

# Research project report Nr 1 for the four-year period (2001-2004)

Project title:

## The kinetics of catalytic surface reactions and self-organization phenomena in advanced materials

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### Summary

*The main task of the present project is to analyze both mechanisms and principles of spatio-temporal structure formation on surfaces by the means of large-scale computer simulations.*

All participants of the project are scientists with the highest qualifications (3 Dr. habil. phys., 2 Dr. phys., 1 PhD student). G. Zvejniaks obtained Dr. rer. nat degree in Osnabrück (Germany) in 2001. His thesis was "Catalytic Surface Reactions: Monte Carlo Simulations of Systems with Creation, Annihilation and Diffusion of Interacting Reactants". PhD thesis defense of MS V. Kashcheyevs is planned for the near future.

Publications and conference presentations published during the review period

Year	Publications	Conference presentations
2001	14	15
2002	16	10
2003	15	20
2004	15	14
<b>2001-2004</b>	<b>60</b>	<b>59</b>

### MAIN RESULTS

1. In collaboration with Braunschweig University, Germany we introduced and studied a microscopic kinetic model for the  $\alpha \rightarrow \beta$  [e.g. hex  $\rightarrow 1 \times 1$  for Pt(100) and  $1 \times 2 \rightarrow 1 \times 1$  for Pt(110)] *surface reconstruction*, investigated by means of both the mean field approximation and Monte Carlo computer simulations. We consider homogeneous phase nucleation, which induces small surface phase defects. These defects can grow or decline via phase border propagation, depending of the surface coverage by an adsorbate CO. Asymmetry in the adsorbate surface diffusion from one surface phase to another gives rise to two critical coverages which determine the intervals of stability of the homogeneous alpha phase, the dynamically stable heterogeneous state and the homogeneous beta phase. Both surfaces show a very similar qualitative behavior regarding the phase transitions, which are in both cases of the second order. As a result, the experimentally observed nonlinear island growth rate and the critical coverages were explained at the quantitative level.

2. We have shown the existence of internal stochastic resonance in a microscopic stochastic model for the oscillating reaction. This stochastic resonance arises directly from the elementary reaction steps of the system without any external input. The lattice gas model is investigated by means of Monte Carlo simulations. It shows the oscillation phenomena and mesoscopic pattern formation. Stochastic resonance arises as the homogeneous nucleation of the individual lattice site states is considered. This nucleation is modeled as a weak noise. As a result, synchronization of the kinetic oscillations is obtained. We show that all characteristics known from research on stochastic resonance are reproduced in our model. We have also shown that the model explains easily several phenomena observed in real experiments. Internal stochastic resonance may thus be an internal regulation mechanism of an extreme adaptability.

3. In collaboration with *Eindhoven University of Technology, the Netherlands* we presented a tool for scaling laws relating the typical space and time scales obtained in microscopic Monte Carlo simulations to both experimental system sizes and relevant diffusion coefficients. One of the most interesting features of surface reactions is that in many cases *pattern formation*, structures with well-defined length scale, sometimes with symmetries and temporal behavior, such as oscillations, traveling waves, spirals, Turing patterns, are observed. An usual approach to a study this pattern formation is reaction—diffusion (RD) equations, which simulate the dynamic behavior of chemical reactions on surfaces. However, these partial differential equations give only approximate solutions and gave in

several cases completely wrong results, because they are based on the local mean field approximation, meaning well-stirred reactants at the microscopic level, ignoring all local correlations between reactants, as well as fluctuations and lateral interactions among adsorbates. The RD equations operate with the coverages, which are macroscopic continuum variables and thus neglect the discrete structure of solids, and do not describe the actual chemical process underlying the pattern formation. An exact method to solve the *master equation* for such systems is the *Monte Carlo* (MC) method. To compare MC simulations with experimental pattern formation, it is necessary to fill the gap between the length scale of the individual particles and the diffusion length. This would be a very large and slow simulation, due to the huge number of particles involved and the fast diffusion rates which means that most of the simulation time is spent for diffusion of particles instead of chemical reactions. Although only the MC simulations provide solutions to the exact master equations for the surface reactions, they are not suitable for efficient parallelization, due to a random selection of lattice sites. However, there is another important approach for simulating the discrete events on the lattices, the Cellular Automata (CA). We have studied under which conditions the CA could reproduce adequately MC simulations of chemical reactions on surfaces. We found that the main requirement is the use of large diffusion coefficients. We performed large-time and large-size computer simulations for *chemical reactions* on surfaces. By using large scale parallel simulations, it is possible to derive scaling laws which allow us to extrapolate results to even larger system sizes and larger diffusion coefficients, thus permitting a direct comparison with real experiments.

4. In collaboration with *Braunschweig University, Germany* we studied *forced oscillations* in a self-oscillating surface reaction model. The harmonic resonance, subharmonic and superharmonic entrainment, quasiperiodic and chaotic behavior are well known to occur in nonlinear self-oscillating systems which are subject to a periodic forcing. Harmonic resonance occurs if the periodic forcing signal has a frequency very similar to that in the undisturbed system 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 with a constant phase difference to the external signal. A microscopic lattice gas model for the catalytic CO+O<sub>2</sub> 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.

5. Theoretical study using *kinetics Monte Carlo* (MC) simulations of the reversible pattern formation during the adsorption of mobile metal atoms on crystalline substrates is performing for the interfaces between transition metals and metal oxide surfaces. In collaboration with *Centre for Materials Science, University College London, UK, Ben Gurion University, Beer Sheeva, Israel, and Technion Institute, Haifa, Israel*, we performed kinetic MC simulations of metal adhesion based on preliminary first principles calculations for the same system. Pattern formation, simulated for submonolayer metal coverage, is characterized in terms of the joint correlation functions for a spatial distribution of adsorbed atoms. A wide range of situations, from the almost irreversible to strongly reversible regimes, is simulated. We demonstrate that the patterns obtained are defined by a key dimensionless parameter: the ratio of the mutual attraction energy between atoms to the substrate temperature.

6. In collaboration with *Braunschweig University, Germany* we studied famous *Anderson localization* problem in one and two dimensions. The problem is solved analytically *via* the calculation of the generalized Lyapunov exponents. This is achieved by making use of a signal theory. In the one-dimensional case all states are localized for arbitrarily small disorder, in agreement with existing theories. In the two-dimensional case for larger energies and large disorder all states are localized but for certain energies and small disorder extended and localized states coexist. The phase of delocalized states is marginally stable. We demonstrate that the *metal-insulator transition* should be interpreted as a first-order phase transition. Consequences for perturbation approaches, the problem of self-averaging quantities and numerical scaling are discussed.

7. The method proposed to handle analytically with the problem of Anderson localization *via* disorder is generalized for higher spatial dimensions  $D$ . In this way the generalized Lyapunov exponents can be calculated analytically and exactly. This permits to determine the phase diagram of the system. For all dimensions  $D > 2$  one finds intervals in the energy and the disorder where extended and localized states coexist: the metal-insulator transition should thus be interpreted as a first-order transition. The qualitative differences permit to group the systems into two classes: low-dimensional systems ( $1 < D < 4$ ), where localized states are always exponentially localized and high-dimensional systems ( $D > D_c=4$ ), where states with non-exponential localization are also formed. The value of the upper critical dimension is found to be  $D_0=6$  for the Anderson localization problem; this value is also characteristic of a related problem - percolation.

8. Frequently problems arise in science, which involve both *additive and multiplicative noise*. The first type is relatively easy to handle with the help of the central limit theorem. The situation changes dramatically with the appearance of multiplicative noise. Well-known examples are the Anderson localization, turbulence, and the kicked quantum rotator. In this field results of the importance comparable to the central limit theorem are still lacking. Moreover, the approaches in general numerical and analytical tools are the rare exception. One of the main problems in the preliminary data analysis is distinguishing the deterministic and noise components in the

experimental signals. For example, in *plasma physics* the question arises when analyzing edge localized modes (ELMs): does observed ELM behavior is governed by a complicate deterministic chaos or just by random processes. In collaboration with *MPI, Garching, Germany*, and *Helsinki University of Technology, Finland* we have developed methodology based on financial engineering principles, which allows us to distinguish deterministic and noise components. We extended the linear auto-regression method (AR) by including the non-linearity (NAR method). As a starting point we have chosen the non-linearity in the polynomial form, however, the method can be extended to any other type of non-linear functions. The best polynomial model describing the experimental ELM time series was selected using Bayesian Information Criterion (BIC). With this method, we have analyzed type I ELM behavior in a subset of 26 ASDEX Upgrade shots. Obtained results indicate that the ELM behavior can be described by a linear AR model. In turn, it means that type I ELM behavior is of a relaxation or random type.

9. Recent technological advances have made possible the study of phase coherent *nanoscale electronic devices* (mesoscopic nanostructures), such as semiconductor quantum dots. A particular effect that has attracted much recent experimental and theoretical attention, is the generation of a dc current through a mesoscopic device by a periodic modulation of the confining potential – quantum charge pumping. A possibility to control the exact number of carriers transferred per cycle leads to important metrological applications. In collaboration with *Tel Aviv University*, we have studied the mechanism of adiabatic charge pumping within a generic non-interacting model. Previous numerical calculations have shown that the pumped charge is close to an integer number of electrons when the pumping contour surrounds a resonance, but the transmission remains small on the contour. We have developed a resonance approximation for adiabatic quantum pumping that gives a quantitative account of the detailed exchange of electrons between the quantum dot and the leads (to the electron reservoirs) during a pumping cycle. Near isolated distinct resonances, we use approximate Breit-Wigner expressions for the dot's Green function to discuss the loading/unloading picture of the pumping: the fractional charge exchanged between the dot and each lead through a single resonance point is related to the relative couplings of the dot and the leads at this resonance. If each resonance point along the pumping contour is dominated by the coupling to a single lead (which also implies a very small transmission), then the crossing of each such resonance results in a single electron exchange between the dot and that lead, ending up with a net quantized charge. When the resonance approximation is valid, the fractional charges can also be extracted from the peaks of the transmissions between the various leads.