# Electrokinetic Manipulation of Coherent Structures in the Belousov-Zhabotinsky Reaction: Theory and Methods


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## Introduction

- The Belousov-Zhabotinsky (or B-Z) reaction is perhaps the most well-known autocatalytic chemical reaction capable of generating coherent structures far from chemical equilibrium.
- The central reaction of the B-Z system is a redox reaction altered by the presence of free bromide ($Br^-$) ions, which manifests itself as an oxidation wave in spatially heterogeneous systems.
- Using electrokinetic phenomena to manipulate the B-Z reaction has led to successful alterations of B-Z wavefronts in the reaction in simple experimental configurations.[1]
- **Coupling the chemical kinetics, hydrodynamics, and electrochemistry of the B-Z reaction through electrokinetic manipulation targeting the free ions can generate novel phenomena in the system.**

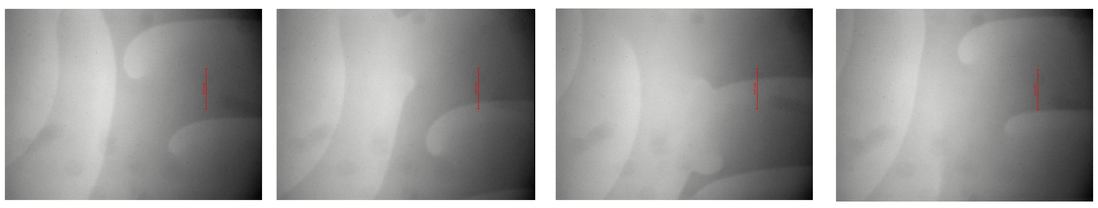
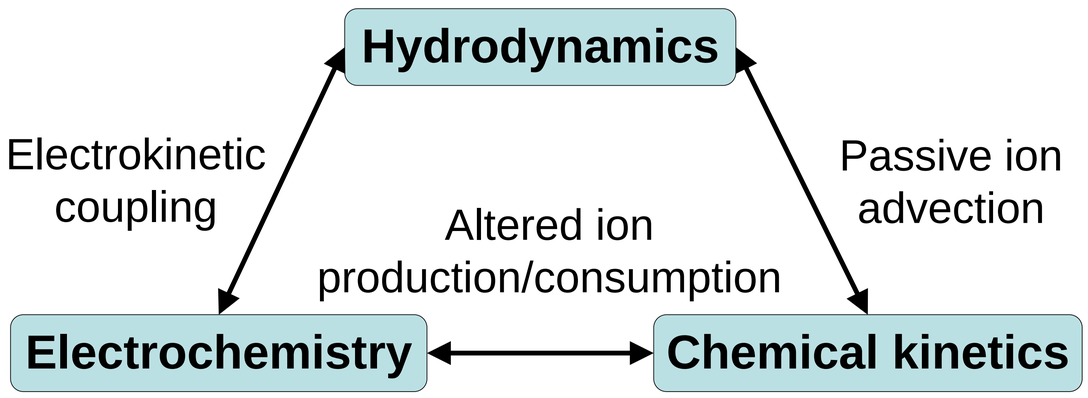


Fig. 1: Time-lapse of B-Z reaction in 50 μm thick microchannel. Bright regions represent oxidation wave reaction mentioned above. Red scale bar is 500 μm.
Complex coherent structure formed by B-Z oxidation wave shown is temporally periodic.

## Mathematical Modeling




- The dynamics of the reagent concentrations $c_i$ can be modeled through a series of reaction-advection-diffusion equations.
- Each component of the equation is coupled to each other through a combination of hydrodynamical, electrochemical, and kinetic effects.
- The equations can be simplified by tracking the projection of a solution onto the space of functions describing a specific coherent structure (like a spiral wave), transforming the equations from a system of PDE's to a system of ODE's.

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (c_i[v + v_i] - D_i \nabla c_i) = R_i(c_{1,2}, \dots)$$

**Advection** **Diffusion** **Reaction**

## Experimental Methods

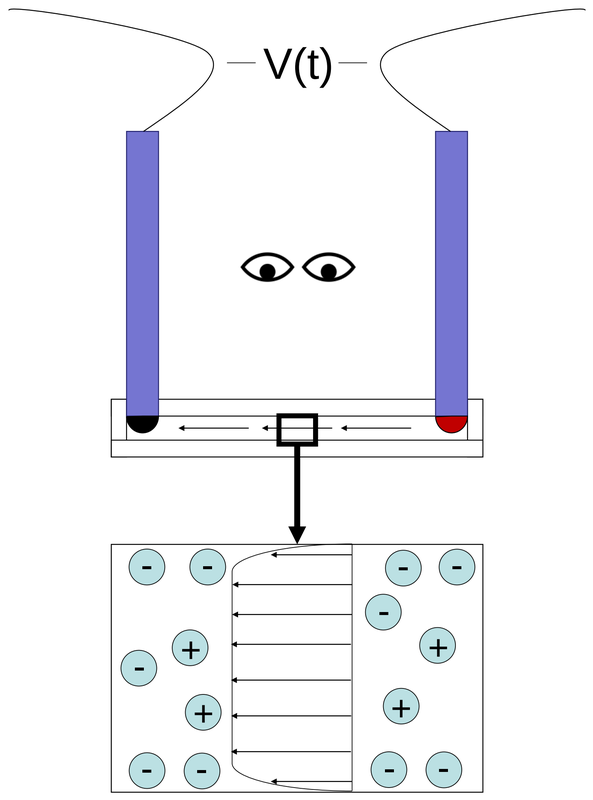



Fig. 2: Schematic of experimental setup, with silver-silver bromide electrodes junctioned across a microchannel filled with B-Z reagents. Observation of coherent structures is top-down. Inset shows sketch of typical fluid velocity profile and ion distribution in the microchannel for a positive voltage.

- The general idea is to generate time-dependent voltages across a glass microchannel filled with the B-Z reagents using silver-silver bromide electrodes.
- The electrodes' electrochemistry leads to local consumption of kinetically relevant ions in the reaction (Br-, etc.)
- Electroosmosis generates a bulk plug flow in the channel, while cations and anions advect differently relative to the bulk flow.
- Surface-reagent electrochemistry disrupts ion distributions, but nearly uniform electroosmotic flow profile doesn't disrupt generated coherent structures.

## Chemical Kinetics

$$H^+ + HBrO_3 + HBrO_2 \rightleftharpoons HBrO_2^+ + BrO_2\cdot + H_2O$$

$$BrO_2\cdot + H^+ \rightleftharpoons HBrO_2^+$$

$$Fe(phen)_3^{2+} + HBrO_2^+ \rightleftharpoons Fe(phen)_3^{3+} + HBrO_2$$

$$2HBrO_2 \rightleftharpoons HOBr + HBrO_3$$

$$H^+ + Br^- + HBrO_2 \rightleftharpoons 2HOBr$$

$$H^+ + Br^- + HOBr \rightleftharpoons Br_2 + H_2O$$

$$H^+ + Br^- + HBrO_3 \rightleftharpoons HBrO_2 + HOBr$$

$$Fe(phen)_3^{3+} + CHBr(COOH)_2 \rightleftharpoons Fe(phen)_2^{2+} + H^+ + \cdot CBr(COOH)_2$$

$$H_2O + \cdot CBr(COOH)_2 \rightleftharpoons H^+ + Br^- + \cdot COH(COOH)_2$$

$$HOBr + CHBr(COOH)_2 \rightleftharpoons CBr_2(COOH)_2 + H_2O$$

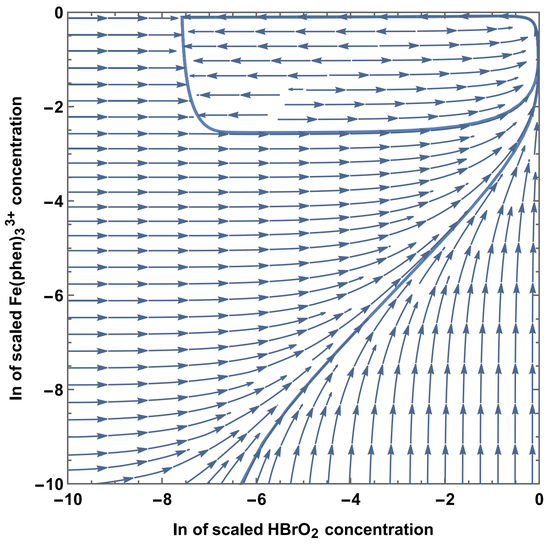
$$Br_2 + CHBr(COOH)_2 \rightleftharpoons CBr_2(COOH)_2 + H^+ + Br^-$$

Above: The dynamics of the ferroin-activated B-Z reaction can be reduced into a 2-D system of equations for its key components. Right: Simulation of reduced mass action kinetics for key B-Z components in accordance with the 2-D model above, described in [3]. $x$ is proportional to the $HBrO_2$ concentration, $y$ is proportional to the ferroin concentration. Quantities are scaled by other reagent concentrations and by reaction rates. The system rapidly converges onto a limit cycle in the upper right of the plot.

$$\dot{x} = \lambda\left[x(1-x) - \gamma\alpha\frac{z}{1-z}\frac{x-\mu}{x+\mu}\right]$$

$$\dot{y} = \beta\left[x - \alpha\frac{y}{1-y}\right]$$

The most comprehensive model for the chemical kinetics of the B-Z reaction uses 80 distinct reactions[2], but the dynamics can be approximated by as little as two autocatalytic reaction processes.[3]




## Summary


The B-Z reaction is an excellent example of an autocatalytic chemical reaction far from chemical equilibrium which generates coherent spatial and temporal structures. However, the full range of phenomena obtained from electrokinetic manipulation of the reaction has not been explored. We outline theoretical and experimental considerations to accomplish this goal and show some motivating results.


## References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