

LECTURE NOTES
IN PHYSICS

R. Haberlandt
D. Michel
A. Pöpl
R. Stannarius
(Eds.)

Molecules in Interaction with Surfaces and Interfaces



Springer

0647.11

M718

R. Haberlandt D. Michel
A. Pöpl R. Stannarius (Eds.)

Molecules in Interaction with Surfaces and Interfaces



E200401659



Springer

Editors

Reinhold Haberlandt, Dieter Michel,
Andreas Pöppel and Ralf Stannarius
Universität Leipzig
Linnéstrasse 5
04103 Leipzig, Germany

R. Haberlandt, D. Michel, A. Pöppel, R. Stannarius (eds.), *Molecules in Interaction with Surfaces and Interfaces*, Lect. Notes Phys. 634 (Springer-Verlag Berlin Heidelberg 2004), DOI 10.1007/b13926

Cataloging-in-Publication Data:

Molecules in interaction with surfaces and interfaces / R. Haberlandt...[et al.] (eds.)
p.cm. – (Lecture notes in physics, ISSN 0075-8450; 643) Includes bibliographical references
and index. ISBN 3-540-20539-X (acid-free paper) 1. Surface chemistry. 2. Molecular dynam-
ics 3. Molecules–Surfaces. 4. Adsorption. 5. Catalysts. I. Haberlandt, R. (Reinhold), 1936 - II.
Series. QD508.M65 2004 541'.33–dc22

Bibliographic information published by Die Deutsche Bibliothek Die Deutsche Bibliothek
lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data is
available in the Internet at <<http://dnb.ddb.de>>

ISSN 0075-8450

ISBN 3-540-20539-X Springer-Verlag Berlin Heidelberg New York

This work is subject to copyright. All rights are reserved, whether the whole or part of the
material is concerned, specifically the rights of translation, reprinting, reuse of illustra-
tions, recitation, broadcasting, reproduction on microfilm or in any other way, and
storage in data banks. Duplication of this publication or parts thereof is permitted only
under the provisions of the German Copyright Law of September 9, 1965, in its current
version, and permission for use must always be obtained from Springer-Verlag. Violations
are liable for prosecution under the German Copyright Law.

Springer-Verlag is a part of Springer Science+Business Media

springeronline.com

© Springer-Verlag Berlin Heidelberg 2004

Printed in Germany

The use of general descriptive names, registered names, trademarks, etc. in this publication
does not imply, even in the absence of a specific statement, that such names are exempt
from the relevant protective laws and regulations and therefore free for general use.

Typesetting: Camera-ready by the authors/editor

Data conversion: PTP-Berlin Protago-TeX-Production GmbH

Cover design: *design & production*, Heidelberg

Printed on acid-free paper

54/3141/ts - 5 4 3 2 1 0

Lecture Notes in Physics

Editorial Board

R. Beig, Wien, Austria
W. Domcke, Garching, Germany
B.-G. Englert, Singapore
U. Frisch, Nice, France
P. Hänggi, Augsburg, Germany
G. Hasinger, Garching, Germany
K. Hepp, Zürich, Switzerland
W. Hillebrandt, Garching, Germany
D. Imboden, Zürich, Switzerland
R. L. Jaffe, Cambridge, MA, USA
R. Lipowsky, Golm, Germany
H. v. Löhneysen, Karlsruhe, Germany
I. Ojima, Kyoto, Japan
D. Sornette, Nice, France, and Los Angeles, CA, USA
S. Theisen, Golm, Germany
W. Weise, Trento, Italy, and Garching, Germany
J. Wess, München, Germany
J. Zittartz, Köln, Germany

Springer

Berlin

Heidelberg

New York

Hong Kong

London

Milan

Paris

Tokyo

Physics and Astronomy

springeronline.com



ONLINE LIBRARY

The Editorial Policy for Edited Volumes

The series *Lecture Notes in Physics* (LNP), founded in 1969, reports new developments in physics research and teaching - quickly, informally but with a high degree of quality. Manuscripts to be considered for publication are topical volumes consisting of a limited number of contributions, carefully edited and closely related to each other. Each contribution should contain at least partly original and previously unpublished material, be written in a clear, pedagogical style and aimed at a broader readership, especially graduate students and nonspecialist researchers wishing to familiarize themselves with the topic concerned. For this reason, traditional proceedings cannot be considered for this series though volumes to appear in this series are often based on material presented at conferences, workshops and schools.

Acceptance

A project can only be accepted tentatively for publication, by both the editorial board and the publisher, following thorough examination of the material submitted. The book proposal sent to the publisher should consist at least of a preliminary table of contents outlining the structure of the book together with abstracts of all contributions to be included. Final acceptance is issued by the series editor in charge, in consultation with the publisher, only after receiving the complete manuscript. Final acceptance, possibly requiring minor corrections, usually follows the tentative acceptance unless the final manuscript differs significantly from expectations (project outline). In particular, the series editors are entitled to reject individual contributions if they do not meet the high quality standards of this series. The final manuscript must be ready to print, and should include both an informative introduction and a sufficiently detailed subject index.

Contractual Aspects

Publication in LNP is free of charge. There is no formal contract, no royalties are paid, and no bulk orders are required, although special discounts are offered in this case. The volume editors receive jointly 30 free copies for their personal use and are entitled, as are the contributing authors, to purchase Springer books at a reduced rate. The publisher secures the copyright for each volume. As a rule, no reprints of individual contributions can be supplied.

Manuscript Submission

The manuscript in its final and approved version must be submitted in ready to print form. The corresponding electronic source files are also required for the production process, in particular the online version. Technical assistance in compiling the final manuscript can be provided by the publisher's production editor(s), especially with regard to the publisher's own \LaTeX macro package which has been specially designed for this series.

LNP Homepage (springerlink.com)

On the LNP homepage you will find:

- The LNP online archive. It contains the full texts (PDF) of all volumes published since 2000. Abstracts, table of contents and prefaces are accessible free of charge to everyone. Information about the availability of printed volumes can be obtained.
- The subscription information. The online archive is free of charge to all subscribers of the printed volumes.
- The editorial contacts, with respect to both scientific and technical matters.
- The author's / editor's instructions.

Preface

Research on the interaction of molecules with surfaces and interfaces plays an important role in various scientific disciplines. This field is of great importance not only for a better understanding of physical and chemical processes in connection with adsorption and catalysis on solid interfaces, but also for the study of the complex properties of molecules on fluid interfaces, as well as for the elucidation of relationships between structure and functionality in macromolecular biological systems. On the basis of long-standing research experience at Leipzig in the field of molecular physics and in studies of liquid and porous solid interfaces, the collaborative research center *Sonderforschungsbereich* (SFB) 294 of the Deutsche Forschungsgemeinschaft, entitled *Moleküle in Wechselwirkung mit Grenzflächen* ("Molecules in Interaction with Interfaces"), was founded at the University of Leipzig in 1994. Since this field is still rapidly growing, it is the aim of these Lecture Notes to present not only the most important results of our research activities but also to include and analyze in a comprehensive way the overall progress in this field, and to point out important methodical achievements.

Within the research field presented in these lecture notes, the *Grenzflächen* (interfaces) exhibit various levels of complexity, and the interactions of molecules with interfaces and the properties of the interfaces themselves have been studied by applying a great variety of modern physical and chemical methods.

Porous solids (such as zeolitic molecular sieves, mesoporous materials, layered materials, and porous glasses), characterized by their large internal surfaces, are comparatively well defined. Thus they lend themselves to use as model systems for the elucidation of fundamental relationships between the structure of the embedded molecules and molecular systems, their conformation, the reorientational and translational mobility, transport processes, and their catalytic properties. Moreover, the internal structure of zeolites may also be modified in a definite manner, for instance by inserting different metal atoms. Hence, we have an interface system where the embedded molecules may be influenced in their electronic density or in their spatial structure without essentially changing the solid surfaces themselves. As is well known, this situation explains also the great importance of porous solids as catalysts and adsorbents with shape-selective properties.

The behavior of fluid interfaces is generally much more complex because in the case of fluid interfaces (such as ordered molecular monolayers, internal and external surfaces of polymer systems, liquid-crystalline thin films, gel systems, and mem-

branes) we arrive at a more complex situation: their properties may change dynamically in response to interactions with molecules in the adjacent bulk phases. Besides the fundamental questions mentioned, the interaction of the associated molecules of molecular systems with the surfaces gives rise to subtle changes of the interface itself, which may lead to new relationships between the structure and properties of the systems considered. This area of research has the potential for important novel results for both, the materials and the life sciences, since such diverse systems as polymer and ferroelectric liquid-crystal phases and biomembrane models are under study. Moreover, complex macromolecular systems are being investigated here, such as cartilage, where the studies are especially concerned with the functionality of the system as a whole, which is determined by the cooperative action of the various compartments. In this sense, the studies are also related to medical questions, such as functional distortions and aging processes. Thus, the variety of systems is a prerequisite for a better understanding of the properties of more complex systems. In this sense, the interdisciplinary character of the research plays an important role, not only with respect to the close cooperation between physicists, biophysicists, and chemists but also including the theoretical work on the basis of molecular dynamic investigations.

One of the aims of studying the interaction between molecules and solid surfaces consists in the possibility of studies on a microscopic level. A large variety of nanoporous materials host channel networks with pore diameters on the order of typical molecular dimensions. Molecular reorientation, diffusion, and reaction under this type of confinement exhibit a number of peculiarities. Because nanoscopic channels may serve as routes of particle propagation in many more systems, with the ion channels in biological membranes and reptation paths in macromolecular systems as two well-known other examples, the interest in these peculiarities is not confined to porous materials.

From the methodical point of view, the work presented in these Lecture Notes strongly benefits also from the great experience achieved in the application of the methods of magnetic resonance and relaxation (NMR and EPR) – initiated in Leipzig by Professors Artur Lösche and Harry Pfeifer about fifty years ago – to complex molecular systems and to solids, and from efforts in specific developments in recent years with respect to modern methods of two-dimensional NMR spectroscopy in solids and systems with restricted internal mobility, and in the development and application of pulsed magnetic field gradient (PFG) NMR techniques and in the use of various pulsed EPR methods. Thus, the development and improvement of modern methods of magnetic resonance also play an essential role in this book.

Besides the application of these magnetic resonance methods, various other physical and chemical methods are also used in the context of this work. Hence, since a broad variety of methods have been developed and applied in the framework of studies of structure, dynamics, transport processes, and reactivity at interfaces with different topologies and properties, it is the aim of this publication also to include a comprehensive description of the methodological background of these interface studies.

The main research activities which are intended to be represented in this publication are characterized by distinct yet interconnected pillars, namely

- the theory of the interactions of guest molecules with surfaces;
- translations and rotational diffusion and dynamics of molecules adsorbed in zeolitic systems;
- the reactivity of the internal surfaces and study of catalytic processes;
- thin films, membranes, and biopolymers in interaction with interfaces;
- supramolecular organization and biological compartmentation.

In total, we intend to show that the great variety of the systems included will contribute to a better understanding of the complex phenomena and may lead to a mutual stimulation of investigations with a strong interdisciplinary character. We hope that the broad scope in the selection of topics will help nonexpert readers to become familiar with the complex field of molecular interactions with interfaces.

The organization of the presentation is as follows:

The *first chapter* “Modeling and Simulation of Structure, Thermodynamics, and Transport of Fluids in Molecular Confinements” (S. Fritzsche, R. Haberlandt, H.L. Vörtler) deals with the molecular modeling and simulation of fluids confined to restricted geometries – such as micropores, porous media, or membranes – and comprises both the equilibrium structural and thermodynamic properties and the transport behavior of the enclosed particles. Recent simulation studies of diffusion processes in zeolites are reported and discussed in some detail. The aim of this chapter is twofold: first, to give a review of recent molecular simulation techniques and the underlying statistical-mechanical concepts, and secondly, to demonstrate the possibilities and limitations of the simulation methods discussed, showing recent results for systems and properties selected from the fields of research of the authors. The statistical mechanics and molecular simulation of inhomogeneous fluids provides basic information about the structure, thermodynamics, and phase behavior of molecules interacting with interphases. Particularly, the molecular modeling of associating (aqueous) phases confined to molecularly rough (hydrophobic and hydrophilic) interface layers is crucial for a theoretical understanding of hydration phenomena at biointerfaces (e.g. biomembranes). The intermolecular forces are modeled between the fluid molecules and the interface molecules in a uniform way, extending novel hierarchical potentials of aqueous bulk fluids (primitive models of association) to interfacial systems. On this basis, molecular models of hydrated interface layers with molecular roughness are simulated. The structural organization and the thermodynamics of the water–interface system are studied.

The *second chapter*, “Diffusion in Channels and Channel Networks” (P. Bräuer, S. Fritzsche, J. Kärger, G. Schütz, S. Vasenkov) may be considered partially as an extension of the first chapter, specifying in detail the theoretical tools for treating molecular propagation and reaction under confinement by channels. With respect to the prospects for experimental observation, it is also closely related to the *third chapter* “Structure-Mobility Relations of Molecular Diffusion in Interface Systems” (J. Kärger, C.M. Papadakis, F. Stallmach), where the potential of PFG (pulsed field gradient) NMR as a very sensitive technique for experimentally tracing these pe-

cularities is described. Beginning with the presentation of some peculiarities of molecular propagation in the individual channels – in particular under the so-called single-file condition (where the individual diffusing species are unable to exchange their positions) – some special features of transport and reaction in mutually intersecting channel arrays are treated, viz. the structure-correlated anisotropy of diffusion and the transport-induced reactivity enhancement by the so-called “molecular traffic control”. In addition to the conventional way of modeling such a situation by dynamic Monte Carlo simulations, initial attempts at an analytic treatment are included.

Both types of theoretical treatment, which are applied to modeling the internal dynamics of single-file systems, are complemented by molecular dynamics (MD) simulations, following the quite general introduction to this method in the first chapter. Key experiments leading to our present knowledge of the real pore structure of nanoporous materials are described, until recently, these materials have been assumed to represent ideal channel host systems, in accordance with their textbook character.

An important question in this context concerns the investigation of structural properties of the inner surfaces of zeolitic molecular sieves. In the *fourth chapter*, “ ^{17}O NMR Studies of Zeolites” (D. Freude and T. Loeser), multiple-quantum magic-angle spinning (MQ MAS) and double rotation (DOR) NMR techniques were applied to structural studies of oxygen-17 enriched zeolites A, LSX, and sodalite. Although oxygen is the most abundant element in the earth’s crust and an important local probe for the characterization of the real structure of internal solid surfaces, only a relatively small number of applications are known. The demand for characterization of inorganic materials and some recently developed experimental techniques are now causing a growing interest in high-resolution solid-state NMR spectroscopy of quadrupole nuclei with half-integer spin, and it is shown here that an additional valuable tool is obtained for the structural probing of the oxygen framework of inorganic materials and for study of the basic properties of porous catalysts as well.

In this context, the spectroscopic characterization of the interaction of adsorbate molecules with surface sites is a major topic in the study of microporous materials. Such studies provide valuable information about the adsorptive and catalytic properties of the surface sites on a microscopic scale. Among the various kinds of adsorption centers on the inner surface of zeolites, acid sites have attracted special interest because they give rise to the unique acid properties of these crystalline solids, making these materials attractive for specially tailored heterogeneous catalytic applications. For catalytic applications of microporous materials, the determination of the structure and concentration of the acid sites, as well as of their acidity, is of the utmost importance. Consequently, in the *fifth chapter*, entitled “Paramagnetic Adsorption Complexes in Zeolites as Studied by Advanced Electron Paramagnetic Resonance Techniques” (A. Pöppl, M. Gutjahr, and T. Rudolf), it is shown that some recently developed techniques of pulsed EPR spectroscopy are valuable tools for the characterization and structural elucidation of electron pair acceptor centers in zeolites, the so-called true Lewis acid sites, constituting, after the Brønsted acid sites, the second major group of acid surface sites in zeolites.

The interaction of adsorbed molecules with adsorption centers in the internal surfaces of porous solids not only may lead to changes in the reorientational and translational mobility of the molecular species but may also influence the molecular conformation. The *sixth chapter*, "Study of Conformation and Dynamics of Molecules Adsorbed in Zeolites by ^1H NMR" (D. Michel, W. Böhlmann, J. Roland and S. Mulla-Osman), is concerned with a combined or alternative application of conventional high-resolution NMR methods and of high-resolution (HR) solid-state NMR techniques, including magic-angle sample spinning (MAS), cross-polarization (CP), high-power decoupling and appropriate multi-pulse sequences for two- or higher-dimensional NMR and multi-quantum spectroscopy. Examples will be given of simple olefins in interaction with inner zeolite surfaces. The conclusions about the correlation times of the internal reorientational and translational dynamics are in complete agreement with the conclusions derived from diffusion coefficients measured by means of PFG NMR as discussed in the *second chapter*. Since the methodical approach of HR MAS NMR for heterogeneous systems presented here is also valuable for the investigation of lyotropic crystalline phases using HR MAS NMR (in chapter 12) and for NMR studies of cartilage (in chapter 13), it seems to be appropriate to elucidate the methodical background of these measurements in some more detail. "Molecular Dynamics of Liquids in Confinement" (F. Kremer and R. Stannarius), is studied in the *seventh chapter* by means of broadband dielectric spectroscopy. With its extraordinary dynamic range (in frequency and intensity), the studies enable one to unravel the subtle interplay between surface and confinement effects for glass-forming liquids. Confining geometries were realized in various ways. Ethylene glycol molecules in zeolites of type sodalite, silicalite-I, and zeolite beta and in an aluminophosphate of type $\text{AlPO}_4\text{-5}$ show a pronounced confinement effect. Propylene, butylene, and pentyleneglycols in nanoporous glasses show interactions with the hydrophilic inner surfaces. In untreated hydrophilic sol-gel glasses, the quasi-van der Waals liquid salol shows a dynamics characterized by an exchange dynamics between a bulk-like phase and an interfacial phase in the vicinity of the pore wall. Confinement effects are also studied in the *eighth chapter*, "Liquid Crystals in Confining Geometries" (R. Stannarius and F. Kremer). In general, the restricted-volume effects that are observed in isotropic liquids confined in porous matrices (seventh chapter) can be found in confined mesogenic materials as well. This contribution will focus on the description of a few selected systems, from a recollection of surface-induced orientation in ordered and disordered systems, via experiments that study the induction or suppression of mesogenic order, to the investigation of dynamic processes in confined liquid crystals. The experiments described in this chapter mainly involve spectroscopic (bulk) methods, polarizing microscopy, and electro-optic measurements.

In the next chapters, thin ordered molecular structures are investigated. The *ninth chapter* deals with "Surfaces and Interfaces of Free-Standing Smectic Films" (H. Schüring and R. Stannarius). Ordered molecular structures with lateral extensions of up to several square centimeters and with uniform thickness can be formed by only a few (even two) molecular layers. Thin free-standing smectic films, with their robust

and stable layer structure, their exceptionally large surface-to-volume ratio, and their macroscopically ordered molecular arrangement, allow one to measure the surface tension of these anisotropic fluids with a variety of methods. In particular, Langmuir's principle can be tested, and contributions to the surface tension can be attributed to individual parts of the molecules. Another aspect is the investigation of the surface tension in the vicinity of liquid-liquid phase transitions. Deviations from the normal temperature dependence, connected with entropic contributions to the surface tension, can be observed. The chapter presents an overview of various methods used for surface tension measurements in liquid crystals, reports on results on the temperature dependence of surface tensions, and deals with interface tensions between different fluid phases derived from the study of isotropic inclusions in thin smectic films. "Pattern Formation in Langmuir Monolayers Due to Long-Range Electrostatic Interactions" (T.M. Fischer and M. Lösche) is the subject of the *tenth chapter*. Langmuir monolayers are monomolecular layers of insoluble amphiphiles at the air/water interface. Molecular self-organization causes these amphiphiles to have their hydrophilic headgroup immersed in the water and their hydrophobic tail dangling into the air. As such, Langmuir monolayers are interesting because, on the one hand, they enable us to study the peculiarities of quasi-two-dimensional (2D) systems. On the other hand, Langmuir monolayers represent half of a lipid bilayer, which in turn is prevalent in biology and forms the local environment where, for example signal cascades and signal transduction reactions occur. The authors report on recent progress in the understanding of the unusual and rather unexpected behavior of a quasi-2D system by reviewing recent experimental results obtained from optical microscopy on equilibrium phase shapes, nonequilibrium phenomena (such as relaxation of the shape after distortions caused by Laser tweezers or local impulse heating), and rheological properties of the system. Long-range electrostatic interactions in Langmuir monolayers cause the development of mesoscopic patterns. Shape transitions and topological transformations triggered by change of the area per molecule, electrostatic contrast, or line tensions between coexisting phases affect the morphology of the monolayer critically: a wealth of nontrivial dynamic reorganization events are observed upon manipulation of these quantities. It is thus clear that Young's equation – established over two centuries ago for 3D systems – does not hold in a straightforward extrapolation to 2D arrays of molecules at interfaces. The theoretical analysis of the underlying molecular interactions leads to a comprehension of the observed phenomena and describes microscopic properties of the system in quantitative terms. The *eleventh chapter* is closely related to the tenth chapter and deals with the "Characterization of Floating Surface Layers of Lipids and Lipopolymers by Surface-Sensitive Scattering" (P. Krüger et al.). Surface-sensitive scattering techniques are employed for the investigation of planar lipid membranes – floating monolayers on aqueous surfaces – to correlate structural, functional, and dynamic aspects of biomembrane models. This chapter surveys recent work on the submolecular structure of floating phospholipid monolayers, where the advent of third-generation synchrotron X-ray sources has driven the development of realistic, submolecular-scale quasi-chemical models, as well as work on more complex systems. The latter includes cation bind-

ing to anionic lipid surfaces; conformational changes of lipopolymers undergoing phase transitions; the conformational organization of phosphatidylinositol and phosphatidylinositides, as examples of physiologically important lipids; and the adsorption of peptides (neuropeptide Y, NPY) and solvents (dimethylsulfoxide, DMSO) onto phospholipid surface layers. The contribution “Studying Lyotropic Crystalline Phases Using High-Resolution MAS NMR Spectroscopy” (A. Pampel and F. Volke), the *twelfth chapter*, focuses on an experimental approach that is based on techniques that were primarily developed for investigations of the liquid-crystalline phases in combination with MAS. These techniques reveal properties that are related to the dynamic, liquid character of liquid-crystalline phase, which may easily be overlooked when these systems are studied with methods intended to observe real solid systems. The reader will be introduced in these methods. Their general applicability and their limits are discussed. Their use is demonstrated with some examples, covering biophysical studies as well as practical applications. The major focus is on problems that are related to molecules interacting with the lipid–water interfaces. The methods discussed, range from two-dimensional NOE spectroscopy for structure determination, via polarization transfer, to the latest development, the combination of MAS with pulsed field gradient NMR spectroscopy to study diffusional properties. Finally, in the *thirteenth chapter*, entitled “NMR Studies of Cartilage – Dynamics, Diffusion, Degradation” (D. Huster, J. Schiller, L. Naji, J. Kaufmann, and K. Arnold), it is shown that the molecular dynamics of biological macromolecules and their interactions with water play a decisive role in the viscoelastic properties of biological tissues. For example, articular cartilage consists of a variety of biopolymers with varying degrees of molecular mobility. Various NMR methods have been used to characterize the physical properties of cartilage on a molecular level. The studies have revealed very heterogeneous molecular dynamics of cartilage, which can serve as a basis for the development of artificial cartilage by tissue engineering methods.

The authors of the various contributions to these Lecture Notes are greatly indebted to their numerous collaboration partners, whether named in the various chapters here, or unnamed. This work would not have been possible without the financial support of the Deutsche Forschungsgemeinschaft (DFG) within the framework of the *Sonderforschungsbereich 294*. We express our sincere gratitude not only to the DFG but also to the University of Leipzig and to the Saxon State Ministry for Science and the Fine Arts for their continuous help and great mutual understanding. Many contributions were stimulated by the close collaboration between different institutes of the university and with numerous colleagues and friends from abroad who cannot be mentioned here. Thank you all very much for the excellent cooperation. In particular, the majority of the scientific work presented in this volume was connected with the preparation of Ph.D. theses and hence with the scientific careers of very talented young researchers. This gives us also the opportunity to express our gratitude to them and to wish them great success in their future scientific activities. In this context, we are glad to congratulate Dr. Christian Rödenbeck for having been awarded the 1999 FEZA Prize for Ph.D. Work in Zeolites or Related Materials by the Federation of European Zeolite Associations. We are greatly indebted to Mrs. Katrin Kunze

for her great efforts in the technical organization of this research project. Above all, we would like to emphasize the excellent work and continuous support by the first spokesman of this SFB, Prof. Dr. Gotthard Klose.

Leipzig,
January 2004

Reinhold Haberlandt
Dieter Michel
Andreas Pöppel
Ralf Stannarius

List of Contributors

Klaus Arnold

Universität Leipzig
Institut für Medizinische Physik
und Biophysik
Liebigstr. 27
04103 Leipzig, Germany
arnold@medizin.uni-leipzig.de

Peter Bräuer

Universität Leipzig
Institut für Experimentalphysik I
Linnéstr. 5
04103 Leipzig, Germany
brauer@chemie.uni-leipzig.de

Thomas M. Fischer

Florida State University
Department of Chemistry
and Biochemistry,
Tallahassee, FL 32306-4390, USA
tfischer@chem.fsu.edu

Dieter Freude

Universität Leipzig
Institut für Experimentalphysik I
Linnéstr. 5
04103 Leipzig, Germany
freude@uni-leipzig.de

Reinhold Haberlandt

Universität Leipzig
Institut für Theoretische Physik
Vor dem Hospitaltore 1
04103 Leipzig, Germany
Reinhold.Haberlandt@
physik.uni-leipzig.de

Siegfried Fritzsche

Universität Leipzig
Institut für Theoretische Physik
Vor dem Hospitaltore 1
04103 Leipzig, Germany
Siegfried.Fritzsche@
uni-leipzig.de

Jörg Kärgner

Universität Leipzig
Institut für Experimentalphysik I
Linnéstr. 5
04103 Leipzig, Germany
Kaerger@physik.uni-leipzig.de

Friedrich Kremer

Universität Leipzig
Institut für Experimentalphysik I
Linnéstr. 5
04103 Leipzig, Germany
kremer@physik.uni-leipzig.de

Mathias Lösche

Universität Leipzig
Institut für Experimentalphysik I
Linnéstr. 5
04103 Leipzig, Germany
loesche@physik.uni-leipzig.de

Dieter Michel

Universität Leipzig
Institut für Experimentalphysik II
Linnéstr. 5
04103 Leipzig, Germany
michel@physik.uni-leipzig.de

André Pampel

Universität Leipzig
Institut für Experimentalphysik II
Linnéstr. 5
04103 Leipzig, Germany
anpa@physik.uni-leipzig.de

Andreas Pöppel

Universität Leipzig
Institut für Experimentalphysik II
Linnéstr. 5
04103 Leipzig, Germany
poeppl@physik.uni-leipzig.de

Heidrun Schüring

Universität Leipzig
Institut für Experimentalphysik I
Linnéstr. 5
04103 Leipzig, Germany
pge91dsf@
studserv.uni-leipzig.de

Ralf Stannarius

Otto-von-Guericke-Universität
Magdeburg
Institut für Experimentalphysik
Universitätsplatz 2
39106 Magdeburg, Germany
ralf.stannarius@
physik.uni-magdeburg.de

Contents

Modeling and Simulation of Structure, Thermodynamics, and Transport of Fluids in Molecular Confinements

<i>Siegfried Fritzsche, Reinhold Haberlandt, Horst Ludger Vörtler</i>	1
1 Introduction	1
2 Statistical Physics	2
3 Structure and Thermodynamics of Confined Fluids	14
4 Transport of Molecules in Nanopores	53

Diffusion in Channels and Channel Networks

<i>Peter Bräuer, Siegfried Fritzsche, Jörg Kärger, Gunter Schütz, and Sergey Vasenkov</i>	89
1 Introduction	89
2 Isolated Channels	90
3 Correlated Diffusion Anisotropy	101
4 Molecular Traffic Control	103
5 Experimental Evidence About the Real Structure of Nanoporous Channel Systems	114
6 Conclusion	121

Structure–Mobility Relations of Molecular Diffusion in Interface Systems

<i>Jörg Kärger, Christine M. Papadakis, Frank Stallmach</i>	127
1 Introduction	127
2 Fundamentals of Self-Diffusion Studies by PFG NMR	128
3 Structure-Related Diffusion in Nanoporous Materials	137
4 Diffusion and Relaxation in Sediments	146
5 Diffusion Under Internal Confinement in Multicomponent Polymer Systems	154
6 Conclusion	158

¹⁷O NMR Studies of Zeolites

<i>Dieter Freude, Thomas Loeser</i>	163
1 Introduction	163
2 Materials and Methods	165
3 Results and Discussion	167
4 Conclusions	180

Paramagnetic Adsorption Complexes in Zeolites as Studied by Advanced Electron Paramagnetic Resonance Techniques

<i>Andreas Pöpl, Marlen Gutjahr, Thomas Rudolf</i>	185
1 EPR Spectroscopy of Adsorbed Molecules in Zeolites	185
2 Pulsed ENDOR and HYSCORE Spectroscopy of Paramagnetic Adsorption Complexes	190
3 Di-Tert-Butyl Nitroxide (DTBN) Adsorption Complexes	195
4 Nitric Oxide (NO) Adsorption Complexes	203
5 Conclusions	212

Study of Conformation and Dynamics of Molecules Adsorbed in Zeolites by ^1H NMR

<i>Dieter Michel, Winfried Böhlmann, Jörg Roland, Samir Mulla-Osman</i>	217
1 NMR Spectroscopy in Heterogeneous Systems	217
2 Analysis of Chemical Shifts	233
3 Two-Dimensional MAS NMR Spectroscopy of Adsorbed Molecules	244
4 Thermal Mobility of Molecules in Zeolites	263
5 Conclusions	270

Molecular Dynamics of Liquids in Confinement

<i>Friedrich Kremer, Ralf Stannarius</i>	275
1 Introduction	275
2 H-Bond-Forming Liquids in Zeolitic and Nanoporous Media	276
3 The van der Waals Liquid Salol in (Lubricated) Nanoporous Sol-gel Glasses	289
4 Conclusions	297

Liquid Crystals in Confining Geometries

<i>Ralf Stannarius, Friedrich Kremer</i>	301
1 Adsorber Geometries and Confinement Effects	301
2 Molecular and Collective Dynamics	306
3 Surface-Induced and Suppressed Order	319
4 Director Configurations in Confined Phases	326

Surfaces and Interfaces of Free-Standing Smectic Films

<i>Heidrun Schüring, Ralf Stannarius</i>	337
1 Introduction	337
2 Surface and Interface Tensions of Thin Smectic Films	340
3 Gas Permeation Through Thin Smectic Films	361

Pattern Formation in Langmuir Monolayers Due to Long-Range Electrostatic Interactions

<i>Thomas M. Fischer, Mathias Lösche</i>	383
1 Introduction	384
2 Wetting in Langmuir Monolayers	384
3 Conclusions	393