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A general cellular automaton model for surface reactions

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Abstract. A general cellular automaton model for surface reactions is introduced that shows almost quantitative agreement with the corresponding Monte Carlo simulations for several surface reaction models. It is generally applicable and can be easily extended to new surface reaction models. The high performance and the parallelism of cellular automaton simulations opens the possibility to investigate long simulation times and systems on large lattices.

1. Introduction

Since the pioneering work by Ziff, Gulari and Barshad [1], who introduced a new model (the ZGB model) for the simulation of surface reaction kinetics in 1986, the frequency and complexity of the research based on their model has increased considerably. Although such models are still very limited in accounting for all of the observed features in real reaction systems they are becoming increasingly powerful techniques in surface reaction studies and may help us to understand the basic elementary reaction steps in the future [2, 3]. In addition to the ZGB model new problems such as the formation of spatiotemporal structures [4], the order of kinetic phase transitions [5–9], energetic adsorbate–adsorbate interaction [10], the occurrence of kinetic oscillations [11–15], and the transition into chaotical behaviour [16] have been investigated. These investigations are very demanding because large lattices and long simulation times are needed in a large number of simulation processes in order to obtain the correct results.

There exist basically two different approaches to simulate physical lattice models. (i) In the Monte Carlo (MC) approach the lattice sites are chosen randomly in a perfectly sequential manner. For long simulation times the mean number of processes is equal for all lattice sites. However, there exists the possibility that a given site is chosen twice or more in succession. MC simulations for surface reaction systems are, in principal, easy to set up but the price to pay for simple programming is the long computation time required. In the MC simulation of the ZGB model most of the computational cost is based on the generation of random numbers for the selection of the sites and on the investigation of all nearest neighbours (NN), checking with which a reaction is possible. (ii) Cellular automata (CA) are a powerful tool to simulate physical and chemical systems at a high level of complexity [17]. The CA approach is discrete in space and time. It is fully parallel and all lattice sites are updated in one single time step. Consequently much fewer random numbers are needed. Natural processes are neither fully parallel nor purely sequential but are a mixture of both types.

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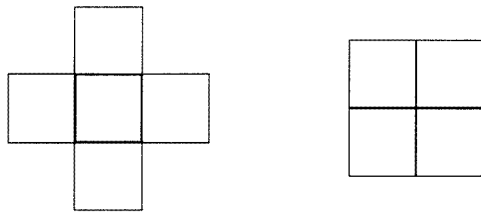


Figure 1. Definition of the von Neumann neighbourhood (left) and of the Margolus block (right). The centre site in the von Neumann neighbourhood has four NNs, whereas in a Margolus block all four sites are NNs to each other.

However, difficulties may arise during this parallel procedure. This generally holds for simulations of lattice gas models because synchronous dynamics such as the parallel update of the states of the lattice sites increases the inherent correlations [18]. A well known problem is the feedback catastrophe in simulating the Ising model [19]. Moreover, the parallel update may lead to the violation of physical laws. In the simulation of surface processes different CA approaches have been used. Chopard and Droz [20] were the first to introduce a CA approach for the $\text{CO} + \text{O}_2$ reaction on metal surfaces. In order to obey the CA laws they were forced to disobey the laws of stoichiometry: one particle may take part simultaneously in the formation of several reactive pairs. A corrected version [21] obeys stoichiometry but still lacks agreement with the ZGB model. Similar problems arise with diffusion processes [17, 22, 23]. Other authors have introduced a CA approach using 2×2 Margolus blocks as a lattice superstructure. The Margolus block is a special form of neighbourhood [24] as compared with the generally used von Neumann neighbourhood (see figure 1). This neighbourhood definition apparently overcomes the above difficulties [25–27] and shows reasonable agreement with results of MC simulations [28]. Although this approach could be extended to other reaction systems [29], an attempt to use it for a $\text{NO} + \text{CO}/\text{Pt}(100)$ reaction model [30, 31] gives incorrect results. In this model with dissociative adsorption of NO (see below in section 2.8) the N atoms form checkerboard-like structures during the MC simulation [31–33] and the system always ends up in an absorbing state. The Margolus block superstructure fails to describe the special structure of N atoms. If one uses the von Neumann neighbourhood the N atoms in such a checkerboard structure are located on sites which are only next NN whereas in a Margolus block two N atoms on sites connected by a corner are NN and react giving N_2 . Therefore the checkerboard structure cannot be formed in a simulation using Margolus blocks. The CA approach using Margolus blocks gives a broad reactive interval which contradicts MC results [34].

Here we introduce a new CA approach which overcomes these problems stated above and gives almost quantitative agreement with the corresponding MC simulations. The paper is organized as follows. In section 2 we give a detailed description of the simulation procedure following the example of the ZGB model. In section 3 some well known surface reaction models are revisited and simulations with fast reaction processes on large lattices are presented. In section 4 conclusions are drawn and prospects are given.

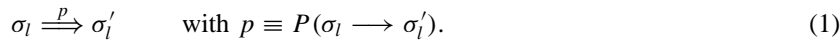
2. The simulation

2.1. Basic arrangement

We model the surface with a two-dimensional lattice with lattice constant a (which is used as the unit length), coordination number z , and side length L . Periodic boundary conditions are applied. Each site can be in state σ , e.g. with $\sigma \in \{0, A, B\}$ for the ZGB model, where 0 stands for an empty site and A and B stand for a site covered with CO and O, respectively.

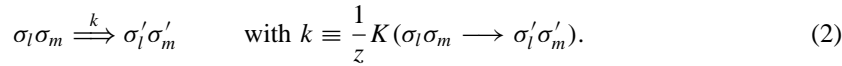
2.2. Transition rates

A kinetic model of the Markovian type is completely defined via its state variables σ and the possible transitions which can occur. In our present CA approach we only consider monomolecular and bimolecular steps and therefore get very simple kinetic definitions of the individual transitions. Monomolecular steps are the simplest processes because only one state variable σ_l changes:



σ_l is the state of lattice site l . p is the transition rate for this process which is independent of the neighbourhood.

Bimolecular steps describe processes which change two state variables σ_l, σ_m . In our model only processes which change the states of two NN sites with $|l - m| = 1$ are considered:



Here k is the corresponding transition rate. Again, the transition rates for these bimolecular processes depend only on the states of the two NN sites.

2.3. A adsorption

The adsorption of a particle A from the gas phase is modelled as in the ZGB model and the rate for A adsorption is given by the gas phase concentration $y = y_A$:



2.4. B_2 adsorption

One B_2 particle is adsorbed with rate $2(1 - y)$ if two empty NN sites are found. Here $y_B = 1 - y$ is the gas phase concentration of B_2 :



2.5. A diffusion

In our model the surface diffusion of A is defined via the transition rate



The diffusion is modelled as a jump of an A particle onto an empty NN site. It can be shown that for the diffusion coefficient of A diffusion on an otherwise empty lattice the equation $D_A = \frac{1}{z} a^2 D$ holds, where a is the lattice constant and z the coordination number of the lattice. Therefore our parameter D corresponds to the frequency factor for the diffusion (all transition rates in the stochastic theory are of dimension $[t]^{-1}$).

2.6. AB reaction

In contrast to the ZGB model we define the reaction constant of the AB reaction via

$$K(AB \rightarrow 00) = R \quad (6)$$

with finite R . In the original ZGB model this parameter is removed because the limit of an infinite reaction constant $R \rightarrow \infty$ is used; but using this limit cannot be described with only monomolecular and bimolecular reaction steps. For example the B_2 adsorption with an A particle on a NN site would lead to the chain process



which corresponds to a trimolecular process. To avoid dealing with such higher order processes we remove the reaction parameter in a different way by simply setting R sufficiently large. We will show that saturation occurs if R exceeds a certain value R' . For $R > R'$ the system behaviour corresponds to a system with infinite reaction constant. For simulations with fast surface diffusion the parameter can be removed by changing the reaction mechanism. In this case reaction occurs when an A particle hops to a NN site which is occupied by B. In this case $R = D$ holds.

2.7. Surface reconstruction

In some simulations below we consider the reconstruction of the catalysts surface. α and β stand for the reconstructed and non-reconstructed surface phase, respectively. Here we consider only the physical properties and neglect the geometric differences of the different phases. In the case of the Pt(100) surface O_2 can only adsorb onto the β phase. In the description of the structural phase transition $\alpha \rightleftharpoons \beta$ stimulated by the presence or absence of A particles one has to distinguish between two processes: (i) spontaneous formation of a nucleus of the α phase in a matrix of the β phase or *vice versa* and (ii) propagation of the border between these two phases including the growth and diminishment of such nuclei. In the simulations presented here we neglect nucleation processes and consider only the phase propagation which depends on the presence or absence of A:

$$K(A_\alpha X_\beta \rightarrow A_\beta X_\beta) = V \quad \text{with } X \in \{0, A, B\} \quad (8)$$

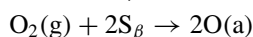
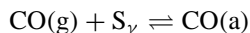
$$K(A_\beta X_\alpha \rightarrow A_\beta X_\beta) = V \quad \text{with } X \in \{0, A, B\} \quad (9)$$

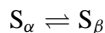
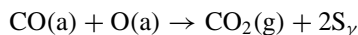
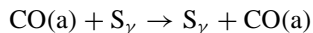
$$K(X_\alpha Y_\beta \rightarrow X_\alpha Y_\alpha) = V \quad \text{with } X, Y \in \{0, B\}. \quad (10)$$

Equations (8) and (9) describe the propagation of the transition $\alpha \rightarrow \beta$ if a particle A exists on at least one of the lattice sites near the phase border. Equation (10) corresponds to the reversed process $\beta \rightarrow \alpha$ under the condition that no A is present. To simplify we assume that the transition rate is equal for both processes. The linear border between the α and β phase moves in one distinct direction dependent on the presence or absence of A, respectively, with velocity $V_{\alpha\beta} = aV/z$, where V is the phase propagation constant. For details see [14, 15].

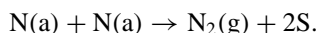
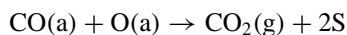
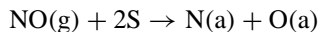
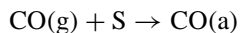
2.8. Kinetic schemes

Summarizing the above transition definitions we simulate the following models written in the more usual form of reaction equations. For the $CO + O_2$ reaction we use





where S stands for a free adsorption site, γ stands for either α or β and (a) or (g) for a particle adsorbed on the surface or in the gas phase, respectively. Note that in the model simulated here O_2 can only adsorb onto sites belonging to the β phase and that the phase propagation $\text{S}_\alpha \rightleftharpoons \text{S}_\beta$ depends on the presence or absence of CO. For additional details see [14, 15]. For the CO + NO reaction model we consider the following elementary reaction steps:



This corresponds to the basic model for the CO + NO reaction which has been discussed in detail elsewhere [31–33].

2.9. Simulation procedure

The simulation is performed in the following way. Instead of choosing every pair of NN sites at random, as is done in MC simulations, we choose only one of the corner lattice sites, e.g. the upper-left corner, and a NN site for it. This is done in accordance with the neighbourhood rules (e.g. the square ($z = 4$) or the triangular lattice ($z = 6$)). The corner site and its NN then build an oriented two-point ‘superstructure’. This ‘superstructure’ is periodically repeated to build a tiled mask over the whole lattice. In the whole process periodic boundary conditions are applied, as is commonly done in such studies. Because transitions are only possible inside such an elementary two-point structure the whole mask can be updated at once, i.e. all two-point structures can be accessed in parallel. With this procedure one saves L^2 random numbers per lattice update which would otherwise be necessary to choose the actual site and its NN site in the MC method. After having generated the ‘superstructure’ mask for each pair of sites a random number is generated. Depending on this random number and the state of the NN sites ($\sigma_l \sigma_m$) the corresponding transition is performed. The sum of all transition rates defines the time unit, i.e. it gives the number of lattice updates necessary for the simulation of one time step. This sum is normalized to unity and the interval [0, 1] is then divided into parts whose lengths are proportional to the individual transition rates. Only transitions in whose interval the random number falls can occur. Therefore the transition rates are mapped onto transition probabilities. The A adsorption as a monomolecular step only changes the state of one site, i.e. considering a 00-pair A adsorbs with rate γ into the first 0 or with equal rate into the second 0. This results in an overall A adsorption rate of 2γ , which is correct because we consider two lattice sites at once. After a full lattice sweep the whole procedure starts over again with a new initial NN site, which is randomly chosen.

2.10. Correlation functions

Investigation of the correlation functions between the species on the surface leads to a deeper insight into the structure of the adsorbate layer. The correlation function g_{ij} between two

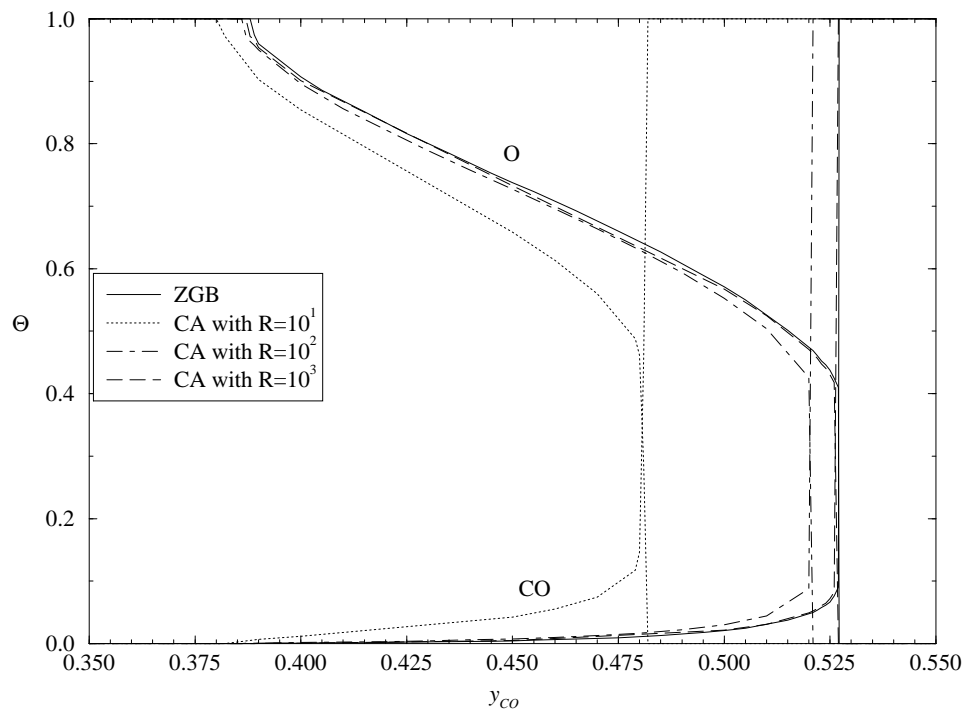


Figure 2. Coverages of CO and O as a function of y_{CO} for the CA approach to the ZGB model on the square lattice with finite reaction constant $R = 10$ (dotted), $R = 100$ (chain), and $R = 1000$ (broken). The result of the original ZGB model is given for comparison (full).

particles i and j is given by

$$g_{ij}(r) = \frac{\langle N_{ij}(r) \rangle}{N_{ij}^*(r)} = \frac{N_{ij}(r)}{z(r)\Theta_j}, \quad i, j \in \{0, A, B\}. \quad (11)$$

It is a measure of the spatial correlation between the (not necessarily different) particles i and j as a function of their distance r on the surface. i and j represent free sites in addition to A , B and the other particles considered in the reaction model. $N_{ij}(r)$ is the number of ij -pairs at a distance r . $\langle N_{ij}(r) \rangle$ is the average value over all particles of type i , whereas $N_{ij}^*(r)$ is the corresponding number of a random particle distribution without correlations ($g_{ij}^*(r) = 1$), which is given by the number $z(r)$ of sites at a distance r from the central site i and the coverage Θ_j of the j particles. (For a more detailed discussion of the correlation function see [35].)

3. Results and discussion

3.1. Similarity with MC simulations

First we examine the original ZGB model [1]. In this model a second-order phase transition from a B poisoned state to a steady state occurs with increasing gas phase mole fraction y of A at $y = 0.387\,368$ [9]. Further increase of y leads to a first-order phase transition into an A poisoned state at $y = 0.525\,60$ [36]. As shown in figure 2 and table 1 large deviations from the original ZGB model exist for small reaction constants ($R = 10$). The CA approach

Table 1. Values of the phase transition points y_1 and y_2 and the width Δ of the reactive interval for the reaction on the regular square lattice with different reaction constants R . The values of our MC simulation corresponding to the work by Ziff, Gulari and Barshad [1] are given for comparison. These correspond to $R \rightarrow \infty$.

R	y_1	y_2	Δ
1	0.340	0.366	0.026
10	0.382	0.481	0.099
100	0.387	0.520	0.133
1000	0.388	0.526	0.138
∞	0.387	0.526	0.139

Table 2. Values of the phase transition points y_1 and y_2 and the width Δ of the reactive interval for the reaction on the regular square lattice with different diffusion constants D . The value of y_2 for $D \rightarrow \infty$ results from the mean-field (MF) approximation.

D	y_1	y_2	Δ
10	0.383	0.512	0.129
100	0.389	0.607	0.218
1000	0.391	0.644	0.253
∞		0.666	

agrees only qualitatively with the MC simulation using an infinite reaction constant. It shows a second-order phase transition at $y_1 = 0.382$ and a first-order phase transition at $y_2 = 0.481$. Our MC simulation which uses the same finite reaction constants gives exactly the same results. A comparison with simulations performed with finite reaction constants by Dumont *et al* [5] shows qualitative agreement with regard to the shift of the phase transition points to lower values and the narrowing of the reactive interval. A quantitative comparison cannot be made because of the different implementation of the adsorption and reaction processes.

For moderate reaction constants ($R = 100$) the results of the CA approach quantitatively agree with those of the ZGB model. In this case the numerical errors in the values of the critical points as well as in the surface coverages are very small (about 1%). For large reaction constants ($R = 1000$) only the value of y_1 shows a small error. The value of y_2 and the surface coverages show excellent agreement with the MC results. The same holds for the extended ZGB model with surface diffusion of A particles. Note that in the case of fast surface diffusion the reaction mechanism is changed in the way described above (i.e. a reaction occurs if A hops to a site covered with B) in order to remove the parameter R because we now have $R = D$. As shown in table 2 the value of y_2 approaches the saturation value $y_2(D \rightarrow \infty) = \frac{2}{3}$ with increasing D similar to the MC simulations performed by other authors [7, 28]. If D or R , respectively, become sufficiently large our CA approach shows excellent agreement with the original ZGB model. Even with moderately large reaction or diffusion constants ($R = 100$ or $D = 100$) the agreement is quantitative. For this reason we can set $R' = 100$ because the system clearly shows saturation even for these moderately large values of R and D .

The next reaction we simulate with our CA approach is the catalytic $\text{NO} + \text{CO}$ reaction model [30–32]. The simulation of this model on a square lattice shows a remarkable behaviour: no steady state reaction exists for any value of y because a special surface

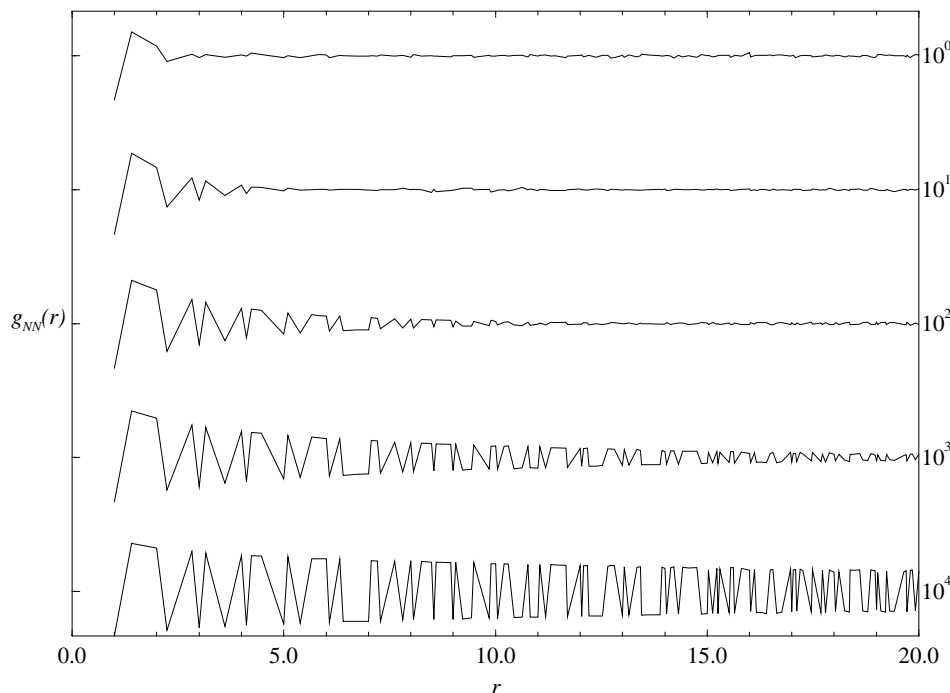


Figure 3. The correlation function $g_{NN}(r)$ on the square lattice for $y_{CO} = 0.23$ and $t = 10^0, 10^1, 10^2, 10^3$ and 10^4 (from top to bottom) determined from the CA simulation. This figure clearly shows the growth of the correlation length with time. In addition one can see that there are hardly any reactive N pairs on NN sites $g_{NN}(r = 1) \approx 0$.

structure of N atoms is built [31–33, 37]. For small and large values of y the system reaches an absorbing state because of large O and CO islands, respectively. In a narrow interval $y \in [0.220, 0.235]$ the coverages of CO and O are of similar magnitude and the system needs very long simulation times to reach poisoning. In this interval large checkerboard structures of N atoms are built covering almost the whole lattice. These structures can directly be seen in the simulation [32] and have been examined via correlation functions [31]. The results of the CA approach presented here coincide with the results of the MC simulation. The coverages as a function of y are the same as in our previous MC study [31] and no differences can be seen in a graphical representation. In the small interval $y \in [0.220, 0.235]$ the N coverage reaches values of $\Theta_N \approx 0.43$ indicating that large N structures are built. Even the microscopic structure and the temporal evolution (see figure 3) of these checkerboard-like structures is described correctly by our CA approach, in agreement with previous results [31, 33]. Although only moderate reaction rates ($R = 100$) are employed hardly any N atoms exist on NN sites ($g_{NN}(r = 1) \approx 0$). The simulation procedure described above can easily be applied to models on the triangular lattice because only the neighbourhood changes. Therefore we ran additional simulations of the NO + CO reaction model with $R = 100$ on this lattice. The CA approach again shows excellent agreement with previous MC results: the system exhibits a second-order phase transition at $y_1 = 0.173$ and a first-order phase transition at $y_2 = 0.344$. These values are qualitatively correct, as a comparison with the values $y_1 = 0.1783$ and $y_2 = 0.3546$ from the original model [31, 32, 38] with

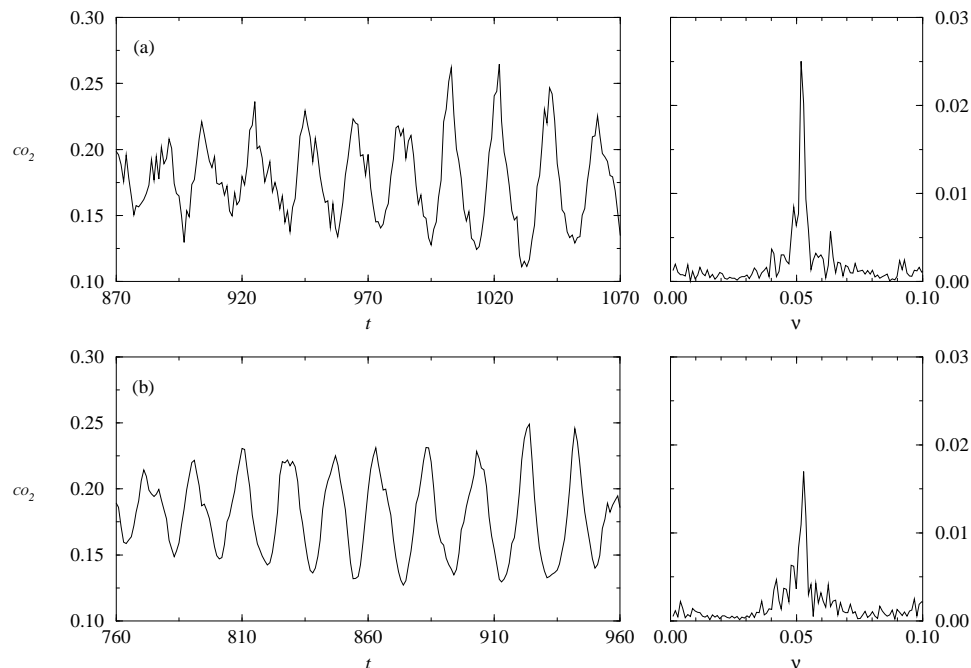


Figure 4. Temporal evolution of the reaction rate R_{CO_2} for the simulation of kinetic oscillation in the catalytic CO oxidation on a Pt(100) surface. (a) Small fluctuations in the oscillations of the reaction rate which occur in the simulation with the CA method presented here. (b) A similar course of a MC simulation where these fluctuations cannot be seen. The right parts show the corresponding power spectra.

infinite reaction constant shows. Again, the value $R = 100$ proves to be sufficient to reach the saturation properties and gives quantitatively correct results with errors of 10^{-2} .

3.2. Temporal behaviour

As shown above the CA approach presented here is in very good agreement with the MC simulation and shows almost equivalent results for steady state properties of such reaction systems. The question that remains is whether the CA approach also shows good agreement for the temporal evolution of the system. The temporal evolution of the correlation functions shown above is at least similar to the results of MC simulations [33]. For the purpose of better comparison we simulated a system which exhibits distinct temporal phenomena, namely kinetic oscillations in the surface coverages and the reaction rate [14, 15]. As shown in figure 4 the results of the CA simulation again show very good agreement even for temporal properties. The power spectra show very similar frequency distributions at almost equal basic frequencies ω_0 . It is important to note that even for two independent MC simulations the frequency distributions are *not* identical but only similar. Therefore the mean kinetic aspects are obtained in agreement with the MC method. A closer look at the temporal evolution of the reaction rate, however, shows a small but systematic difference. In the CA simulation the coverages and reaction rates always show very small fluctuations. These fluctuations arise from the simulation method. Because, in the system considered here, diffusion is the fastest process ($D = 100$) a hopping event takes place in most elementary

Table 3. Relative computational costs for the different simulations methods for the original ZGB model at small ($y = 0.4$) and large ($y = 0.52$) reaction rates. The computational cost for the CA approach for a lattice side length $L = 64$ is set to unity.

L	MC (i)		CA (ii)		MC (iii)		MC (iv)	
	$y = 0.4$	$y = 0.52$	$y = 0.4$	$y = 0.52$	$y = 0.4$	$y = 0.52$	$y = 0.4$	$y = 0.52$
64	0.9	1.5	1.0	1.3	2.5	2.6	0.01	0.07
128	3.8	6.2	4.2	5.2	10.5	11.5	0.05	0.28
256	15.9	27.1	17.8	22.9	47.8	49.5	0.21	1.69
512	194.8	361.3	106.5	128.3	567.5	638.5	2.59	19.30

steps. Reaction is directly coupled to the diffusion because reaction only takes place if an A particle jumps to a site occupied by B . The hopping is restricted to only two instead of four ($z = 4$) or six ($z = 6$) directions, respectively, for a whole lattice update because the orientation of the two-site ‘superstructure’ is determined only once per update. This then leads to bi-directional global diffusion and reaction resulting in these coverage fluctuations. If the same initial NN site determining the orientation of the ‘superstructure’ is chosen twice or more in succession the three other NN sites remain unchecked for the corresponding times of lattice updates. This can lead to an intermediate high density of reactive pairs on NN sites. If the orientation of the ‘superstructure’ is changed in the next lattice sweep these reactive pairs will almost completely be removed resulting in a temporarily high reaction rate and a significant drop in the surface coverages of the reaction partners.

3.3. Computational aspects

After having shown the similarity of our CA approach to MC simulations we now want to focus on the computational aspects such as computational cost and parallelism. In table 3 we compare four different simulation methods.

(i) The ‘normal’ MC simulation with infinite reaction constant as described in the original work of Ziff, Gulari and Barshad [1]. This simulation method has been extended to CO desorption and surface diffusion. It cannot be compared directly to the other methods because it uses a different timescale of so-called Monte Carlo steps (MCS). In this case we compare the time needed for the same number of MCS or our time steps, respectively.

(ii) The CA simulation with a correct timescale based on the sum of the transition rates as described in this article.

(iii) A MC simulation with a correct timescale based on the sum of the transition rates corresponding to the CA method.

(iv) A MC simulation using a correct timescale and infinite reaction rate. In addition the simulation program uses lists for the individual adsorbate particles as described in our previous work [31].

All these simulations have been performed on three different computer systems, all showing very similar relative computational costs. In order to compare the different simulation methods we set the time required for the CA simulation of the ZGB model with $y = 0.4$ on a square lattice of side length $L = 64$ for $t = 100$ time steps to unity. Note, however, that the original MC simulation (i) cannot be compared directly with the other methods because of the different definition of the time unit. As can be seen in table 3 the MC simulation (iv) using lists outperforms all other simulation methods if applied to the original ZGB model [1]. Simulations for $y = 0.4$ and $y = 0.52$ are performed to

investigate the influence of the reaction rate. At $y = 0.52$ the reaction rate is much larger so the simulations using an infinite reaction constant ((i) and (iv)) should significantly slow down compared with those with $y = 0.4$, whereas the computational time for simulation methods (ii) and (iii) using fixed transition rates should increase only very slightly because of the increased counting of particles, updating of lattice sites and so on. This can especially be seen in the timing of the MC method (iv) using lists because in this case not only the sites with the reacting particles have to be found and updated but also the places of the particles in the lists. For the CA simulation (ii) and the MC simulation (iii) a moderate reaction constant of $R = 100$ is applied resulting in results with errors of about 10^{-2} (see above). At first sight the CA approach introduced here has no advantage over the established MC methods. But if one focuses on the computational cost for simulations on large lattices an advantage emerges: as soon as the whole lattice does not fit into the cache memory of the computer (here $L = 512$) the simulation program generates so-called cache misses. If the sites are visited in a random order (MC) the site which is processed after the actual site is far away in most cases. This holds for the spatial order on the lattice as well as for the memory address in the computer. Therefore the next site is not stored in the fast cache memory and must be retrieved from the main memory. As a result the computational cost does not increase by a factor of about 4 (as would be expected for doubling the side length and which can be seen to hold for smaller lattices) but by a factor of about 12. In the CA simulation all sites are updated in one time step without any interaction between the two-point 'superstructures'. Therefore the lattice sites can be accessed in ascending order. This leads to a high rate of so-called cache hits, i.e. in most cases the following site to process is found in the fast cache memory of the computer. Therefore the time increases only by a factor of about 6 in the case of the CA simulation. However, the MC simulation method (iv) using lists is still faster by a factor of 7 because the particles are directly picked from the list and every random number produced is used for a transition. This is not the case for methods (i)–(iii) where many random numbers are rejected during the simulation. On the whole this also holds for the ZGB model with diffusion because of the very small fractional surface coverage of the A (CO) particles.

A completely new situation occurs in simulations where large diffusion constants exist for surface species with large surface coverages. This is the case in the simulation of kinetic oscillations during the catalytic CO (A) oxidation. Here the fractional A coverage varies between very small and very large values [14, 15]. In the MC simulation method (iv) a large part of the computational cost is based on the updating of the sites covered by A and the corresponding list entries, whereas for the CA simulation the situation remains mostly unchanged because of its definition via the transition rates. Indeed the computational cost of the latter only increases by about 2% as compared to the ZGB model. The values in table 4 clearly show that the CA approach is far ahead of the two MC methods, especially for large lattices. In this table the time needed for 100 time steps in a CA simulation of kinetic oscillations in the CO oxidation on Pt(100) with the diffusion constant $D = 100$ and the phase propagation constant $V = 1$ at $y = 0.2$ is given to compare the different simulation methods. For a detailed description of the simulation of the oscillations in the CO oxidation on Pt single-crystal surfaces see [14, 15]. As can be seen only the CA method is convenient for simulating these kinetic oscillations. This holds for simulations with large diffusion constants and even more so for simulations with the combination of large lattices and very fast diffusion.

Table 4. Relative computational costs of the different simulation methods for the simulation of kinetic oscillations in the catalytic CO oxidation on Pt(100). The computational cost of the CA method for the simulation on a lattice of side length $L = 128$ is set to unity. (By multiplying all values by a factor of 4.3 they can be compared with those of table 3.)

L	CA (ii)	MC (iii)	MC (iv)
128	1.0	3.1	2.2
256	4.4	14.8	28.2
512	31.7	228.9	251.4

4. Conclusions

In this paper we have introduced a new CA approach for the simulation of surface reactions. This CA approach shows almost quantitative agreement with the existing MC simulations for the most important reaction systems in the literature. Furthermore it is a general CA because it can be easily adapted to new neighbourhood or transition rules modelling different surfaces or new reaction steps, respectively. It shows a significant reduction of the computational cost for simulations compared with a corresponding MC simulation because much fewer random numbers are needed and because of the better use of the computer's cache memory. This is especially important for simulations on large lattices which do not fit into this cache memory. For simulations of systems, where large fractional surface coverages of very mobile surface species exist, the CA method presented here is the method of choice, especially if these simulations have to be done on large lattices. This is actually the case for our recent simulations of oscillations in surface reactions [14–16]. Surface diffusion is generally the fastest and most prominent process in such reaction systems. Additionally large lattices are needed to describe experimentally observed macroscopic properties correctly. Because of its parallel concept the CA method can be easily implemented on parallel computers and should lead to a large speed-up if the lattice is divided into sufficiently small sublattices which fit into the cache memory of the individual processors.

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