

Modeling the Oscillatory Belousov-Zhabotinsky Reaction through Macroscopic and Microscopic Systems

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1 Introduction

The Belousov-Zhabotinsky reaction (BZ) is a class of oscillating chemical reactions, *i.e.* there are no stable steady state or equilibrium, and the primary reagents have concentrations that are periodic through time [3]. Other notable reactions include the Briggs-Rauscher reaction and the Bray-Liebhafsky reaction [2]. Since Belousov’s original discovery in 1951, various other viable reagents have been discovered, with the bromate oxidizer being the only key chemical. The comprehensive reaction mechanisms for the BZ reaction is incredibly complex and has been the topic of many papers. Due to this complexity, we seek a simplification of the model that preserves the oscillatory and other dynamics of the reaction, which is where the Oregonator comes in. The Oregonator models the BZ reaction through the following reaction scheme [4]:



Where A, B are the reactant species whose concentrations do not change during the reaction, X, Y, Z are the species that undergo oscillatory dynamics, and P, Q are the product species and are insignificant in our simulations. f is the stoichiometric factor and, for the sake of simulation, will be simplified by setting $f = 1$, though the code allows for different integer values of f (see appendix A and B).

I will derive the stiff systems of differential equations that govern the reaction dynamics and simulate this macroscopic system using MATLAB’s variable order solver for stiff differential equations. Note that stiffness will not be proven. The microscopic system will also be simulated and studied using, in part, the law of mass action. I aim to empirically study three properties:

1. Behavior of the oscillating trajectory, *i.e.* whether it’s attracting or repelling.
2. Convergence of microscopic model to macroscopic model as volume of system tends to infinity.
3. Instability of the steady state.

2 Equations

Before derivations and equations, we first define a few terms:

k_i : The reaction rate constant for reaction $i, i \in \{1, \dots, 5\}$. Units are $M^{-1} \text{sec}^{-1}$ for $i \in \{1, \dots, 4\}$ and sec^{-1} for $i = 5$, where M is a measure of concentration (commonly moles per liter). We use the following values, which were experimentally determined in [4]:

$$k_1 = 1.34 M^{-1} \text{sec}^{-1}$$

$$k_2 = 1.6 \times 10^9 M^{-1} \text{sec}^{-1}$$

$$k_3 = 8 \times 10^3 M^{-1} \text{sec}^{-1}$$

$$k_4 = 4 \times 10^7 M^{-1} \text{sec}^{-1}$$

$$k_5 = 1 \text{sec}^{-1}$$

Note that M is a measure of concentration (commonly moles per liter).

X : Refers to concentration of the chemical species X .

N_X : Refers to the number of molecules of X .

V : Refers to the volume of the microscopic system.

2.1 Macroscopic Model

Formula 1 (System of Differential Equations).

$$\begin{aligned}\frac{dX}{dt} &= k_1AY - k_2XY + k_3BX - 2k_4X^2 \\ \frac{dY}{dt} &= -k_1AY - k_2XY + f k_5Z \\ \frac{dZ}{dt} &= k_3BX - k_5Z\end{aligned}$$

Derivation. We assume that for each reaction from R1 to R5, the partial orders of reactions are all 1 which has been confirmed empirically in [4]. *i.e.* for general reactions of the form $aA + bB \longrightarrow C$ with rate constant k , the rate equation is $kabAB$. For dX/dt , we look through reactions R1 to R5 and sum the rate equations of reactions in which X is involved (if X is a product, the sign of the rate equation is inverted):

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

The equations for dY/dt and dZ/dt follow from the same procedure above.

These equations govern the rate at which the concentration for each primary species will change, and are fundamental to our macroscopic model. Given the initial conditions X_0, Y_0, Z_0 and parameters f , we will solve/simulate the system to see oscillatory behavior (see section 3).

2.2 Microscopic Model

On the microscopic scale, we needn't use the differential equations, instead basing our equations on the law of mass action. Instead of using concentrations of chemical species (say X), we use number of molecules (N_X) independently of volume of system (V) and inspect the system reaction by reaction. The rate at which the reactions occurs for this microscopic system is determined as follows:

Formula 2 (Microscopic Rate Equations).

$$\begin{aligned}\text{Rate}_1 &= k_1 N_A N_Y / V \\ \text{Rate}_2 &= k_2 N_X N_Y / V \\ \text{Rate}_3 &= k_3 N_B N_X / V \\ \text{Rate}_4 &= k_4 N_X (N_X - 1) / V \\ \text{Rate}_5 &= k_5 N_Z\end{aligned}$$

Derivation. Given the generic chemical reaction $A + B \longrightarrow C$, let r be the probability per unit time that the above reaction occurs. This term is affected by the V . Now, the expected number of reactions per unit time will be $\text{Rate} = r N_A N_B$. We divide by V to get the expected number of reactions per unit volume per unit time:

$$\frac{r N_A N_B}{V} = r V \frac{N_A}{V} \frac{N_B}{V} = (r V) A B$$

Now, using the macro rate equation from the derivation of formula 1, we have $r = \frac{k}{V}$, where k is the rate constant. Finally, we substitute the above equation and arrive at

$$\text{Rate} = k N_A N_B / V$$

Remark. In the microscopic rate equation for reaction R4, we have $N_X(N_X - 1)$ rather than N_X^2 . This is because the number of pairs for $X + X \longrightarrow Q$ is $N_X(N_X - 1)/2$ through a counting argument, and we get $r N_X(N_X - 1)/(2V) = k X^2$. Using the same argument and the approximation that $(N_X - 1)/V \approx X$, we get $r = 2k/V$ which cancels out the factors of 2.

The above equations, along with the fluctuations in the number of molecules in the system, will be the sole drivers of the oscillatory behavior in the microscopic model.

3 Numerical Method

In the implementations of the macroscopic and microscopic models, a few details should be noted. The equations formula 1 can be simplified through substitution of variables to a simpler and better scaled system. The drawback is that these variables are dimensionless and have no physical meaning, we want to preserve the dimensions so that we can observe convergence of the microscopic model to the macroscopic model numerically instead of visually. A problem that comes with preserving dimensions is scaling, which can be demonstrated by an example: if you are simulating 1mm^3 of chemical A with concentration of 0.06 mol/L , we would have $0.06 \times 6.022 \times 10^{23} / 10^6 = 3.61 \times 10^{16}$ molecules in the system, an overwhelming number. To solve this, we work with minuscule reference volumes such as $10^{-16} L$ (as used in appendix A and B). As such, the rate constants must be scaled accordingly to our chosen reference volume.

3.1 Macroscopic Model

Usually, to simulate formula 1, we would use standard techniques such as the backwards Euler method. However, formula 1 is a known stiff differential equation, *i.e.* certain numerical methods for solving the equation are numerically unstable [1]. To combat this, we use MATLAB’s ode15s solver, which employs a variable-step, variable-order solver based on numerical differentiation formulas of orders 1 through 5 [5]. The details of how ode15s works is beyond the scope of this project.

3.2 Microscopic Model

We use stochastic simulation for our microscopic model. When we say state, we refer to the row vector $N \in \mathbb{Z}^{1 \times 5}$, $N = [N_A \ N_B \ N_X \ N_Y \ N_Z]$. To calculate rates and time until next reaction, we have $\text{Rate}(\vec{N}) = [\text{Rate}_1(\vec{N}) \ \dots \ \text{Rate}_5(\vec{N})]$ from formula 2, and want to describe the probability distribution for the time until next reaction for our stochastic simulation. If we have Rate for a general chemical reaction $A + B \longrightarrow C$, then the time T until a reaction occurs has an exponential distribution with rate parameter $\lambda = \text{Rate}$ and mean $\mathbb{E}[T] = 1/\text{Rate}$. To sample from $\text{Exp}(\text{Rate})$, we use $-\log(\text{rand})/\text{r}$, where $\text{rand} \sim U(0, 1)$. This is because $-\log(\text{rand})$ is an exponential distribution supported on $(0, \infty)$ with mean 1, so multiplying by $1/\text{Rate}$ yields our desired distribution. One can also specify dimensions such as $\text{rand}(1,5)$ to generate vectors and matrices such that all entries are uniformly distributed in $(0, 1)$. We also have a matrix $\text{dN} \in \mathbb{Z}^{5 \times 5}$ such that row i is comprised of immediate changes to the state after reaction i occurs in R1 - R5, *e.g.* $\text{dN}(:, 1) = [-1 \ 0 \ 1 \ -1 \ 0]$.

Given a maximum simulation time of t_{\max} , initial conditions $N_{X_0}, N_{Y_0}, N_{Z_0}$, parameters f, V , and constants, we employ the following algorithm:

Algorithm 1 Microscopic Stochastic Algorithm

```

 $t \leftarrow 0$ 
while  $t < t_{\max}$  do
     $\vec{T} \sim -\log(\text{rand}(1, 5))/\text{Rate}(\vec{N})$   $\triangleright$  “ $\sim$ ” here is sampling, “/” is element-wise division
     $T_{\min} \leftarrow \min_{i \in \{1, \dots, 5\}} \{T_i\}$   $\triangleright \vec{T} = [T_1 \ \dots \ T_5]$ 
     $K_{\min} \leftarrow \arg \min_{i \in \{1, \dots, 5\}} \{T_i\}$ 
     $\vec{N} \leftarrow \vec{N} + \text{dN}(:, K_{\min})^\top$   $\triangleright$  Transpose for dimension matching
     $t \leftarrow t + T_{\min}$ 
end while

```

Note that the notation “ \sim ” is overloaded in this section, meaning it can stand for both “is distributed as” and “is sampled from.”

4 Validation

In order to empirically verify correctness of our models, we will check local results against known results in literature as well as scale up the volume of system to verify convergence of results to that of the macroscopic theory for our macroscopic and microscopic models, respectively.

4.1 Validation of Macroscopic System via Stable Point

We can find a steady state or stable point for the system of differential equations by setting $dX/dt = dY/dt = dZ/dt = 0$ and solving this system of equations. The values obtained are

$$\begin{aligned} X_0 &= 2.4556 \times 10^{-8} \\ Y_0 &= 2.9939 \times 10^{-7} \\ Z_0 &= 1.1787 \times 10^{-5} \end{aligned}$$

which will be used as our initial concentrations.

For reference, we compare our steady state system with an oscillating system with initial concentrations $X_0 = 2.5125 \times 10^{-8}$, $Y_0 = 3 \times 10^{-7}$, $Z_0 = 1.206 \times 10^{-5}$:

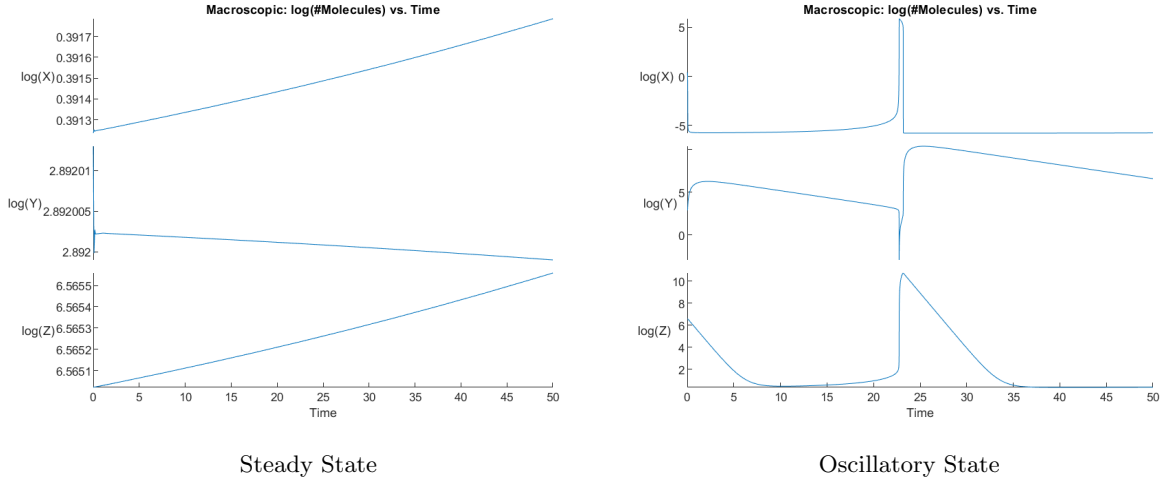


Figure 1: Steady State Validation and Discrimination

We have validated that indeed, our macroscopic system evolves identically to the theoretical system.

Remark. This steady state is actually chaotic and unstable [4], *i.e.* small perturbations in the steady state initial concentrations such as $\widetilde{X}_{ss} = X_{ss} + \epsilon, \epsilon \ll 1$ leads to large deviations from the system with X_{ss} as initial concentration (X_{ss} stands for steady-state concentration of species X) (refer to section 5.1).

4.2 Validation of Microscopic System via Convergence

As mentioned in section 1, we will scale up V and check that the microscopic model converges to the macroscopic model as the stochastic noise is reduced for larger V . Specifically, a fourfold increase in V will lead to a halving of the stochastic noise, so we will increment V by powers of 4. We choose a reference volume of $10^{-17} L$, system volumes of $V \in \{4^0, \dots, 4^5\}$, and initial concentrations of $X_0 = 2.5125 \times 10^{-8}$, $Y_0 = 3 \times 10^{-7}$, $Z_0 = 1.206 \times 10^{-5}$. Note that we use concentrations in the microscopic model, which is then converted to the number of molecules via the equation $N_X = XV$ (X is in our reference volume units), so that we maintain the same parameters as our macroscopic model.

For reference on convergence, below is a graph of the macroscopic model under the same initial conditions:

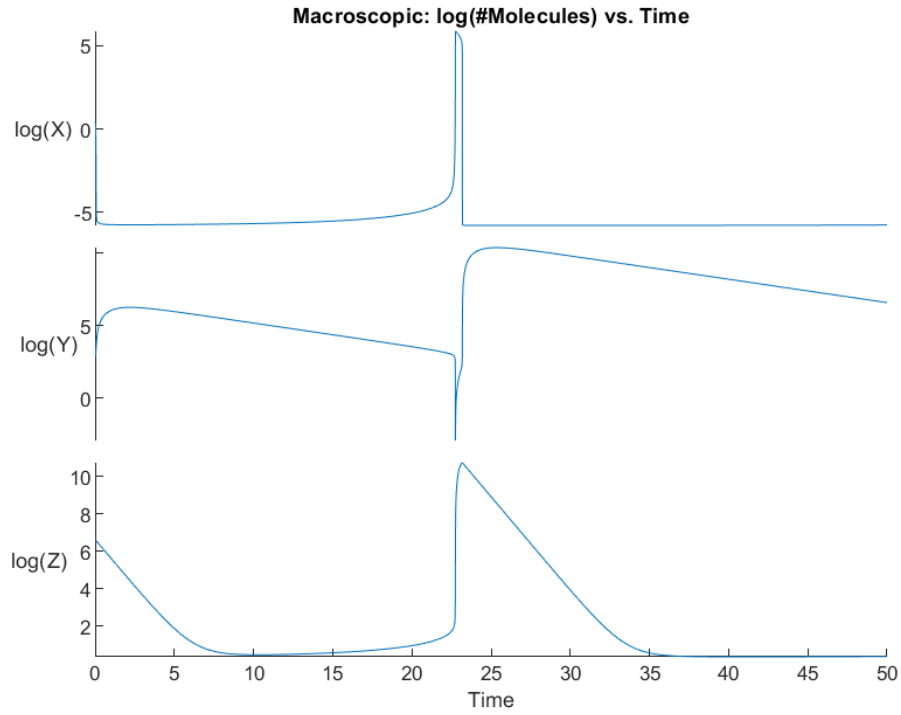
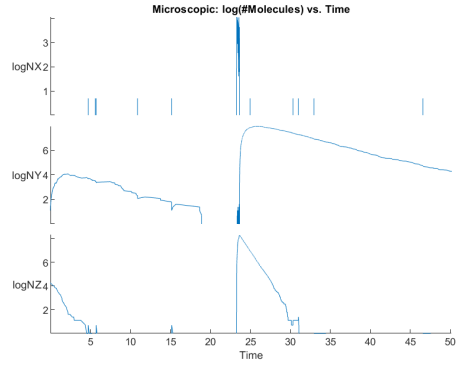
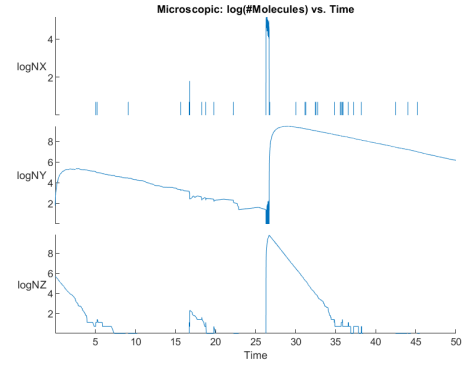


Figure 2: Reference Macroscopic Dynamic

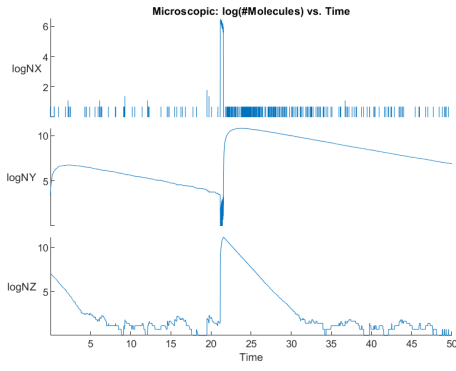
Below are graphs of the microscopic system for varying V :



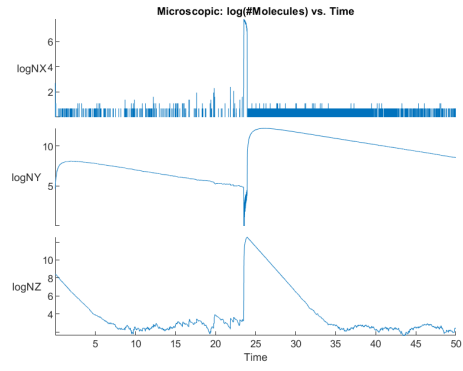
$$V = 4^0$$



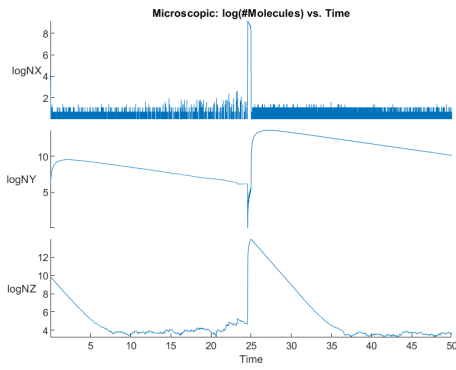
$$V = 4^1$$



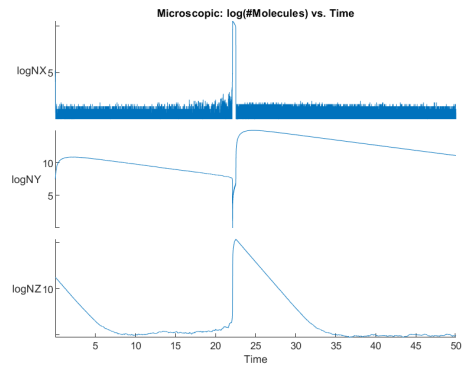
$$V = 4^2$$



$$V = 4^3$$



$$V = 4^4$$



$$V = 4^5$$

Figure 3: Convergence of Microscopic System

Examining figure 3 with respect to figure 2, we see that the increase of V indeed smooth out the noise. Note that $\log(N_X)$ jumps between 0 and 1 a lot as X is often found in low quantities (~ 5) and the stochastic noise oscillates it around that range, causing the jumps. Other than this insignificant detail, we have empirically shown that this convergence holds, thereby answering one of the three questions that this project sought to answer in section 1.

5 Results and Discussion

As question 2 in section 1 has been answered in section 4.2 through the systematic variation of V , we focus our attention on the macroscopic model to determine if our oscillation (or periodic trajectory in \mathbb{R}^3) is attracting. To do so, we choose two parameters: step size ε and number of steps n_s . Then, we construct a 3D cubic lattice in the $\log(X), \log(Y), \log(Z)$ basis defined by the following set:

$$S(\varepsilon, n_s) := \{\varepsilon^k : k \in \{0, \dots, n_s\}\} \times \{\varepsilon^k : k \in \{0, \dots, n_s\}\} \times \{\varepsilon^k : k \in \{0, \dots, n_s\}\}$$

Now, for all $\vec{x} = [X_0 \ Y_0 \ Z_0] \in S(\varepsilon, n_s)$, we solve formula 1 with initial values \vec{x} and plot it to see whether it is pulled into the periodic trajectory.

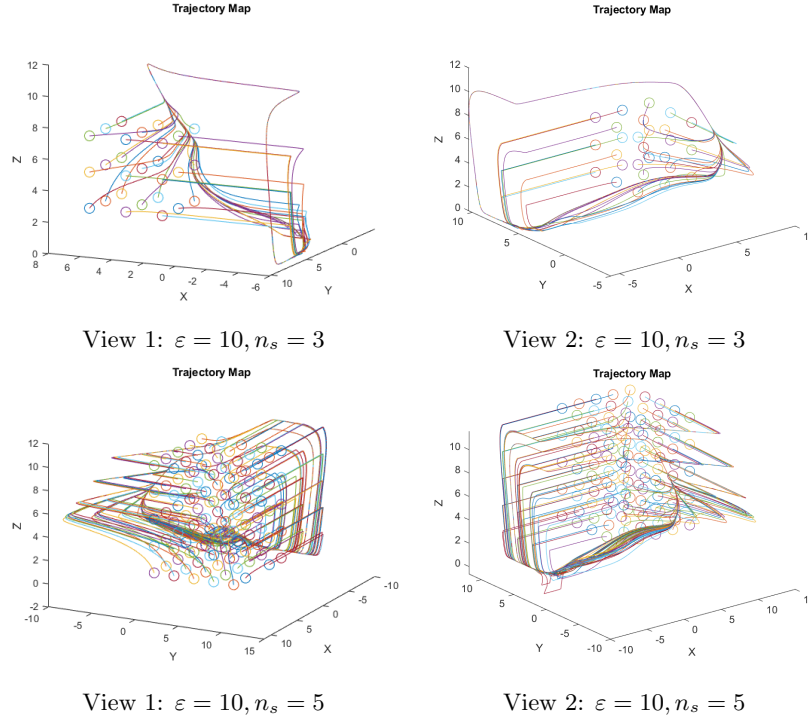


Figure 4: Attractiveness of Periodic Trajectory

Note that the circles are the positions of initial concentrations. Also, the axis labels in figure 4 should

be $\log(X), \log(Y), \log(Z)$ instead of X, Y, Z . Based on figure 4, we see strong empirical evidence that the periodic trajectory, or oscillatory behavior, is indeed attracting.

5.1 Instability of Steady State

Recall our validation method for the macroscopic system in section 4.1. In this section, we empirically verify the instability of the steady state for formula 1 by introducing perturbations around the steady state. Let \vec{x}_{ss} be the vector of initial concentrations of the steady state (with respect to some reference volume), we introduce perturbations of the form $\vec{x}_{ss} + \varepsilon$, where $\|\varepsilon\|_2 \leq r$ for some $r \ll 1$.

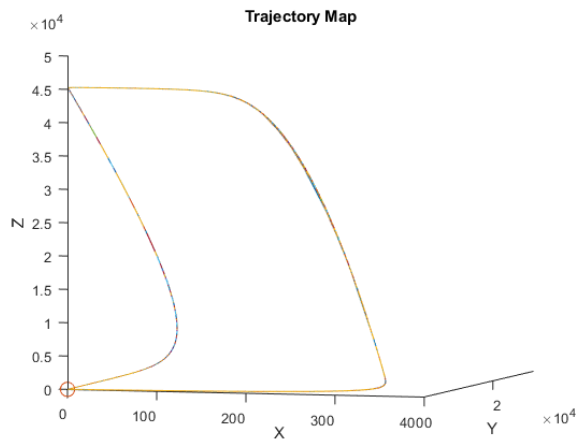


Figure 5: Instability of the Steady State ($r = 0.1$)

Remark. In figure 5, the presence of a periodic trajectory (rather than a single point) implies that the perturbations did, in fact, lead to large deviations in the behavior of the system.

6 Summary and Conclusions

In order to study the properties of the Belousov-Zhabotinsky reaction, we introduced the Oregonator model, allowing for simplification and implementation using both macroscopic and microscopic theory. We have empirically shown

- (1) Convergence of the microscopic model to the macroscopic model with respect to volume of system.
- (2) Attractiveness of the oscillatory trajectory.
- (3) Instability of the steady state.

References

- [1] Richard L. Burden and J. Douglas Faires. *Numerical Analysis*. Wadsworth Publishing Company, fifth edition, 1 1993.
- [2] Irving R Epstein and John A Pojman. *An Introduction to Nonlinear Chemical Dynamics: Oscillations, Waves, Patterns, and Chaos*. Oxford University Press, 11 1998.
- [3] R. J. Field. Oregonator. *Scholarpedia*, 2(5):1386, 2007. revision #91613.
- [4] 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.
- [5] L. F. Shampine and M. W. Reichelt. The MATLAB ODE Suite. *SIAM Journal on Scientific Computing*, 18:1–22, 1997.

A MATLAB Code for Macroscopic System

```

clear all
close all

% Author: Ya Shi (Andrew) Zhang — yashi.zhang@nyu.edu
% Simulate the Belousov–Zhabotinsky Reactions through
% the Oregonator scheme
% i.e. reactions of the form:
% (I)  $A + Y \rightarrow X$  | Rate K1
% (II)  $X + Y \rightarrow P$  | Rate K2
% (III)  $B + X \rightarrow 2X + Z$  | Rate K3
% (IV)  $2X \rightarrow Q$  | Rate K4
% (V)  $Z \rightarrow fY$  | Rate K5
% Where P, Q are products of reaction, f is the stoichiometric
% factor (defaulted to 1 in literature), X is HBrO2, Y is Br(–),
% Z is Ce(4+), and both A and B are BrO3(–). P and Q do not need
% to be modeled as they are products of the reaction.

% Reference Volume
refV = 1e16;
% Avogadro's Constant
NA = 6.02214076e23;
% Time
tspan = [0 100];
% Initial Concentration of [X Y Z] measured in #Molecules/mm3
alpha = 500;
eta = 1;
row = 500;
y0 = [5.025e-11*alpha 3e-7*eta 2.412e-8*row] * (NA/refV);
%[alpha eta row] = [488.68 0.99796 488.68] is an unstable steady state

[t,y] = ode15s(@Oregonator,tspan,y0); % Dynamic Eq. is stiff

% Normal log concentration plot
labels = ["log(X)", "log(Y)", "log(Z)"];
stackedplot(t,log(y), "Title", "Macroscopic: log(#Molecules) vs. Time",...
    "DisplayLabels", labels, "xlabel", "Time")
saveas(gcf,'macro.png');

%figure
%logy = log(y);
% 3d trajectory plot
%plot3(logy(:,1),logy(:,2),logy(:,3));

```

```

function dydt = Oregonator(t,y)
    % Reference Volume
    refV = 1e16;
    % Avogadro's Constant
    NA = 6.02214076e23;
    % Parameter values taken from Oscillations in chemical systems
    % Vector of macro rate constants (1/(# Molecules*Sec))
    k = [1.34 1.6e9 8e3 4e7 1*(NA/refV)] / (NA/refV);
    % Concentrations of [A] and [B] in #Molecules/mm^3
    A = 0.06 * (NA/refV);
    B = 0.06 * (NA/refV);
    % Stoichiometric constant of Y in reaction V
    f = 1;

    dydt = zeros(3,1);
    dydt(1) = k(1)*A*y(2) - k(2)*y(1)*y(2) + k(3)*B*y(1) - 2*k(4)*y(1)*y(1);
    dydt(2) = -k(1)*A*y(2) - k(2)*y(1)*y(2) + f*k(5)*y(3);
    dydt(3) = k(3)*B*y(1) - k(5)*y(3);
end

% Sources: Refer to paper

```

B MATLAB Code for Microscopic System

```

clear all
close all

% Author: Ya Shi (Andrew) Zhang — yashi.zhang@nyu.edu
% Simulate the Belousov–Zhabotinsky Reaction through
% the Oregonator scheme for chemical reactions
% i.e. reactions of the form:
% (I) A + Y → X          | Rate K1
% (II) X + Y → P          | Rate K2
% (III) B + X → 2X + Z   | Rate K3
% (IV) 2X → Q            | Rate K4
% (V) Z → fY             | Rate K5
% Where P, Q are products of reaction, f is the stoichiometric
% factor (defaulted to 1 in literature), X is HBrO2, Y is Br(−),
% Z is Ce(4+), and both A and B are BrO3(−). P and Q do not need
% to be modeled as they are products of the reaction.

refV = 1e17; % Reference Volume
tmax = 50; % Maximum Time
f = 1; % Stoichiometric Factor
NA = 6.02214076e23; % Avogadro's Constant
K = [1.34 1.6e9 8e3 4e7 1*(NA/refV)] / (NA/refV); % Vector of Macro Rate Constants [K1
V = 4^3; % Volume of System
N = zeros(1,5); % State of system
% Initial Number of Chemicals (Converted from dimensionless variables in
% [1]). [alpha eta row] = [488.68 0.99796 488.68] is unstable steady state.
alpha = 500;
eta = 1;
row = 500;
N(1) = 0.06 * (NA/refV) * V; N(1) = round(N(1)); % #Molecules of A
N(2) = 0.06 * (NA/refV) * V; N(2) = round(N(2)); % #Molecules of B
N(3) = alpha * 5.025e−11 * (NA/refV) * V; N(3) = round(N(3)); % #Molecules of X
N(4) = eta * 3e−7 * (NA/refV) * V; N(4) = round(N(4)); % #Molecules of Y
N(5) = row * 2.412e−8 * (NA/refV) * V; N(5) = round(N(5)); % #Molecules of Z

% Change in N when reaction j happens (from I to V)
dN = zeros(5,5);
dN(:,1) = [−1 0 1 −1 0];
dN(:,2) = [0 0 −1 −1 0];
dN(:,3) = [0 −1 1 0 1];
dN(:,4) = [0 0 −2 0 0];
dN(:,5) = [0 0 0 f −1];

```

```

timestate    = zeros(1e8,1);
systemstate  = zeros(1e8,5);

% Main Loop
t = 0;
eventcounter = 1;
while t < tmax
    rate = rates(N,K,V);
    T = (-log(rand(1,5)))./rates(N,K,V);
    [Tmin, Kmin] = min(T);
    N = N + dN(:,Kmin)';
    systemstate(eventcounter,:) = N;
    t = t + Tmin;
    timestate(eventcounter) = t;
    eventcounter = eventcounter + 1;
end

labels       = ["logNX", "logNY", "logNZ"];
stackedplot(timestate(1:eventcounter-1),...
    log(systemstate(1:eventcounter-1,3:5)),...
    "Title", "Microscopic: log(#Molecules) vs. Time",...
    "DisplayLabels", labels, "xlabel", "Time")
saveas(gcf, 'micro.png');

%figure
%plot(timestate(1:eventcounter-1), systemstate(1:eventcounter-1,3), ...
%     'DisplayName', 'X', 'Color', 'r');
%title('NX vs. Time');
%saveas(gcf, 'microX.png');
%figure
%plot(timestate(1:eventcounter-1), systemstate(1:eventcounter-1,4), ...
%     'DisplayName', 'Y', 'Color', 'g');
%title('NY vs. Time');
%saveas(gcf, 'microY.png');
%figure
%plot(timestate(1:eventcounter-1), systemstate(1:eventcounter-1,5), ...
%     'DisplayName', 'Z', 'Color', 'b');
%title('NZ vs. Time');
%saveas(gcf, 'microZ.png');

function rates = rates(N,K,V)
% Takes in the current state of the system (N)
% as well as the vector of reaction coefficients (K)
% to output the probability per unit time that each

```

```

% reaction will occur.
% This specific rate function is for the Oregonator
% class of oscillating chemical reactions

rate1 = abs(K(1) * N(1) * N(4) ) / V; % (K1/V)*NA*NY
rate2 = abs(K(2) * N(3) * N(4) ) / V; % (K2/V)*NX*NY
rate3 = abs(K(3) * N(2) * N(3) ) / V; % (K3/V)*NB*NX
rate4 = abs(K(4) * N(3) * (N(3)-1)) / V; % (K4/V)*(NX)*(NX-1)
rate5 = abs(K(5) * N(5)); % K5*NZ

rates = [rate1 rate2 rate3 rate4 rate5];
end

% Sources: Refer to paper

```