CELLULAR AUTOMATON FOR SURFACE REACTIONS*

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A new algorithm which overcomes some specific difficulties arising in modeling of heterogeneous catalytic processes by cellular automata (CA) technique is proposed. The algorithm was tested with scheme introduced by Ziff, Gulari and Barshad and showed a good agreement with their results. The problem of the physical adequacy and interpretation of the algorithm was discussed.

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1. Introduction

One of the most widespread and developed methods of stochastic simulations in chemistry is Monte-Carlo (MC) method. It has been used with success to investigate equilibrium and dynamic properties of chemical systems (among others, in the study of surface reactions [1]).

Another method, which becomes more and more popular, is the method of cellular automata (CA) [2]. The programs using CA approach are very fast (as they give a natural way for organizing parallel calculations using matrix processors and computers with parallel architecture); also special-purpose cellular automata machines were constructed. In last few years

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CA (formerly used mainly to model spin systems and hydrodynamics) were also applied to study chemical problems (formation of spatial structures and waves, surface reaction kinetics *etc.*) [3].

The aim of the work is to present a new algorithm for CA modeling of the surface reactions. The paper is organized as follows: In Section 2 we will present main features of CA simulating surface reactions and discuss some problems arising in simulations of chemical reactions. In Section 3 the model of Ziff *et al.* will be presented. Section 4 describes CA based on "Margolus blocks". Our algorithm is described in Sections 5–7. In Section 8 the results of simulations using our algorithm will be compared with other approaches. Section 9 contains final remarks and conclusions.

2. CA for surface reactions: main features

In order to define CA we have to specify:

- CA space (a set of "cells" or "nodes", in our case we will use two-dimensional square $n \times n$ lattice with periodic boundary conditions);
- the neighborhood (in our case four nearest neighbors);
- a set of possible states for each element of CA space;
- a set of rules for updating the states.

We will denote the state of the i-th node by S_i. This state can change independently of the neighborhood of the node ("first-order" rule)

$$S_i^{\text{old}} \longrightarrow S_i^{\text{new}},$$

or its evolution can depend on the state of the neighborhood. For example, a "second-order" rule concerns two neighboring cells

$$S_i^{\text{old}} + S_j^{\text{old}} \longrightarrow S_i^{\text{new}} + S_j^{\text{new}}.$$

In the sequel we will consider only first- and second-order rules. Furthermore, we will assume that they are the same for all nodes (homogeneous CA).

The above mentioned definitions apply also for MC simulations. The general difference between MC and CA method is that in the first one we choose nodes for updating at random, while in the latter one the whole space is updated simultaneously. So the algorithm for CA must not depend on the way we scan the lattice.

A successful implementations of CA methods have to overcome some technical problems.

2.1. Oscillations

The first problem becomes clear from consideration of the simplest model of reversible reaction of first order

$$A \underset{k'}{\overset{k}{\rightleftarrows}} B\,. \tag{1}$$

Assume that initially our lattice is filled with A and both reactions occur with probability 1. If we use MC approach we choose cells randomly, and after some number of choices we will have a dynamic equilibrium between A and B species on the lattice. For the CA which treats all cells simultaneously we will get oscillations of reagents; all states will switch back and forth between A and B (so-called *feedback catastrophe*).

2.2. The choice of partner

Another problem appears when we treat a second-order reaction

$$A + A \longrightarrow B + B\,. \tag{2}$$

In MC we use random number generator to choose a partner for a given cell. For CA, the choice of partner should be predetermined in unambiguous way for every cell, otherwise the result of calculations would depend on the way we sweep the lattice.

2.3. The choice of reaction path

Last problem is of the similar nature as the previous one. It may happen that given reagent can take part in more than one reaction

$$\begin{aligned} Z &\longrightarrow A\,, \\ Z &\longrightarrow B\,. \end{aligned} \tag{3}$$

Then our CA should determine unambiguously the products (in MC simulations the products are chosen randomly).

3. The model: ZGB scheme

Let us take as a model system the scheme of irreversible adsorption and surface reaction introduced by Ziff, Gulari and Barshad (ZGB) [4].

$$Z \xrightarrow{k_1} A\,, \tag{4}$$

$$Z + Z \xrightarrow{k_2} B + B\,, \tag{5}$$

$$A + B \xrightarrow{k_3} Z + Z\,. \tag{6}$$

Here Z denotes a "free" cell on the lattice, A — a cell with molecule of "A" reagent adsorbed from the gaseous phase, B — a cell occupied by a "B" molecule which is a product of dissociation of B_2; adsorption of B_2 occurs on two adjacent sites, if both sites are free. As in [4], we assume that reactions (4) and (5) are concurring with probabilities, proportional to partial pressures of A and B_2 gases above the lattice. Reaction (6) has high probability, but in difference with [4], where its probability was equal to one, its value will be defined by peculiarities of CA algorithm. The above model was studied with different methods [4–7].

The characteristic feature of ZGB scheme is the existence of phase transition points in the dependence of stationary concentrations of reagents on the lattice on the ratio of reagents in gaseous phase (curve 1, Fig. 3). So in MC approach we have only one parameter related to partial pressures of reagents

$$Y_a = \frac{k_1}{k_1 + k_2}.$$

It was found [4] that first phase transition which occurs at $Y_1 = 0.389$ is of second order, and the second one, at $Y_2 = 0.527$, is of first order. If $Y_a < Y_1$, the steady state corresponds to the lattice fully poisoned by B; if $Y_a > Y_2$, to the lattice fully poisoned by A reagent. For the interval $Y_1 < Y_a < Y_2$ there is a dynamic equilibrium between Z, A and B on the lattice. Reproducing of results [4] is a good test for any CA algorithm suggested.

4. CA based on "Margolus blocks"

The CA for surface reactions, which uses stoichiometric approach, was proposed in [5]. It treats 2 × 2 Margolus blocks as elementary objects (Fig. 1). The transition to the new state depends on configuration of given block and, sometimes, on random number. All Margolus blocks are updated simultaneously. This algorithm, obviously, solves a problem of parallel organization of calculations. However, difficulties pointed above are not overcome.

A. For the simplest scheme (1) algorithm [5] will give oscillations. Authors did not investigate the problem of temporal correlations with period of the CA step order for ZGB scheme.
B. Neighbor choice is limited by neighborhood definition given by Margolus block. But the choice of neighbor inside the block demands a call for random number generator. Moreover, the conception of blocks may lead to unwished spatial correlations on distances of block size.
C. Random numbers also serve for parallel transitions (4) and (5).

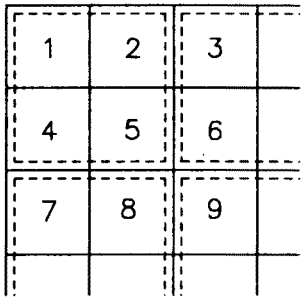

Fig. 1. Lattice subdivision into Margolus blocks (dashed). An illustration of neighborhood.

D. Last note concerns in particular reaction (6). Strictly speaking, we cannot account probability of this reaction equals to one in CA suggested. Cells 5 and 8 (Fig. 1), which are neighbors in physical sense, become Margolus type neighbors only on the third step: 1-st step — block contains 1, 2, 4, 5 cells; 2-nd — 2, 3, 5, 6 cells; 3-d — 5, 6, 8, 9.

However, it should be noted that values of Y_1 and Y_2 in [5] are in close agreement with those of [4].

5. CA with "control lattice"

In our CA we keep the main idea of [5] — we divide our lattice in blocks, but we do it in the stochastic way. Let us call our CA space filled with Z, A and B cells the "work lattice" (WL). We introduce a new lattice, the "control lattice" (CL), which controls transitions on WL in agreement with the kinetic scheme and values of reactions probabilities. The role of CL is to determine if a given transition is allowed for a given cell or pair of cells. The algorithm of our CA is as follows: We sweep the WL comparing it with CL; the comparison determines types of transitions which will possibly occur.

We can classify this algorithm as CA in the sense formulated above, if the result of updating does not depend on the way of sweeping. Therefore CL should not only point out exactly one available reaction, but also determine unambiguously a pair of neighbors in bimolecular transitions. In addition, CL shall assure given probabilities for concurrent transitions (4) and (5).

The simplest CL is organized as follows:

Let us take some values for rate constants k_1, k_2 and k_3 in (4)–(6). We randomly fill WL by masks corresponding to reactions (4)–(6) in such a way that the ratio between the numbers of masks approximates in the best

possible way the ratio of corresponding rate constants. For monomolecular reaction (4) the mask will be one cell, for bimolecular stages (5), (6) it is a randomly oriented pair of cells (Fig. 2). It is known that random filling of lattice with blocked pairs (bimolecular masks) cannot give the full coverage[1], so the process of filling CL by masks is stopped if a given value of coverage is attained.

We begin simulations with some initial distribution of A, B and Z cells in WL (*e.g.* we fill WL only by Z cells). Then we compare WL with CL. If reaction mask in a cell (or in a pair of cells) in CL corresponds to appropriate species in WL, the reaction will occur; if not, the cells in WL will remain unchanged. Obviously, the result of updating of the WL will not depend on the order of sweeping of both lattices. After completing the procedure, CL is randomly shifted and the procedure is repeated.

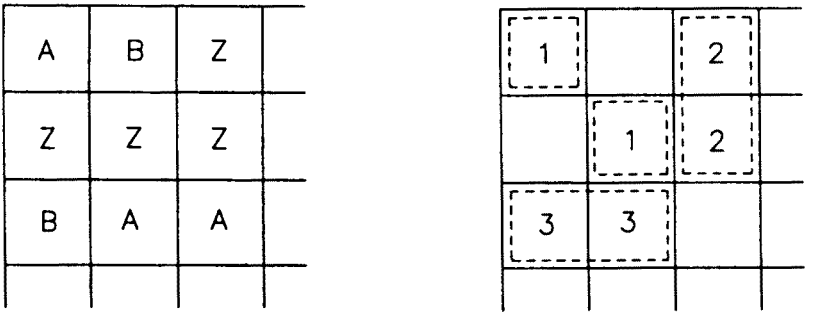

Fig. 2. Work lattice (left) and control lattice with masks of reactions 1–3 (dashed blocks).

The algorithm does not lead to the "feedback catastrophe", even for the scheme (1); if we fill CL randomly with masks of the forward and backward reaction in appropriate ratio (k/k') and fill WL with one species (say A), after first step we will attain dynamic equilibrium, which will be maintained.

The shortcoming of this algorithm is in its comparatively low efficiency: if the number of reactions increases, the relative share of reaction masks in CL decreases and we cannot model adequately processes occurring with high probability (*e.g.* reaction (6) in ZGB scheme).

6. Modified CA algorithm

In some cases when the set of reactions can be divided into subsets in such way that all reactions using common reagents belong to the same

[1] This problem, so called "parking problem", was investigated in [8]. For random distribution of pairs the maximal coverage is 0.907.

subset, we can improve our algorithm in the following way: we introduce for each subset its own CL and fill it by reaction masks only from this subset. It is possible for example in the case of ZGB scheme; reactions (4) and (5) belong to one subset (species Z), reaction (6) — to another one (species A and B). So in this case CL1 will correspond to reactions (4) and (5) — it will be filled by appropriate reaction masks in ratio k_1/k_2, CL2 will be filled by masks of reaction (6).

However, even for fully filled CL2, the probability of reaction (6) cannot be greater than $^1/_4$, because of the fixed orientation of each mask. One can increase this probability by introducing several CL for reaction (6), each one differing from the others in arrangement of masks (there is no mask being in the same position on two or more lattices). We will call them "CL2 layers". For masks consisting of pairs of cells there are at most 7 such layers[2]. To realize the process (6) with probability equal to 1, the total number of masks in all these layers should be $2n^2$.

7. Organization of simulations

We used CA with CL1 for reactions (4), (5) and from 6 to 7 layers of CL2 (denoted CL21,...,CL27) for reaction (6). We filled randomly CL1 with masks for reactions (4) and (5) in ratio k_1/k_2. As a parameter we took (as in ZGB original work) Y_a — the partial pressure of A species.

The coverage S for CL1 is given by

$$S = \frac{m_1 + 2m_2}{n^2},$$

where m_1, m_2 are numbers of masks for reactions (4) and (5) correspondingly, n is the size of the lattice. Note that parameter S has no analogue in MC calculations; it is used in our simulations as an independent parameter. Further, the dependence of results on S will be also discussed.

We started simulations with WL filled with Z. In each cycle, WL was compared with CL1 and all CL2. Then CL1 and all CL2 were randomly shifted (the latter ones simultaneously) and cycle was repeated.

The above algorithm (in spite of its apparent complexity) was 5–6 times faster than the MC algorithm with random number generator calls for each decision, because of the fast diagnostics concerning the possibility of the occurrence of a given reaction and the choice of partners. Numerical experiments were carried out with lattices from 20×20 to 170×170. It was

[2] If we consider two adjacent cells, they can make a pair or make pairs with neighbors (each one with three ones); so if we make pairs randomly, given cells will make a pair at least in seventh attempt.

found that from $n = 40$ critical values Y_1 and Y_2 do not depend on n with accuracy given by CL (this accuracy is of the order $1/n^2$).

8. Results and discussion

Fig. 3 gives dependence of stationary B concentration on Y_a. Curve 1 reproduces results of [4]. It was found that the qualitative behavior of curves is the same, but critical values Y_1 and Y_2 depend on the coverage S of CL1. Low values of S give Y_1 and Y_2 practically the same as the MC algorithm (Fig. 3, curves 1 and 2). When S is large (the coverage close to the maximal one), the values of Y_1 and Y_2 are considerably shifted to the right (Fig. 3, curve 3 against curve 1). Curves 1 and 2 on the Fig. 4 demonstrate Y_1 and Y_2 dependencies on S value.

The increase of Y_1 and Y_2 can be understood by considering two limit cases. First, let us assume that WL is covered only by Z cells, $Y_a = 1/2$ and the coverage S of CL1 is equal to 1. After the first step we would have the B species concentration $C_b = n_b/n^2$ on the WL close to $1/3$, and $C_a = n_a/n^2$ close to 0; as the number of adsorbed B_2 and A would be equal and reaction masks are "well mixed", about a half of B atoms will react with A and desorb, and the other half would rest on the surface. In the MC experiment the ratio of successful attempts of B_2 adsorption to those of A is less than $1/2$because the former needs two free neighbors.

In the opposite case, when there are only few free cells, the B_2 adsorption is also more easy for CA in comparison with MC. Assume the WL is fully covered with B except of two adjacent cells. Let us calculate the probability of B_2 adsorption on those two cells for MC and CA.

For MC the success in the first attempt has a probability

$$p_b = (1 - Y_a)\frac{2}{N}\frac{1}{4} = (1 - Y_a)\frac{1}{2N}, \tag{7}$$

the probability of adsorption of A is

$$p_a = Y_a\frac{2}{N}, \tag{8}$$

and the probability that no adsorption occurred and trials should be continued is

$$p_c = 1 - p_a - p_b. \tag{9}$$

The total probability of success after numerous trials is

$$P_b = p_b + p_c p_b + p_c^2 p_b + \ldots = \frac{p_b}{p_b + p_a}. \tag{10}$$

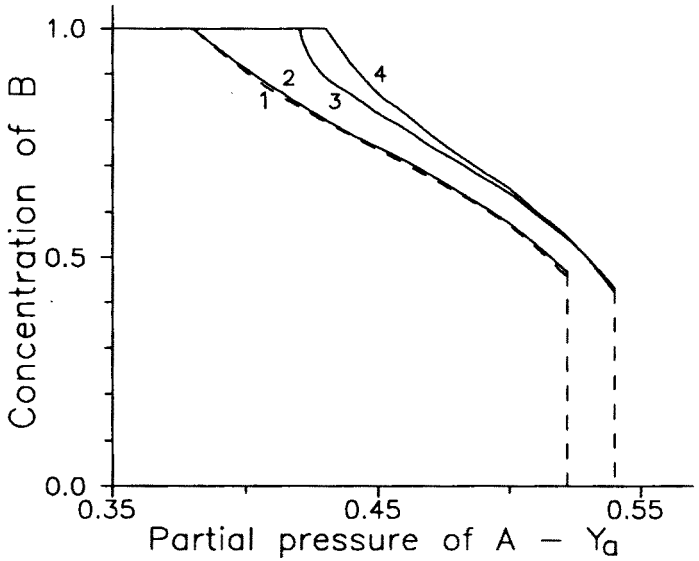

Fig. 3. Stationary B concentrations in dependence on Y_a. Error in Y_1 and Y_2 values is about 0.003. 1 (dashed) — MC-model; $Y_1 = 0.395$, $Y_2 = 0.525$; 2 — CA, $S = 0.1$; $Y_1 = 0.395$, $Y_2 = 0.527$; 3 — CA, $S = 0.8$; $Y_1 = 0.420$, $Y_2 = 0.540$; 4 — CA, $S = 0.8$, fixed CL2, $Y_1 = 0.432$, $Y_2 = 0.540$.

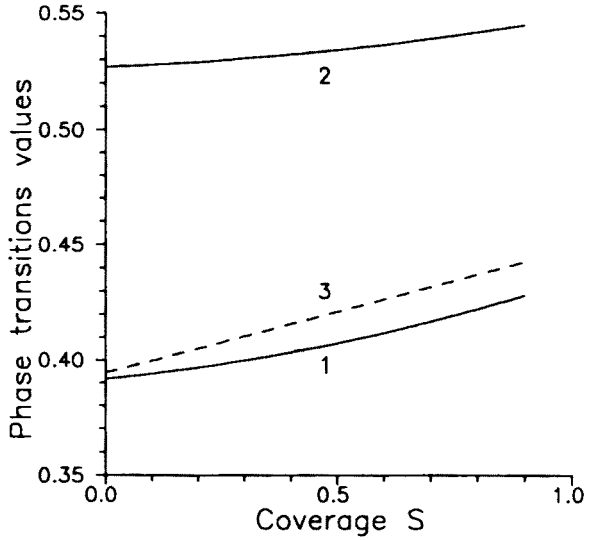

Fig. 4. Dependencies of critical Y values on S. 1 — Y_1 for randomly shifted and fixed CL2; 2 — Y_2 for randomly shifted CL2; 3 (dashed) —Y_2 for fixed CL2.

Substitution of (7), (8) in (10) yields

$$P_b^{\mathrm{MC}} = \frac{1 - Y_a}{1 + 3Y_a}. \tag{11}$$

For CA we have

$$p_b = \frac{n_B}{4N}, \tag{12}$$

where n_B - the whole number of cells in reaction (5) masks in CL1. Multiplier 4 is in denominator here because only $^1/_4$ of B adsorption masks cells on CL1 may be fitted to fill our $2Z$ pair. The probability of hitting of at least one reaction (4) mask to the $2Z$ pair is

$$p_a = \frac{2n_A}{N} - \left(\frac{n_A}{N}\right)^2.$$

It follows from

$$n_B + n_A = N,$$
$$\frac{n_A}{\frac{n_B}{2} + n_A} = Y_a$$

that

$$\frac{n_A}{N} = \frac{Y_a}{2 - Y_a},$$
$$\frac{n_B}{N} = \frac{2(1 - Y_a)}{2 - Y_a},$$

and

$$p_b = \frac{1 - Y_a}{2(2 - Y_a)}, \tag{13}$$

$$p_a = \frac{2Y_a - \frac{Y_a^2}{2 - Y_a}}{2 - Y_a}. \tag{14}$$

Substitution of (13), (14) in (10) yields

$$P_b^{\mathrm{CA}} = \frac{1 - Y_a}{1 + 3Y_a - \frac{2Y_a^2}{2 - Y_a}},$$

what means

$$P_b^{\mathrm{CA}} > P_b^{\mathrm{MC}}.$$

So, it seems that under small, high and average WL fillings simultaneous consideration of B_2 and A absorption in CA gives advantage for B in comparison with molecule by molecule adsorption in MC modeling.

9. Final remarks

As CA with CL takes into account the local properties of the surface, we can use it for modelling of some special features of heterogeneous systems. The inhomogeneous surface (*e.g.* with local defects) can be simulated by CA with suitably chosen CL. Consider for example the ZGB model with *fixed* multi-layered CL2. Then various cells would have different probabilities to take part in reaction (6); in particular, one can get locally groups of cells with small reactivity which can be the "embryos of poisoning". This fact explains the results of numerical experiments (narrowing of region where stationary states with non-zero reaction rate exist - *cf.* Fig. 3, curve 4 *vs* curve 3). The above mentioned mechanism influences only position of Y_1, where the role of cluster formation is definitive (Fig. 4, curve 3 in comparison with curve 1).

The test ZGB scheme is too simplified to make conclusions about more or less physical sense in algorithms compared. However note that CA with "control lattices" gives a natural way to introduce the absolute pressure of reagents by means of S parameter. To continue the theme of "physical sense" of CA with "control lattices" we would like to discuss the peculiarities of interpretation of reaction rates by this algorithm. There is a direction in the theory of heterogeneous catalysis which treats catalytic surface as a dynamical system, governed by some evolution laws. Here we can refer to the model of branched-chain multiplication of active centers [9] and to the cybernetic approach to catalytic act [10]. The latter paper states that the necessary condition for the catalytic reaction is not only the spatial coincidence of reagents, but also the temporal coincidence of their internal states determining the ability of molecules to react. In this approach the probability of chemical act will be connected with the fraction of lattice places which at given moment are able to take part in given reaction. This fraction is just the fraction of corresponding masks given by CL.

By means of our algorithm one can also consider such phenomena as surface diffusion, processes on inhomogeneous and on ordered surfaces, with inhomogeneous reagents distribution (as gaseous beams and surfaces interactions). The surface diffusion act, for example, may be interpreted as exchange of states between two neighboring cells

$$S_a^1 + S_b^2 \longrightarrow S_b^1 + S_a^2 . \qquad (15)$$

We can organize a special CL for surface diffusion with mask which allows (15) for all reagents.

To conclude we want to note the universality of the method, which may be useful also for volume reactions, where the speed of calculations is especially wanted.

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