Spontaneous symmetry breaking in a NO + CO surface reaction model

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Abstract

A simple lattice gas model for the catalytic $CO + NO \rightarrow CO_2 + \frac{1}{2} N_2$ surface reaction is studied by means of a model involving a stochastic cluster approximation. The cluster approximation on an infinite square lattice gives a reactive interval from a second-order phase transition at $y_1 = 0.171$ to a first-order phase transition at $y_2 = 0.319$. The subdivision of the lattice into two chequerboard-like sublattices leads to a third phase transition at $y_{CO} = 0.227$ where the reactive interval ends. This point is the left-hand limit of the domain of spontaneous symmetry breaking where a phase transition from dynamical disorder to static order occurs. © 1997 Published by Elsevier Science B.V.

1. Introduction

The term *hidden symmetry* or *spontaneous symmetry breaking* is well known in almost every field of modern physics [1] from quantum field theory to general relativity. Some examples are models for ferromagnetism [2], anti-ferromagnetism [3,4], diffusion systems [5] and gravitational systems [2]. In general, one can observe quite large fluctuations of one system property before the system settles into a stationary state. In the case of ferromagnetism the system fluctuates around zero magnetization and has no permanent magnetic moment above its Curie point. The system's Hamiltonian is supposed to be spherically symmetric. Cooling down leads to a phase transition and the system spontaneously goes into a state of magnetization. Additionally, one cannot predict the direction of the magnetization because all directions are energetically equivalent (spherical symmetry) and therefore determined by random fluctuations [1]. The Ising model for ferromagnetism shows the same behavior [2] running spontaneously into one state of magnetization, either $+1$ or -1. In this Letter we show that symmetry breaking is a useful term also for the theory of surface reactions, because it gives a general explanation of some phenomena. In addition, it is useful to introduce simple extensions into existing theoretical methods to study this spontaneous symmetry breaking and the possibilities of its descriptions.

In chemical surface reactions one observes kinetical phase transitions of different order, e.g. a change in the surface coverage with the variation of some parameters, which determine the course of the reaction. The question of a theoretical method which is appropriate for the description of the problem is important in all theories of critical phenomena. These theoretical methods can be divided into the following groups. (a) In mean-field (MF) theories [1,6] one only considers globally averaged quantities, e.g. densities, and neglects all spatial correlations between the reactants. (b) In the cluster approximation [7–10]

spatial correlations between nearest neighbors (NN) are taken into consideration. (c) The correlation analysis [11,12] looks at the spatial correlations between two particles λ and μ at all distances $\boldsymbol{r}$. Here one pays attention to the globally averaged quantities and the intermediate range order of λ,μ-states through pair correlation functions $g_{\lambda\mu}(\boldsymbol{r})$. (d) The consideration of the three (four, five and so on) point correlations is another possibility, but, as far as we know, there are no examples in the literature.

There is a simple relation between these methods [7,11,12] because the omission of the intermediate range order in the correlation analysis (i.e. $g_{\lambda\mu}(\boldsymbol{r}) = 1$ for all $|\boldsymbol{r}| > 1$) leads to the equations of the cluster approximation. If one further neglects the correlations between nearest neighbors ($g_{\lambda\mu}(\boldsymbol{r}) = 1$ for all $|\boldsymbol{r}| \geq 1$) one gets the equations of the MF approximation.

A comparison of the results of MF theory and Monte Carlo simulations shows that the primitive MF approximation is a useful tool to fit experimental data but has little relevance as an alternative to simulations in the development of theoretical models of chemical surface reactions [13]. A good example is the $A + \frac{1}{2}B_2 \rightarrow 0$ reaction [14] (ZGB model) which exhibits one second-order phase transition at $y_1 = 0.395$ and one first-order phase transition at $y_2 = 0.525$, whereas the MF approximation leads to a value of $y_1 = 0$. The cluster approximation shows at least a qualitative agreement [7] giving a second order phase transition at $y_1 = 0.258$. A quantitative evaluation with errors within a few 10% in the position of the critical points is possible. The main disadvantage of this approximation is the too simple description of the lattice structure which only takes the coordination number Z into account. Therefore, it proves insufficient for a correct description of the formation of spatial structures on the lattice. Concepts like intermediate range order and correlation length are necessary. The correlation analysis overcomes the disadvantages mentioned above and gives good results in agreement with the simulation [12] (e.g. $y_1 = 0.395$ for the $A + \frac{1}{2}B_2 \rightarrow 0$ reaction). Additionally, the correlation analysis makes the observation of cluster formation and segregation possible.
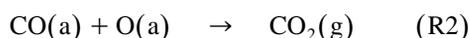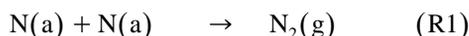
Somewhat more difficult is the correct description of problems with static disorder such as the $A + \frac{1}{2}B_2 \rightarrow 0$ reaction on irregular lattices [15,16] or the

ammonia synthesis on lattices with promoting sites [11,17]. A special problem arises in the description of percolation effects [18]. In these cases not only MF but even the cluster approximation fails and only the correlation analysis gives acceptable results. Entirely new problems occur in the investigation of systems with dynamical disorder (see below). An instructive example is the $CO + NO \rightarrow CO_2 + \frac{1}{2}N_2$ ($A + CB \rightarrow 0$) reaction which is described in detail elsewhere [8,19–22]. Below we only give the basic reaction steps of the simplified model considered here.

Adsorption and desorption steps:

$$CO(g) \quad \rightleftharpoons \quad CO(a) \qquad\qquad (A1)$$
$$NO(g) \quad \rightarrow \quad N(a) + O(a) \qquad (A2)$$
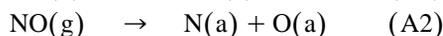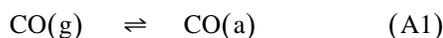
Reaction and desorption steps:

$$N(a) + N(a) \quad \rightarrow \quad N_2(g) \qquad (R1)$$
$$CO(a) + O(a) \quad \rightarrow \quad CO_2(g) \qquad (R2)$$

This simplified model may be valid for Rh(111) at low total coverages because of the fast NO dissociation on this surface. On the triangular lattice ($Z = 6$) the system shows a reactive interval between $y_1 = 0.1783$ and $y_2 = 0.3546$. The values of these phase transition points are discussed in detail in relation to previous results in Ref. [19]. The phase transition at y_1 is of second, the one at y_2 of first order. On the square lattice ($Z = 4$) the system behaves completely differently. No steady-state reaction occurs on a finite lattice in the MC simulations. The reaction always reaches an absorbing (poisoned) state independently of the gas phase concentration y_{CO}. For $y_{CO} < 0.22$ the lattice is mainly covered with O, whereas for $y_{CO} > 0.235$ CO is the predominating species. In the interval $0.22 \leq y_{CO} \leq 0.235$ the system behavior is of special interest, because large chequerboard-like N structures are built and the time to reach an absorbing state depends on the lattice size. This corresponds to the state of perfect antiferromagnetic alignment in the two dimensional Ising model of antiferromagnetism where magnetic spins are arranged in a chequerboard-like manner [1,23]. For the interval mentioned above a special discussion is neccessary (see below).

The NO + CO reaction can be seen as a combination of two reactions, the CO + O and the N + N

reaction. The adsorbed N atoms are obstacles (inactive or perturbation sites) for the CO + O reaction, whereas the CO molecules and the O atoms are inactive sites for the N + N reaction. Contrary to irregular lattices or percolation problems these inactive sites are dynamically distributed over the lattice because they can be produced (NO adsorption) and removed (N$_2$ desorption) within the course of the reaction. An interesting point is that this dynamical disorder transmutes spontaneously into real static order. The randomly distributed N atoms build a regular chequerboard structure. This structure was extensively analyzed by Meng, Weinberg and Evans [8] and its sensitivity against small changes has been investigated in our previous paper [19]. Brosilow and Ziff [22] gave a simple but remarkable proof that the model cannot show any reactive state on a *finite* square lattice of *even* side length L. However, this proof is not valid for a finite square lattice with periodic boundary conditions and L odd, because it is impossible to cover the whole lattice with N atoms in a chequerboard-like manner without reacting N atoms on nearest neighbor sites. The system behavior on an infinite lattice considered here is indeterminate. The cluster approximation shows a remarkable behavior in this case.

2. Results and discussion

In this Letter we do not wish to show the derivation of the equations. One can use the known equations of Dickman [10], Meng et al. [8] or our previous work [7]. For example, we get

$$\frac{d}{dt}\varrho_{AA} = 2 p_A \varrho_{0A} - 2\frac{Z-1}{Z}\frac{\varrho_{AA}\,\tilde{\varrho}_{AB}}{C_0} \qquad (1)$$

for the evolution in time of the A–A nearest neighbor pairs (A = CO). The two-point density $\varrho_{\lambda\mu}$ is the probability of finding one particle λ and one particle μ on a pair of nearest neighbor sites, and $\tilde{\varrho}_{\lambda\mu} = R_{\lambda\mu}\varrho_{\lambda\mu}$ is the corresponding *virtual* two-point density if λ and μ are reactive neighbors with $R_{\lambda\mu} \to \infty$. The one-point density C_λ is simply the surface concentration (fractional coverage) of species λ. The only structure parameter is the coordination number Z. The equations for the correlation analysis are

derived, in general, and independently of the reaction model elsewhere [11].

On the triangular lattice ($Z = 6$) the cluster approximation shows good agreement with the simulation, comparable to the one for the A + $\frac{1}{2}$B$_2$ → 0 reaction. The cluster approximation leads to phase transitions at $y_1 = 0.152 \pm 0.001$ (second-order) and at $y_2 = 0.393 \pm 0.001$ (first-order). Except for numerical differences both the simulation and the cluster approximation give a relatively broad reactive interval. On the square lattice ($Z = 4$) the cluster approximation fails to give qualitatively consistent results. Again it shows a broad reactive interval between a second-order phase transition at $y_1 = 0.171 \pm 0.001$ and a first-order phase transition at $y_2 = 0.3193 \pm 0.0001$, whereas the MC simulation always runs into an absorbing state. The values of y_2 are in qualitative agreement with the analysis in Ref. [8], where the authors get spinodal points at $y_{CO} = 0.3020$ for $Z = 4$ and at $y_{CO} = 0.3877$ for $Z = 6$. The differences in the values of the saturation coverages are extremely large (e.g. $C_N = 0.43$ (MC simulation) and $C_N = 0.21$ (cluster approximation) at $y_{CO} = 0.23$). The origin of this failure requires a fundamental explanation. This then leads to an improvement of the cluster approximation.

In the simulation the growth of the N structures can be directly observed. A statistical evaluation of snapshots of the lattice gives the correlation functions for pairs of surface species as shown in Ref. [19] and in Fig. 1a. These correlation functions clearly show the existence of intermediate range order. The values of the correlation function differ from the asymptotic value ($g_{\lambda\mu}(r) = 1$ for $|r| \to \infty$) on a length equal to the correlation length ξ, which can be seen as the mean size of the N structures. If the reaction runs into an absorbing state, the value of ξ is determined kinetically because the N structures do not have sufficient time to grow. Therefore, it is clear that the direct use of the cluster approximation must lead to large and qualitative errors.

There should not be any theoretical problems with the correlation analysis because it considers spatial correlations for any r. For the correlation analysis we use the general representation of this method [11]. It describes the growth of the chequerboard-like N structures and is an important supplement to the simulation. In the simulation we have a small inter-

val $0.22 \leq y_{CO} \leq 0.235$ where the correlation length ξ is similar to the system size L, $\xi \sim L$. The correlation analysis employs an infinite lattice $L \rightarrow$ which renders an unhindered growth of the N structures possible. This can be seen in the correlation functions and the correlation length increasing with time as $\xi(t) \rightarrow$ (Fig. 1b).

The growth of an infinite structure on an infinite lattice needs an infinite time. Therefore, an absorbing state only exists as a possibility in a certain interval. In this interval an absorbing state cannot be reached within a finite time and the correlation analysis shows non-steady reactive states. Although no theoretical disadvantage exists, the correlation analysis exhibits a practical drawback: the computation time increases with ξ^2 resulting in an upper time limit for the calculations. Therefore, we do not get

Fig. 2. Comparison of the steady-state coverages of the simulation and the correlation analysis (dot-dashed lines).

an absorbing state and do not have any possibility to compare the correlation analysis with the simulation. However, an incomplete verification is a comparison with the simulation results in those intervals, where the correlation analysis leads to an absorbing state (see Fig. 2).

We need a much more primitive theory to get a qualitatively correct description of the system behavior over the whole range of the system parameters. If the correlation length ξ approaches infinity, the N structures grow indefinitely, i.e. the former intermediate range order inside the finite N structures is transformed into a kind of long range order within the infinite N structures. If one divides the square lattice into two chequerboard-like sublattices with the white sites on the first and the black sites on the second sublattice, it is impossible to predict the color of the sites where the N atoms will reside. This infinite N structure is generated because of spontaneous symmetry breaking in the system. Similar unpredictability of symmetry breaking is observed in the theory of anti-ferromagnetism [3], diffusion systems [5], ferromagnetism, self–gravitating systems and quantum field theory [2].

A simple way to take the possibility of symmetry breaking into account in the theory of kinetic phenomena is to generalize the cluster approximation to two (virtual) sublattices [23]. To this purpose we define black (B) and white (W) sites like a chequer-
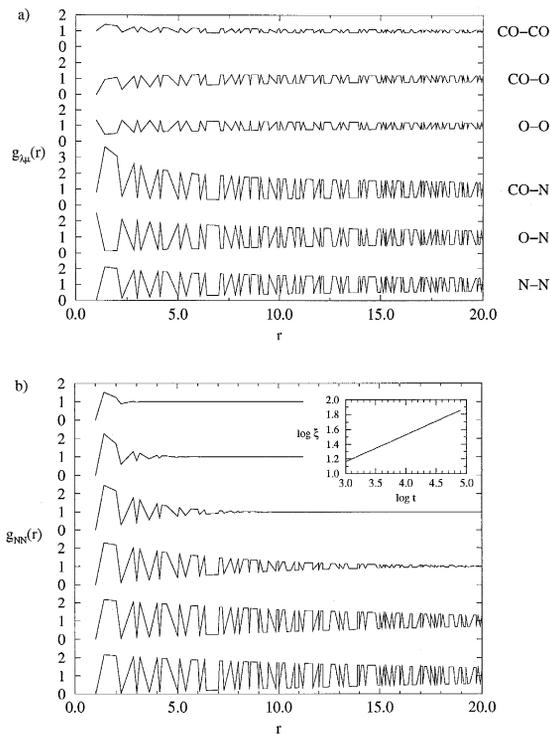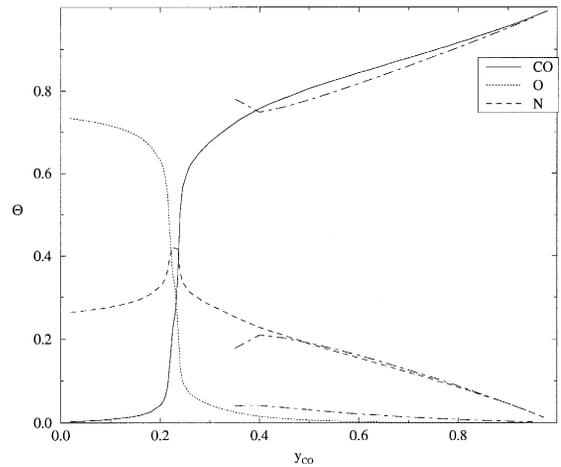

Fig. 1. (a) The correlation functions $g_{\lambda\mu}(r)$ on the square lattice for $y_{CO} = 0.23$ determined from Monte Carlo simulation. (b) The correlation function $g_{NN}(r)$ on the square lattice for $y_{CO} = 0.23$ and $t = 10^0$, 10^1, 10^2, 10^3, 10^4 and 2.5×10^4 (from top to bottom) determined from the correlation analysis. The inset shows the correlation length as a function of time, which can be seen as a measure of the mean cluster size of the N structures.

board on the lattice. In the simple cluster approximation without the sublattices the states of nearest neighbor pairs $\lambda\mu$ and $\mu\lambda$ are identical states. Assuming that the first particle resides on a white and the second on a black site of the lattice, we then have two different pairs $\lambda\mu$ and $\mu\lambda$ (according to $\lambda_W\mu_B$ and $\mu_W\lambda_B$, respectively) in the cluster approximation with the sublattices. This leads to an enlarged number of equations describing the structure of the lattice in more detail. For example the evolution of the A–A nearest neighbor pairs now reads

$$\frac{d}{dt}\varrho_{AA} = p_A(\varrho_{A0} + \varrho_{0A}) - \frac{Z-1}{Z}\frac{\varrho_{AA}\,\tilde{\varrho}_{AB}}{C_{A_W}}$$
$$- \frac{Z-1}{Z}\frac{\varrho_{AA}\,\tilde{\varrho}_{BA}}{C_{A_B}}, \qquad (2)$$

where C_{A_W} and C_{A_B} denote the densities of particle λ on the white and black sites, respectively. The equations of the new cluster approximation formally give the same solution as those in the old 'symmetric' approximation. To initiate the symmetry breaking we have the following possibilities. (a) The use of an unsymmetrical scheme to solve the equation automatically leads to symmetry breaking. This could be done by calculating the solutions for the white sublattice before calculating the solutions for the black sublattice for each time step (or vice versa). The small numerical differences grow with time and soon give completely new results. Outside the domain of symmetry breaking the small differences vanish quickly. (b) One can introduce a small asymmetry into the initial conditions such as creating a small difference δC in the particle densities on both sublattices and solve the equations simultaneously. Again in the region without symmetry breaking this difference should disappear with time. (c) Only steady-state solutions can be investigated under the condition that these solutions are stable.

In this work we use the second method setting the initial difference to $\delta C = 10^{-15}$ ($C_{N_W}/C_{N_B} = 1 + 10^{-9}$ with $C_{N_B} = 10^{-6}$ at $t = 0$) in the density of N atoms. The results for the steady-states are independent of δC, even the temporal evolution does not vary with different values of δC. In Fig. 3 the coverages are shown as a function of the CO gas
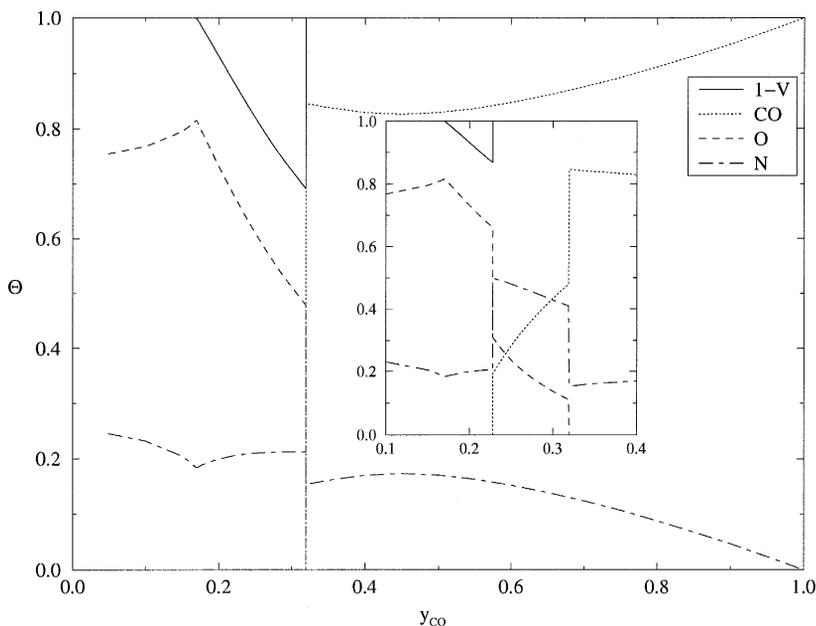

Fig. 3. Phase diagram of the NO + CO reaction in the symmetric cluster approximation. The inset shows the phase diagram for the cluster approximation on the two sublattices in the interval where symmetry breaking exists. The fractional coverages Θ of CO (dotted line), O (dashed line), N (dot-dashed line), and the total coverage (1-V, solid line) are shown.

phase concentration y_{CO}. Now the sublattice model exhibits three phase transition points.

At $y_1 = 0.171 \pm 0.001$ there is a second-order phase transition from poisoned to steady reactive states giving the left-hand limit of the reactive interval. The reactive interval ends at $y_2 = 0.2276 \pm 0.0001$ with a first-order phase transition. y_2 is the right-hand limit of the reactive interval and the left hand limit of the domain of symmetry breaking. This domain ends at $y_3 = 0.3193 \pm 0.0001$ with another first-order phase transition into a region, where symmetry breaking ceases to play a role. In the interval $y_{CO} \in (y_2, y_3)$ the symmetric solution is unstable. The symmetry breaking results in the slow process of N structure formation (increasing correlation length ξ). The cluster approximation is not able (even with the sublattices) to describe this phenomenon correctly, but as an important result the unsymmetrical solution can be compared qualitatively with the results of the correlation analysis. This is shown in Fig. 4. At $t \approx 1000$ the N structure on one sublattice begins to predominate over the N structure on the other sublattice. The growth continues until the first sublattice is almost covered by N at $t \approx 2500$. Because the cluster approximation neglects

intermediate range order the growth of the N structures is fast and the kinetic phase transition into the absorbing state cannot be described correctly.

The cluster approximation reaches the steady state with an N structure covering one of the two sublattices ($C_N = 0.5$), whereas the correlation analysis still is in an unsteady-state. The cluster approximation with symmetry breaking gives the densities for the case that the intermediate range order has changed into a long range order, therefore it shows the solution of the correlation analysis for $t \rightarrow$.

One final question remains. Although the width of the reactive interval is reduced when we consider the symmetry breaking, it still exists, whereas the simulation always runs into an absorbing state. At first we wish to emphasize that simulation is not always a verification of analytical results because of the limitation to a finite lattice, which is often a severe limitation. The analytical theories always regard processes on an infinite lattice. Thus it should be considered whether and how strongly the results of the simulation depend on the lattice size and whether a property, observed in the simulation, really has a physical meaning.
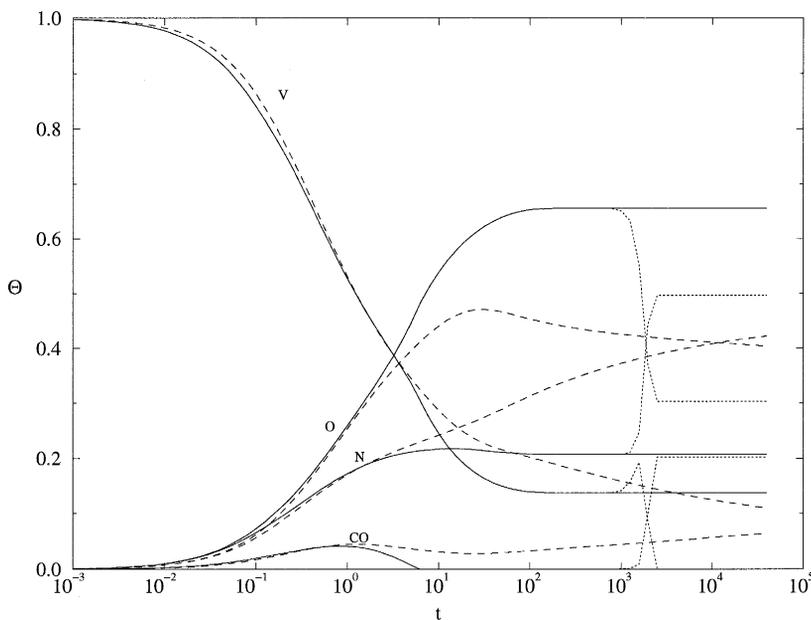
The models for chemical reactions investigated

Fig. 4. Evolution of the coverages with time for the symmetric (solid line) and the sublattice cluster approximation (dotted line) and for the correlation analysis (dashed line).

with Monte Carlo simulations usually are relatively simple. Only the basic reaction steps are taken into account, e.g. only adsorption without desorption. The back processes are neglected and consequently the model gets a characteristic feature. Many states Q (particle distributions on the lattice) can be reached through processes $Q' \to Q$. These states Q cannot be neglected, because no back process $Q \to Q'$ is considered. In the ZGB model without desorption only two states Q exist (a fully covered lattice, either with A or B). In a simulation on a finite lattice these states Q can always be reached in finite time [23]. For each model this time is a random variable (see Fig. 5) depending on the weight of the state Q and the system size. [8,19]

These significant effects of the finite lattice can be removed by introducing a small change to the kinetic parameters. This can be done by allowing back processes $Q \to Q'$ with a small rate $k \to 0$, e.g. a weak desorption. Slight changes in the parameters

should cause only slight changes in the phase diagram. In the simulation of the NO + CO reaction a slow N + O recombination (note that no molecular NO exists on the surface) followed by NO desorption with a desorption constant of $K_{NO} = 10^{-3}$ leads to a completely different behavior [19] from the basic model without desorption. In the phase diagram a reactive interval appears for $0.2095 \leq y_{CO} \leq 0.2395$. At $y_{CO} = 0.238$ the densities of vacant sites and N atoms are $C_0 = 0.114$ and $C_N = 0.325$ instead of $C_0 = 0$ and $C_N = 0.432$, respectively, in the simulation without desorption. This is a change of about 0.1 in both densities. Such a (large but finite) jump in the variables caused by a weak change in the parameters points to results dominated by effects of the finite system size instead of physically reasonable results.

Recapitulating, we can say that there *may* be a steady reactive state on the infinite square lattice for this model system. The stability analysis of this
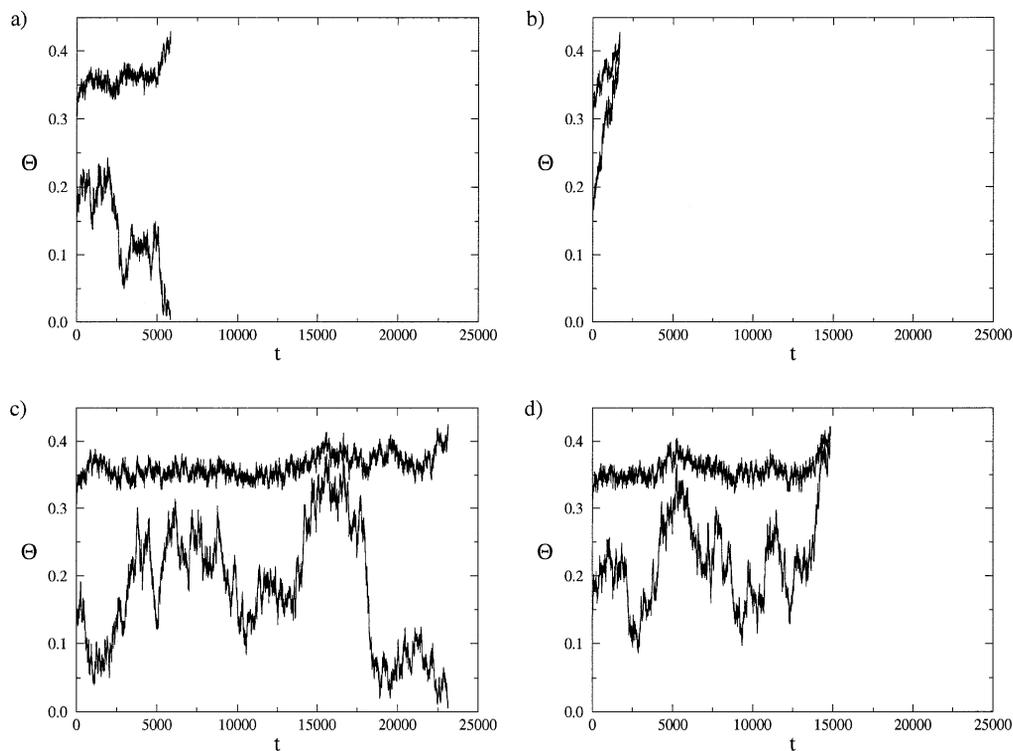

Fig. 5. Temporal evolution of the N coverages C_N in the MC simulation on a 64×64 square lattice. Only the total N coverage (upper curve) and the N coverage on the white lattice sites are shown. The N coverage on the black lattice sites is therefore given by the difference of both.

special interval in Ref. [19] as discussed above, the qualitative prediction of a reactive steady-state in our cluster approximation and the infinite time to reach an absorbing state in the correlation analysis are clear hints, but we have no proof. The cluster approximation is not exact but it makes it possible to qualitatively investigate systems, where the finite lattice as a deficiency of MC simulations leads to unphysical results.

Acknowledgements

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