

An Overview of the Belousov-Zhabotinsky Chemical Oscillations

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This paper reviews the Belousov-Zhabotinsky reaction and the Oregonator. Specifically, this paper explores how the Oregonator captures the characteristic behaviors of the Belousov-Zhabotinsky reaction through the existence of the limit cycle and excitability. The paper also briefly discusses the history and significance of the Belousov-Zhabotinsky reaction.

I. INTRODUCTION

The Belousov-Zhabotinsky (BZ) reaction, named after Soviet chemists Boris Belousov (1893 - 1970) and Anatol Zhabotinsky (1938 - 2007), are an important example of a large class of chemical oscillators. The reaction was first discovered by Belousov in 1951 in his attempt to mimic glycolysis, an oscillatory biochemical process in which glucose is metabolized. Using a mixture of potassium bromate, cerium(IV), sulfate, malonic acid, and citric acid in dilute sulfuric acid at appropriate proportions, Belousov found that the solution color spontaneously oscillated between clear and yellow rather than reaching an equilibrium state. This behavior was so peculiar that Belousov's contemporaries refused to publish his results, citing the apparent violation of the second law of thermodynamics, which states that a system must attain a preferred equilibrium state [1]. Belousov ultimately managed to publish his results, but in a less reputed and non-peer-reviewed journal. Belousov's reaction was further studied in 1961 by Zhabotinsky and only gained popularity in the Western scientific community after a conference in Prague in 1968[2].

Today, the BZ reaction remains popular among academics. It is not only a prime example for non-equilibrium thermodynamics but is also a nonlinear system which exhibits excitability and oscillatory behaviors. Following its emergence into the scientific canon, mathematical models for the reaction also attract significant interest. The most notable examples of these models are the *Brusselator*, proposed by Ilya Prigogine and his collaborators at the Universit Libre de Bruxelles, and the *Oregonator*, proposed by Richard Field and Richard M. Noyes at the University of Oregon. While the Brusselator helped motivate interest in chemical pattern formation, it does not model a realistic BZ reaction. The Oregonator, on the other hand, captures many aspects of a true chemical oscillator including limit cycle and dynamics and excitability.

When taking place in an appropriate geometry, the BZ reaction becomes a *reaction-diffusion system* which gives rise to pattern-forming *chemical waves* [1]. Unlike sound waves or electromagnetic radiation, however, these waves

do not interfere the same way sound of electromagnetic waves do, i.e., they do not obey the principles of superposition. In a different setting, the BZ reaction manifests as oscillations. This paper treats focuses mainly on BZ oscillations with an emphasis on the Oregonator, a mathematical model for the reaction.

II. THE OREGONATOR

The Oregonator is a system of two coupled ordinary differential equations [3]:

$$\epsilon \dot{U} = U(1-U) - fV(U-q)/(U+q) \quad (1)$$

$$\dot{V} = U - V \quad (2)$$

where U, V represent the concentrations of HBrO_2 and Ce^{4+} , respectively. The Oregonator provides a realistic mechanism linking limit cycle dynamics to a real-world chemical oscillator. The equilibrium concentrations are attained whenever $\dot{U} = \dot{V} = 0$. These solutions are given by the following expressions:

$$U_{\text{eq}} = \frac{1}{2} \left[1 - q - f + \sqrt{(1 - q - f)^2 + 4q(1 + f)} \right]$$
$$V_{\text{eq}} = U_{\text{eq}}. \quad (3)$$

The equilibrium solutions are given by intersecting the following the nullclines $\dot{U} = 0$ and $\dot{V} = 0$:

$$V = \frac{U(1-U)(U+q)}{f(U-q)} \quad (4)$$

$$V = U \quad (5)$$

It is clear that the first nullcline depends only on the parameters f and q , and the second nullcline is independent of all model parameters. For the rest of this paper, we will assume q is fixed unless stated otherwise. As we will see later, by varying f , the model exhibits markedly different behaviors.

A. Limit Cycle

The Oregonator captures the oscillatory behavior of the BZ reaction through the existence of the *limit cycle* for certain combinations of the parameters f, q , and ϵ . A

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limit cycle is an attractor, a solution for the Oregonator towards which the system tends to evolve in the large-time limit, which shows up as a closed trajectory in phase space. When a limit cycle is present, the system converges to no fixed point.

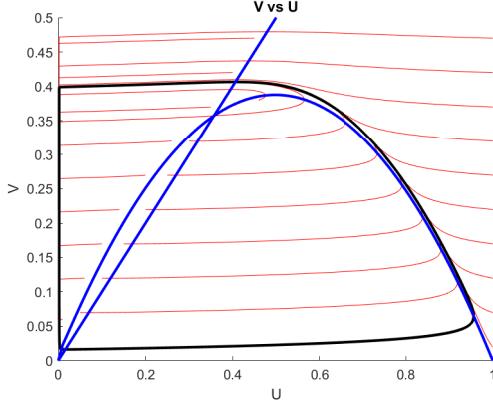


FIG. 1: Limit cycle (black) and nullclines (blue), for $f = 0.65, \epsilon = 10^{-2}, q = 0.002$. All trajectories converge to the limit cycle, including points near the equilibrium solution. Points to left of the $V = U$ nullcline converge the limit cycle from the right, and vice versa. The system does not converge to a fixed point.

Figure 1 shows the phase portrait of the system at $f = 0.65, \epsilon = 10^{-2}$, and $q = 0.002$. All phase trajectories, except for the equilibrium trajectory at $U_{\text{eq}} = V_{\text{eq}} = 0.3572$ (which is the intersection between two nullclines highlighted in blue), converge to the counter-clockwise limit cycle highlighted in black. All trajectories which begin below the parabolic nullcline first evolve towards an increase in U , while those above the parabolic nullcline first evolve towards a depletion in U . For example, Figure 2 shows how the system evolves following the initial condition given by $U_0 = 0.2, V_0 = 0.26$.

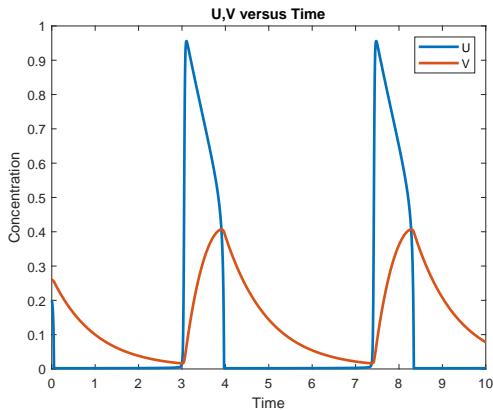


FIG. 2: Oscillations in concentration of U, V in time is the presence of a limit cycle. The system evolves from the initial condition $U_0 = 0.2, V_0 = 0.26$

Just to emphasize the fact that *all* trajectories, no matter how close to the equilibrium solution, converge the limit cycle, we consider the initial condition $U_0 = U_{\text{eq}} + 10^{-7}$ and $V_0 = V_{\text{eq}} + 4 \times 10^{-8}$. To put into context, this initial condition corresponds to the just some trace perturbation from the equilibrium solution. Figure 3 shows that this slight perturbation from the equilibrium sends the system into an oscillation. Thus, it is clear that in reality, one almost never observes the equilibrium state of the system when the model parameters are right for the limit cycle to appear.

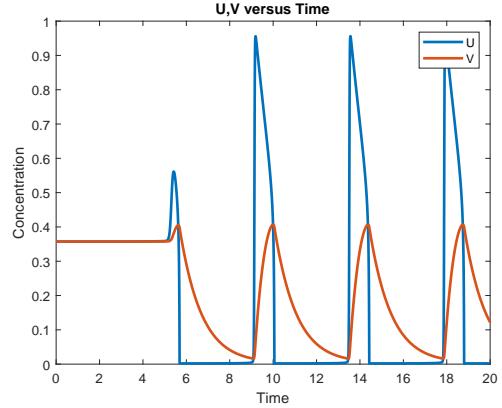


FIG. 3: Oscillations in concentration of U, V in time is the presence of a limit cycle. The system evolves from the initial condition $U_0 = U_{\text{eq}} + 10^{-7}, V_0 = V_{\text{eq}} + 4 \times 10^{-8}$

B. Hopf Bifurcation

The Hopf bifurcation, in the context of this paper, is a critical point in the parameter space (f, q, ϵ) at which the limit cycle appears. So far, we have assumed that $f = 0.65, \epsilon = 10^{-2}$, and $q = 0.002$, at which point the model has a limit cycle shown in Figure 1. For simplicity, let us assume that q, ϵ are fixed. By varying f , we will see that the limit cycle disappears when f is too small or too large. For example, consider the case where $f = 2.45$. Figure 4 shows that solutions now converge to fixed point. f is too large, and the limit cycle no longer exists.

The limit cycle also disappears when f is too small. Consider the case where $f = 0.505$. The initial condition $U_0 = V_0 = 0.6$ evolves and spirals towards the fixed point shown in Figure 5. To see how the system reaches a stable equilibrium in the large-time limit, we can also look at how U evolves in time in Figure 6.

It is possible to map out all the combinations of (f, q, ϵ) for which the Oregonator has a limit cycle. This can be done through careful stability analysis of the Oregonator as well as numerics. For the sake of simplicity, however, we will not cover how this is done.

The Hopf bifurcation is not unique to the Oregonator. Not surprisingly, this bifurcation also appears in the BZ

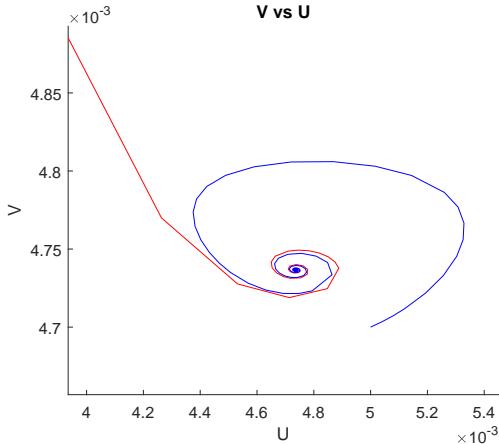


FIG. 4: $f = 2.45$. Solutions converge to a stable fixed point: the red line denotes initial condition $U_0 = V_0 = 4 \times 10^{-3}$; the black line denotes the initial condition $U_0 = 5 \times 10^{-3}, V_0 = 4.7 \times 10^{-3}$.

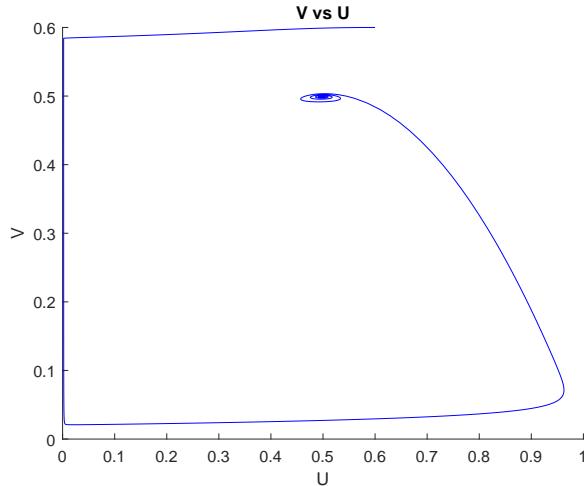


FIG. 5: $f = 0.505$. Solutions converge to a stable fixed point: the red line denotes initial condition $U_0 = V_0 = 4 \times 10^{-3}$; the black line denotes the initial condition $U_0 = 5 \times 10^{-3}, V_0 = 4.7 \times 10^{-3}$.

reaction, as well as in the Brusselator, the Hodgkin-Huxley model, and the FitzHugh-Nagumo model. In fact, these models are closely related and share a number of common characteristics including *excitability*, which we will cover in the next subsection.

C. Excitability

An excitable system is a nonlinear system which can be characterized by the following two properties. For small perturbations away from the equilibrium state, the system responds monotonically with the perturbations. However, when the perturbation is suffi-

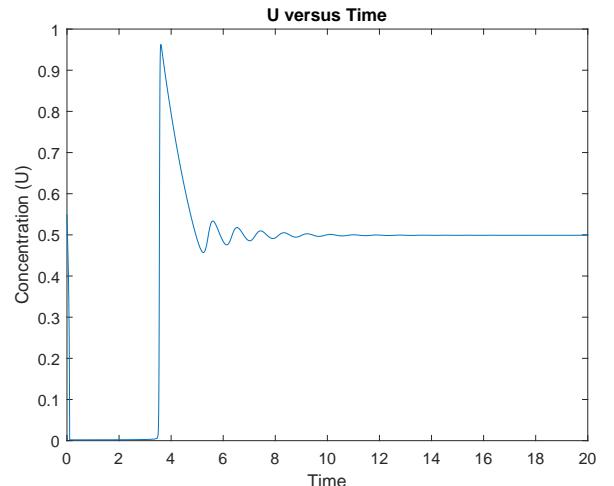


FIG. 6: $f = 0.505$. The concentration in U approaches a stable fixed point.

ciently large (beyond some threshold), the system becomes *excited* and undergoes a markedly different, more extreme, trajectory.

In this subsection we shall see that the Oregonator, under appropriate conditions, can be an excitable system. From the preceding subsections, we have seen that the Oregonator can exhibit limit cycles for certain values of (f, q, ϵ) . When a limit cycle exists, all solutions except for the equilibrium converges to the limit cycle. As a result, for any perturbation from the equilibrium state, the system eventually behaves the same way. It is thus clear that the system cannot be excitable in this case.

This leaves the only remaining possibility: the system can become excitable when no limit cycles exist. It remains for us to find evidence of excitability in the Oregonator when (f, q, ϵ) is beyond the Hopf bifurcation. To this end, we consider the combination $(f, q, \epsilon) = (3, 0.002, 0.01)$. The Oregonator in this case exhibits no limit cycle, according to the phase portrait shown in Figure 7. Solutions might follow a similar trajectory as in the case with the limit cycles, but since these trajectories are not closed curves, they are not limit cycles. Rather, all trajectories converge to the equilibrium point $(0.004, 0.004)$ of the model (Figure ??).

With these, we can now find evidence of excitability in the system. To this end, we consider how the system evolves from a neighborhood around the equilibrium solution. Particularly, we consider the set of initial conditions of the form $(U_0, V_0 - \delta)$ where $\delta \in [0, 3.7 \times 10^{-4}]$. Figure 8 shows the phase trajectories associated with these initial conditions, with the nullclines highlighted in blue. The equilibrium is again the intersection of the two nullclines. Figures 8 and 9 combined show how the system evolves under this set of initial conditions. It is clear that the system possesses two characteristically distinctive behaviors, despite having very similar initial conditions:

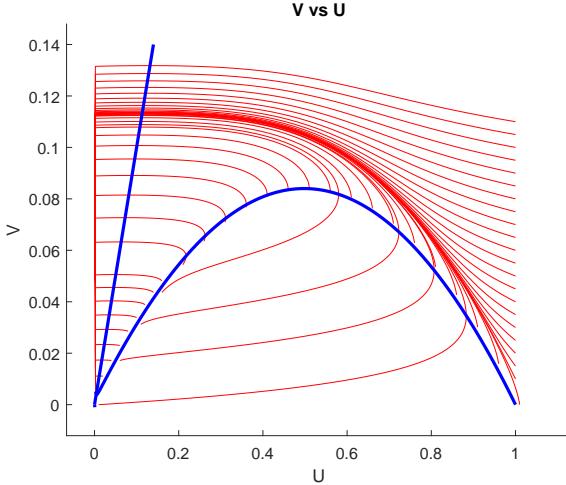


FIG. 7: No limit cycle present when $(f, q, \epsilon) = (3, 0.002, 0.01)$. All solutions converge to the equilibrium point $(0.004, 0.004)$. No phase trajectory is a closed curve.

- For small perturbations from the equilibrium, the system *immediately* returns to the equilibrium state (appearing as small convex curves above the parabolic nullcline in Figure 8). In this case we say that the system is not excited.
- When the perturbation is sufficiently large, the system undergoes a markedly different trajectory than an immediate return to the equilibrium state (appearing as D-shaped curves in Figure 9). In this case we say that the system is excited.

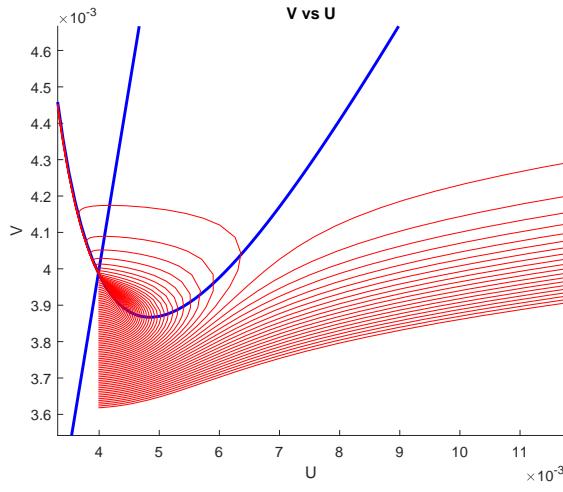


FIG. 8: How the system evolves under various initial conditions. Here $(f, q, \epsilon) = (3, 0.002, 0.01)$. The region of interest is a small neighborhood of the origin.

Figure 10 further illustrates the transition from an unexcited to an excited state of the system. When the perturbation is small, the maximum in V remains in a

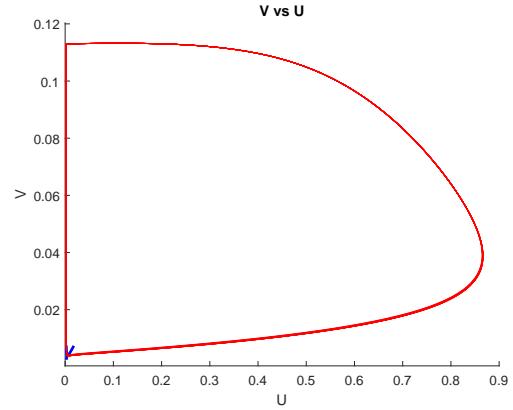


FIG. 9: How the system evolves under the same set of initial conditions. The region of interest now contains all phase trajectories generated from these initial conditions. The blue line in the bottom left corner is the linear nullcline in Figure 8.

neighborhood of the initial condition (and the equilibrium value). However, when the perturbation in V exceeds a threshold value between 2.5×10^{-4} and 3×10^{-4} , the concentration U possesses a large spike as a function of time. Since V also behaves similarly as V , in phase space we have a large D-shaped trajectory.

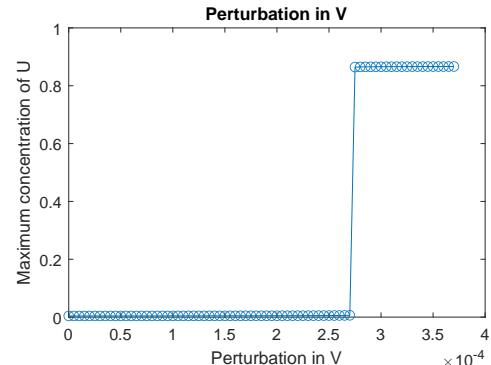


FIG. 10: Plot of the maxima in V at various perturbation amplitudes. Perturbations beyond a threshold value between 2.5×10^{-4} and 3×10^{-4} excite the system.

III. DISCUSSIONS

A. BZ reaction as real-world manifestations of the limit cycle and excitability of the Oregonator

The Oregonator captures not only the oscillatory behavior through the existence of the limit cycle but also the excitability of the BZ reaction. These two phenomena appear under different experimental settings. BZ oscillations occur when the reactants are constantly mixed in order to maintain uniform chemical concentrations

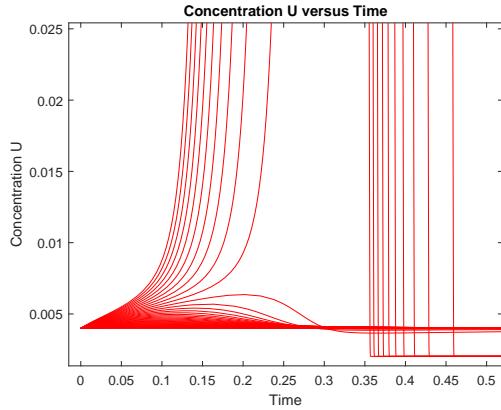


FIG. 11: Concentration U as a function of time. For perturbations beyond the threshold value, U has a large spike and eventually returns to the equilibrium value.

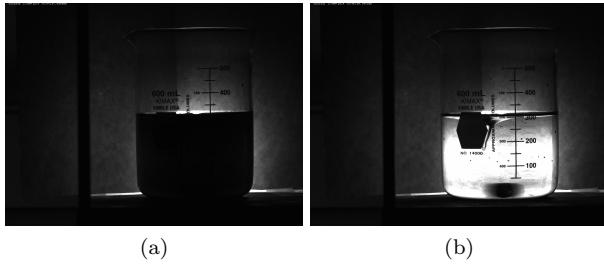


FIG. 12: The solution oscillates between the two states (a) and (b). Constant stirring is required.

throughout the medium in which the reaction takes place. Figure 12 shows a flask containing the reaction at two different points in time, and Figure 13 shows how the color of the solution oscillates in time. We notice that these oscillations occur at regular intervals, but are not strictly periodic.

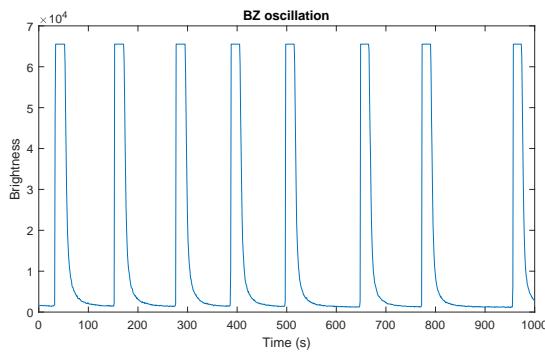


FIG. 13: Brightness of the solution in Figure 12 as a function of time. Notice that these oscillations do not occur with a constant period.

In the absence of vigorous stirring, diffusion be-

comes important, and the system becomes an excitable, pattern-forming, *reaction-diffusion system*. Figure 14



FIG. 14: The solution oscillates between the two states (a) and (b). Constant stirring is required.

shows a typical pattern and how it evolves in time.

Here, the reaction generates traveling chemical waves. Unlike sound or electromagnetic waves, these waves do not necessarily obey the principle of superposition. For instance, two BZ wavefronts annihilate each other when they meet. The pattern-forming property is due to the interplay between reaction and diffusion. Turing patterns are a classical example of patterns formed through such a process.

B. BZ reaction in Non-equilibrium thermodynamics

The second law of thermodynamics states that a system must tend towards higher entropy, i.e., coffee never unstirs itself into water, sugar, and coffee beans. This law guarantees for every chemical reaction a preferred direction towards a preferred equilibrium state. The BZ reaction, despite having seemingly perpetual oscillations, is no exception. The oscillations eventually diminish and vanish. Given sufficient time, the system will reach a stable equilibrium state at which its total entropy is higher than that before the reaction took place.

In spite of this, the BZ reaction is still interesting because of its peculiar path towards equilibrium. Likewise, many fascinating processes, such as the formation of life or the creation of societies, take place in out-of-equilibrium states. [1]

Acknowledgments

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