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Cellular-automaton approach to a surface reaction

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A cellular-automaton model for a surface reaction is introduced that describes the chemical reactions correctly. The phase-transition points and the order of the phase transitions agree well with the results of Ziff, Gulari, and Barshad via a Monte Carlo simulation [Phys. Rev. Lett. **56**, 2553 (1986)]. The high performance of the cellular automaton leads to a more precise determination of the critical exponent β at the second-order phase transition ($\beta=0.58$), which thus appears to belong to the universality class of Reggeon field theory.

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INTRODUCTION

Cellular automata (CA) are a very powerful tool to describe complex physical properties. They thus give the possibility to obtain more detailed insight into the dynamics of such systems. Many different systems such as crystal growth or magnetic systems (Ising model) have been studied with the help of CA models. A very important and different aspect is the modeling of surface reactions which in a Monte Carlo (MC) simulation exhibit kinetic or nonequilibrium phase transitions [1]. But these reaction systems have so far eluded a correct treatment via the CA approach because if the CA rules are obeyed the stoichiometry of the reaction is treated incorrectly. The study of the universality class of these systems is also of great importance for the basic understanding of dynamical phenomena. A study of systems such as the Schlögl model [2], the directed percolation [3], and the Reggeon field theory [4] has revealed that these systems belong to the same universality class: the universality class of Reggeon field theory. There are also suggestions that surface reactions may belong to this universality class [5,6].

An example of a surface reaction is the reaction of CO and O over a Pt surface. Ziff, Gulari, and Barshad [1] introduced a MC simulation which takes only a few important steps into account. In their simulation the surface is represented as a two-dimensional square lattice with periodic boundary conditions. A gas phase containing CO and O_2 with the mole fraction of y_{CO} and $y_O=1-y_{CO}$, respectively, sits above this surface. Adsorption can occur if a randomly selected site on the surface is vacant. Because the adsorption of O_2 is dissociative an O_2 molecule requires two adjacent vacant sites. If a CO molecule is a nearest neighbor of an O atom reaction occurs and the product molecule desorbs immediately after formation. The three basic steps are

$$\mathrm{CO(gas)} \rightarrow \mathrm{CO(ads)}\,, \tag{1}$$

$$\mathrm{O_2(gas)} \rightarrow \mathrm{2O(ads)}\,, \tag{2}$$

$$\mathrm{CO(ads)+O(ads)} \rightarrow \mathrm{CO_2(gas)}\,. \tag{3}$$

Ziff, Gulari, and Barshad found in their simulations two kinetic phase transitions with regard to y_{CO}. For low values of y_{CO} the surface is completely covered with O ($y_{CO}\le y_1=0.395$) and for higher values with CO ($y_{CO}\ge y_2=0.525$). A reactive phase exists only in the interval $y_1<y_{CO}<y_2$. The phase transition at y_1 is of second order and at y_2 of first order.

The CA is a model which is discrete in time and space. The transition rules for all cells are the same and the update is simultaneous. During this fully parallel procedure difficulties can arise. A well-known problem is the Ising model [7]. Simultaneous update of all spins (or cells) leads to the *feedback catastrophe.* To get the correct physical behavior one must divide the lattice like a checkerboard on which white and black cells are updated in alternate order. In a reaction system this technique does not work, however.

Chopard and Droz [8] introduced a CA approach for the system $CO+O_2$ on a metal surface. In order to obey the CA laws they were forced to disobey the laws of stoichiometry in the reaction: A particle may take part simultaneously in the formation of several reactive pairs. Therefore the values of y_1 and y_2 are shifted to higher values ($y_1=0.5761$ and $y_2=0.6515$) and both phase transitions are of second order.

Berryman and Franceschetti [9] have developed a CA model for the reversible $A+B\rightleftharpoons C$ reaction which involves the Margolus block rotation to describe diffusion and reaction. They studied anticorrelations in this reaction. In contrast to their work we have source terms and dissociation, but we neglect diffusion so far. In a MC simulation we studied diffusion in the $CO+O_2$ reaction [10].

Here we present a CA approach which describes the steps of adsorption and reaction correctly. We obtain the value of y_1 and y_2 and the character of the phase transition in good agreement with the MC simulation. We found that the results of the sequential and of the parallel approach are numerically nearly identical but we cannot show the identity of these models analytically. Beney, Droz, and Frachebourg [11] studied similar models and in one dimension they found no difference in the values of the critical exponents obtained by a sequential and by a parallel model but they observed small changes in the values of the critical points. These observations are confirmed by our results.

The performance of the parallel CA approach is very good, so that the simulation can be performed on large lattices because the large number of unsuccessful attempts (which are unavoidable in a MC simulation) does not appear. Therefore a lot of computer time is saved in the CA model. Moreover the fully parallel approach can be implemented on special purpose computers (such as the CAM-6) or better on a computer with full parallel architecture (e.g., the Connection Machine) which offers a magnitude of computational resources.

Therefore the CA approach offers a way to follow the temporal evolution of the system. Near y_1 (the second-order phase transition) long-range correlations and fluctuations play a crucial role. Because of the critical slowing down at this point many iterations are necessary to describe the behavior of the system correctly.

THE SIMULATION

Above we mentioned that the trick with the Ising model does not work with chemical reactions. The lattice must thus be divided in another way as in the Ising model to get the correct stoichiometry for the system. We divide the lattice into Margolus blocks [12] containing 2×2 cells as elementary cells. Thus the neighborhood here is the cells in a Margolus block; and any cell in a Margolus block is a neighbor of the three other cells. The definition of the neighborhood is clearly different from the neighborhood used by Ziff, Gulari, and Barshad: All Margolus blocks are updated simultaneously. The transition rules are shown in Fig. 1. The probability for each transition depends on the mole fraction y_{CO}, on the statistical weights of the individual configurations, which are taken as classical, and on the initial state of the cell. Similarly to the MC approach two vacant cells are necessary to adsorb an O_2 molecule. For example, the probability for the adsorption of one CO molecule into an empty Margolus block depends on the probability of selecting a CO molecule from the gas phase (y_{CO}) and on the number of vacant cells in the Margolus block which determines the number of different adsorption states. In an empty Margolus block there exists four different possibilities. Therefore the (unnormalized) probability for this event is $4y_{\mathrm{CO}}$. Only one of the possible configurations is shown in Fig. 1. The same comment applies to the other rules. The probability for simultaneous adsorption of two CO molecules depends on y_{CO}^2 (probability that both selected particles are CO molecules) and on the number of adsorption configurations (there are 12 possibilities for a classical particle). A last example: the probability for adsorbing an O_2 molecule in an empty Margolus block depends on the probability that the selected gas phase molecule is an O_2. This is y_{O} $(=1-y_{\mathrm{CO}})$, and the distinct number of configurations for adsorbing a classical O_2 is 12. Each Margolus block is changed during a sweep through the lattice. The probability for a block to remain in its previous state is zero if it is not fully occupied. If we would use other rules which allow a Margolus block to remain unchanged we would have to introduce an arbitrary parameter, namely, the probability that a Margolus block remains unchanged. This cannot be determined from any physical or plausible model. But this parameter has to be fixed in order to normalize the probabilities. We have avoided this unphysical approach. If the lattice is completely covered by one or the other species (which means poisoning of the catalyst surface) the system remains in this state with unit probability (this transition is not shown in Fig. 1), which is in agreement with the original model of Ziff, Gulari, and Barshad. This rule that no block remains unchanged unless it is fully occupied by only one species is rather different from Monte Carlo simulations in which at each time step only a single cell is updated and most cells consequently remain unchanged. CA and Monte Carlo approaches are thus extreme cases. It should be pointed out that the adsorption on a surface in an experiment occurs on many sites essentially simultaneously but not on all. Yet the Monte Carlo simulations of Ziff, Gulari, and Barshad describe in a simplified way certain aspects of the experiment and we are going to see that the CA approach does so too.

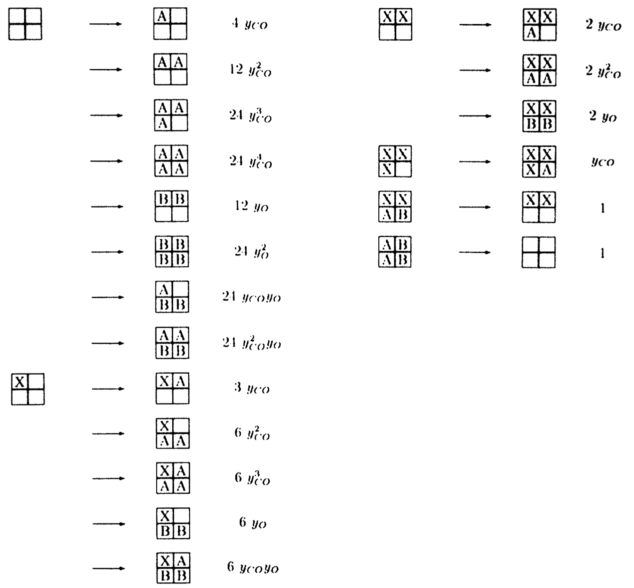

FIG. 1. CA transition rules for the $\mathrm{CO}+\mathrm{O}_2$ reaction. *A* denotes a CO molecule, *B* an O atom, and *X* any occupied site. y_{CO} is the mole fraction of CO molecules in the gas phase. The probability of adsorption depends on y_{CO} and on the number of different adsorption configurations in a Margolus block.

After the calculation of the transition probability a random number is generated and a transition for the current initial state is selected. For a particular initial state the sum of all transition probabilities is normalized to 1. Such a CA is called a probabilistic or stochastic CA. After one sweep through the lattice, the Margolus block (the window in which transitions take place) is shifted by one cell to the right, then down, then left, and then up to get all different configurations inside a Margolus block. In the simulation we use a lattice of 256×256 sites with cyclic boundary conditions. One independent run consists of 10000 updates for the lattice (consisting of adsorption, Margolus block shifting). For each value of y_{CO} many independent runs are performed (near y_1 10000 and for $y_{\mathrm{CO}} > y_1$ only a few hundred runs are made). To test the system for relaxation to the steady state we enlarge the number of lattice updates up to 50000. We find no significant change in the values of the coverages compared to the simulations with 10000 lattice updates. During the simulation many random numbers must be generated. To be sure that no recurrences occur we use two different random number generators: (1) a random number generator from the numerical algorithms group (NAG) library and (2) a very fast random number generator introduced by Kirkpatrick and Stoll [13]. The recurrence cycle for the random number generator (1), e.g., is 10^{17}. For a 256×256 lattice with 50000 updates and 10000 independent runs we need 3×10^{13} random numbers. This is well below the recurrence of the numbers from the random number generator. In addition no significant difference in the results occur using these two different random number generators.

RESULTS

In Fig. 2 the coverage of the surface by CO and O and the reaction rate R are shown as a function of y_{CO}. The jump in the reaction rate R at y_1 arises due to the phase transition, because for $y_{\mathrm{CO}} < y_1$ the lattice is completely covered by O (which means poisoning) and therefore the reaction comes to a stop. In this irreversible model no further change can occur and the reaction rate R is lowered to zero.

Near y_1 hundreds of data points were collected with many independent runs. Because of the scale of the figure these have not been plotted. The error bars in the neighborhood of y_1 and y_2 are so small that they cannot be represented on the scale. In the interval $y_1 < y_{\mathrm{CO}} < y_2$ which is of less interest the data are less accurate because of a smaller number of independent runs. We obtain the critical values $y_1 = 0.3915 \pm 5 \times 10^{-4}$ and $y_2 = 0.514 \pm 0.001$, which are in very good agreement with the results of the MC procedure of Ziff, Gulari, and Barshad. The values for the critical points obtained by the sequential model of Ziff, Gulari, and Barshad and by our parallel approach are not identical. Similar differences were also found by Beney, Droz, and Frachebourg [11] for one-dimensional systems with sequential and parallel updating. One reason for the discrepancy may be the use of larger lattices in the CA simulations which gives more accurate results. But other explanations of an intrinsic type cannot be ruled out. The character of the kinetic phase transitions is also conserved in the CA approach; it is second order at y_1 and first order at y_2. The fact that the transition at y_2 takes place in a finite interval has solely to do with the finite lattice. It has been shown that at y_2 a mean-field theory is valid [14] and in a mean-field theory the O coverage becomes imaginary demonstrating first-order behavior. The phase diagram is very similar to the figure obtained by Ziff, Gulari, and Barshad [1].

Near the second-order phase transition at y_1 the coverage Θ of CO and O scale as

$$1 - \Theta_{\mathrm{O}} \sim (y_{\mathrm{CO}} - y_1)^{\beta_{\mathrm{O}}} \text{ and } \Theta_{\mathrm{CO}} \sim (y_{\mathrm{CO}} - y_1)^{\beta_{\mathrm{CO}}} . \tag{4}$$

Meakin and Scalapino [15] found $\beta_{\mathrm{O}} \approx 0.61$ and $\beta_{\mathrm{CO}} \approx 0.69$ via a MC approach. Within the uncertainty of their simulations they believed that their results indicate that $\beta_{\mathrm{O}} = \beta_{\mathrm{CO}}$. A mean-field ansatz [16] predicts $\beta_{\mathrm{O}} = \beta_{\mathrm{CO}} = 1$, showing that the behavior of the system near the second-order phase transition is not of mean-field character but is dominated by long-range correlations and fluctuations. Grinstein, Lai, and Browne [5] and Jensen, Fogedby, and Dickman [6] argued that the second-order phase transition belongs to the universality class of

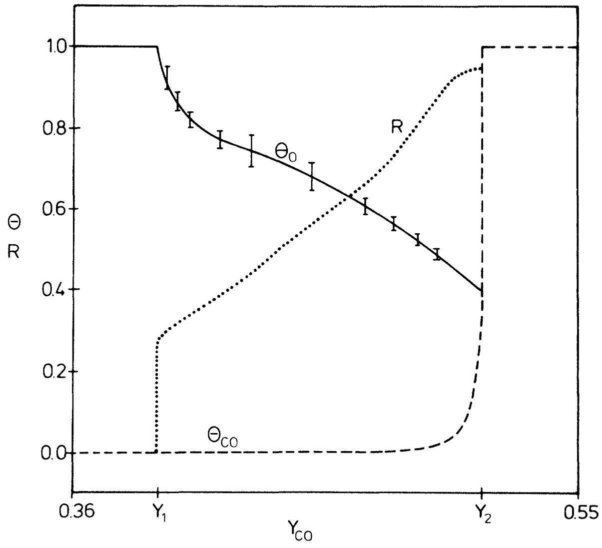

FIG. 2. Phase diagram for the occupation of the surface by CO and O and the reaction velocity R (in arbitrary units) as a function of the mole fraction y_{CO} in the gas phase. The error bars show the uncertainty in the values of Θ_{O}. Near the phase-transition points y_1 and y_2 no error bars are plotted because they are so small that they cannot be represented on the scale. The same holds for the error bars of Θ_{CO} and R. For more details see the text.

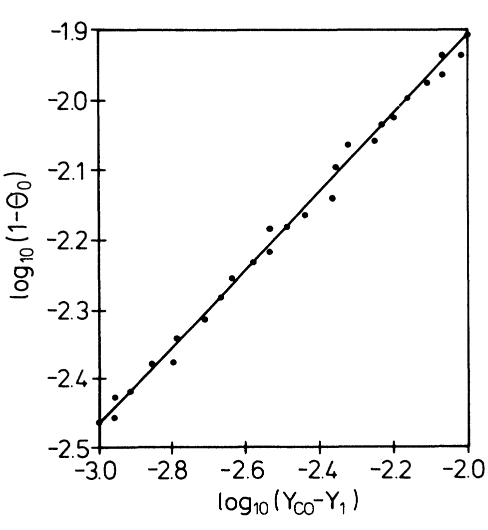

FIG. 3. Log-log plot for Θ_{O} in the vicinity of the phase-transition point y_1.

Reggeon field theory, for which the critical exponent is $\beta \approx 0.58$. Chopard and Droz [8] obtained $\beta = 0.55 \pm 0.05$, which is in agreement with the value of the Reggeon model, but this has to be regarded with some skepticism because the stoichiometry is not correct and therefore this model describes another reaction system and is not equivalent to the model of Ziff, Gulari, and Barshad.

It is thus required to arrive at a more precise value of β to clarify this point. But to this end it is necessary to determine the value of the phase-transition point, y_1, more accurately than it was possible so far. This has turned out to be difficult because of the critical slowing down at y_1. Therefore many iterations (10000 to 50000) and many independent runs (10000) must be performed to obtain the correct value of β. From the simulation it was found that if y_1 is known with an accuracy of 2×10^{-3} then the error of β is obtained to be 0.06 in a small interval near y_1. We attempted to achieve an accuracy of 5×10^{-4} in y_1. This results (via a log-log plot) in a value of $\beta_{\mathrm{O}} = 0.58 \pm 0.02$ and $\beta_{\mathrm{CO}} = 0.58 \pm 0.03$ in the interval $y_{\mathrm{CO}} - y_1 = [10^{-3}, 10^{-2}]$ (see Fig. 3). It should be apparent that at such a precision one should control the dependence of y_1 and thus β on the system size beyond the present 256×256 for the cellular automaton. Because the main goal of this paper is to show a CA model which fulfills the rules of a surface reaction correctly, calculations with a 512×512 matrix with many time steps and many independent runs which would be time consuming have not been performed. The result for β is in good agreement with the result predicted by the Reggeon field theory. Within the accuracy of the calculations both values of β, i.e., β_{CO} and β_{O} are equal.

CONCLUSIONS

We conclude that the CA approach can also be applied to surface chemical reactions that so far have proved to be rather difficult to treat correctly. Thus the CA approach can be set up to be equivalent to the MC simulation, but it is much faster. Thus larger systems can be treated and critical exponents estimated more reliably. We expect that the cellular-automaton presented here is generally applicable to surface chemical reactions.

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