Modeling chemical reactions by forced limit-cycle oscillator: synchronization phenomena and transition to chaos

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Abstract

The lattice limit-cycle (LLC) model is introduced as a minimal mean-field scheme which can model reactive dynamics on lattices (low dimensional supports) producing non-linear limit cycle oscillations. Under the influence of an external periodic force the dynamics of the LLC may be drastically modified. Synchronization phenomena, bifurcations and transitions to chaos are observed as a function of the strength of the force. Taking advantage of the drastic change on the dynamics due to the periodic forcing, it is possible to modify the output/product or the production rate of a chemical reaction at will, simply by applying a periodic force to it, without the need to change the support properties or the experimental conditions.

1. Introduction

Chemical reactive dynamics on low dimensional lattices have been in the focus of attention in recent years due to a variety of applications in Physical Chemistry and especially in heterogeneous catalysis [1–4]. When the reactive species come into contact with the catalytic surface a variety of non-linear phenomena is observed ranging from multistability and bifurcations up to chaotic oscillations.

To model reactive systems in general, the chemical kinetic equations have been used since the 1970s with considerable success in predicting the general macroscopic characteristics of the reaction evolution [5]. More recently, an attempt is made to take into account the local characteristics of the catalyst and to quantify the effect of the locality of interaction in the macroscopic development of the reaction, using a multitude of methods ranging from exact calculations [6] up to numerical simulations [7–9].

In earlier works the current authors and coworkers have developed models which incorporate some of the local characteristics of the reactive process within the mean-field model itself. In particular the fact that the reactions take place only on the catalytic surface whose total area is conserved (catalytic sites where particles are adsorbed and empty catalytic sites) can be incorporated within the mean field kinetic equations with the form of a conservation condition. As was shown in a number of works (see for example [6], [10], [11]) such reactive schemes can lead to periodic oscillations of the concentrations of the components which take part in the reactions. In particular, the lattice

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Lotka–Volterra reactive scheme has presented center-like oscillations because the correspondent system of equations was conservative [10], while the lattice limit cycle (LLC) model has lead to limit cycle mean field behavior for a considerably large region of the parametric space [11].

The models developed above involve two interacting species plus the empty catalytic sites, which amounts into only two independent components and thus the corresponding phase space is two-dimensional. Consequently, the most complex non-linear behavior expected was the appearance of limit cycle oscillations. Before attempting to investigate systems involving a higher number of reactive species in order to complexify further the dynamics and to investigate transitions to chaos we posse the question about the possibility of chaotic dissipative behavior in two components chemical systems under mean-field modeling.

As it is known the minimal dimension of phase space for chaos is three. Hence, if we consider the whole space of chemical reactions as a single oscillator, two components could not lead to chaotic oscillations of averaged concentrations. One possible way for mean field modeling of two components’ reactions which demonstrate chaotic behavior in experiments is to divide the reactions space into several subspaces each of which can be considered in the framework of the mean field approach. This approach naturally leads to arrays of interacting oscillators with diffusive (or may be some other) couplings and hence to a task of synchronization of oscillators. As a result of the interactions the coupled oscillators can demonstrate more complex (quasiperiodic and chaotic) behavior than the single one.

Dynamic features common to coupled reacting systems have been considered in a number of works (see for example [13], [14]). There the authors investigated different phenomena which take place in coupled and in periodically forced oscillators. They have found that the coupled reacting systems demonstrate typical synchronous behavior which is common feature for coupled oscillators in general. In this work we generalize/extend the LLC model, by adding a periodic external force which acts selectively only on one of the reactants. The extended mean-field model represents two-dimensional oscillator with periodic external force. Our investigations show that the chosen model demonstrate classical phenomena of synchronization of periodic oscillations and transition to chaotic oscillations.

In the next section the autonomous LLC model is recapitulated and each dynamical behavior and phase space structure are presented. In Section 3 the non-autonomous system is investigated, the complexity of its phase space is explored and various transitions to chaos are demonstrated. In the concluding section the main results are recapitulated, conclusions related to the impact of chaotic oscillations in reactive systems are drawn and open problems are discussed.

2. Autonomous system of four-molecular reactions

Let us consider the reactions on lattice of the type [11]:

\[
\begin{align*}
2X + 2Y & \xrightarrow{k_1} 3Y + S \\
X + S & \xrightarrow{k_2} 2X \\
Y + S & \xrightarrow{k_3} 2S
\end{align*}
\]

where \( X \), \( Y \) and \( S \) are molecules of type \( X \) and \( Y \) and empty lattice sites respectively, while \( k_1 \), \( k_2 \) and \( k_3 \) are the kinetic constants of the corresponding reactions.

Multimolecular MF reactive schemes have been used in chemical kinetics since the early 1970s and they have been very successful in predicting complex oscillatory dynamics and spatial pattern formations as observed in experiments [5]. In particular, quadrilamolecular models have been used since early 1980s to explore the possibility of obtaining sustained oscillations in surface reactions [12–14]. Experimentally, quadrilamolecular reactive steps have been proposed to describe the “vacancy models” [2]. In these models increase in the number of vacant sites leads to increase of the autocatalytic behavior leading further to oscillatory behavior. Well known vacancy models are the \( \text{NO} + \text{CO}, \text{NO} + \text{NH}_3 \) and \( \text{NO} + \text{H}_2 \) reactions all using the Pt surface as catalyst [2]. In all of them an autocatalytic behavior related to the vacant sites is observed and this explains, amongst other non-linear phenomena, the “surface explosion” phenomena observed frequently in heterogeneous catalysis: i.e. narrow peaks of the product concentrations at regular temporal intervals.

In the mean-field approach the kinetic equations for the evolution of the relative concentrations of the molecules \((x, y)\) and of the empty sites \((s)\) can be written as [11]:

\[
\begin{align*}
\frac{dx}{dt} &= \frac{2k_1}{3} y - k_2 x \\
\frac{dy}{dt} &= \frac{2k_1}{3} x - k_3 y \\
\frac{ds}{dt} &= k_2 x - k_3 y
\end{align*}
\]
\[
\begin{align*}
\frac{dx}{dt} &= -2k_1x^2y^2 + k_2xs \\
\frac{dy}{dt} &= k_1x^2y^2 - k_3ys \\
\frac{ds}{dt} &= k_1x^2y^2 - k_2xs + k_3ys
\end{align*}
\]

(2)

It is easily shown that a condition of conservation is fulfilled:

\[\frac{dx}{dt} \frac{dy}{dt} + \frac{ds}{dt} = 0\]

and hence, \(x + y + s = \text{const.}\) Choosing this constant value as 1: \(x + y + s = 1\) and substituting this in Eq. (2) the dimension of the system is reduced to two:

\[
\begin{align*}
\frac{dx}{dt} &= -2k_1x^2y^2 + k_2x(1 - x - y) \\
\frac{dy}{dt} &= k_1x^2y^2 - k_3y(1 - x - y)
\end{align*}
\]

(3)

Eq. (3) describe the behavior of the mean concentrations of the reactions (1). It can be written in a simpler form if dimension of the parameter’s is reduced to two, using the following time rescaling: \(\tau = k_1t\). Using notation \(\dot{x} = \frac{dx}{d\tau}\) the system (3) is rewritten in the new form:

\[
\begin{align*}
\dot{x} &= -2x^2y^2 + x(1 - x - y) \\
\dot{y} &= x^2y^2 - \beta y(1 - x - y)
\end{align*}
\]

(4)

where \(\alpha = k_2/k_1, \beta = k_3/k_1\).

We will consider the system (4) with positive values of parameters and dynamical variables because the variables \(x\) and \(y\) represent relative chemical concentrations. The system (4) has four fixed points:

1. A trivial point \(P_1 = (0; 0)\) is saddle with eigenvalues \(\lambda_1 = \alpha, \lambda_2 = -\beta\).
2. Two semi-trivial points: \(P_2 = (1; 0)\) is unrobust point with \(\lambda_1 = -\alpha, \lambda_2 = 0\) and \(P_3 = (0; 1)\) is unrobust point with \(\lambda_1 = 0\) and \(\lambda_2 = \beta\).
3. A non-trivial point \(P_4 = \left(\frac{\beta}{\alpha}, \frac{\beta}{\alpha}, \frac{\beta}{\alpha}, \frac{\beta}{\alpha}\right)\). Contrary to points \(P_1, P_2,\) and \(P_3\), the location and type of \(P_4\) depends on the values of the parameters. Depending on \(\alpha\) and \(\beta\) this point can be (a) stable node, (b) stable focus, (c) unstable focus (see Fig. 1(a)). Loss of stability of the equilibrium leads to birth of periodic oscillations via Andronov–Hopf bifurcation. The region of the presence of oscillations (which coincides with the region of unstable focus) is shown in Fig. 1(b).

Typical structure of the phase space in the region of our interest is presented in Fig. 2. It is seen that fixed points \(P_2\) and \(P_3\) have non-robust character. Trajectories approach them from one side and depart from a different one. An attracting limit cycle is located around the non-trivial fixed point. At the moment of its birth, through Andronov–Hopf bifurcation of the point \(P_4\), the oscillations have infinitesimally small amplitude and near-harmonic shape. As the parameters’ values drift away from the bifurcation values the amplitude of the oscillations increase and the trajectory spends a long time in the neighborhood of the invariant manifolds \((x = 0)\) and \((y = 0)\). Its shape becomes triangle-like and oscillations are unharmonic (Fig. 3).

The chosen dynamical system behaves as typical dissipative periodic self-oscillator. It demonstrates a rather complex phase space structure with several fixed points (including non-robust ones), one of which can give rise to periodic motion. The amplitude of oscillations of concentrations varies from 0 to almost 1 (for \(x\) variable). The reduced dimensionality of the phase space does not allow the development of more complex regimes which can be observed in real experiments. In reality the space of reactions can be influenced of neighboring/external sources. This leads to a model of periodically forced oscillator where the phase space dimensionality is equal to three. Hence, the modified mean-field
model with presence of external periodic force can demonstrate more complex types of behavior: quasiperiodic and chaotic.

3. Behavior of non-autonomous model

We modify the original model of the LLC oscillator (3) by adding a periodic term to the right hand side of the first equation:
\[
\frac{dx}{dt} = -2k_1x^2y^2 + k_2x(1 - x - y) + a \sin \omega t \\
\frac{dy}{dt} = k_1x^2y^2 - k_3y(1 - x - y)
\]

(5)

where \(a\) is amplitude and \(\omega\) is frequency of external force.

External forcing on dissipative self-oscillators may produce a variety of complex dynamical behaviors depending on the type of the forcing and for that reason has been extensively studied in the literature (see for example [15,16]). The external oscillatory term used in Eq. (5) is the simplest form of periodic forcing and mimics an external force field, such as exposure of the system to a source of periodic radiation, which affects the production of one of the two species or excites its reactivity. In the current section we wish to investigate how this periodic perturbation will modify the dynamics and how the phase portrait is affected under the influence of the external force. This is technologically important since we may modify the output of the reactive system at will, only by applying a simple periodic external force without the need to fabricate sophisticated catalytic materials or to apply specific experimental conditions which are sometimes hard and/or expensive to achieve.

Using the same procedure as for the autonomous system we transform Eq. (5) to two-parameters form:

\[
\dot{x} = -2x^2y^2 + xz(1 - x - y) + A \sin \Omega t \\
\dot{y} = x^2y^2 - \beta y(1 - x - y)
\]

(6)

Here \(A = a/k_1\) and \(\Omega = \omega/k_1\). We have chosen the values of the parameters \(x = 0.0413, \beta = 0.0667\) connected to developed oscillatory regime in the autonomous case with frequency of self-oscillation \(\Omega_0 = 0.0407\) and amplitude of time-series \(x(t)\) about 0.225. The amplitude \(A\) and the frequency \(\Omega\) of the external force serve as control parameters. We vary them in intervals \(0 \leq \Omega \leq 0.15\) and \(0 \leq A \leq 0.01\). The upper bound of the frequency corresponds to approximately \(3.5\Omega_0\). For values of \(A \approx 0.01\) (the exact threshold value depends on the frequency \(\Omega\)) the trajectory diverges to infinity. It is seen that the dynamics of the system in the chosen regime of dynamical variables is very slow and leads to very low frequency of self-oscillations and to small values for the time derivatives of the dynamical variables. The amplitude of autonomous oscillations of the derivative \(\dot{x}\) is approximately \(\approx 0.0114\). Therefore we chose very small absolute values of the amplitude of the external force \(A\). The value of the amplitude of the “real” force \(a = k_1A\) can become large if we chose large values for the parameter \(k_1\).

We investigate the system (6) at frequencies of the external force close to the frequency of self-oscillations. In this case the oscillator demonstrates typical regimes of synchronization with different rotation numbers and regimes of
quasiperiodic behavior corresponding to ergodic two-dimensional tori. The structure of regions of synchronizations represents standard structure of “Arnold’s tongues” which lean on the line \( A = 0 \) (Fig. 4). As it is seen from the figure the structure of the parameters plane is characterized by overlap of resonance regions. As a result in the region of overlap the system demonstrates developed multistability with a variety of stable regimes coexisting at the same parameters values. By properly choosing the initial conditions we can obtain the desired behavior.

Increasing the amplitude of the force leads to complexifying the oscillating regimes. Outside the regions of synchronization we observe transition from quasiperiodic oscillations to chaotic through tori breaking. Inside the tongues typical route to chaos is period-doubling cascade on base of the stable limit cycle which locates on the torus surface at lower value of the force. The structures of the synchronization tongues are rather complex with lines of abrupt bifurcations and intermittency between several regimes. The typical structure is shown in Fig. 5 for the 1:1 synchronization area. The region of main resonance is bounded by lines \( l_1 \) and \( l_2 \). Inside them, and up to line \( l_3 \), a stable periodic cycle \( 1C_1 \) appears. In the low part of the tongue the cycle is located on the torus surface. Its phase portrait is represented in Fig. 6(a). The period of the cycle is equal to the period of the external force.

The boundaries \( l_1 \) and \( l_2 \) has complex structures and consist of several bifurcational lines. The lower parts of the lines \( l_1 \) and \( l_2 \) (up to points \( P_{sn} \)) are lines of saddle-node periodic bifurcations. On these lines the stable limit cycle \( 1C_1 \) merges with saddle cycle located on the torus surface and then both the cycles vanish. Over this point on the line \( l_1 \) the system demonstrates abrupt transition from the cycle \( 1C_1 \) to quasiperiodic oscillations which are accompanied by hysteresis. With backward parameter changing the system returns to periodic oscillations \( 1C_1 \) on line \( l_4 \). Appeared on the line \( l_4 \) torus smoothly transforms to periodic cycle \( 1C_2 \) through backward Hopf bifurcation on the line \( l_5 \). This line leans to the another resonance tongue with rotation number 1:2 (the line and the boundary of the 1:2 resonance are marked by dots). Both bifurcational lines \( l_4 \) and \( l_5 \) merge in the point \( P_{bn} \). Over it, on the line \( l_6 \) we observe abrupt transition from the cycle \( 1C_2 \) to the original resonance \( 1C_1 \) cycle. The right boundary has another structure. Over the point \( P_{sn} \) the boundary \( l_2 \) can be divided to two intervals with different types of synchronization loss. The interval between points \( P_{sn} \) and \( P_{an} \) is characterized by abrupt transition with hysteresis between lines \( l_2 \) and \( l_7 \). At larger amplitude of the force, above the point \( P_{bn} \), the synchronization loss occurs on line \( l_4 \) through Hopf bifurcation of the cycle \( 1C_1 \). The line of the Hopf bifurcation leans to the line \( l_1 \) (point \( P_{b} \)) which bounds the region of existence for the cycle \( 1C_1 \) from top. On the line \( l_5 \) the limit cycle \( 1C \) undergoes the period-doubling bifurcation. As a result the limit cycle becomes saddle one and the trajectory develops into a stable period-two cycle \( 2C \) (Fig. 6(b)). On the point \( P_{bd} \) (Fig. 5) the line \( l_2 \) of the Hopf bifurcation of the \( 1C \) cycle merges with the line of its period-doubling bifurcation. This merging takes place only from right-to-left (higher to lower frequencies). From the reverse side, the lines \( l_1 \) and \( l_3 \) develop parallel to each other. When the force amplitude \( A \) is further increased there is a next period-doubling bifurcation (line \( l_6 \) in Fig. 5) after which we observe a period-four cycle \( 4C \) (Fig. 6(c)). The cascade of period-doubling

Fig. 4. Regions of synchronization with different rotation numbers on the plane \( \Omega/\Omega_0 - A \) (\( \Omega_0 \) is the frequency of autonomous oscillations). The region of main resonance (1:1) is marked by grey color.
bifurcations is finished by transition to chaos (dotted line $l_9$ in Fig. 5). In the chaotic region there are band-merging bifurcations which lead from many band chaotic attractors $2^n A$ to a one-band attractor $1A$. In the region of many band chaotic attractors one can observe windows of periodicity. Phase portraits of different many band chaotic oscillations are shown in Fig. 6(d)–(f). Evolution of regimes inside the synchronization region is finished on line $l_{10}$ (from the left side of the point $P_{ua}$) by abrupt transition to oscillating regimes coexisting with the one-band chaotic attractor $1A$. From the right side of the point $P_{ua}$ on the line $l_{10}$ the one-band chaotic attractor merges with another chaotic set and chaotic behavior becomes more developed. The line $l_6$ over the point $P_{ua}$ divide the region of existence of the developed chaos and of regular oscillating regimes. On this line we observe intermittency process between chaotic and periodic oscillations.

Outside the regions of synchronization we can observe transitions to chaos from regimes of quasiperiodic oscillations. This process takes place at values of the external force $A' = 0.0025$. Fig. 7 represents the phase portraits (left column) and the stroboscopic sections (right column) corresponding to sequential stages of the process of the transition from ergodic torus to chaotic attractor.

This rich complex structure is developed on the LLC model by simple exposure of it to an external periodic force. The original limit cycle behavior develops complex regimes including multiple tori with transitions to chaos through either period doubling bifurcations or through tori breaking. Inverse transitions take place from many band chaotic attractors for high values of the external periodic force amplitude. This analysis shows that it is possible to complexify the behavior of the limit cycle in a reactive system and to obtain certain dynamical characteristics at will, without modifying the experimental conditions other than exposing the system into an external periodic force.

Comparison of the yield of $x$-particles in the reactions with and without external force influence is presented in Fig. 8 and Table 1. The time-series of the concentration $x(t)$ is shown for gradually increasing amplitude of the force $A$. All calculations are inside the region of the main resonance with $\Omega = 0.0365$. The influence of the force leads to both complexifying the shape of oscillations from simple one-periodic at $A = 0$ (Fig. 8(a)) till two-periodic at $A = 0.00272$ (Fig. 8(b)), weakly chaotic at $A = 0.00281$ (Fig. 8(c)) and strongly chaotic at $A = 0.00283$ (Fig. 8(d)) and to increasing of the amplitude of the oscillations from $\approx 0.4$ till $\approx 0.8$. Quantitative results are shown in Table 1, where the average yield $x_{av}$ on particles $X$ is computed over 30 cycles of oscillations (in the case $A = 0$). In the forth column of the same table the relative $x$-yield is computed. The yield increases rapidly with increasing amplitude $A$ of the force and the susceptibility, represented here by the derivative of the $x$-yield with respect to the external forcing, $dx/dA$, increases exponentially fast as we enter the region of developed chaos. As expected, the maximum instantaneous yield $x_{max}$, which can be important in applications, is also achieved in the region of chaotic oscillations, as seen in the last column of Table 1.

Abrupt changes in the outflux of certain species can be generated for specific values of the external force amplitude. In Fig. 9 an abrupt transition is shown when the amplitude of the force crosses a critical value $A_c$. Fig. 5. The structure of region of main resonance (1:1).
above which the system enters the regime of developed chaos. The value $A_c$ depends on the frequency $\Omega$. In Fig. 9 the mean outflux of $x$ and $y$ are presented as a function of $A$ for given frequency $\Omega = 0.041$. The transition point for the given frequency is $A_c \simeq 0.0037$. Such transitions are very important in applications where by varying the external force field one can accelerate the production of a given product and in some cases even change the specificity of the reaction.
Fig. 7. Transition from quasiperiodic to chaotic oscillations (phase portraits and stroboscopic section): (a,b) smooth torus ($A = 0.00246$, $\Omega = 0.0481$); (c,d) beginning of the transition ($A = 0.002461$, $\Omega = 0.0481$); (e,f) chaotic attractor ($A = 0.00248$, $\Omega = 0.0481$).

<table>
<thead>
<tr>
<th>$A$</th>
<th>Regime</th>
<th>$x_{av}$</th>
<th>$x_{av}/x_0$</th>
<th>$x_{max}$</th>
</tr>
</thead>
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<tr>
<td>0.0</td>
<td>Limit cycle</td>
<td>0.481</td>
<td>1.000</td>
<td>0.713</td>
</tr>
<tr>
<td>0.00272</td>
<td>Two-cycle</td>
<td>0.545</td>
<td>1.133</td>
<td>0.948</td>
</tr>
<tr>
<td>0.00281</td>
<td>Weak chaos</td>
<td>0.553</td>
<td>1.150</td>
<td>0.957</td>
</tr>
<tr>
<td>0.00283</td>
<td>Strong chaos</td>
<td>0.595</td>
<td>1.237</td>
<td>1.027</td>
</tr>
</tbody>
</table>

Table 1
Average $x$-yield as a function of the amplitude $A$ of the force for $\omega = 0.00365$
4. Conclusion

We have considered the dynamical features of a two-component quadrinolecular reactive system, the LLC model, in the presence of periodic external influence using the mean-field approach. The autonomous model demonstrates limit cycle behavior from near-harmonic to strictly unharmonic periodic oscillations. The non-autonomous model demonstrates typical phenomena of synchronization of periodic oscillations with structure of the parameters’ plane common in forced oscillatory systems. It demonstrates a route from regular to chaotic oscillations through cascade of period-doubling bifurcations (inside tongues of synchronization) and from quasiperiodic oscillations (outside the tongues). In the region of overlap of synchronization tongues the system demonstrate developed multistability.

This analysis shows that it is possible to take advantage of the drastic changes in the dynamical behavior of the reactive system under the periodic forcing and to gradually modify its behavior to obtain complex dynamical features at
will. Experimentally this can be done only by simple exposure of the apparatus to a periodic external force without modifying otherwise neither the catalyst properties nor the conditions of the experiment.

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