Журнал в журнале – для студентов и преподавателей

Изв. вузов «ПНД», т.11, № 2, 2003 УДК 517.39

CHAOTIC DYNAMICS OF CHEMICAL REACTIONS IN LOW-DIMENSIONAL SUBSTRATES: MEAN-FIELD AND MONTE-CARLO APPROACHES

A. Efimov, A. Shabunin, V. Astakhov, A. Provata

Complex reactive dynamics on low-dimensional lattices is studied using mean-field model and Monte-Carlo simulation. We consider four-species cyclic chemical reactions on one- and two-dimensional catalytic supports. The resulted mean-field model is conservative. Depending on parameters it shows quasi-periodic or chaotic oscillations. One-dimensional lattice does not demonstrate oscillating behavior due to the geometric restrictions. Lattice Monte-Carlo simulations on two-dimensional lattices show locally emergence of chaotic oscillations which are resulted from complex motions and interactions of clusters of homogeneous species. The properties of the oscillations depends on the size of the lattice.

Introduction

For the last decades the dynamics of chemical reactive systems on low-dimensional supports have been in the focus of attention due to their extensive applications in catalytic processes [1-8]. For interpretation of the basic mechanisms underlying the formation of spatiotemporal patterns observed in such processes different models have been proposed [3,5,6]. Methods of non-linear dynamics offer the possibility of analyzing these models and predicting some essential features of their behavior. Basic approaches for similar models are the mean-field and the Monte-Carlo simulation methods. The first one describes the space of reactions as a whole without considering local interactions (if they are present) i.e. description on macrolevel. The other one takes into account processes in the every site of the system and describes local behavior with many interesting phenomena such as clustering, wave propagations etc. Hereunder it uses description on mesolevel. Comparison between these two approach is a subject of the present work. We investigate regular and chaotic behavior of cyclic chemical reactions on lattices with dimensionality one and two in the mean-field and Monte-Carlo approaches. As it was shown in reference [5] similar systems demonstrate different behavior depending on geometry of the lattice. The differences in obtained results can be explained by the fact that the geometry and the dimensionality of the lattice strongly influence the behavior of the investigated system. In the present work we investigate a system of reactions with four interacting components. Mean-field approach leads to conservative dynamical system, which reflects the dynamics of average concentrations of substances. Depending on the parameters and the initial concentrations this model demonstrate

regular (quasi-periodic) or chaotic behavior. The Monte-carlo simulation of the processes on the lattice demonstrates complex motion of spatial clusters of homogeneous species. Results obtained by these methods have both similarities and some differences. Most of the effort in this study is focused in this comparison of the obtained results to a better explanation of spatiotemporal behavior of the system.

Conservative chaos in four-component reactions

We consider systems of cyclic chemical reactions in the form [7,8]

$$\begin{gathered} X + Y \xrightarrow{k_1} 2Y, \quad Y + Z \xrightarrow{k_2} 2Z, \quad Z + U \xrightarrow{k_3} 2U, \\ U + S \xrightarrow{k_4} 2S, \quad S + X \xrightarrow{k_5} 2X \end{gathered} \tag{1}$$

where X, Y, Z, U are reactive components and S are emptylattice sites respectively while k_1, k_2, k_3, k_4 and k_5 represent the kinetic constants of the corresponding reactions. To get mean-field equations we suppose that the probability of the every reaction in the scheme (1) depends on the products of the correspondent components. The standart technique leads to five differential equations for the concentrations of the molecules x, y, z, u and the empty sites s respectively. Using the conservation condition $x+y+z+u+s$=const with const=1 leads to four-variables equations for relative concentrations:

$$\begin{aligned} dx/dt &= -k_1xy + k_5x(1-x-y-z-u), \\ dy/dt &= k_1xy - k_2yz, \\ dz/dt &= k_2yz - k_3zu, \\ du/dt &= k_3zu - k_4u(1-x-y-z-u). \end{aligned} \tag{2}$$

Considered system is conservative: it is seen that it has an integral of motion

$$x^{k_2k_4}y^{k_3k_5}z^{k_1k_4}u^{k_2k_5}(1-x-y-u-z)^{k_1k_3} = K. \tag{3}$$

Its phase space has the following equilibrium points and sets: the trivial point: P_1=(0;0;0;0); semi-trivial equilibrium lines P_2=(0;0;z;0), P_3=(0;y;0;0), P_4=(0;y;0;1-y), P_6=(x;0;1-x;0) (when the space of reactions is poisoned by one substance) and one nontrivial equilibrium point $P_7 = (k_2k_4/A;\ k_3k_5/A;\ k_1k_4/A;\ k_2k_5/A)$ where $A=k_1k_3+k_2k_4+k_3k_5+k_1k_4+k_2k_5$. The region of our interest (from the point of view of chemical reactions) is bounded by invariant manifolds: x=0, y=0, z=0, u=0 and $x+y+z+u$=1 which do not allow phase trajectories to leave the region. The dynamics of the system (2) depends on five parameters: k_1, k_2, k_3, k_4 and k_5. However, their number can be reduced to four by appropriate renormalization

$$\begin{aligned} \dot{x} &= -xy + \delta x(1-x-y-z-u), \\ \dot{y} &= xy - \alpha yz, \\ \dot{z} &= \alpha yz - \beta zu, \\ \dot{u} &= \beta zu - \gamma u(1-x-y-u-z), \end{aligned} \tag{4}$$

where $a=k_2/k_1$, $\beta=k_3/k_1$,$\gamma=k_4/k_1$, $\delta=k_5/k_1$, $\tau=k_1t$, $\dot{x}=dx/d\tau$. Dynamics of the system (4) is similar to the one of system (2) up to a time scale. Depending on parameters values and

initial conditions the system (4) demonstrates two qualitatively different types of behavior: quasi-periodic, when the phase trajectory locks on a two-dimensional torus (cases of many-band tori also take place), and conservative chaos. Fig. 1 represents a

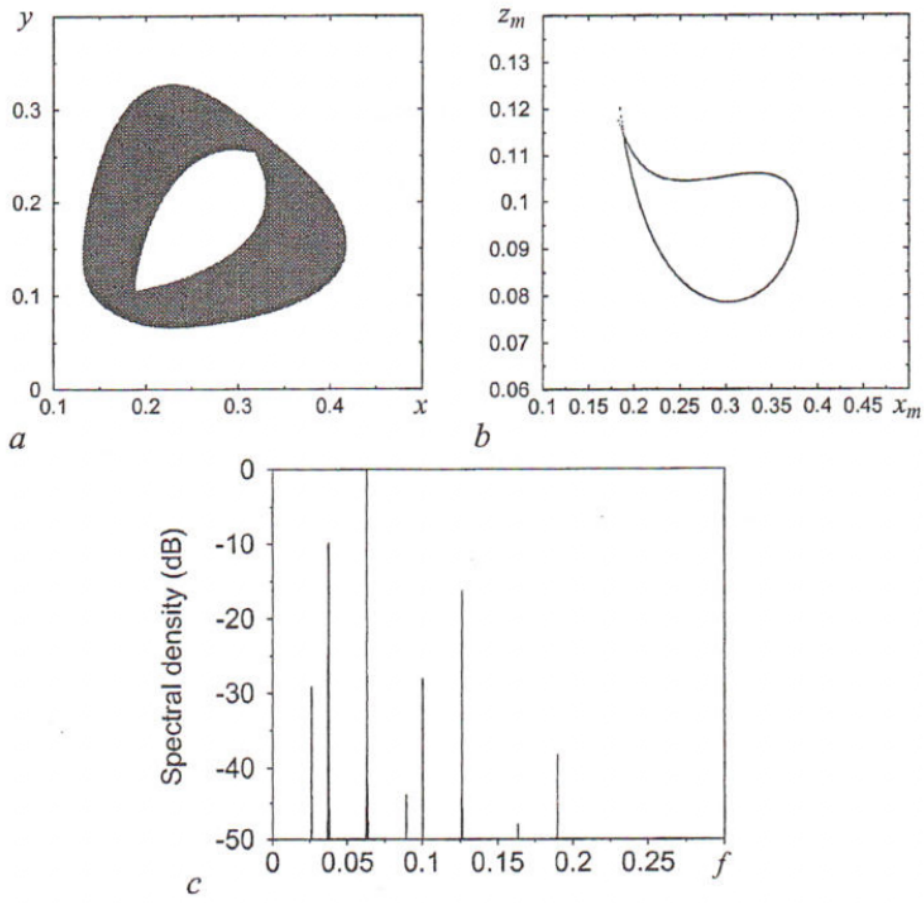

Fig. 1. A projection of the phase portrait (*a*), a Poincare section (*b*) and power spectrum (*c*) of oscillations in the system (4) for parameters α=1.5, β=1.0, γ=1.0, δ=1.0 and initial values x_0=0.2, y_0=0.1, z_0=0.11, u_0=0.3

typical example of quasi-periodic behavior: phase portrait (*a*), Poincare section (*b*) and power spectrum (*c*) of the oscillations. In the fig. 2 we see an example of the chaotic behavior. Contrary to dissipative systems, attractor-like behavior is impossible in this case. Hence, every mentioned oscillatory regime depends not only on the values of the parameters but also on the choice of initial conditions. Therefore, we cannot describe the evolution of the system solely based on the parameters because at the same parameters values infinite number of quasi-periodic and chaotic limit sets exist. Fixing the values of the parameters we can observe regular and chaotic regimes coexisting at different initial values. Contrary, fixing initial values we can built regions of existence of typical oscillating regimes on the plane of the parameters. The last case is represented in fig. 3 where we built the region of quasi-periodic behavior on the plane of the parameters α and β. In the figure, regions of quasi-periodic oscillations are located inside the «tongues» marked by «○» and «◇». It is seen that the shapes of the regions are similar for two different initial values. In both cases chaotic oscillations take place at large and at small values of the parameter α. The regions of regular behavior become more narrow with

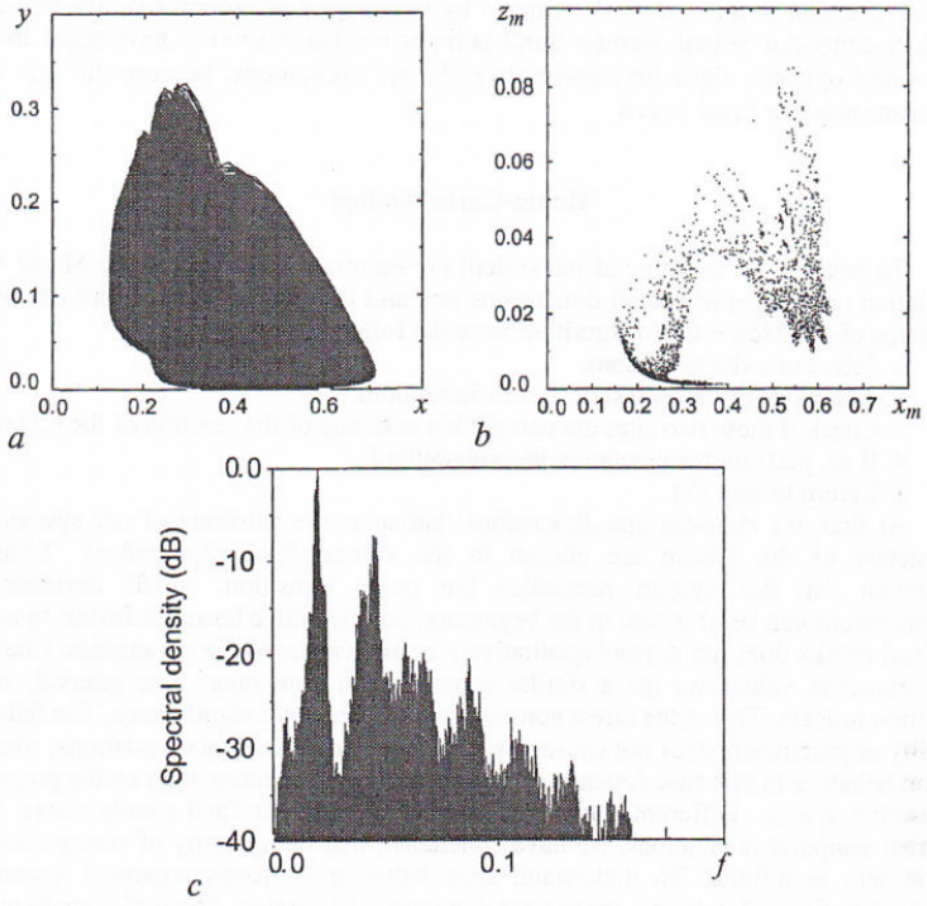

Fig. 2. A projection of the phase portrait (*a*), a Poincare section (*b*) and power spectrum (*c*) of oscillations in the system (4) for parameters α=5.98, β=1.0, γ=1.0, δ=1.0 and initial values x_0=0.2, y_0=0.1, z_0=0.11, u_0=0.3

decreasing of the parameter β, and at small β (β<0.1) quasi-periodic oscillations are not observed. To be sure that we deal with conservative chaotic dynamics we have built the Lyapunov exponents on the trajectory of the system. Fig. 4 demonstrates dependence of all four exponents on the parameter α for the same initial values used in fig. 3. Two of the

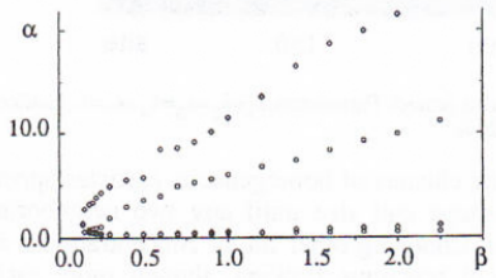

Fig. 3. Boundaries for regions of quasi-periodic behavior for the initial values: x_0=0.2, y_0=0.1, z_0=0.11, u_0=0.3 (○) and x_0=0.4, y_0=0.1, z_0=0.11, u_0=0.3 (◇) on the plane of parameters β - α. The other parameters are fixed in the values: γ=1, δ=1

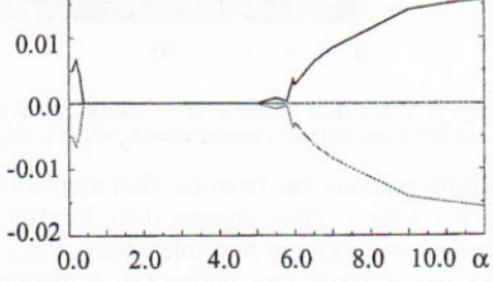

Fig. 4. Dependence of the Lyapunov exponents on the parameter α for initial values x_0=0.2, y_0=0.1, z_0=0.11, u_0=0.3. The other parameters are fixed in the values: β=1, γ=1, δ=1

exponents are always equal to zero: one of them is along the trajectory and the other is in normal direction to the surface determined by the integral of motion (3). The remaining two exponents can be both zero for quasi-periodic oscillations or can have equal absolute values and opposite signs for conservative chaotic oscillations, because the sum of all exponents must be equal to zero.

Monte-Carlo Method

To analyze the dynamic of the system (1) on micro level we use the Monte-Carlo simulation on lattices of spatial dimensions one and two with free boundary conditions. The steps of our Monte-Carlo algorithm were the following:

1. Select one site at random.
2. Select one of its nearest neighbors in random.
3. Check if these two sites are compatible with any of the reaction of the scheme.
4. If so, perform the reaction with probability k_i.
5. Return to step (1).

At first, we consider one-dimensional lattice as the substrate of our system. The parameters of the system are chosen in the values: $k_1=k_2=k_3=k_4=k_5=1$. Temporal realization for this system resembles the noise transition. Small deviations of concentrations can be observed in the beginning, but the lattice becomes frozen soon. The obtained results does not depend qualitatively on the values of the parameters. Changing the parameters values we get a similar behavior, but with other time intervals of the transition process. This is the direct consequence of parameter significance. The failure of equality of parameters does not cause any noticeable or fundamental variations, since the system behavior in this case depends on initial configuration more, than on the proportion of reaction speeds. Different initial values lead to different final steady states. From different temporal realizations, we have concluded, that the quantity of steady states for this system is infinite. To understand such behavior of four-component system we demonstrate figure 5, where a space-time dynamic is illustrated. The initial configuration

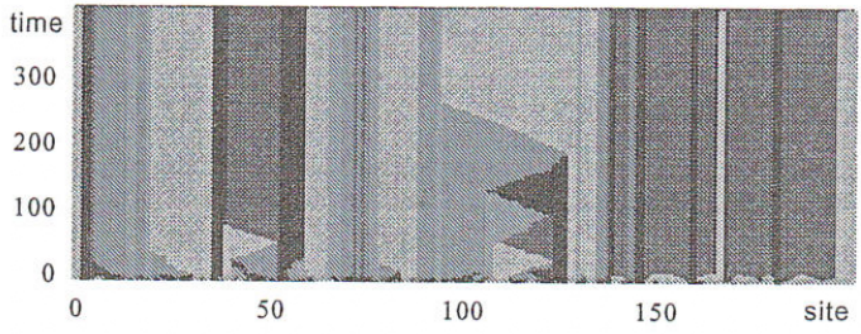

Fig. 5. Space-time dynamic of one-dimensional lattice.protect Parameters:$k_1=k_2=k_3=k_4=k_5=1$. Lattice size 200 sites. Initial concentrations:$X_0=Y_0=Z_0=U_0=20\%$

is fully random, but from the first moments the clusters of homogeneous particles appear in the lattice. They change their location, shape and size until any two neighboring clusters will contain non-interacting particles. Choosing other initial concentrations, we did not observe any noticeable deviations in reactions flowing, though more rapid transitions to the steady state are possible.

Let us consider now two-dimensional lattice. The behavior of the concentrations is now qualitatively different compare to the one-dimensional case. Lattices of sufficiently large size demonstrate chaotic oscillations of concentrations which do not transit to a

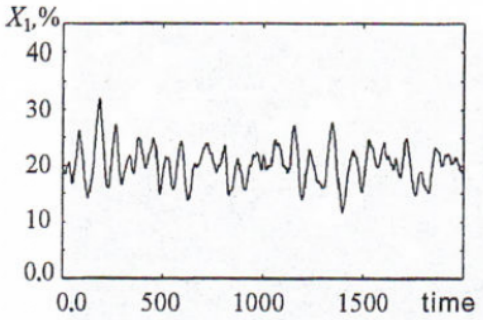

Fig. 6. Time evolution conservative chaotic dynamics on a two-dimensional lattice. Parameters: $k_1=k_2=k_3=k_4=k_5=1$. Initial concentrations: $X_0=Y_0=Z_0=U_0=20\%$. Lattice size 128×128 sites

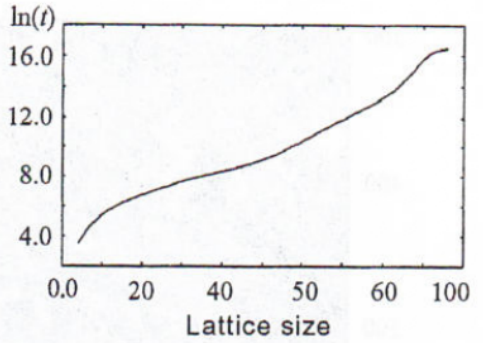

Fig. 7. Dependence of lifetime of oscillations on lattice's size in semi-logarithmic scale. Parameters: $k_1=k_2=k_3=k_4=k_5=1$. Initial concentrations: $X_0=Y_0=Z_0=U_0=20\%$

steady state during reasonable observation times. Typical time-series of concentrations is demonstrated in fig. 6. Lattices of smaller sizes demonstrate temporal chaotic behavior (similar to the described in the fig. 6) which is finished by transition to poisoning of the whole lattice by some substance. The life-time of oscillations depends on both lattice size and chosen initial conditions. Choosing initial concentrations far from equilibrium state leads to shorter life-time. The averaged dependence of the life-time of oscillations on the size of the lattice is shown in fig. 7 (in semi-logarithmic scale). The amplitude of the concentrations of the oscillations depends on the lattice size. When increasing the lattice size the amplitude of oscillations is reduced. Alternatively, if we observe only a smaller part of the lattice of a particular size we see oscillations of larger intensity. For example, in fig. 8 there are time-series of concentrations of substance X built on 10×10 and 50×50 sub-lattices of the original 128×128 lattice. At equal values of parameters the point of nontrivial equilibrium has coordinates $P_7(0.2;0.2;0.2;0.2)$. It means that each substance occupies the lattice on 20% and remaining 20% of sites are empty. In dynamical model this relates to the steady state of the system. In Monte-Carlo simulations we observe oscillations of concentrations of all substances near the value of 20% with some amplitudes. These oscillations are stable with respect to choice of the particular initial conditions while their averaged values remain the same. The temporal averages of the concentrations are equal to the equilibrium values of the dynamical model.

The mean-field dynamical model is conservative with an integral of motion

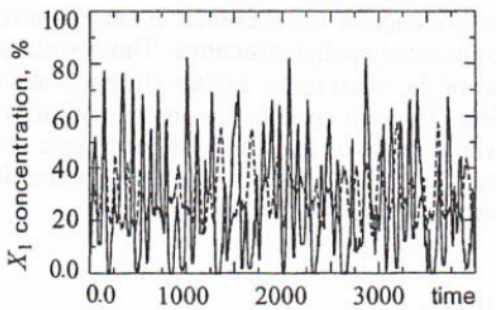

Fig. 8. Oscillations on sub-lattices of the whole lattice of 10×10 sites (solid line) and 50×50 sites (dashed line). The full lattice is 128×128 sites

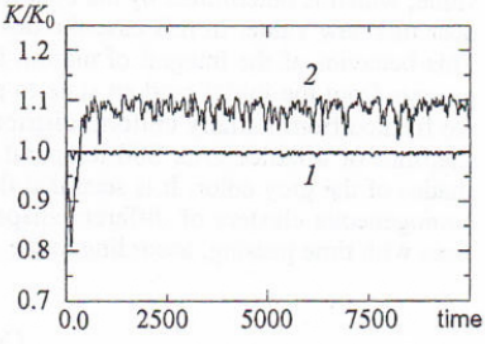

Fig. 9. Dependence of the integral of motion (3) on time for two different sets of initial concentrations: $X=Y=Z=U=20\%$ (curve *1*) and $X=20\%$, $Y=10\%$, $Z=10\%$, $U=30\%$ (curve *2*) on lattice 500×500. The values of the parameters: $k_1=k_2=k_3=k_4=1$

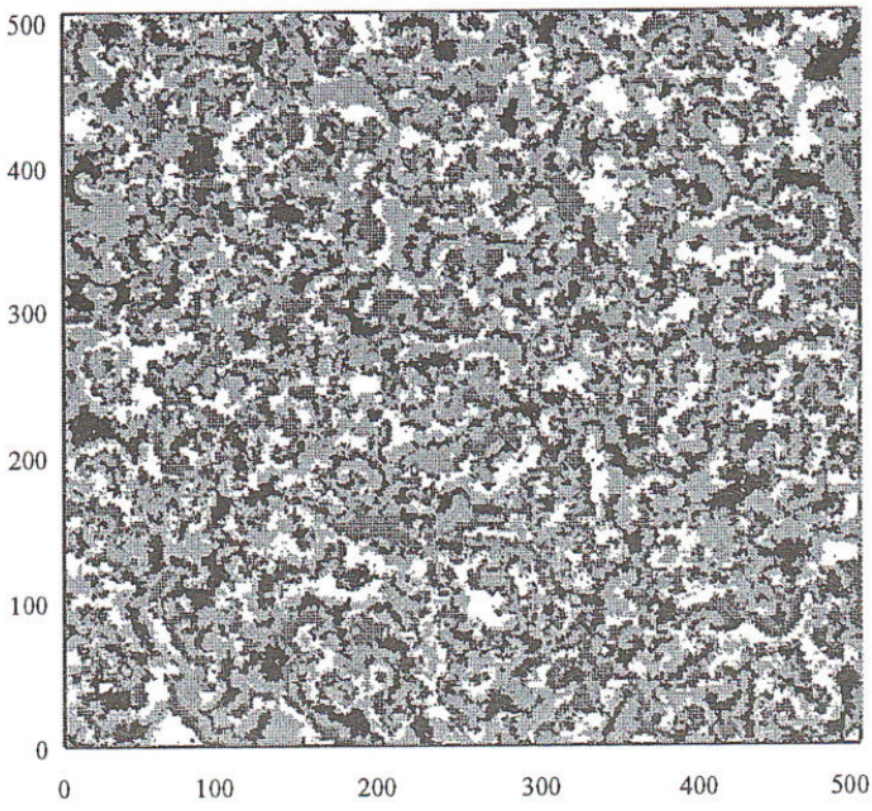

Fig. 10. Space realization for two-dimensional lattice. Parameters: $k_1=k_2=k_3=k_4=k_5=1$. Initial concentrations: $X_0=Y_0=Z_0=U_0=20\%$. Lattice size 500×500 sites. Snapshot of a lattice through 500 temporal units after initial filling

determined by (3). Is this characteristic preserved with time in Monte Carlo simulations? In fig. 9 we show the values of (3) per the value of the integral in the initial moment of time. When initial concentrations are chosen near the equilibrium state the integral is close to its initial value $K_0=K(0)$ (see the curve *1* in the fig. 9) and its deviation remain very small. Choosing initial concentration farther from the equilibrium state we observe departure of the integral from its initial value during very short interval to another steady value, which is determined by the concentrations. Then, the value of the integral oscillate near this new value. In this case the deviations become much larger (curve *2* in fig. 9). This behavior of the integral of motion is an evidence of the presence of some transient process from the initial random state to more ordered spatial structures. These structures are formed from initially uniform distribution of the substances. Figure 10 represents the snapshot of a lattice after 500 temporal units. Different species are shown by different shades of the grey color. It is seen that the whole space of the reactions becomes a set of homogeneous clusters of different shape and size. The clusters move and change their sizes with time passing, according to the scheme of reactions (1).

Conclusion

The mean-field model of the four-components cyclic reactive system demonstrates both chaotic and quasi-periodic behavior. Because the system is conservative and has no attractors its phase space has infinite number of chaotic and torus-like limit sets co-

existing at the same parameters values. In real conditions any small noise being present in the system (for example due to small fluctuations of the system's parameters) will lead to wandering of the trajectory from one limit set to other and hence to intermittent behavior. Using Monte-Carlo simulation on a two-dimensional substrate we observe complex random-like behavior of the average concentrations, the amplitude of which depends on the size of the lattice. The lifetime of these oscillations depends on spatial dimension and size of the lattice. The one-dimensional lattice demonstrates only short transient oscillations to one of the steady states. Two-dimensional lattices demonstrates permanent chaotic oscillations if the size of the lattice is sufficiently large. The oscillation is a result of interaction and relative motion of clusters of homogeneous substances which are formed during the initial time interval.

Acknowledgments

The authors acknowledge support by NATO Collaborative Linkage Grant PST.CLG. 977654. A.E., A.S and V.A. would like to acknowledge support from Civilian Research & Development Foundation (Grant REC-006).

References

1. *Ertl G.* // Science. 1991. Vol. 254. P. 1750.
2. *Voss C., Kruse N.* // Applied Surface Science. 1994. Vol. 87/88. P. 127.
3. *Zhdanov V.P.* // Surface Science. 1999. Vol. 426. P. 345.
4. *Ertl G., Freund H.* // Physics Today. 1999. Vol. 52. P. 32.
5. *Provata A., Nicolis G., Baras F.* // Journal of Chemical Physics. 1999. Vol. 110. P. 8361.
6. *Liu D.J., Evan J.W.* // Phys. Rev. Lett. 2000. Vol. 84. P. 953.
7. *Picard G., Johnson T.W.* // Phys. Rev. Lett. 1982. Vol. 48. P. 1610.
8. *Frachebourg L., Kapivsky P.L., Ben-Naim E.* // Phys. Rev. E. 1996. Vol. 54. P. 6186.

Saratov State University, Russia
Institute of Physical Chemistry,
National Research Center
«Demokritos», Athens, Greece

Поступила в редакцию 28.02.03

ХАОТИЧЕСКАЯ ДИНАМИКА ХИМИЧЕСКИХ РЕАКЦИЙ НА РЕШЕТКАХ НИЗКОЙ РАЗМЕРНОСТИ: СРАВНЕНИЕ МЕТОДОВ СРЕДНЕГО ПОЛЯ И МОНТЕ-КАРЛО

А. Ефимов, А. Шабунин, В. Астахов, A. Provata

В работе рассматривается сложная динамика химических реакций, происходящих на решетках низкой размерности, состоящих из молекул катализатора. Для схемы циклических реакций в приближении среднего поля строится система дифференциальных уравнений, описывающая консервативный осциллятор. В зависимости от выбора параметров и начальных значений модель среднего поля демонстрирует квазипериодические или хаотические колебания. Локальная динамика реакций моделируется методом Монте-Карло для решеток размерности один и два. Сопоставляются результаты моделирования методами среднего поля и Монте-Карло.

Efimov Anton Viktorovich, student of the fourth course of the Radiophysics and Nonlinear Dynamics Department of the Saratov State University. Fields of scientific interests are nonlinear oscillations and wave theory, application of nonlinear dynamics methods for problems of chemical physics.

Редакция приносит свои извинения Сергею Павловичу Курдюмову за ошибку, допущенную в журнале «Известия вузов.ПНД», 2003, т. 11, № 1 стр. 98.

Следует читать:

ПРОЛОГ

СИНЕРГЕТИКА И СИСТЕМНЫЙ АНАЛИЗ

С.П. Курдюмов, Г.Г. Малинецкий