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Trigger Mechanism of Self-Oscillations and Effect of Molecule Self-Organization in the Course of Monte Carlo Modeling of a Bimolecular Catalytic Reaction

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In the Ziff, Gulari, and Barshad (ZGB) model of the catalytic reaction $2A + B_2 = 2AB$, we have investigated by Monte Carlo (MC) simulation oscillatory kinetics and spatial–temporal self-organization caused by jumpwise variations in the catalytic properties of the surface. The following conditions were used. The adsorbed B_2 particles did not dissociate and did not react until A-coverage was less than the critical coverage Θ_A^{kr}. When, however, A-coverage reached Θ_A^{kr}, the adsorbed B_2 particles dissociated instantly into B particles and reacted with the adjacent A particles. It has been found that in a certain region of Y_A (a ratio of partial pressures of A and B_2 in the gas phase) oscillatory kinetics is controlled mainly by one compact cluster of A particles. We have established the specific mechanism of A-clusterization. We found also that in a certain region of Y_A our stochastic system demonstrates a route to chaos which is very similar to "intermittency" (P. Manneville and Y. Pomeau scenario).

INTRODUCTION

The complex dynamics of heterogeneous catalytic reactions far from equilibrium is of great interest for practical applications as well as for fundamental science. These reactions may exhibit many phenomena of nonlinear dynamics: various types of oscillations, which vary from periodic, to quasi-periodic, to chaotic, and various types of dissipative structures (*1–3*). It is well established that these phenomena arise as a direct result of nonlinearities within the reaction. Several mechanisms which are responsible for this complex dynamics have been proposed: the dependence of the heat of adsorption on coverage (*4–7*), the slow reversible oxidation of catalytic surface (*8, 9*), adsorbate-induced surface reconstruction (*10–14*), and cluster formation (*15–17*).

An important role in understanding complex dynamics belongs to simple models which allow one to investigate the mechanisms in great detail and, hence, can provide a basis for more elaborate models.

One of the most studied models of the Langmuir–Hinshelwood catalytic reaction $2A + B_2 = 2AB$ is the ZGB model introduced by Ziff *et al.* (*18*). This is a nonequilibrium model which exhibits phase-transition-like behavior. The only parameter in this model, Y_A (a ratio of partial pressures of A and B_2 reagents in the gas phase), sets the probabilities for which two reactive species (A or B_2) collide with the surface. It has been shown that steady states with nonzero reaction rate exist in a certain region of this parameter and that outside of this region the surface becomes completely covered with A or B particles. This model has been studied in great detail in several works (*18–24*).

In the present work we investigate the dynamics of the ZGB model under conditions of jumpwise changes of the catalytic properties of the surface which can arise from surface reconstruction induced by reagent adsorption. Until the fractional cov-

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erage of A particles, Θ_A, reaches the critical value Θ_A^{kr}, the B_2 particles adsorb nondissociatively and do not react with A particles. But when Θ_A becomes equal to Θ_A^{kr}, then the B_2 particles adsorb dissociatively and react immediately with adjacent A particles. In some ways the system simulated bears resemblance to the CO oxidation on Pt(100), where jumpwise variations of the catalytic properties of the surface induced by CO adsorption have been found.

We found that in a certain region of Y_A the specific clusterization of A reagent occurs. In this case the sustained self oscillations of the reaction rate are controlled mainly by one compact cluster of A particles. The growth of the cluster leads to the increase in oscillation rate that leads, in turn, to the decrease in the cluster size and vice versa, i.e., the cluster plays the role of a feedback. We found also that in a certain range of Y_A our stochastic system demonstrates a transition to chaos which is very similar to "intermittency" (P. Manneville and Y. Pomeau scenario (*25*)).

MODEL DESCRIPTION

We have simulated the bimolecular reaction on the catalyst surface between A and B_2 reagents through the classical Langmuir–Hinshelwood mechanism consisting of the following steps.

1. *Reagent Adsorption.* In the adsorption process, A species occupy single sites, while B_2 particles occupy a pair of adjacent (nearest neighbor) sites. If surface A-coverage is below Θ_A^{kr}, the adsorbed B_2 particles do not dissociate. B_2 adsorption becomes dissociative only when $\Theta_A \geq \Theta_A^{kr}$. On the other hand, the character of the A particle adsorption does not change.

2. *Reagent Desorption.* Desorption of the adsorbed A, B, and B_2 particles does not occur and A and B particles can leave the surface in the form of AB product only.

3. *Reaction.* The reaction can occur only between A and B particles; nondissociated B_2 particles do not react. The reaction between A and B particles occurs with unity probability every time when a pair of A and B happen to be in the nearest neighbor position. AB particles immediately leave the surface, vacating two sites.

4. *Surface Reconstruction.* When A-coverage reaches Θ_A^{kr}, surface reconstruction is supposed to occur. As a result of reconstruction, all B_2 particles on the surface dissociate into B particles which react with the adjacent A particles.

If as a result of the reconstruction cycle the A-coverage becomes less than Θ_A^{kr}, the B particles remaining on the surface do not reassociate, but continue to react with A particles which appear on adjacent sites due to subsequent adsorption. On the other hand, the adsorption of B_2 particles becomes nondissociative. They do not react with A molecules until $\Theta_A < \Theta_A^{kr}$.

If after the reconstruction cycle A-coverage still remains equal to or greater than Θ_A^{kr}, the adsorption of B_2 particles becomes dissociative. They adsorb on the surface in the form of B particles and react with adjacent A particles. Thus, at $\Theta_A < \Theta_A^{kr}$ there can be sites occupied by A, B, and B_2 particles as well as vacant sites, while at $\Theta_A \geq \Theta_A^{kr}$ there could be sites occupied by A and B particles and vacant sites.

As one can see, in our model, surface reconstruction is a hypothetic phenomenon. We only postulate its influence upon reagent adsorption.

To simulate the surface we used a 300 × 300 square lattice with periodic boundary conditions and conventional simulation algorithm described in detail elsewhere (*18*). We investigated the model at one value of $\Theta_A^{kr} = 0.3$. The simulations were usually run to 1000 Monte Carlo steps (MCS) and in some cases up to 40,000 MCS to insure that the cluster of A particles is stable and does not continue to grow. We measured the reaction rate as the number of reacted AB pairs per MCS per one lattice site. In comparing the oscillation rates obtained at various values of Y_A, it is not convenient to measure the oscillation frequencies in Monte Carlo steps because MCS has different time cost depending on the value of Y_A. For our aims it is more convenient to express the oscillation frequencies directly in seconds using the ratio between MCS and real time. Note that one MCS corresponds, in our model, to 90,000 (300 × 300) random adsorption trials (on the average one trial per site) and equals the real time interval $\tau = 1/(1 + Y_A)$.

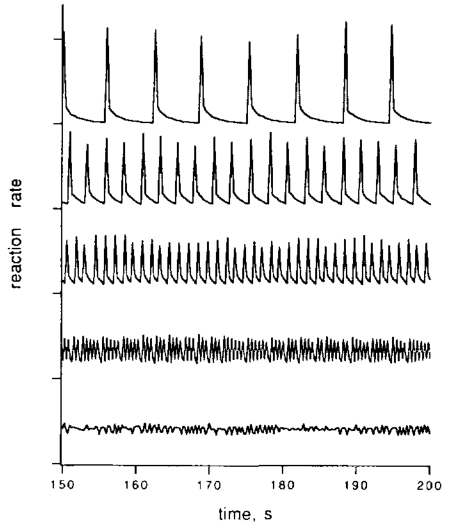

FIG. 1. Reaction rate as a function of time for various Y_A: (a) $Y_A = 0.6$, (b) $Y_A = 0.7$, (c) $Y_A = 0.85$, (d) $Y_A = 1.0$, and (e) $Y_A = 1.1$.

RESULTS AND DISCUSSION

The simulations show that self-sustained periodic oscillations of the reaction rate occur in the region $Y_1 \leq Y_A \leq Y_2$, where $Y_1 = 0.59 \pm 0.01$ and $Y_2 = 1.05 \pm 0.01$. Outside this region self-sustained oscillations do not exist and the system goes into steady states with zero reaction rate. At $Y_A > Y_2$ all surface is completely covered with A particles, while at $Y_A < Y_1$ it is covered with A, B, and B_2 particles. In the latter case, despite the presence of A and B particles on the surface, reaction between them is impossible because they are separated by sites occupied by B_2 particles. We did not aim to determine the boundaries of the oscillation region with maximum accuracy. Within our accuracy (±0.01) the size of the oscillation region, in our model, is approximately the same as that of the region of steady states with nonzero reaction rate in the ZBG model. The time dependencies of the reaction rate for several values of Y_A are shown in Fig. 1. The oscillations are periodic peak oscillations with small random irregular perturbations in frequencies and amplitudes that are caused by the stochastic nature of the system. As one can see from Fig. 1, the oscillation frequency increases as Y_A increases. The reason for that is evident because the oscillation frequency is determined by the time of accumulation of A particles on the surface. The average oscillation frequency as a function of n_A ($n_A = Y_A/(Y_A + 1)$ is the mole fraction of A particles in the gas phase) for the entire oscillation region is shown in Fig. 2. The curve in Fig. 2 has two parts, each part being practically linear and having its own slope. It indicates that in the region of large values of n_A there appears an additional factor which effectively influences the oscillation rate. This additional factor is associated with the appearance of a cluster of A particles. We

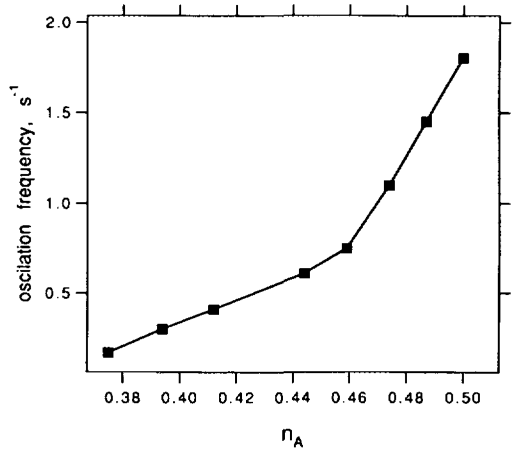

FIG. 2. Dependence of the average oscillation frequency on the mole fraction of A reagent in the gas phase.

have studied this effect thoroughly. The degree of A-clusterization at $Y_A = 0.6$ and $Y_A = 1.0$ is shown in Figs. 3a and 3b, respectively. The histograms show the fraction of A particles having 0, 1, 2, 3, and 4 nearest neighbors, respectively. As one can see, there is no clusterization at $Y_A = 0.6$, while it is very considerable at $Y_A = 1.0$. In the latter case, the summary fraction of A particles with 4 and 3 nearest neighbors is about 0.8 and, hence, these A particles are members of a compact cluster.

The time dependence of the clusterization of A particles at $Y_A = 1.0$ is shown in Fig. 4. The curves in Fig. 4 labeled 3 and 4 correspond to the fraction of A particles with 3 and 4 nearest neighbors, respectively. One can see that at the beginning the fraction of A particles with 4 nearest neighbors grows gradually while the fraction with 3 neighbors decreases gradually. It indicates that the density of the A-cluster increases with time. Eventually both curves become time independent. We continued simulation runs up to 40,000 MCS and did not see any evolution of these curves.

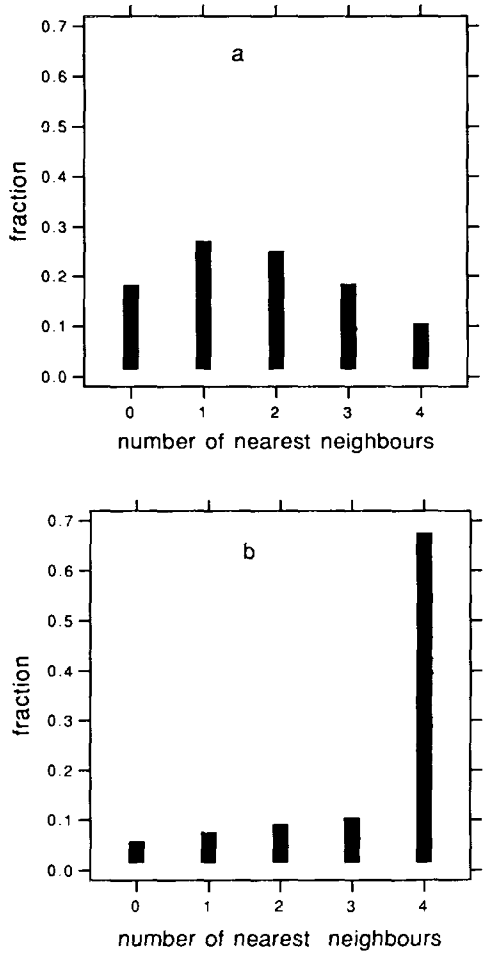

FIG. 3. Degree of clusterization of A particles, i.e., the fraction of A particles having 0, 1, 2, 3, and 4 nearest neighbors: (a) $Y_A = 0.6$, and (b) $Y_A = 1.0$.

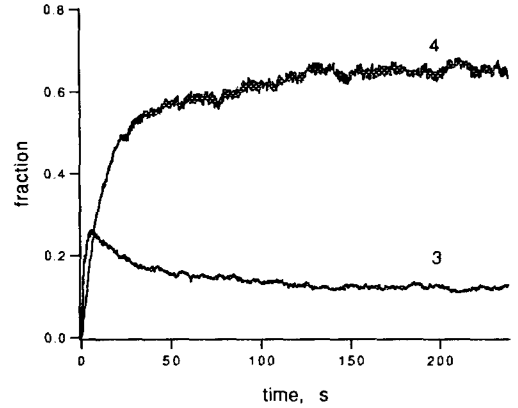

FIG. 4. Fraction of A particles having 3 (curve 3) and 4 (curve 4) nearest neighbors as a function of time at $Y_A = 1.0$.

Now we explain the mechanism of cluster formation in detail. First, we consider the case $Y_A = 0.6$, low pressure of A reagent, when there is no clusterization, and analyze the situation on the surface just after completing an oscillation. In the course of the previous reconstruction cycle all B_2 particles have dissociated into B particles, and some of them have reacted with A particles and left the surface. The A-coverage dropped below the critical value (0.3) and the surface returned to its nonreconstructive state. Under these conditions initially a rapid growth of B_2-coverage occurs, since, first, many vacant sites are available and, second, at $\Theta_A < \Theta_A^{kr}$ the adsorbing B_2 particles do not dissociate and do not react. At the same time A-coverage grows very slowly because a considerable part of the adsorbing A particles react with B particles remaining on the surface. The sites vacated due to the reaction are mainly occupied by B_2 particles. At the moment when A particles at last have got a possibility to accumulate effectively, only a few vacant sites remain on the surface. These vacant sites are mainly the isolated "holes" remaining after two-site B_2 particle adsorption. Thus, practically all the adsorbed A particles have B_2 nearest neighbors and, hence, must "die" in the next oscillation, so the accumulation of A particles after every oscillation starts practically from zero. It is evident that no A-clusterization occurs under these conditions.

A different situation takes place at Y_A = 1.0 (high pressure of A reagent). Here the adsorption rate of A particles is considerably higher. Now, just after completing an oscillation, A particles have a possibility to accumulate rather effectively on a nonreconstructed surface. They can occupy the sites not only among B_2 particles but also in the neighborhood of each other forming small random islands. The formation of such A islands favors keeping A particles (inside the islands) and leads to an increase in oscillation frequency. The increase in oscillation frequency leads to a disappearance of small islands while the large islands continue to grow. It is evident that the largest island has the greatest advantage. Finally, after several hundred oscillations, such a process leads to the formation of one stable cluster of A particles. Eventually, a steady state is reached when the average number of A particles adsorbed between two subsequent oscillations at the cluster boundaries is approximately equal to the average number of A particles leaving these boundaries during oscillation. Of course, the above picture is not such a perfect one. The stochastic nature of this process is evident. Sometimes we observed two clusters approximately equal in size.

Let us emphasize the specificity of described mechanism of A-clusterization. "Clustering effect" in the absence of attractive lateral interactions and surface diffusion has been studied in several works in two MC models of catalytic reactions, $A + B = AB$ (*20, 27, 28*) and $2A + B_2 = 2AB$ (*21, 22*). It has been shown that such clusterization is caused by irreversible reagent adsorption and the fact that reaction removes AB pairs. However, the A-clusterization in our model is caused not only by these reasons. As one can see from above, *it is also caused by the jumpwise variations of the catalytic properties of the surface induced by adsorption*. It is well known that in the ZGB model, just in this region of Y_A A-clusterization does not occur (*18, 21*) because A-coverage is about zero. Thus the specific A-clusterization appears to be due to the fact that A particles have a possibility to accumulate effectively in the intervals between reaction cycles. At the same time, the growth of the A-cluster is restricted by the reaction cycles during which A-coverage tends to zero. We performed ten simulation runs, each one up to 40,000 MCS, at Y_A = 1.0, where the A-clusterization is high, and did not see that the A-cluster continued to grow.

The influence of cluster formation on oscillatory kinetics can be manifested in many ways. In Ref. (*15*) it was supposed that reversible CO blocking of the Pt surface was the reason for the unstable behavior of the CO oxidation reaction. In Ref. (*17*) oscillatory behavior of the reduction of NO by NH_3 over the Pt(100) single-crystal surface has been studied. The authors showed that the oscillatory kinetics can be described by a model in which NO forms densely packed islands within which only few sites are available for NO dissociation. NO and NH_3 react with each other at the boundaries between NO islands and areas with vacant sites where NO and NH_3 dissociation can occur. Thus, in this model, NO islands determine vacant sites required for dissociation. In Ref. (*16*) various island models of catalytic oxidation of carbon monoxide and carbon monoxide–olefin mixtures have been studied. It was shown that in a certain case the size of the CO and O islands rises and falls during oscillations and that the aperiodic behavior may result from the fact that the maximum size that the islands reach in each cycle does not remain constant. In Ref. (*27*) the dynamic behavior of an MC model of the catalytic reaction A + B = AB has been studied for small lattices. The authors state that, in the case of a certain reversibility in reagent adsorption, chaotic oscillations in the reaction rate are caused by reagent clusterization.

However, the mechanism of clusterization described in the present paper and the influence of the arisen A-cluster on the oscillatory kinetics, to our knowledge, do not have analogies. This A-cluster is an example of the dissipative structure which arises and develops under nonequilibrium conditions of trigger oscillations.

Consider the behavior of the system outside the oscillation region. At large values of Y_A, the increase in oscillation frequency can no longer prevent cluster growth and the cluster covers the entire surface. This situation is shown in Fig. 5b. At $Y_A = 1.2$, the surface is covered completely by A particles. The situation at small values of Y_A is shown in Fig. 5a. In this case ($Y_A = 0.57$), after two or three oscillations, the surface is covered completely by a mixture of A, B, and B_2 particles. Despite the presence of A and B particles on the surface, reaction between them is impossible because they are separated by sites with B_2 particles.

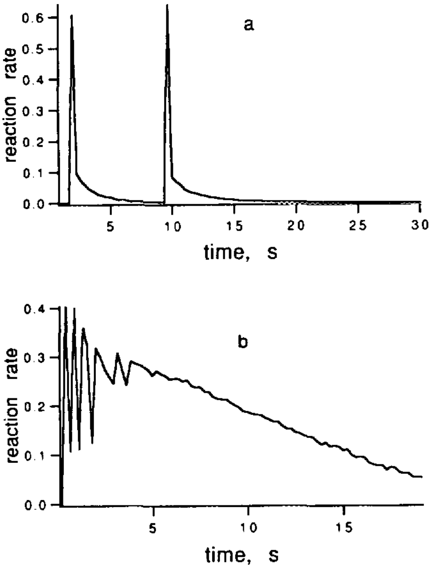

FIG. 5. Behavior of the system outside the region of the existence of oscillations: (a) $Y_A = 0.57$ and (b) $Y_A = 1.2$.

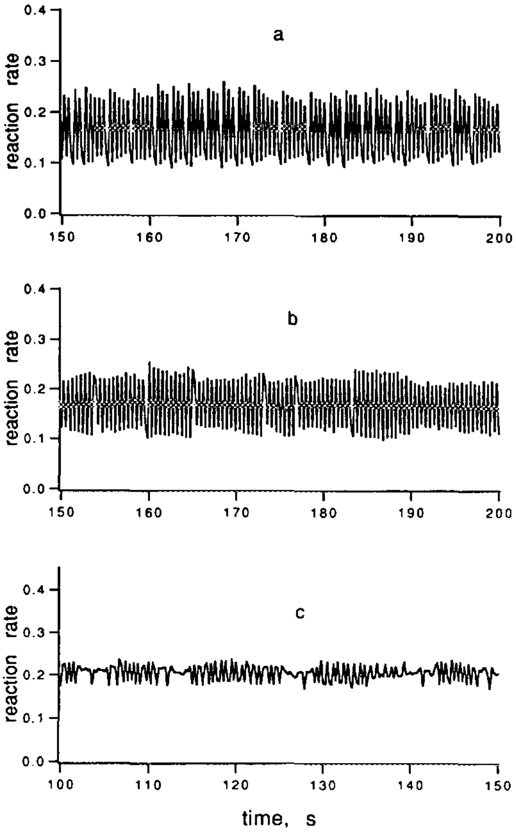

FIG. 6. Three consecutive states of the system in the course of the transition to chaos: (a) $Y_A = 1.0$, (b) $Y_A = 1.04$, and (c) $Y_A = 1.1$.

When Y_A approaches the right boundary of the oscillation region, the system demonstrates a transition to chaos via a scenario that is very similar to "intermittency" (*25*). Figure 6 shows three consecutive states in evolution of the system. As can be seen, the periodic series of oscillations is interrupted by random delays. Such "intermittency-like" behavior is somewhat unexpected in our stochastic model because it is well known that intermittency arises from deterministic chaos. Chaotic oscillations of reaction rate in MC models of catalytic reactions A + B = AB (*27*) and $2A + B_2 = 2AB$ (*26*) have already been observed, but in both cases the route to chaos was like "order through fluctuation" (*29*). We probed different sequences of random numbers and found that the above picture could shift slightly but it was always reproduced qualitatively. The shifts arise due to the finite size of the system and they do not have to be observed in a system of sufficiently large size. We believe that the scenario observed is the intrinsic feature of our stochastic model.

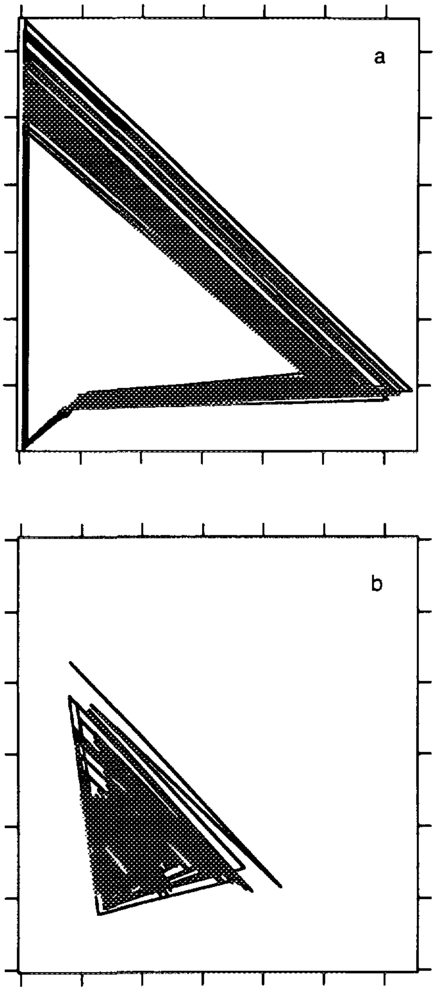

FIG. 7. Phase portraits: (a) $Y_A = 0.6$ and (b) $Y_A = 1.04$.

We applied the time-delay method (*30*) so as to demonstrate more clearly the dynamics of the system. The time-delay method allows one to construct "phase portraits" of the system from time series. To this effect we plotted a value of the reaction rate at time t, $r(t)$, versus $r(t + \tau)$, where τ is an arbitrary but fixed delay time. Two portraits, at $Y_A = 0.6$ and $Y_A = 1.04$, are shown in Fig. 7. At $Y_A = 0.6$ (Fig. 7a), the temporal behavior of the system is essentially regular. The fact that movement of the system follows several trajectories reflects the effect of fluctuations. At $Y_A = 1.04$, however, the picture of movement is quite different. Once an A-cluster formed (after several hundred oscillations), all trajectories gathered in some region of "phase space," covering the region practically uniformly (Fig. 7b). Temporal behavior of the system, in this case, becomes unpredictable.

CONCLUSION

We have investigated the ZGB model under conditions of jumpwise variations of the catalytic properties of the surface and have established the specific mechanism of A-clusterization. We found that in a certain region of Y_A the oscillatory kinetics is controlled mainly by one compact cluster of A particles which plays the role of a feedback. We found also that our model demonstrates an "intermittency-like" transition to chaos. We believe that these findings have some theoretical interest.

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