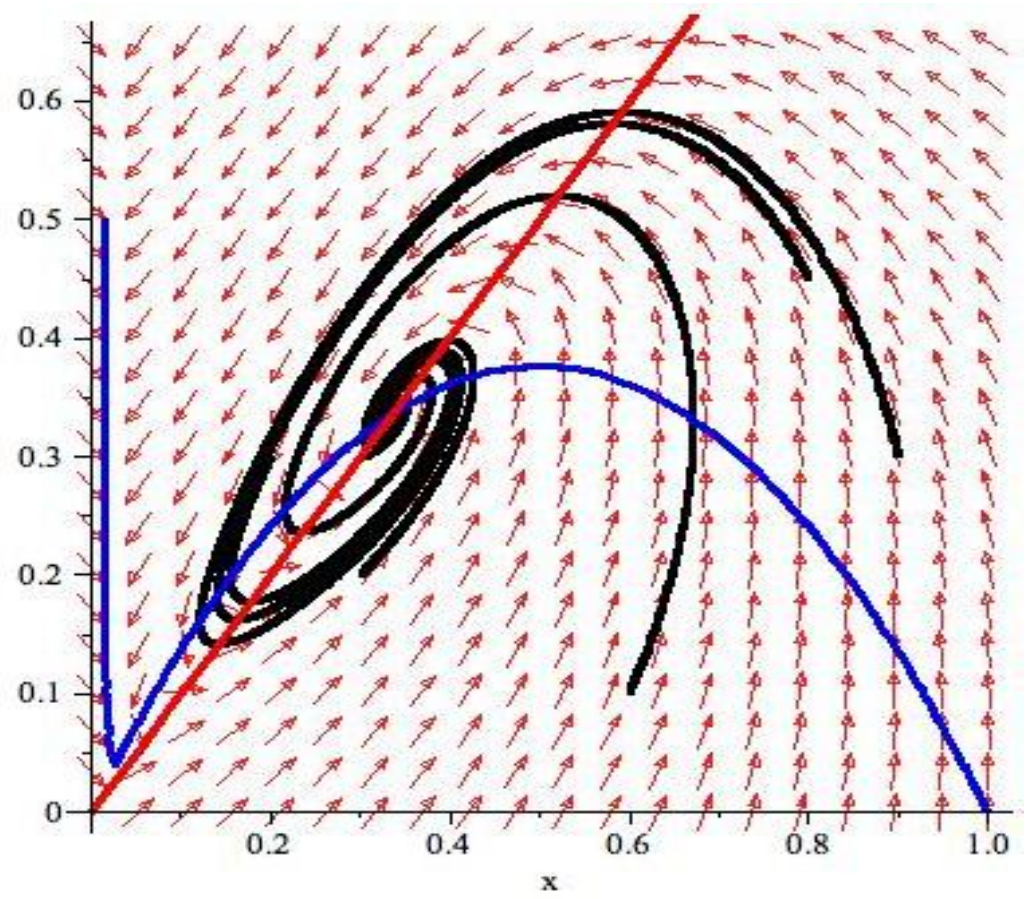




Mathematical Analysis

- Question: What effect does varying initial concentrations have on the limit cycle?
- It turns out that this system has a Hopf Bifurcation:
  - A Hopf Bifurcation is a qualitative change in the phase portrait that occurs as the real parts of eigenvalues of the Jacobian matrix for the system (evaluated at a fixed point) change from negative to positive.
  - Assuming that q is fixed, we will find that the limit cycle will exist only for certain values of f and ε.

Mathematical Analysis



- For example, if we increase ε to 0.6 (and keep q and f the same) then the limit cycle vanishes.
- Note that the fixed point is now stable.

Mathematical Analysis

What values of ε and f will produce oscillations?

1. Compute the positive fixed point (x^*, z^*) by solving the system $\frac{dx}{d\tau} = 0, \quad \frac{dz}{d\tau} = 0$ to obtain

$$x^* = \frac{1}{2}\left(1 - f - q + \sqrt{f^2 + (1+q)^2 + f(6q-2)}\right), \quad z^* = x^*.$$

Mathematical Analysis

2. Compute the Jacobian matrix for the system, evaluated at the fixed point:

$$J(x^*, z^*) = \begin{bmatrix} \frac{1}{\varepsilon}\left(1 - 2x^* - \frac{2fx^*q}{(q+x^*)^2}\right) & \frac{f(q-x^*)}{\varepsilon(q+x^*)} \\ 1 & -1 \end{bmatrix}.$$

Mathematical Analysis

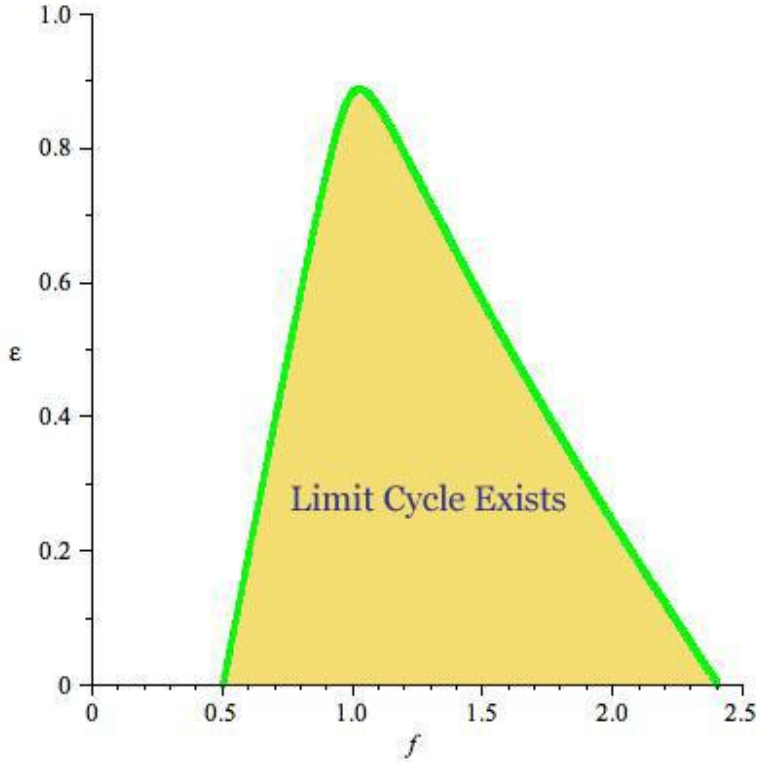
3. The critical value for ε will occur when the real part of the eigenvalues for the Jacobian matrix are equal to zero. This means the trace of the Jacobian will be zero.

$$trace(J) = -\frac{1}{\varepsilon}\left(1 - 2x^* - \frac{2fx^*q}{(q+x^*)^2}\right) = 0$$

$$\Rightarrow \varepsilon = 1 - 2x^* - \frac{2fx^*q}{(q+x^*)^2}$$

Mathematical Analysis

4. We can graph this result in the ε-f plane to obtain a region in which oscillations will occur.



References

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- Holmes, M.H., *Introduction to the Foundations of Applied Mathematics*.
- Strogatz, Steven H., *Nonlinear Dynamics and Chaos*.
- Winfree, A.T., The Prehistory of the Belousov-Zhabotinsky Oscillator.