Bachelor Technical Project:

Echo Behaviour in large population of Chemical Oscillators

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Chapter 1

Introduction

In this project we have studied the dynamical behaviour of Belousov-Zhabotinsky (BZ) oscillators. Studies of the BZ oscillators have shown a variety of collective dynamical behaviors, such as phase clusters, dynamical quorum sensing and chimera states.
Another phenomena that has been discovered in a system of large populations of BZ oscillators is the Echo phenomenon. Where the experiments and numerical results shows that if the BZ system if perturbed two times at a time difference of τ, then the system shows a measurable response at τ time after the second perturbation. The system somehow stores the information of the perturbations in their phase structure, and that can be seen by measuring the Global Order Parameter (R) in the form of echo. I have tried to analyze this phenomenon through simulation using modified ZBKE model for two variables.

Chapter 2

Experimental results

Experimental and theoretical studies have revealed that Echo phenomenon can be observed with large number of oscillators in photosensitive BZ system[1]. The experiment was performed in such a way that it was made sure that over 1000 of oscillators get simultaneously perturbed.

2.1 Chemistry of the experiment

[1] In the oscillatory array, the photosensitive oscillators are catalyst-loaded beads of about 200 μm in diameter, each of which is fixed on a film of polydimethylsiloxane(PDMS), which is then positioned in an open reactor that is continually replenished with a catalyst-free BZ solution.

The BZ oscillators are individually monitored with a CCD camera, where the gray level is proportional to the concentration of the oxidized catalyst, $Ru(bpy)_3^{3+}$, and they are illuminated with a spatial light modulator (SLM) for a prescribed duration and intensity. The illumination generates the excited form of the reduced catalyst, $Ru(bpy)_3^{2+*}$, which initiates a sequence of photo chemical reactions that produce the autocatalyst $HBrO_2$

2.2 Coupling and Perturbation

To have the oscillators in oscillatory state a background illumination ϕ_0 is chosen. The photosensitive BZ system allows global coupling of the oscillators by a simple feedback scheme, with the projected light intensity given by

$$\phi_j = \phi_0 + k(\bar{I} - I_j)$$

where k is the coupling strength, I_j is the transmitted intensity of j^{th} oscillator, $\bar{I}$ is the average transmitted light intensity of all N oscillators, and ϕ_j is the projected light intensity on j^{th} oscillator. In this experiment perturbations are applied by increasing the light intensity to ϕ_p for 3.4 s. During an experiment, the first perturbation is applied 168 s after introducing the coupling. The second perturbation is then applied τ seconds later, with τ chosen to be between 6 and 10 times the mean oscillator period[1].

2.3 Phase and Order parameter of Oscillator

The state of each oscillator j is characterized by a phase variable θ_j, which is defined as

$$\theta_j = \frac{(t - t_n)}{(t_n - t_{n-1})}$$

where $t_n < t$ denotes the time closest to t at which I_j is maximum. Also the phase is defined so that $\theta \to \theta + 1$ corresponds to one oscillation.

To see the collective behaviour of all the oscillators we have to look at a global parameter, here we obtain a Kuramoto order Parameter, which is defined as

$$R(t) = \frac{1}{N} \mid \sum_j exp(2\pi\iota\theta_j) \mid$$

which may be thought of as macroscopically quantifying the degree of synchronization of the system, in terms of oscillator phase. The order parameter R(t) as a function of time observed experimentally is shown in the Fig. 2.1. We can see that at the time of perturbation the order parameter increases as the oscillators are phase synchronized. we note that the duration of applied perturbation is small relative to the mean period and the delay time τ

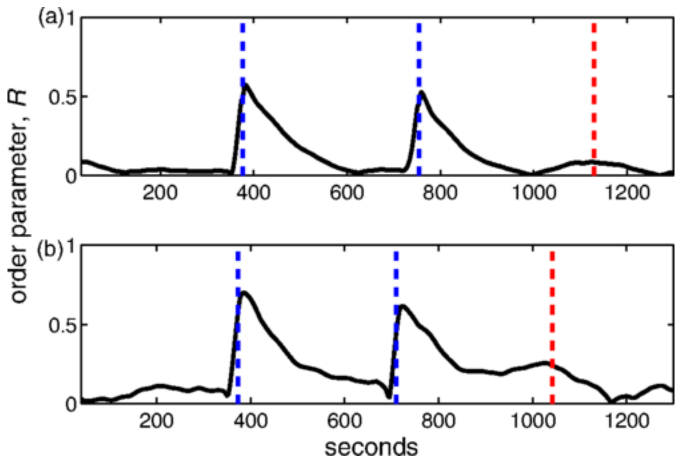

Figure 2.1: Experimental measurements illustrating echo behavior in populations of Belousov-Zhabotinsky (BZ) oscillators. The order parameter R is calculated from the phases of the oscillators and plotted as a function of time. The phases of the oscillators are determined using linear interpolation between consecutive peak times. An echo is exhibited in the magnitude of the order parameter R at time $t_p + 2\tau$ for a system perturbed at times t_p and $t_p + \tau$. (a) uncoupled system, k = 0, with t_p = 376 s, $\tau = 378s$, and N = 1295. (a) coupled system, k = 0.25, with t_p = 373 s, $\tau = 336s$, and N = 1001. In these experiments, the critical coupling strength for the onset of synchronization is $k_c = 0.70$. Average natural period and standard deviation: (a) $T_0 = 36.5 \pm 3.2$ and, (b) $T_0 = 42.6 \pm 8.2s$

2.4 Observed Echo

As we can see in Fig 2.1[1]. following each perturbation, there is decrease in order parameter. This happens due to heterogeneity in frequency of the oscillators. At the perturbation the phases of the oscillators drops to zero giving rise to the order parameter, after that each oscillator oscillates with its own frequency, which leads to a decrease in order parameter. The echo is observed at time 2τ after the first perturbation. Echo behavior in an experiment with weak coupling is shown in Fig. 2.1(b). As is expected, the phase dispersion of the coupled oscillators is now slower following each perturbation.

Chapter 3

Simulation

To gain insight into the echo phenomenon, we try to simulate the system. The system is modelled using the Zhabotinsky-Bucholtz-Kiyatkin-Epstein (ZBKE) model [4], modified to describe the photosensitive, discrete BZ oscillator system [3][2].

In the simulation each oscillator is described by concentration of two key species, $HBrO_2$ and oxidesed form of catalyst $Ru(bpy)_3^{3+}$. The reaction that happens between these two leads to oscillations in their concentration, which further leads to oscillations in the light emitted by each oscillator.

3.1 ZBKE Model

As said earlier each oscillator is described by concentration of two key species. Now say concentration of these two species $HBrO_2$ and $Ru(bpy)_3^{3+}$ be X and Z respectively. In the photoexcitable model, an increase in light intensity leads to increased production of bot bromous acid $HBrO_2$ and and the oxidized form of catalyst, $Ru(bpy)_3^{3+}$.

The concentration of $Ru(bpy)_3^{3+}$ corresponds to the transmitted light intensity (I_j) of the micro-oscillators in the experiment. Also an approximate Gaussian frequency distribution in the oscillator population is produced by varrying the stoichiometric factor(q) in the ZBKE model for the individual oscillators. The equations involved:

$$\epsilon_1 \frac{\mathrm{d}X}{\mathrm{d}t} = \phi - X^2 - X + \epsilon_2 \gamma U_{ss}^2 + U_{ss}(1-Z) + \left[\frac{\mu - X}{\mu + X}\right]\left[\frac{q\alpha Z}{\epsilon_3 + 1 - Z} + \beta\right] \quad (3.1)$$

$$\frac{\mathrm{d}Z}{\mathrm{d}t} = 2\phi + U_{ss}(1-Z) - \frac{\alpha Z}{\epsilon_3 + 1 - Z} \quad (3.2)$$

$$U_{ss} = \left(\frac{1}{4\gamma\epsilon_2}\right)\left(\sqrt{(16\gamma\ X\epsilon_2 + Z^2 - 2Z + 1)} + Z - 1\right) \quad (3.3)$$

$$\phi_j = \phi_0 + k * (\overline{Z} - Z_j) \quad (3.4)$$

where $\gamma = 1.2$, $\alpha = 0.1$, $\beta = 1.7 * 10^{-5}$, $\mu = 2.4 * 10^{-4}$, $\epsilon_1 = 0.11$, $\epsilon_2 = 1.7 * 10^{-5}$, $\epsilon_3 = 1.6 * 10^{-3}$, q = Gaussian distribution with mean=0.7, sigma=0.0625.

3.2 Simulation Results

when we solve these equation we can see in the Fig. 3.1(a) that the concentration of $HBrO_2$ and $Ru(bpy)_3^{3+}$ oscillates over time.
Now as we have defined above the phase of each oscillator (θ_j) as :

$$\theta_j = \frac{(t - t_n)}{(t_n - t_{n-1})}$$

where $t_n < t$ denotes the time closest to t at which I_j is maximum. As the concentration of $Ru(bpy)_3^{3+}$ is directly proportional to the transmitted light intensity (I_j), we say t_n to be the n^{th} maxima of $[Ru(bpy)_3^{3+}]$. In the Fig. 3.1(b) we can see that theta varies linearly with time.

3.3 Perturbation

In order to see echo, we have to perturb the system. In the experiment, the perturbation was of the form light, they were illuminated with a spatial light modulator (SLM) for a prescribed duration and intensity. In the simulation ϕ_j is the projected light intensity. So while perturbing the system, we set $\phi = \phi_p$ for 3.4 sec. In Fig. 3.2(a) you can see a sudden rise in the concentration of $Ru(bpy)_3^{2+*}$, due to which the phase of the oscillator (θ_j) drops to zero, as can be seen in Fig. 3.2(b).

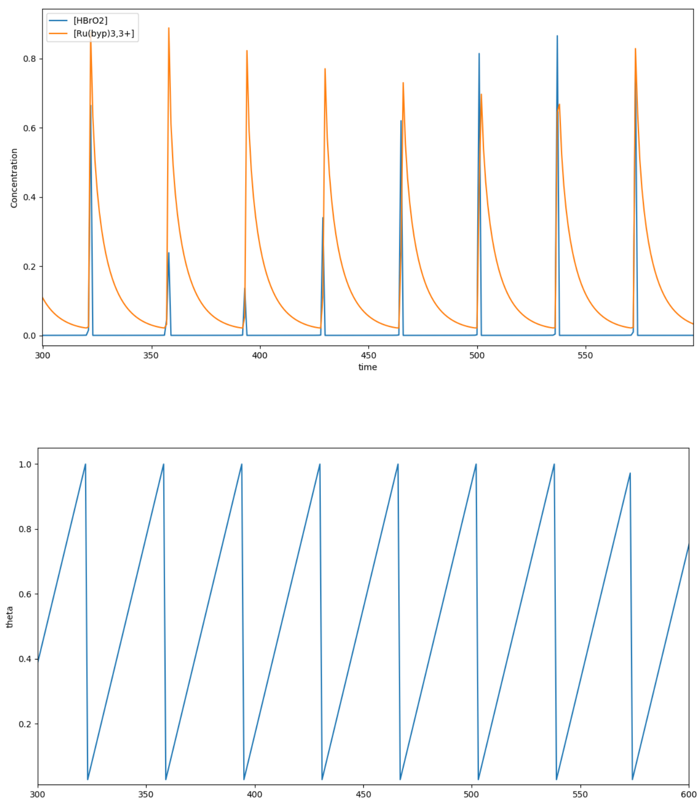

Figure 3.1: The figure shows the oscillations in the concentration of the two key species, due to which the phase of the oscillator oscillates between 0 to 1.(a). Concentration of $[HBrO_2]$, $[Ru(bpy)_3^{2+*}]$ vs time, (b) Theta vs time

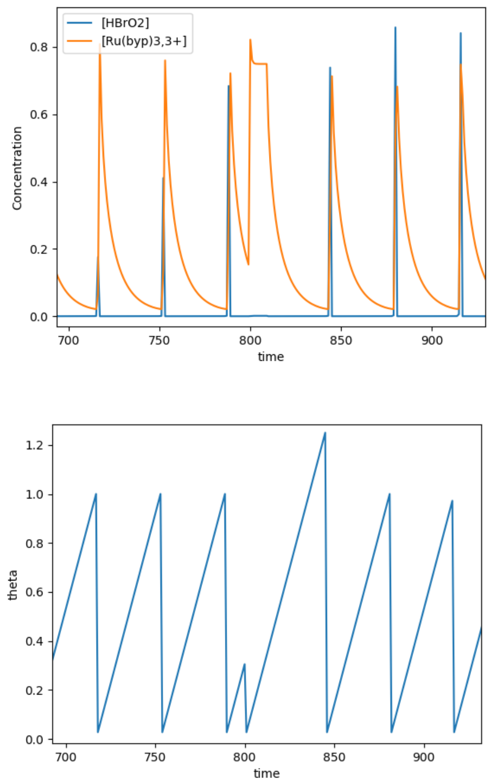

Figure 3.2: Perturbation is given at t=800 with ϕ_p=0.147, (a). Concentration of $[HBrO_2]$, $[Ru(bpy)_3^{2+*}]$ vs time, (b) Theta vs time

3.4 Echo in Simulation

Figure 3.3 shows the order parameter R as a function of time from simulations of an uncoupled system (k = 0). The system was perturbed by momentarily increasing the light intensity (ϕ) to ϕ_p=0.147 at $t_p = 3000$, and again at $\tau = 840$ later. Each perturbation is followed by a rapid dispersion, with corresponding decrease in global order parameter. As we can see in the figure, an increase in order parameter is exhibited at time $t_p + 2\tau$, the echo.

Figure 3.4 shows the simulation result of coupled system. The figure shows how introduction to coupling leads to slower phase dispersion of the oscillators following each perturbation.

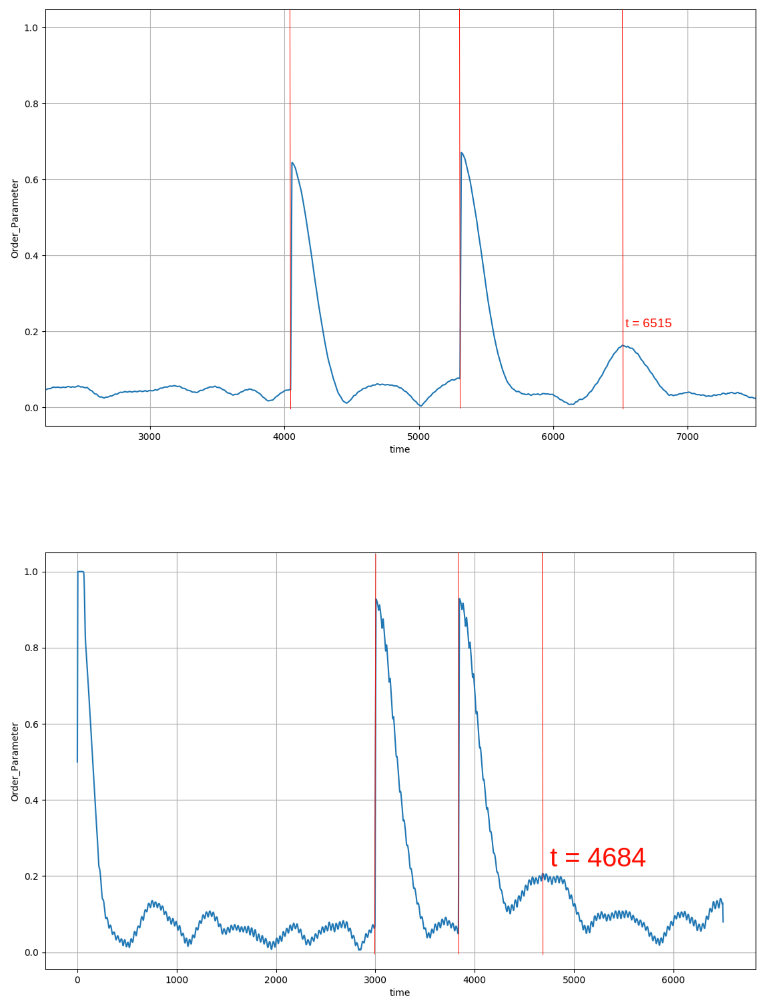

Figure 3.3: (a).Simulations of the modified ZBKE model illustrating echo behaviour in populations of uncoupled photosensitive BZ oscilators. The Order parameter R is calculated from the phases of the oscillators and plotted as a function of time. An echo is observed at time $t_p + 2\tau$ for a systen perturbed at t_p and $t_p + \tau$, System with K=0, N=5000, ϕ_p=0.147, t_p=4059, τ=1260, Echo is observed at t = 6515 $\approx t_p + 2\tau$
(b). System with k = 3.35 * 10^{-4}, N = 500, ϕ_p=0.147, t_p = 3000, τ = 840, Echo is observed at t = 4684 $\approx t_p + 2\tau$ Note the slower phase dispersion following each perturbation.

Chapter 4

Conclusion

After analyzing the dynamics of a BZ oscillator and its response to any perturbation, we modelled a system of N oscillators using ZBKE Model for two variables, and observed Echo in both coupled and uncoupled system.

We observed Echo in the Order parameter, note that the magnitude of the order parameter at echo is less than that at perturbation, implying that the phase of some not all of the oscillators are getting synchronized. To understand this phenomenon Phase Analysis [1] of the system is done, where it is explained how the information that Perturbation have previously occurred remains encoded within the phase structure of the Oscillators.

4.1 Observation of Two Echoes

While simulating for uncoupled system, instead of two perturbation, the system was perturbed three times but with different time difference, say at say at t_{p1}, $t_{p1} + \tau_1$ and at $t_{p1} + \tau_1 + \tau_2$ and as you can see in Fig. 4.1 two different echoes are observed. First echo is observed due to 2nd and 3rd perturbation at t=6515, τ_2 time later than the 3rd perturbation. And second echo is observed at t=8106, τ_1 time later than the 1st perturbation. It is interesting to observe that how the information of all the perturbations are stored in the phase structure of the oscillators.

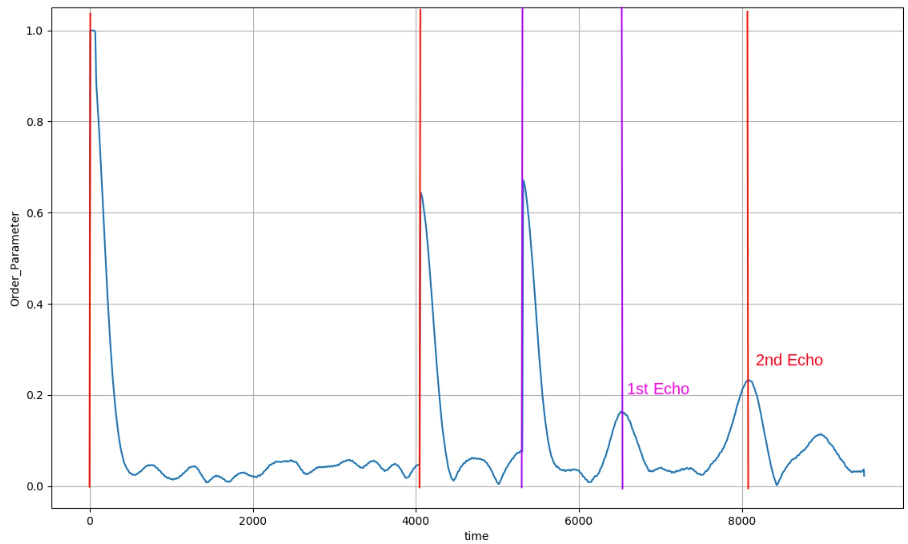

Figure 4.1: System with K=0, N=5000, ϕ_p=0.147, Perturbation is given at t_{p1}=0, $t_{p1}+\tau_1$ and at $t_{p1}+\tau_1+\tau_2$ with τ_1=4050 and τ_2=1260. Two echoes at different times are observed. first at t=6515 due to 2^{nd} and 3^{rd} perturbation, and second echo is observed at t=8106 due to 1^{st} and 2^{nd} perturbation.

4.2 Future Scope

There are lot of things that are not analyzed due to low computational power. We have simulated for only 500 oscillators in coupled system whereas for 5000 oscillators in uncoupled system. As it takes a lot of time to solve coupled differential equation. Due to which we couldn't analyze the effect of noise in the system. All this problems can be solved by parallelizing the code for coupled system. Also a theoretical analysis has to be done to generalize the phenomenon of multiple echoes.

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