RESEARCH PAPER

PCCP
www.rsc.org/pccp

Forced oscillations in a self-oscillating surface reaction model

O. Kortlüke,[a] V. N. Kuzovkov[ab] and W. von Niessen[a]

[a] *Institut für Physikalische und Theoretische Chemie, Technische Universität Braunschweig, Hans-Sommer-Straße 10, 38106, Braunschweig, Germany*
[b] *Institute of Solid State Physics, University of Latvia, 8 Kengaraga Street, LV – 1063, RIGA, Latvia. E-mail: kuzovkov@latnet.lv*

Received 16th September 2003, Accepted 21st January 2004
First published as an Advance Article on the web 13th February 2004

A microscopic lattice gas model for the catalytic $CO + O_2$ reaction on Pt(110) subject to external periodic forcing is studied by means of cellular automaton simulations. Harmonic resonance, subharmonic and superharmonic entrainment, quasiperiodic as well as chaotic behavior are among the observed phenomena in this model when the gas phase concentration of CO as an external control parameter is periodically varied and interacts with the self-oscillating reaction system.

Harmonic resonance, subharmonic and superharmonic entrainment, quasiperiodic and chaotic behavior are well known to occur in nonlinear self-oscillating systems which are subject to periodic forcing. Harmonic resonance occurs if the periodic forcing signal has a frequency ν_{ex} very similar to the one of the undisturbed system ν_0 and results in an amplification of the oscillations. In this case the so-called phase locking occurs, *i.e.* the system oscillates with the response frequency $\nu_r = \nu_{ex}$ with a constant phase difference to the external signal. In the case of the subharmonic and superharmonic entrainment the ratio of the frequencies is given by $\nu_r/\nu_{ex} = T_{ex}/T_r = p/q$ where p and q are generally small integers. ν_r (T_r) and ν_{ex} (T_{ex}) are the frequencies (periods) of the response signal of the system and the external forcing signal, respectively. For quasiperiodic and chaotic behavior no simple and fixed relation exists between ν_r and ν_{ex}. These phenomena have been observed and theoretically investigated in a large number of systems including Josephson junctions, nonlinear electric conductors, hydrodynamic systems, biological oscillators, homogeneous and heterogeneous[1,2] chemical reactions. Although there exists a large number of studies the field of forced non-linear systems is still open.

In this report we concentrate on the heterogeneously catalyzed $CO + O_2$ reaction on the Pt(110) surface. The reaction has been investigated in great detail (for a review see ref. 3) and especially the behavior under periodic forcing has been experimentally studied about 10 years ago by Eiswirth and Ertl.[1] In this study all the above mentioned resonance phenomena could be observed with the exception of chaos because of limited experimental resolution. Model calculations have been performed using a phenomenological approach *via* the mean field (MF) approximation by Krischer *et al.*[4] In this study the so-called three-variable model[5] for the $CO + O_2$ reaction which describes the macroscopic kinetics correctly has been extensively investigated under periodic forcing. The main attention was attributed to the bifurcation structure and the details of the individual entrainment bands (Arnol'd tongues) in this three-variable model which is represented by a system of three coupled non-linear differential equations.

Quite in general almost every theoretical study of forced non-linear oscillators is based on idealized systems which can be represented by rather simple systems of equations. In addition these models generally do not consider fluctuations and spatial correlations, although these are known to occur and to have a large influence in real systems. We here present a cellular automaton (CA) simulation of a lattice gas model for a self-oscillating system[6–10] subject to external periodic forcing. Because of the simulation procedure the model contains fluctuations and spatial correlations by its very nature. We show that it is possible to use such simulations for the investigation of systems which exhibit very complex temporal behavior. We do this by reproducing first the experimental results given in ref. 1 at a qualitative level without using any parameter taken from or fitted to experiment. This is the obligatory prior condition in order to get physically clear and self-contained results. We then show that additional entrainment bands result from our model simulation which were not detected in experiments because of experimental limitations.

The model[6–10] reproduces correctly oscillatory regimes for both Pt(100) and Pt(110) surfaces by changing only one parameter (sticking coefficient). Experiments on the CO oxidation on Pt(100) show irregular oscillations in the reaction rate in the form of wave trains, whereas regular and synchronized oscillations are generally found on Pt(110). In addition, no regular patterns or oscillations on the mm scale have been observed on Pt(100) in the domains between the traveling reaction fronts, whereas on Pt(110) a rich variety of spatiotemporal patterns has been found. Resonance phenomena for the two surfaces are also quite different. These exemplary results should demonstrate that it is no case easy to predict or reproduce experimental findings. Thus serves as a justification for the here presented studies.

In our model for the periodically forced self-oscillating CO oxidation on Pt(110) we use the square lattice as a model for the catalyst surface with the lattice constant $a = 1$. Each lattice site stands for an individual surface atom which can belong to the α (reconstructed, 1×2) or β (non-reconstructed, 1×1) phase. The gas phase consists of particles A (CO) and B_2 (O_2) with the dimensionless concentrations y and $1 - y$, respectively. Molecules A adsorb molecularly onto the surface with rate y independent of the phase the adsorption site belongs to. Molecules B_2 adsorb dissociatively with rate $2(1 - y)$ or $(1 - y)$ on sites belonging to the β or the α phase, respectively. For the B_2 adsorption directly on the phase border the geometric mean of these rates is used. This qualitatively agrees with the experimentally obtained ratio of the O_2 sticking coefficients on the different phases. In addition A is able to diffuse *via* hopping to nearest neighbor (NN) sites with rate D and to

DOI: 10.1039/b311257h

desorb from the surface with rate k. The growth and decline of the individual phases occurs only directly at the phase border. Consider two lattice sites at the phase border where one site belongs to the α phase and one to the β phase. If at least one site is covered with A the β phase grows with rate V by switching the site in the α state into the β state. If no A is present at the phase border the β site is turned into an α site with the same rate. Therefore the growth of the phases is modeled as a phase border propagation. This phase border propagation mechanism mimics the growth of the β phase because of the larger adsorption energy of CO on the 1×1 phase as on the hex phase.

The above described transitions are written in the more common form of reaction equations, which are given below:

$$\begin{aligned} \mathrm{CO(g)} + {}^{*\chi} &\rightleftharpoons \mathrm{CO(a)}, \\ \mathrm{O_2(g)} + 2^{*\alpha} &\rightarrow 2\mathrm{O(a)}, \\ \mathrm{O_2(g)} + 2^{*\beta} &\rightarrow 2\mathrm{O(a)}, \\ \mathrm{CO(a)} + {}^{*\chi} &\rightarrow {}^{*\chi} + \mathrm{CO(a)}, \\ \mathrm{CO(a)} + \mathrm{O(a)} &\rightarrow \mathrm{CO_2(g)} + 2^{*\chi} \\ {}^{*\alpha} &\rightleftharpoons {}^{*\beta}. \end{aligned}$$

Here * stands for a free adsorption site, χ stands for either α or β and (a) or (g) for a particle adsorbed on the surface or in the gas phase, respectively.

The periodic forcing is introduced *via* a sinusodial variation of the A gas phase concentration y. Note that in this case also the concentration of B_2 varies. We use randomly distributed phases with coverages of $\Theta_\alpha = \Theta_\beta = 0.5$ as the initial lattice condition. It has been shown elsewhere[6,7] that these initial conditions lead to a dynamically heterogeneous stable state which allows us to neglect nucleation as the process for the formation of initial phase defects. In the present study we use $y = 0.49$, $D = 300$, $k = 0.1$ and $V = 1$ as the standard parameters if not stated differently. The only control parameters are the amplitude S and the frequency ω of the varied gas phase concentration y of A as the external forcing parameter. For details of the model and the simulation procedure see refs. 6–11.

This microscopical model is able to explain some of the most important experimental results for both surfaces, Pt(100) and Pt(110), such as critical coverages,[9,12,13] local oscillations and pattern formation,[6,7] global synchronization mechanisms,[8] and the resulting transition into the limit cycle.[6,8] Our model is the first one for catalytic reactions on reconstructing single crystal surfaces with completely local definitions of the elementary reaction processes. By a local definition is meant that all possible microscopic transitions take place on only one (monomer adsorption and desorption) or two nearest-neighbor lattice sites (dissociative dimer adsorption, diffusion, reaction, reconstruction). An adapted version[14] of the model for the NO + CO reaction on Pt(100) is able to describe the Feigenbaum transition into chaos which has been observed in experiment.[15]

As a first and very important result we get excellent agreement with experiment.[1] We ran more than 800 independent simulations in order to confirm the phase diagram of the entrainment bands given in Fig. 1 of ref. 1. The resonance behavior regarding the phase and the amplitude in the harmonic entrainment band can be described as well.

Outside the region of harmonic entrainment we detect not only two subharmonic (1/2, 2/3) (see Fig. 1) and seven (4/1, 7/2, 3/1, 5/2, 2/1, 5/3, 3/2) superharmonic entrainment bands, which were previously found in experiment,[1] but also three additional (4/3, 8/3, 9/2) superharmonic entrainment bands. There seem to be additional bands for larger $q > 3$ but the data are not completely conclusive in this case.

It should be mentioned here that a quantitative comparison of the phase diagram resulting from experiment[1] and from our present CA simulation is not quite correct. In the experiment[1] one has obtained a periodic forcing of the system *via* a low-amplitude (about 1%) modulation of the partial pressure of O_2. As already mentioned above, the periodic forcing in our paper is introduced *via* a variation of the parameter y. It should be noted that in this case also the concentration (and partial pressures) of A = CO, y, and $B_2 = O_2$, $(1 - y)$, vary. The differences between the results from this model and experiment appear, however, to be small, although definitely present. The modulation of the parameter y also lies in the low-amplitude region (about 1%). The ranges of phase locking in the diagram of Fig. 1 of the present paper and Fig. 1 of ref. 1 are also quite similar. Although the number of independent simulations was quite large in our paper (more than 800) this is insufficient to determine the boundaries of the phase diagram precisely. This also applies to the phase diagram resulting from experiment, Fig. 1 of ref. 1: both diagrams can only roughly be determined. For this reason we consider further information with a better quality and this is the time series in the form as given in Fig. 5 of ref. 1. Our essential result is here that we did not find from the CA simulation model specific effects. All phenomena correspond to the general picture of nonlinear dynamics. To illustrate this point let us restrict first to two examples: the superharmonic entrainment bands (5/3) and (2/1), which were clearly seen also in experiment.[1] Additionally we consider the superharmonic entrainment band (4/3), which has not been detected in experiment.[1] We are going to show that the superharmonic entrainment band (4/3) simply represents a case which again has nothing to do with the definition of the model.

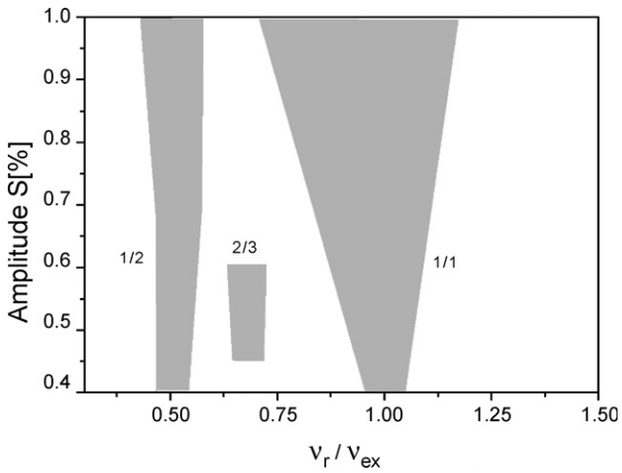

Fig. 1 Phase diagram showing phase locking response (gray) as a function of amplitude (S) and frequency of the y perturbation ($y = 0.49$, $D = 300$, $V = 1$).

In Fig. 2 a time series of the superharmonic 5/3 entrainment is shown as an example. Because of fluctuations inherent to the system the heights of the individual response amplitudes show variations but the basic structure of the response signal can be clearly seen in the time series as well as in the power spectrum. Outside the entrainment bands a constant phase relationship between the perturbation and response signal does not exist. The phase relation is continuously shifted either forward or backward from period to period. This causes a complete phase shift within a certain number of cycles and leads to beats in the response signal. The beat period is the time required for a phase shift of one complete period, *i.e.* the time in which the phase difference returns to its initial value.

In Fig. 3 such a beat period is shown for a simulation in the region of the 2/1 entrainment edge. In the 2/1 entrainment band one has alternating large and small amplitude signals and 12 forcing periods are attended with 24 response periods. In the case shown in Fig. 3 the large (first) amplitude signal

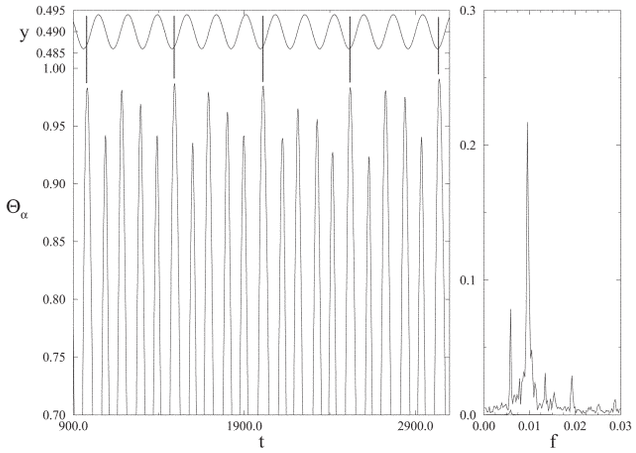

Fig. 2 Time series and power spectrum of 5/3 superharmonic entrainment ($y = 0.49$, $D = 300$, $V = 1$, $S = 3.5 \times 10^{-3}$, $\omega = 2\pi \times 5.7 \times 10^{-3}$).

starts to decline and the small (second) amplitude signal starts to grow until the proportions are reversed. After 12 forcing periods the phase relation has returned (not exactly but within our resolution) to its initial value. However, this time the response signal runs only through 23 instead of 24 periods, *i.e.* one period is suppressed on account of the continuous shift of the phase difference. This is the phenomenon of the so-called frequency-pulling. The ratio $n{:}2n-1$ (*e.g.* 12:23 as shown in Fig. 3) holds for the high-frequency edge of the 2/1 entrainment band. At the other (low-frequency) edge of the 2/1 entrainment band the phase difference is shifted to the other direction. This then leads to a ratio of $n{:}2n+1$, *e.g.* 12:25 which has been observed in experiment.[16]

The individual entrainment bands widen with increasing amplitude of the forcing signal.[4,16] Unfortunately in the experiment the 4/3 entrainment band has not been detected due to experimental limitations. However, it was shown in the theoretical analysis of the bifurcation structure of the three-variable model[4] that the 4/3 entrainment band should exist and that there is significant overlap of the entrainment bands between 1/1 and 3/2 for forcing amplitudes sufficiently widening the individual bands. As shown in Fig. 4, our model supports the existence of the 4/3 entrainment band as well as the overlap of the individual entrainment bands. After the induction period the system exhibits 4/3 entrainment for a short time. Then a very fast transition into the 3/2 entrainment occurs which is stable for at least $T = 5000$. Therefore it may be very difficult to detect the 4/3 entrainment band in experiment.

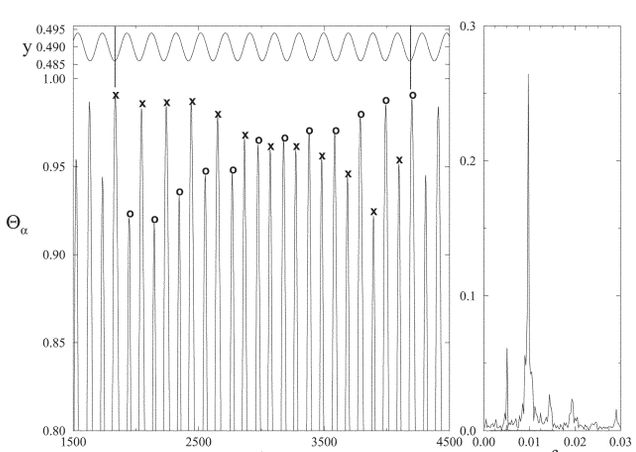

Fig. 3 Time series and power spectrum of quasiperiodic oscillations near the high-frequency 2/1 entrainment edge ($y = 0.49$, $D = 300$, $V = 1$, $S = 4.0 \times 10^{-3}$, $\omega = 2\pi \times 5.05 \times 10^{-3}$).

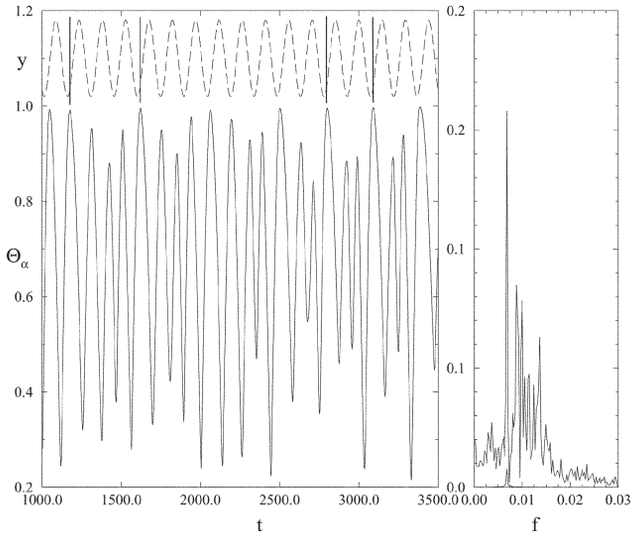

Fig. 4 Time series and power spectrum of a simulation within the overlapping region of the 4/3 and 3/2 entrainment band ($y = 0.49$, $D = 300$, $V = 1$, $S = 7.5 \times 10^{-3}$, $\omega = 2\pi \times 6.75 \times 10^{-3}$).

In this paper we have shown that our self-consistent stochastic model is able to correctly describe the experimentally observed resonance phenomena without any parameters taken from experiment. It therefore can be used as an addition to experiment for the qualitative investigation of heterogeneous surface reactions.

Acknowledgements

The authors acknowledge financial support from the Deutsche Forschungsgemeinschaft *via* fellowships for V. K. Part of this work was supported by the Fonds der Chemischen Industrie and the European Center of Excellence in Advanced Materials Research and Technology (Contract No. ICA-1-CT-2000-7007).

References

1 M. Eiswirth and G. Ertl, *Phys. Rev. Lett.*, 1988, **60**, 1526.
2 R. R. Sadhankar and D. T. Lynch, *Chem. Eng. Sci.*, 1996, **51**, 2061.
3 R. Imbihl and G. Ertl, *Chem. Rev.*, 1995, **95**, 697.
4 K. Krischer, M. Eiswirth and G. Ertl, *J. Chem. Phys.*, 1992, **97**, 307.
5 K. Krischer, M. Eiswirth and G. Ertl, *J. Chem. Phys.*, 1992, **96**, 9161.
6 V. N. Kuzovkov, O. Kortlüke and W. von Niessen, *J. Chem. Phys.*, 1998, **108**, 5571.
7 O. Kortlüke, V. N. Kuzovkov and W. von Niessen, *J. Chem. Phys.*, 1999, **110**, 11 523.
8 O. Kortlüke, V. N. Kuzovkov and W. von Niessen, *Phys. Rev. Lett.*, 1999, **83**, 3089.
9 V. N. Kuzovkov, O. Kortlüke and W. von Niessen, *Phys. Rev. Lett.*, 1999, **83**, 1636.
10 O. Kortlüke, *J. Phys. A: Math. Gen.*, 1998, **31**, 9185.
11 G. Zvejnieks and V. N. Kuzovkov, *Phys. Rev. E*, 2001, **63**, 51 104.
12 V. N. Kuzovkov, O. Kortlüke and W. von Niessen, *Phys. Rev. E*, 2001, **63**, 23 101.
13 V. N. Kuzovkov, O. Kortlüke and W. von Niessen, *Phys. Rev. E*, 2002, **66**, 11 603.
14 O. Kortlüke, V. N. Kuzovkov and W. von Niessen, *Phys. Rev. Lett.*, 1998, **81**, 2164.
15 G. Veser, F. Mertens, A. S. Mikhailov and R. Imbihl, *Phys. Rev. Lett.*, 1993, **71**, 935.
16 M. Eiswirth, K. Krischer and G. Ertl, *Surf. Sci.*, 1988, **202**, 565.