Department of Physical Chemistry  Director until Nov. 2004: Gerhard Ertl
Acting Director: Gerard Meijer

Group leaders:
Markus Eiswirth
Tobias Hertel (Habilitation) until 31.12.2003
Josef F. Holzwarth (Habilitation) until 30.11.2005
Karl Jacobi (Habilitation) until 31.10.2004
Alexander S. Mikhailov
Bruno Pettinger
Harm H. Rotermund (Habilitation)
Wilfried Schulze (Habilitation) until 28.02.2005
Rolf Schuster (Habilitation) until 31.07.2004
Mau-Scheng Zei until 31.12.2004

Guest scientists, staying for at least six months, paid by the FHI:
Tae-Geun Noh Takayuki Suzuki
Gennaro Picardi Yevgenyi Temko
Alexei L.N. Pinheiro Ming Chun Xu
Bin Ren Dai Zhang

Guest scientists, staying for at least six months, paid from external funds:
Sergio Alonso EU Marie Curie Fellowship
Sabine Azouani-Couderc DFG Fellowship
Sarah L. Horswell EU Marie Curie Fellowship
Raymond E. Kapral AvH Awardee
Hiroshi Kori AvH Fellowship
Alan C. Luntz AvH Awardee
Ursula A. Paulus DFG Fellowship
Oliver Rudzick DFG Fellowship
Pablo Sánchez Bodega AvH Fellowship
Yuichi Togashi JSPS Fellowship

Graduate students: 6
Diploma students: 1
Technicians: 6
Recent Developments in the Department of Physical Chemistry

Director until 11/2004: Gerhard Ertl, Acting Director: Gerard Meijer

Since the last meeting of the Fachbeirat the following changes occurred among the staff scientists:

– Gerhard Ertl retired from his position as Director in October 2004.
– Tobias Hertel became Associated Professor of Physics at the Vanderbilt University, Nashville, TN, USA, in January 2004.
– Josef F. Holzwarth will retire in November 2005.
– Rolf Schuster became Professor of Physical Chemistry (C3) at the Technische Universität Darmstadt in August 2004.
– Mau-Scheng Zei retired at the end of 2004.

As the Fachbeirat is well aware, the offer by the President of the MPG, Peter Gruss, to Lynn Gladden from Cambridge University, of a Directorship at the Fritz Haber Institute as Head of the Department of Physical Chemistry was not accepted, so that this position has not yet been filled. At present, Gerard Meijer is the Acting Director while Harm H. Rotermund takes care of current affairs.

The work of the remaining groups concentrates on theoretical and experimental studies on aspects of nonlinear dynamics in various interface reactions, in part within the framework of DFG Sfb 555: “Komplexe nichtlineare Prozesse” as well as on the development of Raman spectroscopy of nanoscale objects.

1. Complex systems

Engineering of self-organizing chemical systems cannot be based on the same principles as traditional chemical technology. Application of rigid controls may destructively interfere with the fine interactions between the elements of a system responsible for its self-organization. Instead, spontaneous activity of a system could be steered in a desired direction by applying weak control impulses and imposing various feedbacks. In this manner, transitions between different organization states can be initiated and new forms of collective behavior can be achieved. The aim of this project is to explore, theoretically and experimentally, new directions in chemical engineering. In continuation of the previous research, pattern formation in the CO oxidation reaction on
platinum, under global delayed feedback and periodic forcing through the gas phase, have been studied. These investigations have been extended to composite materials created by microlithography. The second research direction involves local manipulation and control of reaction patterns by focused laser beams on microlithographically modified catalytic surfaces.

The activities in the area of nonlinear dynamics and complex surface reactions have been broadened and moved towards important practical applications by starting experimental and theoretical research on critical nonequilibrium phenomena during the onset of pitting corrosion. In a way, this has been a move back to the roots of the institute, when during the nineteen twenties optical investigations of the passivity of iron and steel had been performed by L. Tronstad (Nature 124, 373, 1929) under the guidance of Fritz Haber and Herbert Freundlich. Recently front propagation in the regime of metastable pitting on stainless steel has been visualized, for the first time, by utilizing simultaneously contrast-enhanced optical microscopy and elliptical microscopy for surface imaging (EMSI). While the contrast-enhanced optical microscopy allows real time in situ observations of the creation of single pits at the diffraction limit (about 2 µm), EMSI images at the same time show the depletion of the oxide layer, although, due to experimental restrictions, only at a spatial resolution of about 20 µm.

Parallel theoretical investigations have led to a new view on the development of corrosion, in which diffusion-mediated interactions between metastable corrosion pits play a key role. The sudden onset of corrosion is rationalized as a critical phenomenon involving an autocatalytic explosion of corrosion pits. Theoretical analysis and numerical simulations of the proposed mathematical models reproduce the experimental observations well.

Further experimental studies with electrochemical systems concerned the propagation of potential excitations in the course of an electrochemical reaction (formic acid oxidation on platinum). On a thin Pt ring electrode small sections were insulated, which caused various novel effects such as period-doubled pulses, trapped oscillatory states and, in particular, pronounced velocity changes, which may serve as models for ‘saltatory’ conduction across the Ranvier nodes in nervous systems.

On the theoretical level, nanoscale pattern formation was studied for surface chemical reactions with promoters, and for Langmuir monolayers formed by organic lipid or amphiphilic molecules disposed on a water–air interface. The patterns representing stationary periodic structures or traveling waves are maintained and controlled in such systems by chemical reactions, illumination or transmembrane flows.
In another activity, research was focused on enzymes acting as cyclic protein machines. Statistical methods for the analysis of experimental data of single-molecules fluorescence correlation spectroscopy have been developed and applied to determine the operation mechanism of the enzyme cholesterol oxidase. Similarly, stochastic simulations of pattern formation and molecular cycle synchronization phenomena in enzymic arrays have served to shed light on these complex phenomena.

In an even more abstract sense, progress has been made in predicting dynamic instabilities from a chemical reaction mechanism by using concepts from algebraic topology as analytic tools. One can define certain algebraic structures (polynomial rings) as the kinetic terms of a reaction mechanism (rewritten in binomial form). After a change of basis these can be solved for their roots in the form of a deformed toric variety, allowing solutions for the multiplicity of the states and the location of bifurcations. In this way, a complete mechanistic classification of chemical oscillators including competitive autocatalyses and nonautocatalytic systems could be achieved. The methods were successfully applied to a number of real systems, such as oscillating Langmuir-Hinshelwood mechanisms (e.g. CO oxidation), the electrocatalytic oxidation of formic acid, the peroxidase oscillator and the calcium oscillations in cilia during olfactory response. The latter system is interesting because it includes refractoriness with respect to a stimulus without exhibiting excitability (Eiswirth, Mikhailov, Rotermund).

2. Raman spectroscopy

The sensitivity of Raman spectroscopy can be immensely enhanced by the excitation of surface plasmons by primary (visible) light, but this surface-enhanced Raman spectroscopy (SERS) is restricted to rough surfaces of silver or gold. Another approach, that of tip-enhanced Raman spectroscopy (TERS), is based on the optical excitation of localized surface plasmons between the Au (or Ag) tip of a scanning tunneling microscope and any (smooth) arbitrary surface, whereby a very strong local field enhancement is achieved in the cavity. Spectra from various adsorbed organic and inorganic molecules were recorded in this way. With the dye malachite green isothiocynate, as few as 200 molecules underneath the tip can be ‘seen’ by this technique. Using the ClO$_4^-$ stretch vibration, the dependence of the TER band intensity on the distance to the substrate was recorded. For a tip radius of 20 nm the TERS signal was found to decrease by one order of magnitude for 10 nm vertical displacement of the tip. Thus, a powerful tool for vibrational spectroscopy with spatial resolution in the nanometer regime is being developed (Pettinger).
Publications of the Department of Physical Chemistry

Late 2003


Habilitation

Dissertationen


2004


**Dissertationen**


**Diplomarbeit**


**2005**


Suzuki, T., Y. Temko, M.C. Xu and K. Jacobi: Atomic structure of InAs quantum dots on GaAs(112)A. Surf. Sci., accepted.


Dissertationen


Noh, Tae-Geun: Spatiotemporal pattern formation in the electro-oxidation of formic acid on Pt. Effect of electrode geometry and lowered symmetry. FU Berlin 2005.

Department of Physical Chemistry

Invited Lectures at Conferences

Markus Eiswirth
“Nonautocatalytic oscillators and olfactory response”.

Gerhard Ertl

Josef F. Holzwarth


Alexander S. Mikhailov


“What is a society?” Symposium on Oscillations, Chaos, and Network Dynamics, Kyoto, Japan, November 2004.


“Nonequilibrium structures in reactive soft matter”. Workshop Developments of Nonequilibrium Physics in Material and Biological Sciences, Kyoto, October 2005.

Bruno Pettinger

“Tip-Enhanced Raman Spectroscopy at Single Crystalline Metal Surfaces. Recent Developments and Perspectives for Electrochemical Applications”,

“Hydroxide Adsorption of Ag(hkl) Electrodes Studied by in-situ SHG and ex-situ LEED”.
10th International Conference on Electrified Interfaces, Spa, Belgium, 11-16 July 2004.

“Tip-enhanced Raman spectroscopy at single crystalline metal surfaces. Hints for surface restructuring and surface chemistry”.
2nd ISE Spring Meeting, Xiamen, China, 7-10 March 2004.

Harm H. Rotermund

“Real time imaging and control of pattern formation during catalytic surface reactions”. International Symposium on Advanced Physical Fields, Tsukuba, Japan, March 2004.


“Shedding light on surface reactions: Real time imaging and control of pattern formation during catalysis”. Ringberg Meeting, Tegernsee, Germany, September 2004.


“Die CO-Oxidation unter die Lupe genommen: Raum-zeitliche Strukturbildungen bei
nichtlinearen Oberflächenreaktionen und der Einfluss äußerer Randbedingungen”. WE-
Heraeus-Ferienkurs “Dynamik in dün nen Schichten und Grenzflächen”, Magdeburg,
Germany, September 2004.

“Reaction diffusion systems”. Surface Science Summer School, University of
Nottingham, UK, August 2005.

“Patterns in surface reactions: the oscillatory case – experiments”. Int. Workshop on
Nonlinear Pattern Dynamics in Complex and Reactive Fluids far from Equilibrium”,
Kyoto, Japan, September 2005.

Invited Seminars and Colloquia (selection)

Markus Eiswirth

Topological methods for chemical reactions.

Stoichiometric network analysis.

Gerhard Ertl

ETH Zurich, Feb. 2004
Katholieke Universiteit Leuven, March 2004
University of Wales, Cardiff, April 2004
Technische Universität Darmstadt, April 2004
Rheinisch-Westfälische Technische Hochschule Aachen, December 2004
California Institute of Technology, Pasadena, Jan. 2005
Université de Paris, April 2005
University of Uppsala, June 2005
Universität Karlsruhe, December 2005.
Alexander S. Mikhailov

Taming Winfree turbulence of scroll waves in excitable media.
University of Hiroshima, Japan, November 2004.

Sudden onset of corrosion as a nonequilibrium critical phenomenon.

Nonequilibrium pattern formation in reactive soft matter.

Sudden onset of corrosion as a nonequilibrium critical phenomenon.
University of Sapporo, Japan, February 2005.

Are enzymes molecular machines?
FOM Inst. for Atomic and Molecular Physics (AMOLF), Amsterdam, September 2005.

Bruno Pettinger

Tip-Enhanced Raman Spektroskopie an Einkristallinen Gold- und Platin-Elektroden.
Seminar at the Institute of Physical and Theoretical Chemistry, (Prof. Baltruschat),
University Bonn, 12 November 2004.

In situ Raman Spectroscopy: Fundamentals and Applications.
IMPRS-Colloquium “Modern Methods in Heterogeneous Catalysis”
3 December 2004.

Lecture at Dept. of Chemistry and Applied Biosciences (Prof. Zenobi), ETH Zürich,
Switzerland, 28 April 2005.

A Fine Needle Boosts Raman Scattering (Tip-enhanced Raman spectroscopy (TERS)).
ICSOS 8, Munich, Germany, 18-22 July 2005.

Lecture at UK Summer School 2005, The University of Nottingham, UK,

Harm H. Rotermund

Some twists and turns in the path of improving surface activity.
University of Delaware, Newark, August 2003.
Control of catalytic surface reactions by local laser heating.
Dalhousie University, Halifax, Canada, August 2003.

Putting surface reactions under a magnifying glass:
Real time imaging of catalytic reactions.

Spatio-temporal addressing of surface activity.
University of Hokkaido, Sapporo, Japan, March 2004.

Photoemission Electron Microscopy:
PEEM and other tools to image catalytic surface reactions.

Phenomena in nonlinear dynamics: From pattern formation during catalytic surface
reactions to pitting corrosion of stainless steels.
Colloquium, Dalhousie University, Halifax, Canada, September 2004.

From metastable pitting corrosion to propagating fronts on stainless steels.
Dalhousie University, Halifax, Canada, May 2005.

Chaos und Ordnung auf Oberflächen.
Europaschule Reutershagen, Rostock, June 2005.

Rost an Edelstahl.
Christophorusschule, Rostock, June 2005.

Oberflächenreaktionen unter die Lupe genommen.
Visit of the winners ‘Jugend forscht’ at the FHI, August 2005.

Real time imaging methods in heterogeneous catalysis.
Lecture series at the FHI, December 2005.

Other activities

Members of the department served widely in editorial boards of journals and in advisory
and organizing committees of conferences, as well as referees for numerous research
proposals and journals.

In particular:

– Josef F. Holzwarth is the European Editor of Langmuir.

– Alexander S. Mikhailov is the Mentor of the Minerva Junior Research Group on
  Biological Computation, Weizmann Institute, Rehovot, Israel. He is also Editor-in-
