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Long Range Correlations in Chemical Oscillations

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Abstract: The purpose of the present study is to determine whether a long range correlation is present in BZ (Belousov-Zhabotinskii) reaction and how this correlation varies with the change in concentration of the solution. To explore the dynamics of the system with change in concentration, phase space plot and power spectrum are studied. Hurst exponent is estimated using log log plot and R/S technique. We discuss the results which uncover how the system changes from an excitable steady state to a limit cycle.

Key words: BZ reaction, Hurst exponent, concentration.

1. Introduction

Long range correlations have been found in a wide number of systems including biological, physical, economical, geological, and urban systems [1]. A system is said to exhibit long-range correlations when some physical properties of the system are correlated at different times (or positions) and the corresponding correlation function decays much slower than exponentially as a function of time or distance. In physics and mathematics, long-range correlations typically refer to a power-law decay of the correlation function. The mechanism for generating such long-range correlations is not always obvious. Usually, long-range correlations are a result of the collective behavior of a complex system (under unique conditions), with the multiple components interacting through "local" (short-range) interactions. Recognizing the ubiquity of long range power law correlations can help us in our efforts to understand nature.

In this study we discuss the relevance of these concepts in the context of oscillating reactions, the most intriguing of chemical reactions. One of the most commonly demonstrated oscillating reactions is BZ (Belousov-Zhabotinskii) reaction. The experiment displays a variety of dynamical phenomena illustrating some of the key concepts of nonlinear dynamics. Oscillating reactions are best understood within the context of nonlinear chemical dynamics models that are used to predict the overall behavior of complex systems. In this type of reaction, a mixture of chemicals goes through a sequence of color changes, and this sequence repeats periodically. The reactions can be conveniently manipulated by adjusting the dynamic control parameters like the initial concentration of each reagent or the temperature. As a result, chemical media can shed some interesting new light on various nonlinear behaviors encountered in nature [2-6].

BZ reaction [7, 8] is always at the centre of scientific interest even five decades after its discovery. The reaction involves the oxidation of an organic species such as malonic acids (malonic acid, MA = $HO_2CCH_2CO_2H$) with a solution of acidified bromate (H^+/BrO_3^-) in the presence of a 1-electron transfer redox catalyst. The redox catalyst can be, for instance, an Fe^{2+}/Fe^{3+} couple. The two oxidation states have different colours, allowing the change of oxidation state to be observed visually. Complexation of Fe^{2+} with the 1,10-phenanthroline ligand gives the species known as *ferroin* which has a red colour. The oxidised *ferroin* form is blue. The detailed mechanism for the

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BZ reaction is given in Ref. [9].

The classical, cerium-ion-catalyzed reaction system was first elucidated by Field et al. [10]. The complex reaction was reduced to some coupled elementary pseudoreactions. Field and Noyes were able to construct a simplified mathematical model [11], now known as the Oregonator, which exhibits oscillatory limit cycles. The model also successfully describes the fascinating features of the complex phenomena seen in the BZ reaction, both temporal, such as excitability [12, 13], bistability [14], stirring effects [15, 16], quasiperiodicity, and chaos [17, 18], and spatial, including traveling waves [19], target and spiral patterns [20, 21], scroll rings [22], and their orientation dynamics in advective fields [23]. In our study, we will, in particular review the evidence supporting the presence of long range correlation in this reaction.

2. Theory

Spectrophotometric technique is the most widely and convenient technique employed to study this reaction. If there are absorbing species, ultraviolet and/or visible spectrophotometry offers rapid response time and high sensitivity for monitoring concentrations. The absorption of light in the visible and near ultraviolet regions of spectrum by a solution is governed by a photo physical law, known as the Lambert-Beer law, according to which, when a beam of monochromatic radiation of suitable frequency passes through a solution, it is absorbed by the solution. As a result, the intensity of emergent light is considerably reduced than that of the incident light (I_0), and this decrease in intensity depends upon the thickness (b) and concentration (c) of the absorbing solution, i.e.

$$ln\, {}^{I}/_{I_0} = \alpha bc \qquad (1)$$

Where α is proportionality constant. Changing to the common log, we have,

$$A = log\frac{I}{I_0} = \varepsilon bc \qquad (2)$$

where, ε is called the absorption coefficient or extinction coefficient of the absorbing medium. It is characteristic of the solute and depends on the nature of the solvent, temperature and the wavelength of the radiation employed. If the concentration c of the solution is expressed in $moll^{-1}$ and path length b in cm, then ε is referred to as molar absorption coefficient. Spectrometer may detect the percentage transmittance of light radiation when light of certain intensity and frequency range is passed through the sample. Thus the instrument compares the intensity of the transmitted light with that of the incident light transmittance T, is related to the absorbance A, as

$$A = -logT \text{ , or, } T = 10^{-A} = 10^{-\varepsilon bc} \qquad (3)$$

The analysis in this article will focus on one of the BZ reaction in an open reactor in stirring condition 0.5 mM 80 mL aqueous solution of $KBrO_3$, 1 mM 100 mL aqueous solution of malonic acid, 0.5 mM 70 mL aqueous solution of KBr and 5 NH_2SO_4 are poured into a 500 mL beaker containing 400 mL of triple dist. water and continuously stirred with a magnetic stirrer. After the disappearance of yellow-brown colour (bromine), 2 mL of ferroin solution are added to the mixture. Ferroin indicator shows a red colour after the addition and the colour of the solution turns to a blue after about 75 s, which will again disappear after a short time and a mixed red colour will reappear. The colour oscillates between red and blue. This oscillatory change in colour of the reaction mixture is measured by UV absorption spectroscopy.

JASCO V-650 spectrophotometer was used to acquire the UV-vis absorption spectra at 298 K. At first the absorption spectrum of water was taken in a sample cuvette of 1 cm path length along with the same volume of water in the reference cuvette. In case each experiment base line is corrected with respect to triple distilled water.

3. Analysis

Our analysis begins with a careful study of the raw signal which gives the different values of absorbance

consecutively in time at a particular wavelength. These allow us to shed light on the correlation between chemical oscillations and spatio-temporal dynamics, how the peak wavelength evolves with time. Data were collected at intervals of 0.1 s until 14,000 data points were obtained. In the BZ reaction Br^{-1} levels are extremely dynamic as shown by absorbance measurements. Observed color changes in the presence of ferroin, a redox indicator, support this interpretation of the cyclical absorbance data. The absorbance of the system was related with ratio of $[Fe^{3+}]/[Fe^{2+}]$. The concentrations Fe^{3+} and Fe^{2+} were changed by each reaction involved in the system, thus tracing the changes of ratio $[Fe^{3+}]/[Fe^{2+}]$ was an entrance of studying the mechanisms.

Fig. 1 shows the wavelength of maximum absorbance. This wavelength at which the absorbance is greatest is the most suitable wavelength for study. The spectrophotometer is more sensitive to absorbance changes at this wavelength. Thus, the wavelength of maximum absorbance is typically used for the analysis. From Fig 1, it has been found that 540 nm is the most suitable wavelength for study.

Fig. 2 shows the effect of concentration on the absorbance data. The amplitude and the number of oscillations are associated with the initial reactant's concentration. The higher is the initial concentration of malonic acid, the larger is the absorbance. Also the number of oscillations becomes less as the concentration decreases. The higher amplitude of oscillation corresponds to the oxidation state, the lower amplitude corresponds to the reducing state. For 100% concentration, we see that there is a sharp oxidation which is accompanied visually by a sharp red to blue colour change-followed by a slower "recovery" back to the reduced state. Over the five oscillations shown in this trace, there is little observable variation in the amplitude of the oscillation in this species. These trends are apparent from the data.

The most powerful appeal of the use of the phase space is its graphical vividness. This goes along with how changes over time series chart are transformed into spatial patterns in phase space. The phase space thus obtained is used to characterize the trajectory of the evolution of the system. Fig. 3 depicts the phase space plots for different concentration of the solution.

It is seen that the frequency of oscillation decreases in time as reagents are consumed. From a dynamical

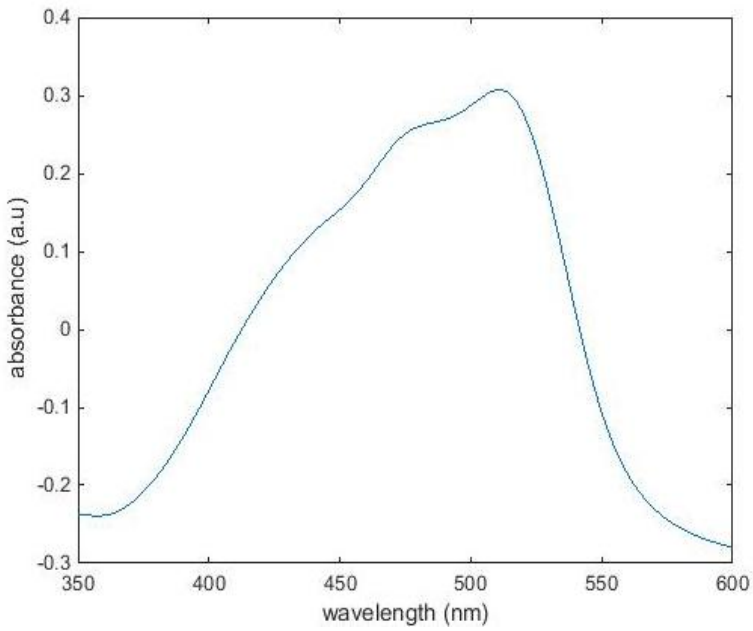

Fig. 1 Maximum absorbance vs. wavelength.

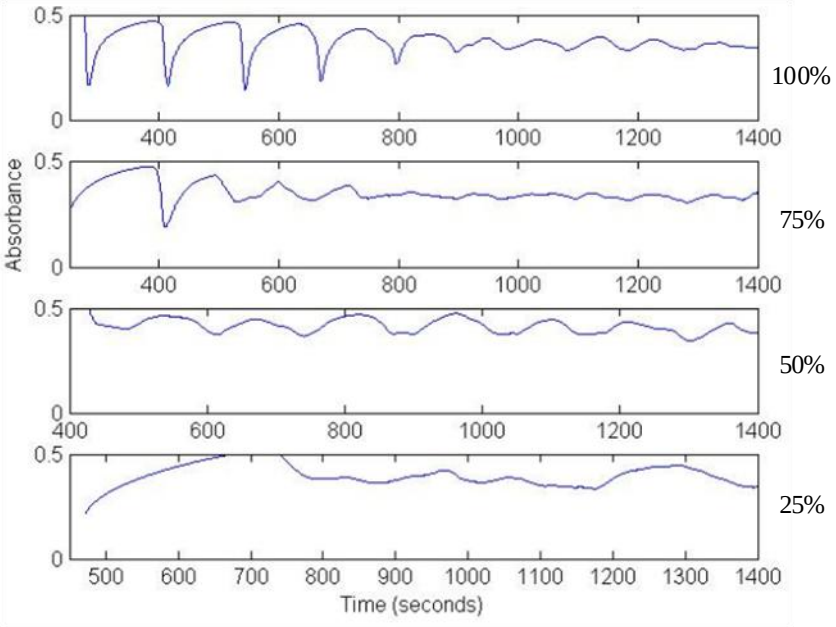

Fig. 2 Raw signals for different concentrations.

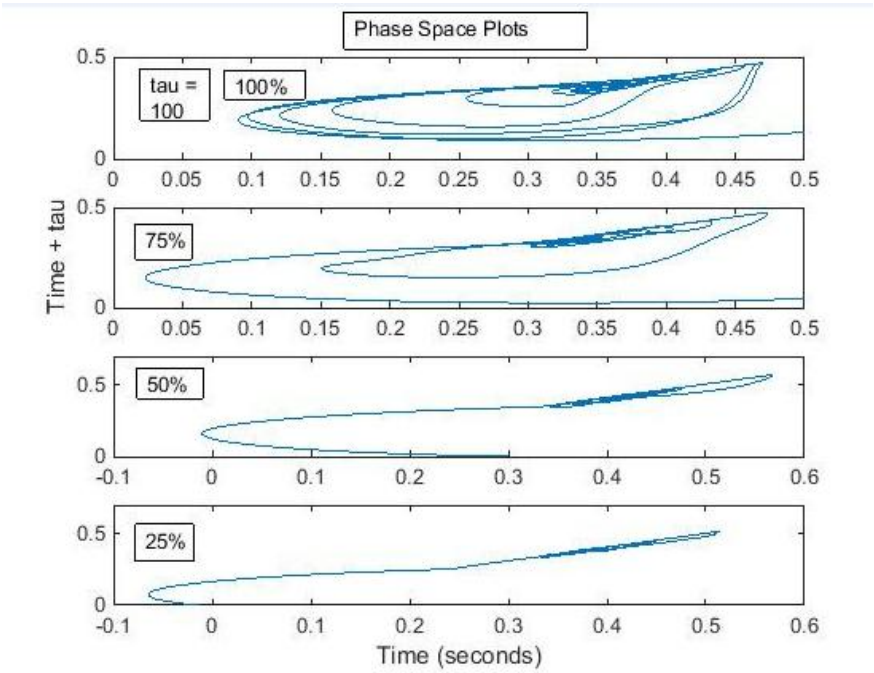

Fig. 3 Phase space plots for different concentrations.

point of view the trajectory in phase space should be a slowly winding spiral. This is endorsed in first trajectory which is for 100% concentration. As the concentration decreases, the number of oscillations decreases. For 25% concentration the signal becomes almost stationary and the trajectory is approximately a limit cycle in phase space. The phase space plots are shown for 75% and 50% concentration.

BZ reaction oscillates with a natural frequency which depends on the chemical condition. In order to obtain deeper insights into system dynamics, power spectral density of the absorbance is plotted for different concentration of the solution. It is observed that for all concentrations, strong peaks are observed

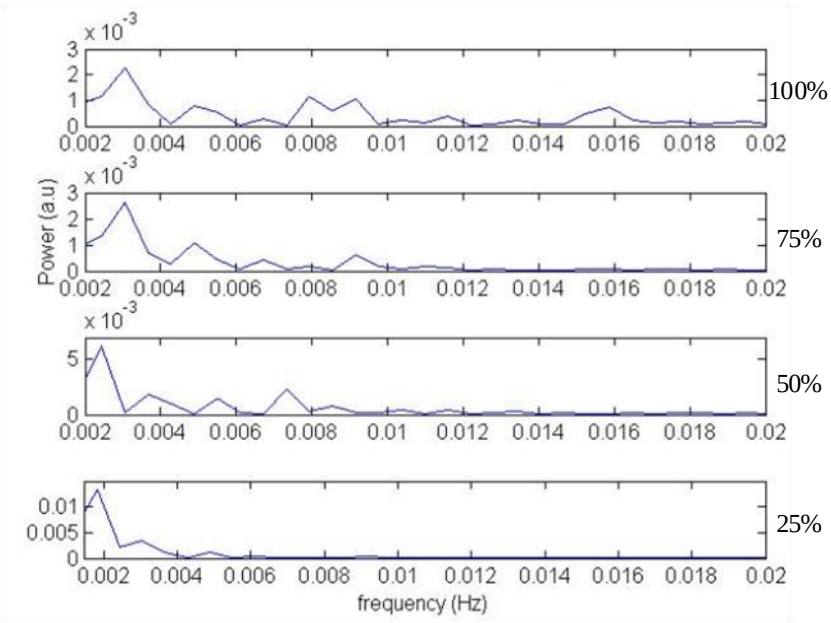

Fig. 4 Power spectrum for different concentrations.

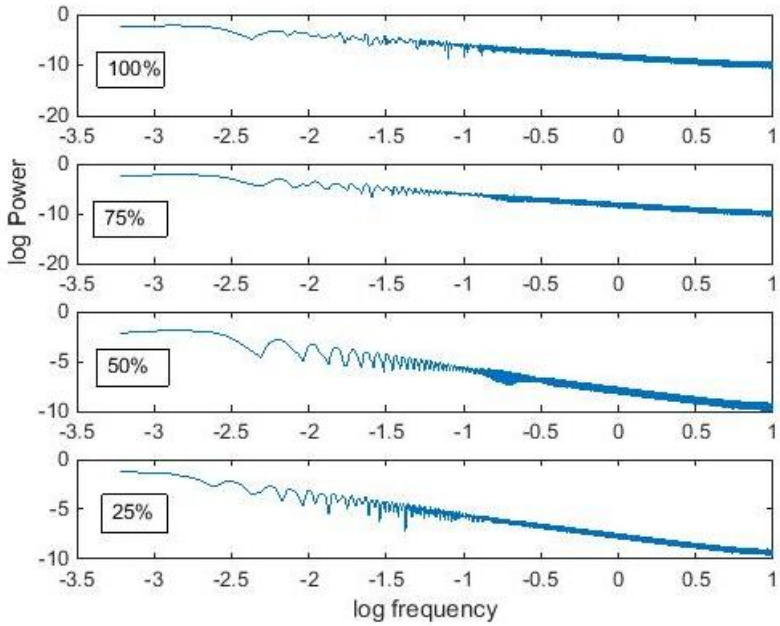

Fig. 5 Log power vs. log frequency for different concentrations.

at low frequencies. As concentration decreases, the power in the high frequency range decreases. This is shown in Fig. 4.

Since data with long memory appear quite frequently in many different areas of science and engineering, many methods have been proposed to estimate the key scaling parameter, the Hurst exponent. The common method of estimating the Hurst exponent is from the slope of the log power vs. log frequency plot. The slope β of the log-log plot of Power(f) vs. Frequency, when $f \to 0$, is related to the Hurst exponent through $H = (1+\beta)/2$. The Hurst exponent is calculated for different concentration. It is observed that H is well above 0.5 which is indicative of considerable persistence. It is found that the value of H is increasing from 0.69 for 25% concentration to 0.91 for 100%

Table 1 Concentration vs. Hurst exponent.

Concentration	Hurst exponent
25%	0.69
50%	0.73
75%	0.89
100%	0.91

concentration. This indicates the existence of a long-range correlation with increase in concentration. As the concentration decreases, the rate of the BZ reaction decreases due to decrease in the collision rate among the BZ substrate. As a result, the degree of persistence also decreases. In Fig. 5, the log power is plotted against log frequency for different concentration. The slope is calculated and the H values obtained are as follows:

The Hurst exponent calculated from R/S method varies from 0.96 to 0.98 in all the cases. So, it indicates that Hurst exponent calculated by R/S method matches with that calculated by the former method only at higher concentrations.

4. Conclusion

The results presented in this work show the dynamic behavior of the BZ reaction. The oscillating chemical reactions are highly sensitive to external perturbations. The reaction is perturbed by adding known amount of water to the reactants while monitoring the change produced in the oscillating pulse. It is interesting to note that the oscillatory regime decreases as we go on adding water thereby decreasing the concentration of the reactants in a closed system. Upon variation of the concentration, we see the evolution of the system from an excitable steady-state to a limit cycle.

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