Oscillation Phenomena Leading to Chaos in a Stochastic Surface Reaction Model

O. Kortlüke,[1,*] V. N. Kuzovkov,[2,1] and W. von Niessen[1]

[1]*Institut für Physikalische und Theoretische Chemie, Technische Universität Braunschweig,*
Hans-Sommer-Straße 10, 38106 Braunschweig, Germany
[2]*Institute of Solid State Physics, University of Latvia, 8 Kengaraga Street, LV-1063 RIGA, Latvia*
(Received 6 April 1998)

A microscopic lattice gas model for the CO + NO reaction on Pt(100) is studied by means of Monte Carlo simulations. It shows different kinetical phenomena such as steady state reaction, damped, regular, and irregular oscillations, as well as a transition into chaotical behavior via the Feigenbaum route. Because of its small number of parameters, each with a specific physical meaning, it enables the investigation of the whole parameter regime leading to a deeper insight to the mechanisms which create the oscillations and chaotical behavior. [S0031-9007(98)07025-2]

Surface reactions are of enormous importance for heterogeneous catalysis. Besides this practical importance one finds many complex and fascinating phenomena such as pattern formation and self-organization [1–3], regular and irregular oscillations [4–6], as well as chaotical behavior [5,7–9] even for apparently simple reactions over simple low index single crystal surfaces. Comprehensive reviews are given in Refs. [10,11]. Especially for the CO + O_2 reaction on Pt(110) the chaotical behavior has been clearly identified in extensive numerical analyses [8,12] of the time series of the experimental reaction rate. Single crystal systems generally exhibit a transition from regular to chaotic oscillations via a Feigenbaum scenario, i.e., a sequence of period doublings [10]. This transition is achieved by varying only one control parameter: the CO partial pressure in the case of the CO + O_2/Pt(110) or the temperature in the case of the CO + NO/Pt(100) reaction. The mathematical models which have been proposed for oscillations in the CO + O_2 [13,14] and the CO + NO [6,15] reaction are of mean field (MF) type and cannot explain chaotical behavior. The model for the chaotical behavior in the latter one [16,17] is a somewhat methodical model with only one reacting species and delay induced chaos (see also Refs. [18–20]).

We introduce a very simple microscopic model, which is based on Monte Carlo (MC) simulations and therefore includes all spatial correlations. It has only four parameters with a clear physical meaning. This model considers surface reconstruction and shows all types of oscillations. Increasing the gas phase mole fraction y_{CO} of CO as the only control parameter one gets steady state reaction, damped, regular, and irregular oscillations and finally a transition to chaos via the Feigenbaum scenario. After breakdown of the chaotical behavior steady state reaction occurs again in correspondence with experimental results.
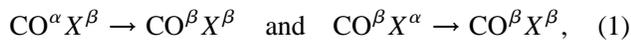
Our work has a second background which is methodical. Chaos is normally treated with rather simple equations (e.g., two nonlinearly coupled oscillators, the Hénon-Heiles system). Therefore it is very interesting to investigate whether it would also be possible to describe chaos in stochastic systems which are realized by MC simulations. A stochastic system contains noise by its very nature, which will be superimposed on any oscillations that might occur and on the chaos. One might suppose that a discovery of chaos in such systems is impossible. We show for the first time that chaos is possible and can in fact be detected. The absence of explicit equations in the MC procedure is certainly a difficulty. MC simulations might correspond most closely to a hierarchy of master equations (nonlinear partial differential equations) with all correlations included and then mapped onto a finite lattice. But this still precludes using the well established tools in research on chaos. On the other hand a success of our approach will widen substantially the possibilities to describe chaos in complex systems. This is of fundamental importance. It should be mentioned that a theoretical modeling of chaos in surface reactions is so far lacking with the exception of MF type models in Refs. [16,17] (CO + NO, see above) and Ref. [20] (NO + H_2). These mathematical models are contradictory with regard to the origin of the oscillations and the chaotical behavior. The former uses the surface reconstruction; the latter is based on the nonlinear dependence of the NO dissociation on the number of vacant sites on the surface. From experiment it appears to be established that surface reconstruction is essential to the oscillations in the CO + O_2 and the CO + NO reaction. The authors of Ref. [20] suggest that this might be different for NO + H_2. But this is not yet settled because both models are described in the MF approximation, which neglects all correlations, and use somewhat artificially introduced nonlinearities.

We examine the CO + NO → CO_2 + $\frac{1}{2}N_2$ reaction on Pt(100) with the $\alpha \rightleftharpoons \beta$ structural transformation in the high temperature oscillation regime [5] where surface reconstruction occurs. The occupation of the lattice is denoted by X with $X \in \{0, CO, O, N\}$ which stands for an empty site, a site occupied by CO, O, or by N, respectively. In addition the site itself belongs to the phase χ with

$\chi \in \{\alpha, \beta\}$, where α and β stand for the reconstructed *hex* and the nonreconstructed 1×1 phase, respectively. The simulation uses the principal rules of the Ziff, Gulari, and Barshad model [21]; i.e., CO or NO particles are chosen randomly from the gas phase with probability y or $1 - y$, respectively, with $y \in [0, 1]$.

We want the simplest possible model for the CO + NO reaction on Pt(100) including surface reconstruction. This model contains the following elements: (a) CO adsorbs on the sites of the α and β phase. (b) NO adsorbs dissociatively on the β phase into two nearest neighbor (NN) sites and does not adsorb on the α phase. (c) CO diffuses via hopping between NN sites and desorbs. (d) Reaction occurs between CO + O and between N + N on NN sites; the reaction products CO_2 and N_2 desorb instantly. (e) The structural phase transition $\alpha \rightleftharpoons \beta$ is stimulated by the presence or absence of CO and is described in this Letter as a phase border propagation:

$$CO^\alpha X^\beta \rightarrow CO^\beta X^\beta \quad \text{and} \quad CO^\beta X^\alpha \rightarrow CO^\beta X^\beta, \quad (1)$$

$$Y^\alpha Z^\beta \rightarrow Y^\alpha Z^\alpha, \quad (2)$$

with $X \in \{0, CO, O, N\}$ and $Y, Z \in \{0, O, N\}$. For simplification we assume that the transition rate is equal for both processes and given by the phase propagation velocity V.

The following arguments should explain the chosen procedure if not apparent by itself.

As to (b), in the experiment NO adsorption is found to be dominantly dissociative on the nonreconstructed 1×1 Pt(100) surface and nondissociative on the *hex* substrate [10]. In our model molecular NO does not directly take part in any reaction step but can only dissociate or desorb. The lifting of the reconstruction because of NO in addition to CO should lead only to quantitative effects. Thus we may neglect molecular NO adsorption in order to get the simplest model possible.

As to (c), CO diffuses very fast at the relevant reaction temperatures, whereas O and N are rather immobile.

As to (e), it is known from experiment that the surface phases are homogeneous on a mesoscopic length scale. Therefore the process of spontaneous nucleation of one surface phase must be significantly slower than the phase propagation and is neglected in our model.

The following parameters are chosen. The only control parameter is y, the CO mole fraction in the gas phase. All other parameters stay fixed at the following values: Diffusion constant $D = 1000$; reaction constant $R = D$ (because of this large value only small quantitative deviations to a model with an infinite reaction rate occur [22]); desorption constant $K = 0.1$; phase propagation velocity $V = 1$.

One additional detail of the MC approach has to be addressed. Because it is almost impossible to model a local change of geometry in lattice simulations (e.g., the transition from $z = 4$ to $z = 6$) on a microscopic length scale we consider only the *physical* difference of the surface

phases, i.e., the different NO dissociation probabilities. We simulate this model on the square ($z = 4$) and triangular ($z = 6$) regular lattices with a side length of $L = 256$. The sites belonging to the α and β phase are distinguished via an additional marker. This geometric simplification is admissible because in our model the lattice geometry plays only a minor role (see below). If our model describes the real surface reaction with surface reconstruction at least qualitatively correct, the results of a model with changes in the local surface geometry should lie in between the results below as an interpolation of the two regular lattices.

On both the square and the triangular lattice a broad reactive interval exists once surface reconstruction is included. The results on the square lattice agree qualitatively with the results on the triangular lattice and are very surprising if compared to the basic reaction model without surface reconstruction which does not show a reactive interval [23]. Surface reconstruction and the ensuing oscillations thus drive the system from a nonreactive to a reactive state. All types of kinetic phenomena mentioned below occur on the square lattice. As in the basic model [23] part of this lattice is covered with checkerboard like N atom adsorbate structures (which are an artifact of the model) and a strong disturbance of the system results. Therefore the transition into chaotical behavior cannot be seen as clearly as for the triangular lattice to which we restrict in the following.

For small values of y the reaction system shows an almost constant reaction rate (see Table I). If y increases damped oscillations occur as shown for the triangular lattice in Fig. 1. With further increase of y the damping decreases until the system reaches a limit cycle at $y = 0.25$. For even larger values of y the oscillations remain regular in shape but now show a very narrow principal peak before the regular one of the reaction rate. This peak can be explained as follows: For smaller values of y there is a larger probability for NO molecules to reach the surface. But because of the smaller CO coverage, Θ_{CO}, arising from the smaller values of y the coverage of the β phase, Θ_β, is

TABLE I. Existence regimes of different kinetic phenomena for the square and triangular lattices. Listed are the values of the CO mole fraction y in the gas phase. Note that these values are rough estimates because the transitions from one type to another are continuous. For values of $y < 0.05$ CO desorption hinders the CO coverage to reach sufficiently large values to initiate the $\alpha \rightarrow \beta$ reconstruction. Because we neglect spontaneous phase nucleation the system reaches a homogeneous α phase and further NO adsorption and therefore reaction is impossible.

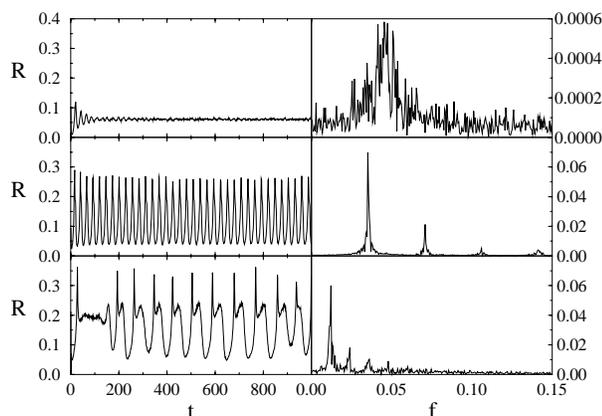|	Square lattice	Triangular lattice
Constant reaction	$0.05 - 0.14$	$0.05 - 0.14$
Damped oscillations	$0.15 - 0.24$	$0.15 - 0.20$
Regular oscillations	$0.25 - 0.31$	$0.21 - 0.34$
Chaotical behavior	$0.32 - 0.33$	$0.35 - 0.355$

FIG. 1. Reaction rate of the CO_2 production. On the left side the temporal evolution of reaction rate, on the right side the corresponding power spectra are shown. At a CO gas phase mole fraction of $y = 0.150$ the system exhibits only damped oscillations (top). With $y = 0.250$ the system reaches a limit cycle (middle). For larger values of y a shoulder peak appears in the reaction rate ($y = 0.345$, bottom). The other parameters are kept constant at $D = R = 1000$, $K = 0.1$, and $V = 1$.

FIG. 2. Period doubling as part of a transition into chaotical behavior via a Feigenbaum scenario. The CO_2 reaction rate, the coverage of the β phase, and the surface coverages of CO (dotted line), O (dashed line), and N (dot-dashed line) are shown on the left side (from top to bottom). The right side shows the corresponding power spectra. The CO gas phase mole fraction is $y = 0.349$; the other parameters are kept constant at $D = R = 1000$, $K = 0.1$, and $V = 1$.

also small. This leads to a reduced adsorption probability for NO and the O coverage Θ_O is almost zero even at $y = 0.25$ because the O atoms are effectively removed by the very mobile CO molecules. Therefore only one reaction peak occurs per cycle. With increasing values of y the coverage of the β phase also increases to an almost homogeneous β phase with $\Theta_\beta \approx 1.0$. In this case NO can adsorb dissociatively into holes of the CO continent. The reaction of CO with O introduces further vacancies which permit further NO adsorption. This is the autocatalytic vacancy creation [24] ("surface explosion") which leads to the steep first peak in the reaction rate.

When CO is completely removed the $\beta \rightarrow \alpha$ surface phase transiton occurs resulting in increased adsorption of CO and decreased adsorption of NO. Now the removal of O atoms starts leading to the shoulder peak. After that CO adsorption is favored. The values of Θ_{CO} and Θ_β increase and the whole cycle starts over again.

We thus understand the complex double peak structure of the oscillations. A similar behavior can be seen in Fig. 2 for $y = 0.349$, where a transition to chaotical behavior occurs. The first period doubling can clearly be seen in the temporal evolution of the coverages of CO, O, and the β phase, as well as in the power spectra of the β phase and the reaction rate. Here the principal peak of the reaction rate with its shoulder is followed by another principal peak with only a very small shoulder. Unfortunately, this period doubling cannot be explained in such a simple way as above. However, the peak at the half of the frequency can clearly be seen in the power spectra. Of course, in a stochastic simulation fluctuations are always present and the period doubling cannot be expected to be as pure as in a system of coupled differential equations showing a Feigenbaum transition into chaos. This especially holds
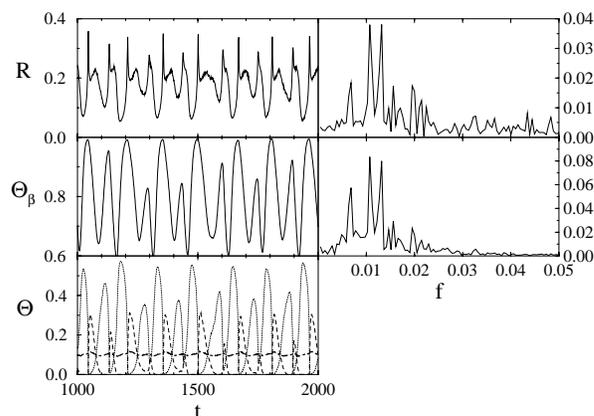
for the second and further period doublings which appear as indications in our simulations. There is a second period doubling at $y \approx 0.351$ (see Fig. 3) whose trace is also seen in the power spectra as a peak at a fourth of the original frequency. The observation of further period doublings would require changing the control parameter by about 10^{-4} or less. This is exceedingly difficult due to fluctuations and the attempts remained not completely conclusive.
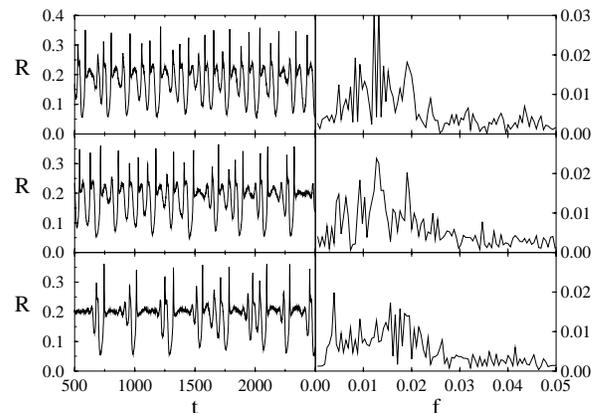

FIG. 3. Reaction rate of the CO_2 production. On the left side the temporal evolution of reaction rate, on the right side the corresponding power spectra are shown. For values of the CO gas phase mole fraction of $y = 0.351$ (top) oscillations occur which are not completely irregular yet. The power spectrum shows a second period doubling. At $y = 0.353$ (middle) completely irregular oscillations occur corresponding to the chaotic regime of the Feigenbaum scenario. At $y = 0.356$ (bottom) the plateaus of moderate reaction can clearly be seen. The other parameters are kept constant at $D = R = 1000$, $K = 0.1$, and $V = 1$.

Increasing the value of y up to $y = 0.353$ one gets a chaotical behavior which should lie in the chaotic regime of the Feigenbaum scenario. For slightly larger values $y = 0.356$ a new form of order appears. First irregular oscillations occur, then after an extended period with moderate and nearly constant reaction rate wild fluctuations appear, followed by another period of constant reaction. Increasing further the control parameter y these periods between the fluctuations become more extended until for $y = 0.357$ a constant steady state reaction with $\Theta_\beta = 1$ is reached. The system now corresponds to the basic model with fast CO diffusion [23]. All these types of oscillations and kinetical phenomena have been observed in experimental studies where three period doublings have been demonstrated [5]. The route to chaos via period doublings leading to chaotic oscillations (Feigenbaum scenario) is quite apparent from our simulations. It would, however, be desirable to calculate the Lyapunov exponents and other quantities from a time series in order to clearly indentify the chaotic behavior. For this purpose the data are not yet sufficient because of the inherent fluctuations. This requires further work.

In summary, with the CO $+$ NO surface reaction model presented here we have been able to simulate and describe the various types of kinetic phenomena occurring in the real CO + NO surface reaction over single crystal surfaces. A transition from damped over regular oscillations into chaotical behavior has been achieved for the first time with a lattice gas Monte Carlo simulation for surface reactions. With our MC model, which corresponds most closely to a set of master equations (coupled nonlinear partial differential equations) including *all* spatial correlations but transferred to a finite lattice, it is possible to describe these complex phenomena correctly and to investigate their origin. Because these simulations are not too demanding to carry out it is possible to examine different and more complex model systems. This opens a route to the investigation of chaos in more complex systems than possible previously.

*Corresponding author.
Electronic mail: O.Kortlueke@tu-bs.de

[1] H. H. Rotermund, W. Engel, M. Kordesch, and G. Ertl, Nature (London) **343**, 355 (1990).
[2] S. Jakubith, H. H. Rotermund, W. Engel, A. von Oertzen, and G. Ertl, Phys. Rev. Lett. **65**, 3013 (1990).
[3] G. Veser and R. Imbihl, J. Chem. Phys. **96**, 7155 (1992).
[4] G. Veser and R. Imbihl, J. Chem. Phys. **100**, 8483 (1994).
[5] G. Veser and R. Imbihl, J. Chem. Phys. **100**, 8492 (1994).
[6] Th. Fink, J.-P. Dath, R. Imbihl, and G. Ertl, J. Chem. Phys. **95**, 2109 (1991).
[7] G. Veser, F. Mertens, A. S. Mikhailov, and R. Imbihl, Phys. Rev. Lett. **71**, 935 (1993).
[8] M. Eiswirth, Th.-M. Kruel, G. Ertl, and F. W. Schneider, Chem. Phys. Lett. **193**, 305 (1992).
[9] P. D. Cobden, J. Siera, and B. E. Nieuwenhuys, J. Vac. Sci. Technol. A **10**, 2487 (1992).
[10] R. Imbihl and G. Ertl, Chem. Rev. **95**, 697 (1995).
[11] M. Eiswirth, in *Chaos in Chemistry and Biochemistry,* edited by R. J. Fields and L. Györgyi (World Scientific, Singapore, 1993).
[12] M. Eiswirth, K. Krischer, and G. Ertl, Surf. Sci. **202**, 565 (1988).
[13] R. Imbihl, M. P. Cox, G. Ertl, H. Müller, and W. Brenig, J. Chem. Phys. **83**, 1578 (1985).
[14] K. Krischer, M. Eiswirth, and G. Ertl, J. Chem. Phys. **96**, 9161 (1992).
[15] R. Imbihl, Th. Fink, and K. Krischer, J. Chem. Phys. **96**, 6236 (1992).
[16] N. Khrustova, G. Veser, A. Mikhailov, and R. Imbihl, Phys. Rev. Lett. **75**, 3564 (1995).
[17] N. Khrustova, A. S. Mikhailov, and R. Imbihl, J. Chem. Phys. **107**, 2096 (1997).
[18] V. P. Zhdanov, Phys. Rev. Lett. **78**, 4303 (1997).
[19] R. Imbihl and A. S. Mikhailov, Phys. Rev. Lett. **78**, 4304 (1997).
[20] A. G. Makeev and B. E. Nieuwenhuys, J. Chem. Phys. **108**, 3740 (1998).
[21] R. M. Ziff, E. Gulari, and Z. Barshad, Phys. Rev. Lett. **56**, 2553 (1986).
[22] O. Kortlüke, J. Phys. A (to be published).
[23] O. Kortlüke and W. von Niessen, J. Chem. Phys. **105**, 4764 (1996).
[24] Th. Fink, J.-P. Dath, M. R. Bassett, R. Imbihl, and G. Ertl, Surf. Sci. **245**, 96 (1991).