Chaos to periodicity and periodicity to chaos by periodic perturbations in the Belousov–Zhabotinsky reaction

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Abstract

A three-variable model of the Belousov–Zhabotinsky reaction system subject to external sinusoidal perturbations is investigated by means of frequency spectrum analysis. In the period-1 window of the model, the transitions from periodicity to chaos are observed; in the chaotic window, the transitions from chaos to periodicity are found. The former might be understood by the circle map of two coupled oscillators, and the latter is partly explained by the resonance between the main frequency of the chaos and the frequency of the external periodic perturbations.

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1. Introduction

In the past two decades, nonlinear dynamic behaviors such as periodic oscillations and chaos in chemical reaction systems have been the subject of intensive investigations in both experiment and theory [1–3]. The theoretical descriptions of these nonlinear dynamic behaviors are often based on the nonlinear differential equations of mass action kinetics. By using this phenomenological method, numerous kinetic models for real and ideal reaction systems have been investigated exhibiting fruitful dynamic behaviors, so many nonlinear phenomena observed in real chemical reaction systems can be readily understood and interpreted.

Besides studying single nonlinear chemical systems, the effects of perturbations have also been widely studied in the field of nonlinear chemistry since new phenomena could be explored. Perturbations are often classified as periodic and random ones. In the early studies, much theoretical and experimental work was carried out on the periodically perturbed nonlinear chemical reactions, and some fascinating phenomena, such as entrainment of oscillatory systems, quasi-periodic and chaotic responses, and generation of new limit cycles, were found [4]. The phenomenon of critical slowing down was also found in periodically perturbed chemical oscillations [5]. Moreover, Schneider et al. experimentally observed the phenomenon of chemical resonance when they investigated the Belousov–Zhabotinsky (BZ) and peroxidase–oxidase (PO) reaction systems, which were perturbed sinusoidally on the focus close to a Hopf bifurcation point [6–8]. Recently, the studies on chemical stochastic resonance, where noise can improve the signal-to-noise ratio when the signal passes through a nonlinear chemical system, have attracted considerable attentions [9–15]. There, the systems located in focus near Hopf bifurcation were perturbed by random noise plus a periodic signal [9–11] or by random noise only [12–15]. It is worth noting that most of above mentioned work on effects of periodic perturbations involved the dynamic regions either of stationary states or oscillatory states or between them.

Nonlinear systems in chaotic region, perhaps the most interesting dynamic region, have also been extensively investigated under perturbations. Among them, however, chemical systems are much less studied than physical ones. The
most significant effect found in this field is chaos control where chaotic motions can be commonly converted into regular motions such as periodic motions or steady states. Many studies have been carried out in physical models [16–21] and real physical systems [22,23]. For example, proper periodical perturbation of one of the parameters in the Lorenz equations would decrease the magnitude of the maximum Lyapunov exponent in the chaotic region to be below zero [18]. Chemically, Schneider et al. obtained the chaos control by periodic perturbations in some experiments and numerical simulations [24,25]. Recently, this chaos control technique has been proved to be useful for the control of friction at the nanoscale [26]. Besides chaos control, some other interesting phenomena were found as well [27,28]. Very recently, for example, two coupled periodically driven double-well Duffing oscillators were found to exhibit imbricated period-doubling bifurcation, symmetry-breaking, sudden chaos and a great abundance of Hopf bifurcations [28].

As a well-studied prototype in nonlinear chemical studies, the BZ reaction can show rich nonlinear dynamic behaviors such as period-1, period-3, chaos, and period-doubling bifurcation. It has mathematical models of the ordinary differential equations with the dimension changing from three to higher. Oregonator is a three-variable model of the BZ reaction which does not show chaos by itself. However, chaos can be induced by an external periodic force in it [29]. In the present work, we numerically investigate the effects of sinusoidal perturbations on another three-variable BZ model [30], which is a modified version of Oregonator. It can well account not only for the chaotic behavior but also for the evolution of dynamic behavior with the change of the control parameter value in the real BZ reaction. The control parameter will be sinusoidally modulated in the dynamic regions of period-1 and chaos, respectively. And the perturbation amplitude is chosen in such a way that it can make the system always remain in the dynamic regions of period-1 and chaos, respectively. By frequency spectrum analysis, we find the transitions from periodicity to chaos in the period-1 window and the transitions from chaos to periodicity in the chaotic window.

2. Model

The chemical scheme of the modified Oregonator model is given in Table 1. Considering the reaction rates and flow rate, the dynamic evolution equations of the studied system can be written as

\[
\begin{align*}
\frac{dX}{dt} &= -k_1HXY + k_2AH^2Y - 2k_3X^2 + 0.5k_4A^{0.5}H^{1.5}(C - Z)X^{0.5} - 0.5k_5XZ - k_7X \\
\frac{dY}{dt} &= -k_1HXY - k_2AH^2Y + \alpha k_6ZV - k_7Y \\
\frac{dZ}{dt} &= k_4A^{0.5}H^{1.5}(C - Z)X^{0.5} - k_5XZ - \alpha k_6ZV - \beta k_7MZ - k_7Z \\
\frac{dV}{dt} &= 2k_1HXY + k_2AH^2Y + k_3X^2 - \alpha k_6ZV - k_7V,
\end{align*}
\]

(1)

here \(k_i\) is the flow rate.

If one variable changes on a faster timescale than the others in several reaction steps, quasi-steady-state approximation could be used, i.e. \(d(\text{variable})/dt = 0\). In this model, \(X\) and \(Y\) are both such kind of variable, but we only let \(dY/dt = 0\) since it will make the model simpler and work better [30]. Thus, \(Y\) is eliminated in Eq. (1) by calculating \(\tilde{y}\) as the root of \(d\tilde{y}/dt = 0\).

\[
\tilde{y} = \frac{\{xk_6V_0\exp((k_1HX_0x + k_2AH^2 + k_7))\}}{Y_0}.
\]

Until now, the dimension of Eq. (1) has been decreased to three. Then, the equations reduced are nondimensionalized by

Table 1

<table>
<thead>
<tr>
<th>Chemical scheme of a model of the BZ reaction</th>
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<tbody>
<tr>
<td>Reactions</td>
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<tr>
<td>(1) (Y + X + H \rightarrow 2V)</td>
</tr>
<tr>
<td>(2) (Y + A + 2H \rightarrow V + X)</td>
</tr>
<tr>
<td>(3) (2X \rightarrow V)</td>
</tr>
<tr>
<td>(4) (0.5X + A + H \rightarrow X + Z)</td>
</tr>
<tr>
<td>(5) (X + Z \rightarrow 0.5X)</td>
</tr>
<tr>
<td>(6) (V + Z \rightarrow Y)</td>
</tr>
<tr>
<td>(7) (Z + M \rightarrow )</td>
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</table>

The chemical identities of the components are: \(Y \equiv \text{Br}^-,\) \(X \equiv \text{HBrO}_2,\) \(Z \equiv \text{Ce}(IV),\) \(V \equiv \text{BrCH(COOH)}_2,\) \(A \equiv \text{BrO}_3^-,\) \(C \equiv [\text{Ce}_{\text{tot}}],\) \(H \equiv H^+,\) \(M \equiv \text{CH}_2(COOH)_2.\) The concentration of the main reactants \((A, H\) and \(M)\) and the total concentration of cerium ions \((C)\) are fixed.
Continuing increasing plotted in Fig. 2(a), showing a clear main peak at
with Gyorgyi and Field’s result [30]. Small-amplitude, sinusoidal period-1 oscillations develop as \( k_1 \) is increased to
3.163 \( \times 10^{-4} \) s\(^{-1}\). A sequence of period-doubling bifurcations follows, and chaos is reached at \( k_1 \approx 3.230 \times 10^{-4} \) s\(^{-1}\). Continuing increasing \( k_1 \) to 3.300 \( \times 10^{-4} \) s\(^{-1}\), period-3 is reached, and then another chaos follows.

3. Results

The bifurcation diagram with \( k_1 \) increasing from 3.000 \( \times 10^{-4} \) s\(^{-1}\) to 3.500 \( \times 10^{-4} \) s\(^{-1}\) is shown in Fig. 1, which agrees with Gyorgyi and Field’s result [30]. Small-amplitude, sinusoidal period-1 oscillations develop as \( k_1 \) is increased to 3.163 \( \times 10^{-4} \) s\(^{-1}\). A sequence of period-doubling bifurcations follows, and chaos is reached at \( k_1 \approx 3.230 \times 10^{-4} \) s\(^{-1}\). Continuing increasing \( k_1 \) to 3.300 \( \times 10^{-4} \) s\(^{-1}\), period-3 is reached, and then another chaos follows.

3.1. The effect of sinusoidal perturbations on the period-1 system

\( k_1 \) is modified as \( k_1(t) = k_{01}(1 + a \sin 2\pi \omega t) \), where \( k_{01} \) is a constant component, and \( a \) is the amplitude of the sinusoidal perturbation with frequency \( \omega \). We fix \( a \) to be 0.01 and scan \( \omega \) in a certain range. In the period-1 window, we select the case of \( k_{01} = 3.100 \times 10^{-4} \) s\(^{-1}\). The perturbed regime in the bifurcation diagram (denoted by \( \text{p} \) in Fig. 1) thus has the range of \( k_1 = 2.360 \times 10^{-4} \) s\(^{-1} \). The frequency spectrum for the period-1 of \( k_{01} = 3.100 \times 10^{-4} \) s\(^{-1}\) is plotted in Fig. 2(a), showing a clear main peak at \( \omega = 62.93 \) Hz with the peak height of 29.32. We let \( \omega \) increase from 0 to 300 Hz with the interval of 1 Hz. The peak height at the main frequency as a function of \( \omega \) is plotted in Fig. 3. As

Table 2
Parameters used in Eq. (2) [30]

| Rate constants \((k_i)\) for reactions (1)-(7) | 
|---|---|
| \( k_1 = 4.0 \times 10^3 \) M\(^{-1}\) s\(^{-1}\) | \( k_2 = 2.0 \) M\(^{-3}\) s\(^{-1}\) |
| \( k_3 = 3000 \) M\(^{-1}\) s\(^{-1}\) | \( k_4 = 55.2 \) M\(^{-2}\) s\(^{-1}\) |
| \( k_5 = 7000 \) M\(^{-1}\) s\(^{-1}\) | \( k_6 = 0.09 \) M\(^{-1}\) s\(^{-1}\) |
| \( k_7 = 0.23 \) M\(^{-1}\) s\(^{-1}\) | 

Other parameters

\( A = 0.1 \) M, \( M = 0.25 \) M, \( H = 0.26 \) M,
\( C = 8.33 \times 10^{-4} \) M, \( z = 666.7, \beta = 0.3478 \)

\[ \tau \equiv t/T_0, \quad x \equiv X/X_0, \quad z \equiv Z/Z_0, \quad v \equiv V/V_0 \]

with the scaling [30]

\[ T_0 = (10k_2AHC)^{-1}, \quad X_0 = k_2AH^2/k_5, \]
\[ Y_0 = 4k_2AH^2/k_5, \quad Z_0 = CA/(40M), \quad V_0 = 4AHC/M^2. \]

Finally, the dimensionless rate equations become

\[
\frac{dx}{d\tau} = T_0 \{ -k_1HY_0x\dot{y} + k_2AH^2Y_0/X_0y - 2k_3X_0x^2 + 0.5k_4A^{0.5}H^{1.5}X_0^{-0.5}C/Z_0x^2 - 0.5k_2Z_0xz - k_1x \}
\]
\[
\frac{dz}{d\tau} = T_0 \{ k_4A^{0.5}H^{1.5}X_0^{-0.5}C/Z_0 - z \} x^0.5 - k_5X_0xz - \alpha k_1Y_0\dot{v} - \beta k_1\dot{z} - k_5z \}
\]
\[
\frac{dv}{d\tau} = T_0 \{ 2k_1HX_0Y_0\dot{y} + k_2AH^2Y_0/V_0\dot{y} + k_3X_0^2/V_0x^2 - \alpha k_0V_0\dot{v} - k_1v \}.
\]

The parameters used in Eq. (2) are listed in Table 2. See Ref. [30] for more details about the model.

Eq. (2) are solved numerically using the Gear method. To obtain frequency spectra, 16,384 points at intervals of 0.001 s are used for fast Fourier transformation. By frequency spectra analysis, we can get the response curve of the peak height at the main frequency (the height of the highest peak in a frequency spectrum) to the frequency of sinusoidal perturbation. Here, the magnitude of the peak height at the main frequency in a frequency spectrum can reflect the degree of order for the data analyzed. As the data comes from a period-1 motion, the frequency distribution should only converge to the fundamental frequency and its harmonics. As the data comes from an aperiodic motion, the frequency distribution would disperse in a wider range of frequency. In both cases, the sum over the peak heights in the frequency spectrum is essentially conserved. Therefore, the peak height at the main frequency of the periodic data is clearly higher than that of the aperiodic data, and the more irregular the data is the lower the peak height at the main frequency is. There should exist a critical value for the peak height at the main frequency, above which the data is periodic.

mentioned above in the model section, there should exist a critical value for the peak height at the main frequency, above which the analyzed data is periodic. We find out that the critical value is about 15 in this work. Fig. 3 shows that there appear some valleys whose peak heights are below 5 when $\omega$ goes beyond 90 Hz. These low-value peak heights all

Fig. 3. Bifurcation diagram obtained from numerical simulations for the model in Table 1. Notations used are: p1, period-1 oscillations; p2, period-2 oscillations; p3, period-3 oscillations; pd, sequence of period-doubling bifurcations; ch, a chaotic regime; pr1, perturbed regime in the period-1 window; pr2, perturbed regime in the chaotic window.

Fig. 2. Characteristics of period-1 (p1) and induced chaos (ich) in the period-1 window: (a) frequency spectrum, p1; (b) frequency spectrum, ich; (c) limit cycle, p1; (d) strange attractor, ich; (e) Poincaré section, ich; and (f) return map, ich.
correspond to chaotic oscillations. We choose the case at $\omega = 178$ Hz as an example. Its frequency spectrum, phase-space diagram, poincaré section, and return map are shown in Fig. 2(b), (d–f). They all show the characteristics of chaos.

![Frequency Spectrum](image)

Fig. 3. Peak height at the main frequency in frequency spectrum as a function of perturbed frequency $\omega$ of $k_{\omega} = 3.100 \times 10^{-4}$ s$^{-1}$. The peaks whose heights are above the upper dashed line correspond to periodic oscillations. The peaks whose heights are below the lower dotted line correspond to chaotic oscillations.

![Frequency Spectra](image)

Fig. 4. Characteristics of chaos (ch) and induced periodicity (ip) in the chaotic window: (a) frequency spectrum, ch; (b) frequency spectrum, ip; (c) strange attractor, ch; (d) limit cycle, ip; (e) poincaré section, ch; and (f) return map, ch.
3.2. The effect of sinusoidal perturbations on the chaotic system

In the chaotic window, $k_{t_0}$ is same modulated as in the period-1 window, and $a$ is still fixed to be 0.01. We select the case of $k_{t_0} = 3.400 \times 10^{-4}$ s$^{-1}$. So the perturbed regime in the bifurcation diagram (denoted by pr$_2$ in Fig. 1) has the range of $k_{t_1} = 3.320 \times 10^{-4}$ s$^{-1}$–$3.68 \times 10^{-4}$ s$^{-1}$. The frequency spectrum for the chaos of $k_{t_0} = 3.400 \times 10^{-4}$ s$^{-1}$ is plotted in Fig. 4(a), which distributes in a wide range of frequency with the highest peak height of 4.16. Likewise, we let $\omega$ increase from 0 from 300 Hz with the interval of 1 Hz. The peak height at the main frequency as a function of $\omega$ is plotted in Fig. 5, in which eight sharp peaks whose heights above 15 appear, showing the occurrence of periodic behavior. We take the case of $\omega = 178$ Hz as an example (note it has the same perturbation frequency as in the example above for the period-1 window), and its frequency spectrum and phase-space diagram are respectively shown in Fig. 4(b) and (d). Obviously, a stabilized periodic motion is obtained.

4. Discussion

The effect that the periodic perturbation can induce chaos for the period-1 system might be understood by the circle map of two coupled oscillators. In the circle map, chaos can occur if the coupling strength is large enough. Our results in the period-1 window may be this case considering that one coupling oscillator is the BZ system and the other is the external periodic perturbation. In addition, we should note in Fig. 3 that besides those peak heights below 5 there are also some ones between 5 and 15 which correspond to quasi-periodic oscillations. Thus, the case here seems like that in Ref. [31], where the single Bonhoeffer–van der Pol neuron, driven by a sinusoidal external stimulus shows periodic, quasi-periodic and chaotic states.

As the sinusoidal perturbation is added to the chaotic system, the above result shows that we obtain eight induced periodic motions at the perturbation frequencies 26, 40, 62, 107, 122, 131, 178 and 242 Hz. The main frequency in the frequency spectrum of the controlled chaos is 59.50 Hz. We find out that four frequencies, i.e., 62, 122, 178 and 242 Hz, are basically of times of the main frequency, indicating the occurrences of resonance. Kraus et al. studied the effects of sinusoidal perturbations on the chaotic states in the seven-variable model of the BZ reaction and found out that this resonant chaos control was also effective [24].

5. Conclusion

Numerical study of a three-variable model for the BZ reaction in flow system shows the double-face of periodic perturbations, i.e., the transitions from periodicity to chaos in the period-1 window and the transitions from chaos to periodicity in the chaotic window both occur when the external sinusoidal perturbation is imposed on the control parameter. From the experimental point of view, the model used in this study is realistic enough to reproduce the experimentally observed behavior of the BZ reaction. And an experimental realization of the way used in this work is simple. Thus, it would be interesting if our results can be tested in the real experiments.
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References