Modeling the Oscillatory Belousov-Zhabotinsky Reaction

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Overview

Simplified Reaction and Goal

Simplification of the original reaction that preserves its mechanics [1]:

$$\mathrm{A} + \mathrm{Y} \rightleftharpoons \mathrm{X} \qquad (k_1)$$
$$\mathrm{X} + \mathrm{Y} \rightleftharpoons \mathrm{P} \qquad (k_2)$$
$$\mathrm{B} + \mathrm{X} \rightleftharpoons 2\,\mathrm{X} + \mathrm{Z} \qquad (k_3)$$
$$2\,\mathrm{X} \rightleftharpoons \mathrm{Q} \qquad (k_4)$$
$$\mathrm{Z} \rightleftharpoons f\,\mathrm{Y} \qquad (k_5)$$

A, B are reactant species. X, Y, Z are oscillatory species. P,Q are product species. $f \in \mathbb{Z}$ is stoichiometric constant. Want to study 3 things:

- Study behavior of oscillating trajectory (attracting or repelling)
- Convergence of microscopic model to macroscopic model
- Instability of steady state

Macroscopic Model

Formula (System of Differential Equations)

Given X_0, Y_0, Z_0, f, the Oregonator can be modeled macroscopically as follows:

$$\frac{dX}{dt} = k_1AY - k_2XY + k_3BX - 2k_4X^2$$
$$\frac{dY}{dt} = -k_1AY - k_2XY + fk_5Z$$
$$\frac{dZ}{dt} = k_3BX - k_5Z$$

Above is stiff (standard techniques are numerically unstable), so we use MATLAB's ode15s solver: variable-step variable-order solver.

Microscopic Model

Formula (Microscopic Rate Equations)

Given $N^{(0)} = \begin{bmatrix} N_A^{(0)} & N_B^{(0)} & N_X^{(0)} & N_Y^{(0)} & N_Z^{(0)} \end{bmatrix}$, V, *the Oregonator can be modeled microscopically as follows:*

$$\mathrm{Rate}_1^{(t)} = k_1 N_A^{(t)} N_Y^{(t)} / V$$
$$\mathrm{Rate}_2^{(t)} = k_2 N_X^{(t)} N_Y^{(t)} / V$$
$$\mathrm{Rate}_3^{(t)} = k_3 N_B^{(t)} N_X^{(t)} / V$$
$$\mathrm{Rate}_4^{(t)} = k_4 N_X^{(t)} (N_X^{(t)} - 1) / V$$
$$\mathrm{Rate}_5^{(t)} = k_5 N_Z^{(t)}$$

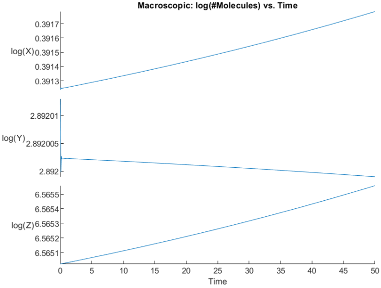
Microscopic Algorithm

Algorithm Microscopic Stochastic Algorithm

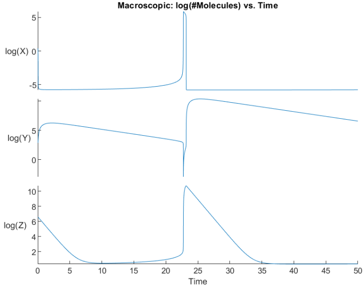
$t \leftarrow 0$
while $t < t_{\text{max}}$ **do**
  $\vec{T} \sim -\log(\text{rand}(1,5))/\mathrm{Rate}(\vec{N})$
  $T_{\text{min}} \leftarrow \min_{i \in \{1,\ldots,5\}}\{T_i\}$
  $K_{\text{min}} \leftarrow \arg\min_{i \in \{1,\ldots,5\}}\{T_i\}$
  $\vec{N} \leftarrow \vec{N} + \mathrm{dN}(:\ K_{\text{min}})^{\top}$
  $t \leftarrow t + T_{\text{min}}$
end while

Macro Model Validation (Stable Point)

For $f = 1, X_0 = 2.4556 \times 10^{-8}, Y_0 = 2.9939 \times 10^{-7}, Z_0 = 1.1787 \times 10^{-5}$, the Oregonator should not be oscillatory.



Steady State

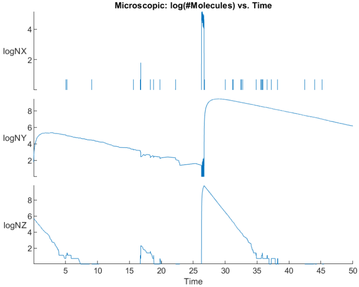


Oscillatory State

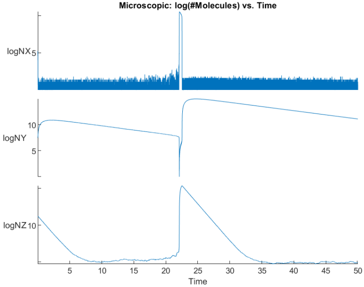
Figure: Validation and Discrimination

Micro Model Validation (Convergence) - Question 1

By increasing V, we expect to see convergence towards the macroscopic model.



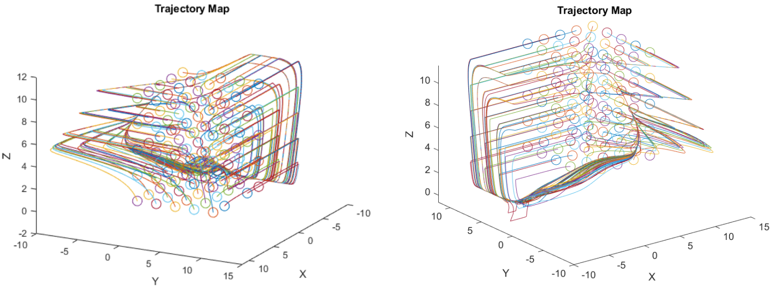
$V = 4^1$



$V = 4^5$

Attracting Oscillator - Question 2

Visualize path trajectories for initial values in $S(\varepsilon, n_s) := \{\varepsilon^k : k \in \{0, \ldots, n_s\}\} \times \{\varepsilon^k : k \in \{0, \ldots, n_s\}\} \times \{\varepsilon^k : k \in \{0, \ldots, n_s\}\}$.



View 1: $\varepsilon = 10, n_s = 5$ View 2: $\varepsilon = 10, n_s = 5$

Figure: Attractiveness of Periodic Trajectory

Instability of Steady State - Question 3

Let $\vec{x_{ss}}$ be initial concentrations of steady state. Introduce perturbations of the form $\vec{x_{ss}} + \varepsilon$, where $\|\varepsilon\|_2 \leq r$ for some $r \ll 1$.

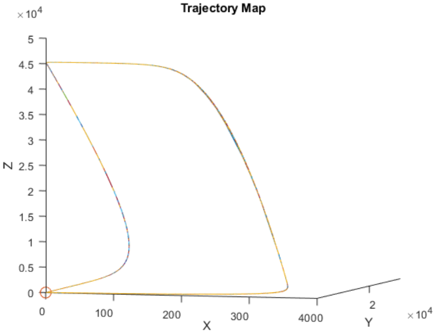


Figure: $r = 0.1$

References

Richard J. Field and Richard M. Noyes.
Oscillations in chemical systems. IV. Limit cycle behavior in a model of a real chemical reaction.
The Journal of Chemical Physics, 60(5):1877–1884, 1974.