Modelling Nonlinear Chemical Oscillators with Inhibitory Coupling

Jacob Gold, Adam Wang, Camille Girabawe, Kyle Harrington, Seth Fraden
Brandeis University
Waltham, MA, USA

***Abstract*—We investigate the nonlinear, oscillatory Belousov-Zhabotinsky (BZ) reaction by constructing a computationally efficient Kuromoto-based model to predict its behavior. We treat each BZ droplet as a chemical oscillator that is coupled to its neighbors through diffusion and generate the coupling function used in our model. We then test our model with experimental data for a series of one-dimensional 60 micron diameter BZ droplets. The RMS error between the measured phases of the droplets and our simulation is 0.118 radians.**

Keywords—Kuromoto, Nonlinear chemical oscillator, Belousov-Zhabotinsky

I. Introduction

Nonlinear oscillators are found in a variety of biological systems including neural networks, circadian clocks, and the vascular system [1, 2]. The Belousov-Zhabotinsky (BZ) is one such chemical oscillator that can be used as a model for these systems. Its nonlinear, oscillatory behavior is attributed to autocatalytic oxidation producing an indicator in the absence of inhibitor, which is a byproduct of this oxidation. The presence of inhibitor stops the oxidation, which ceases production of inhibitor. The inhibitor is then consumed and over time the oxidation resumes, creating a cycle. In a system of several BZ droplets separated by oil, only the inhibitor diffuses through to neighboring drops and prevents their oxidation, introducing inhibitory coupling between drops [3]. This inhibitory coupling allows for stable behavior that could provide a basis for computation through a chemical substrate [4].

II. Field Körös-Noyes Model

The most common method of simulating the BZ reaction is through the Field-Körös-Noyes (FKN) model that represents the chemical dynamics as a system of partial differential equations (PDEs). Each PDE dictates the rate of change of a certain reactant, one such example being of the form

$$dx/dt = -k_1 xy + k_2 y - 2k_3 x^2 - k_4 x + k_r w^2 + k_{red} wx, \quad (1)$$

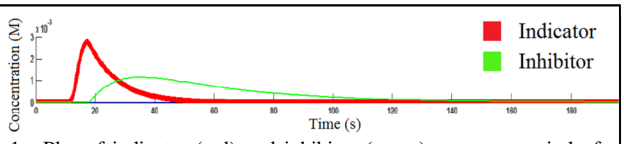

Fig. 1. Plot of indicator (red) and inhibitor (green) over one period of approximately 200 seconds generated by the FKN model.

where k_i are constants and the other variables are reactants. The full model is quite precise and involves seven PDEs but as a result, the computation time needed for FKN is enormous, even for simple systems comprised of a few drops [3]. Fig. 1 shows a plot of indicator and inhibitor concentration over one period generated by the FKN model.

III. Kuramoto Model

A more generalized model for coupled oscillators that depends only on one parameter, the phase, is Kuromoto:

$$d\theta_i/dt = \omega_i + K \sum_{j \neq i} \sin(\theta_j - \theta_i). \quad (2)$$

Here $d\theta_i/dt$ is the frequency of the i-th droplet with natural frequency ω_i. The Kuromoto phase model is a great simplification as compared to FKN, with only one differential equation to solve. The summation accounts for global coupling, based on the difference in phase between all drops where K is a constant. Kuromoto-based models that exhibit local coupling have also been studied with similar form as (2), but with a summation over only nearest neighbors [5].

IV. Adapted Kuromoto Model

We extend [5] by introducing a coupling function that does not depend on the difference in phase due to the reaction's nonlinearity. Since BZ demonstrates local inhibitory coupling, we search for a coupling function $H(\theta_i, \theta_j)$ that depends on the phase of two drops with a summation over only nearest neighbors:

$$d\theta_i/dt = \omega_i + \sum_{j=i-1}^{i+1} H(\theta_i, \theta_j). \quad (3)$$

Such a model allows for the simulation of large systems while capturing the inhibitory coupling BZ exhibits.

V. Inhibitory Coupling Function

Our coupling function must measure the deviation between the effective frequency of a drop and its natural, uncoupled frequency. To calculate it, we define the effective frequency of the i-th droplet $\omega_{i,\,eff}$ in terms of the rate of change of inhibitor concentration dM/dt. Our coupling function depends on the phase of each drop, which means there exists a bijection. Thus, we can extract from dM/dt

$$\omega_{i,\,eff} / \omega_i = (dM/dt)_c / (dM/dt)_{uc}, \quad (4)$$

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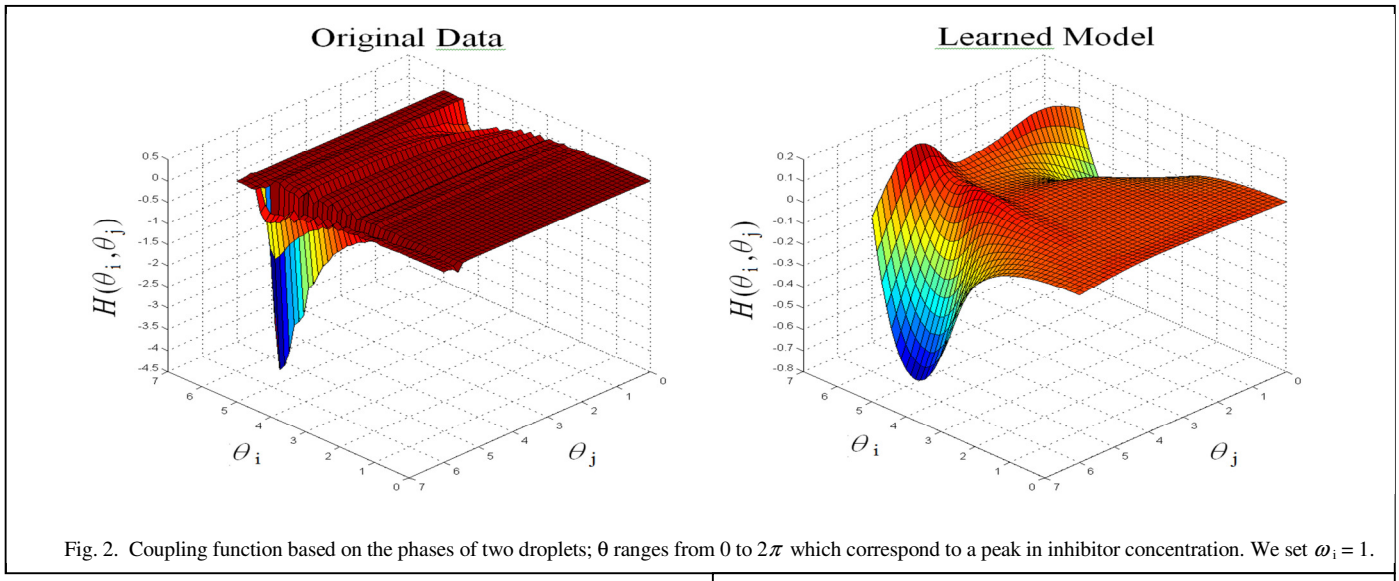

Fig. 2. Coupling function based on the phases of two droplets; θ ranges from 0 to 2π which correspond to a peak in inhibitor concentration. We set $\omega_i = 1$.

where the subscript c is for two coupled drops and the subscript uc is for a single uncoupled drop. We can re-arrange (4) to find the effective frequency and deduce our coupling function

$$H(\theta_i,\theta_j) = \omega_{i,\,\mathrm{eff}}(\theta_i,\theta_j) - \omega_i. \qquad (5)$$

We measured the coupling function by simulating a simple two-drop system separated by oil using the FKN model at various initial phases. The effective frequency and therefore coupling function were calculated numerically. Plotted in Fig. 2 is our coupling function described by (5). It is mostly negative as expected, since we have inhibitory coupling. From (3), we see that negative H corresponds to a smaller frequency, and thus a longer period caused by the diffusion of inhibitor. Furthermore, there is primarily one range of phases where the drop is significantly affected by coupling, which is approximately 1 radian below peak indicator concentration. As we see by comparing to Fig. 1, this range corresponds to approximately 10 seconds before a spike in indicator. This result is physically sound, since inhibition of indicator just before the peak will maximize the period increase.

VI. Results and Discussion

With initial conditions taken from experimental data, we are able to predict the phase of a particular BZ droplet in a one-dimensional (1D) arrangement of multiple droplets to 0.118 RMSE. Fig. 3 shows a plot of the phase of the simulated and experimentally measured drop. When predicting the phase of all drops in the capillary, the average phase drift between simulated and actual data is 0.401 radians per oscillation. We suspect this is the result of heterogeneity in the drops in the experimental data; our model assumes the frequency of each droplet is the same.

VII. Future Work

We intend to adapt our Kuromoto-based model to a 2D hexagonal lattice with a coupling function that depends on the phase of seven drops. Such a system is more enlightening and pertinent to real world biological systems. We also intend to investigate the nature of the inhibitory coupling, strong or weak, to characterize the limits and applications of our model.

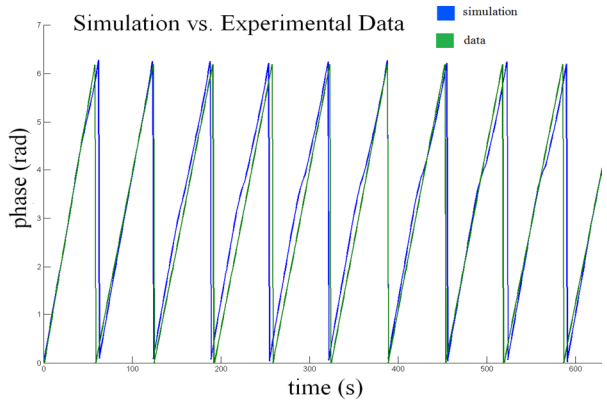

Fig. 3. Plot of phase over time for data collected in a physical experiment and simulation with the same initial conditions. Experimental phase found from interpolating between indicator peaks. RMSE of 0.118 radians.

Acknowledgments

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