

**GEOMETRIC STRUCTURES
OF PHASE SPACE IN
MULTIDIMENSIONAL CHAOS
APPLICATIONS TO CHEMICAL REACTION
DYNAMICS IN COMPLEX SYSTEMS**

ADVANCES IN CHEMICAL PHYSICS

VOLUME 130

PART A

Edited by

**M. TODA, T. KOMATSUZAKI, T. KONISHI,
R. S. BERRY, and S. A. RICE**

Series Editor

STUART A. RICE

Department of Chemistry
and
The James Franck Institute
The University of Chicago
Chicago, Illinois



**WILEY-
INTERSCIENCE**

AN INTERSCIENCE PUBLICATION
JOHN WILEY & SONS, INC.

**GEOMETRIC STRUCTURES OF PHASE SPACE IN
MULTIDIMENSIONAL CHAOS**

A SPECIAL VOLUME OF ADVANCES IN CHEMICAL PHYSICS
VOLUME 130

PART A

EDITORIAL BOARD

- BRUCE J. BERNE, Department of Chemistry, Columbia University, New York, New York, U.S.A.
- KURT BINDER, Institut für Physik, Johannes Gutenberg-Universität Mainz, Mainz, Germany
- A. WELFORD CASTLEMAN, JR., Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania, U.S.A.
- DAVID CHANDLER, Department of Chemistry, University of California, Berkeley, California, U.S.A.
- M. S. CHILD, Department of Theoretical Chemistry, University of Oxford, Oxford, U.K.
- WILLIAM T. COFFEY, Department of Microelectronics and Electrical Engineering, Trinity College, University of Dublin, Dublin, Ireland
- F. FLEMING CRIM, Department of Chemistry, University of Wisconsin, Madison, Wisconsin, U.S.A.
- ERNEST R. DAVIDSON, Department of Chemistry, Indiana University, Bloomington, Indiana, U.S.A.
- GRAHAM R. FLEMING, Department of Chemistry, University of California, Berkeley, California, U.S.A.
- KARL F. FREED, The James Franck Institute, The University of Chicago, Chicago, Illinois, U.S.A.
- PIERRE GASPARD, Center for Nonlinear Phenomena and Complex Systems, Brussels, Belgium
- ERIC J. HELLER, Institute for Theoretical Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, Cambridge, Massachusetts, U.S.A.
- ROBIN M. HOCHSTRASSER, Department of Chemistry, The University of Pennsylvania, Philadelphia, Pennsylvania, U.S.A.
- R. KOSLOFF, The Fritz Haber Research Center for Molecular Dynamics and Department of Physical Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel
- RUDOLPH A. MARCUS, Department of Chemistry, California Institute of Technology, Pasadena, California, U.S.A.
- G. NICOLIS, Center for Nonlinear Phenomena and Complex Systems, Université Libre de Bruxelles, Brussels, Belgium
- THOMAS P. RUSSELL, Department of Polymer Science, University of Massachusetts, Amherst, Massachusetts, U.S.A.
- DONALD G. TRUHLAR, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota, U.S.A.
- JOHN D. WEEKS, Institute for Physical Science and Technology and Department of Chemistry, University of Maryland, College Park, Maryland, U.S.A.
- PETER G. WOLYNES, Department of Chemistry, University of California, San Diego, California, U.S.A.

**GEOMETRIC STRUCTURES
OF PHASE SPACE IN
MULTIDIMENSIONAL CHAOS
APPLICATIONS TO CHEMICAL REACTION
DYNAMICS IN COMPLEX SYSTEMS**

ADVANCES IN CHEMICAL PHYSICS

VOLUME 130

PART A

Edited by

**M. TODA, T. KOMATSUZAKI, T. KONISHI,
R. S. BERRY, and S. A. RICE**

Series Editor

STUART A. RICE

Department of Chemistry
and
The James Franck Institute
The University of Chicago
Chicago, Illinois



**WILEY-
INTERSCIENCE**

AN INTERSCIENCE PUBLICATION
JOHN WILEY & SONS, INC.

Copyright © 2005 by John Wiley & Sons, Inc. All rights reserved.

Published by John Wiley & Sons, Inc., Hoboken, New Jersey.
Published simultaneously in Canada.

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400, fax 978-646-8600, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services please contact our Customer Care Department within the U.S. at 877-762-2974, outside the U.S. at 317-572-3993 or fax 317-572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print, however, may not be available in electronic format.

Library of Congress Catalog Number: 58:9935

ISBN 0-471-70527-6 (Part A)
ISBN 0-471-71157-8 (Part B)
ISBN 0-471-71158-6 (Set)

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

CONTRIBUTORS TO VOLUME 130

- YOJI AIZAWA, Department of Applied Physics, Faculty of Science and Engineering, Waseda University, Tokyo, 169-8555, Japan
- R. STEPHEN BERRY, Department of Chemistry, The University of Chicago, Chicago, Illinois 60637, USA
- JENS BREDEBECK, Max-Planck-Institut für Strömungsforschung, D-37073 Göttingen, Germany. *Present address:* Physikalisch-Chemisches Institut, Universität Zürich, CH-8057 Zürich, Switzerland
- LINTAO BU, Department of Chemistry, Boston University, Boston, Massachusetts, 02215, USA
- MASSIMO CENCINI, Dipartimento di Fisica, Università di Roma “la Sapienza” and Center for Statistical Mechanics and Complexity INFM UdR Roma 1 Piazzale Aldo Moro 5, I-00185 Roma, Italy
- STAVROS C. FARANTOS, Institute of Electronic Structure and Laser Foundation for Research and Technology, Hellas, Greece; and Department of Chemistry, University of Crete, Iraklion 711 10, Crete, Greece
- HIROSHI FUJISAKI, Department of Chemistry, Boston University, Boston, Massachusetts, 02215, USA
- JIANGBIN GONG, Department of Chemistry and The James Franck Institute, The University of Chicago, Chicago, Illinois 60637 USA
- SERGY YU. GREBENSHCHIKOV, Max-Planck-Institut für Strömungsforschung, D-37073 Göttingen, Germany
- HIROSHI H. HASEGAWA, Department of Mathematical Sciences, Ibaraki University, Mito, 310-8512, Japan; and Center for Studies in Statistical Mechanics and Complex Systems, The University of Texas at Austin, Austin, Texas 78712, USA
- SEIICHIRO HONJO, Department of Basic Science, Graduate School of Arts and Sciences, University of Tokyo, Komaba, Meguro-ku, Tokyo, 153-8902, Japan
- KYOKO HOSHINO, Nonlinear Science Laboratory, Department of Earth and Planetary Sciences, Faculty of Science, Kobe University, Nada, Kobe, 657-8501, Japan

- KENSUKE S. IKEDA, Department of Physical Sciences, Faculty of Science and Engineering, Ritsumeikan University, Kusatsu, 525-8577, Japan
- CHARLES JAFFÉ, Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506-6045, USA
- MARC JOYEUX, Laboratoire de Spectrométrie Physique (CNRS UMR 5588), Université Joseph Fourier, Grenoble 1, F-38402 St. Martin d'Hères Cedex, France
- KUNIHICO KANEKO, Department of Basic Science, College of Arts and Sciences, University of Tokyo, Komaba, Meguro-ku, Tokyo, 153-8902, Japan
- SHINOSUKE KAWAI, Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto, 606-8502, Japan
- TAIZO KOBAYASHI, Department of Physical Sciences, Ritsumeikan University, Kusatsu, 525-8577, Japan
- TAMIKI KOMATSUZAKI, Nonlinear Science Laboratory, Department of Earth and Planetary Sciences, Faculty of Science, Kobe University, Nada, Kobe, 657-8501, Japan
- TETSURO KONISHI, Department of Physics, Nagoya University, Nagoya, 464-8602, Japan
- DAVID M. LEITNER, Department of Chemistry and Chemical Physics Program, University of Nevada, Reno, Nevada 89557, USA
- YASUHIRO MATSUNAGA, Nonlinear Science Laboratory, Department of Earth and Planetary Sciences, Faculty of Science, Kobe University, Nada, Kobe, 657-8501, Japan
- TAKAYUKI MIYADERA, Department of Information Sciences, Tokyo University of Science, Noda City, 278-8510, Japan
- TERUAKI OKUSHIMA, Department of Physics, Tokyo Metropolitan University, Minami-Ohsawa, Hachioji, Tokyo, 192-0397, Japan
- YOSHIKAZU OHTAKI, Department of Mathematical Sciences, Ibaraki University, Mito, 310-8512, Japan
- YOSHITSUGU OONO, Department of Physics, University of Illinois at Urbana-Champaign, Urbana, Illinois, 61801-3080, USA
- JESÚS PALACIÁN, Departamento de Matemática e Informática, Universidad Pública de Navarra, 31006 Pamplona, Spain
- STUART A. RICE, Department of Chemistry and The James Franck Institute, The University of Chicago, Chicago, Illinois 60637 USA
- SHINJI SAITO, Department of Chemistry, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8602, Japan

- MITUSADA M. SANO, Graduate School of Human and Environmental Studies, Kyoto University, Sakyo, Kyoto, 606-8501, Japan
- SHIN'ICHI SAWADA, School of Science and Technology, Kwansai Gakuin University, Sanda, 669-1337, Japan
- REINHARD SCHINKE, Max-Planck-Institut für Strömungsforschung, D-37073 Göttingen, Germany
- NORIHITO SHIDA, Omohi College, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya, 466-8555, Japan
- YASUSHI SHIMIZU, Department of Physical Sciences, Ritsumeikan University, Kusatsu, 525-8577, Japan
- AKIRA SHUDO, Department of Physics, Tokyo Metropolitan University, Minami-Ohsawa, Hachioji, Tokyo, 192-0397, Japan
- JOHN E. STRAUB, Department of Chemistry, Boston University, Boston, Massachusetts, 02215, USA
- Y-H. TAGUCHI, Department of Physics, Faculty of Science and Technology, Chuo University, Bunkyo-ku, Tokyo, 112-8551, Japan; and Institute for Science and Technology, Chuo University, Bunkyo-ku, Tokyo, 112-8551, Japan
- KIN'YA TAKAHASHI, The Physics Laboratories, Kyushu Institute of Technology, Iizuka, 820-8502, Japan
- TOSHIYA TAKAMI, Institute for Molecular Science, Okazaki, 444-8585, Japan
- KAZUO TAKATSUKA, Department of Basic Science, Graduate School of Arts and Sciences, University of Tokyo, Komaba, 153-8902, Tokyo, Japan
- MIKITO TODA, Physics Department, Nara Women's University, Nara, 630-8506, Japan
- TURGAY UZER, Center for Nonlinear Science, School of Physics, Georgia Institute of Technology, Atlanta, GA 30332-0430, USA
- DAVIDE VERGNI, Istituto Applicazioni del Calcolo, CNR Viale del Policlinico 137, I-00161 Roma, Italy
- ANGELO VULPIANI, Dipartimento di Fisica, Università di Roma "la Sapienza" and Center for Statistical Mechanics and Complexity INFM UdR Roma 1 Piazzale Aldo Moro 5, I-00185 Roma, Italy
- LAURENT WIESENFELD, Laboratoire d'Astrophysique, Observatoire de Grenoble, Université Joseph-Fourier, BP 53, F-38041 Grenoble Cédex 9, France
- YOSHIYUKI Y. YAMAGUCHI, Department of Applied Mathematics and Physics, Kyoto University, 606-8501, Kyoto, Japan

TOMOHIRO YANAO, Department of Complex Systems Science, Graduate School of Information Science, Nagoya University, 464-8601, Nagoya, Japan

PATRICIA YANGUAS, Departamento de Matemática e Informática, Universidad Pública de Navarra, 31006 Pamplona, Spain

MEISHAN ZHAO, Department of Chemistry and The James Franck Institute, The University of Chicago, Chicago, Illinois, 60637 USA

INTRODUCTION

Few of us can any longer keep up with the flood of scientific literature, even in specialized subfields. Any attempt to do more and be broadly educated with respect to a large domain of science has the appearance of tilting at windmills. Yet the synthesis of ideas drawn from different subjects into new, powerful, general concepts is as valuable as ever, and the desire to remain educated persists in all scientists. This series, *Advances in Chemical Physics*, is devoted to helping the reader obtain general information about a wide variety of topics in chemical physics, a field that we interpret very broadly. Our intent is to have experts present comprehensive analyses of subjects of interest and to encourage the expression of individual points of view. We hope that this approach to the presentation of an overview of a subject will both stimulate new research and serve as a personalized learning text for beginners in a field.

STUART A. RICE

PREFACE

The study of chemical reactions covers a variety of phenomena, ranging from the microscopic mechanisms of reaction processes through structural changes involving macromolecules such as proteins, to biochemical networks within cells. One common question concerning these seemingly diverse phenomena is how we can understand the temporal development of the system based on its dynamics.

At the microscopic level, chemical reactions are dynamical phenomena in which nonlinear vibrational motions are strongly coupled with each other. Therefore, deterministic chaos in dynamical systems plays a crucial role in understanding chemical reactions. In particular, the dynamical origin of statistical behavior and the possibility of controlling reactions require analyses of chaotic behavior in multidimensional phase space.

In contrast, conventional reaction rate theory replaces the dynamics within the potential well by fluctuations at equilibrium. This replacement is made possible by the assumption of local equilibrium, in which the characteristic time scale of vibrational relaxation is supposed to be much shorter than that of reaction. Furthermore, it is supposed that the phase space within the potential well is uniformly covered by chaotic motions. Thus, only information concerning the saddle regions of the potential is taken into account in considering the reaction dynamics. This approach is called the transition state theory.

Recently, however, experimental studies have cast a doubt on this assumption (see Ref. 1 for a review). For example, spectroscopic studies reveal hierarchical structures in the spectra of vibrationally highly excited molecules [2]. Such structures in the spectra imply the existence of bottlenecks to intramolecular vibrational energy redistribution (IVR). Reactions involving radicals also exhibit bottlenecks to IVR [3]. Moreover, time-resolved measurements of highly excited molecules in the liquid phase show that some reactions take place before the molecules relax to equilibrium [4]. Therefore, the assumption that local equilibrium exists prior to reaction should be questioned. We seek understanding of reaction processes where the assumption does not hold.

The problem requires analyses of phase-space structures in systems with many degrees of freedom. In particular, appreciating the global structure of the phase space becomes essential for our understanding of reactions under nonequilibrium conditions. In order to make this point clear, we briefly summarize the present status of the study.

Since the 1980s, concepts and results from nonlinear physics have been incorporated into studies of unimolecular reactions. (For a review, see Rice and co-workers' contribution in this volume.) In particular, concepts established for systems with two degrees of freedom have played an important role in defining the reaction rate based on dynamics [5]. The concept of transition state has been examined from the standpoint of dynamical system theory, and reformulated in terms of normally hyperbolic invariant manifolds (NHIMs). While transition states in the conventional sense are situated in configuration space, NHIMs corresponding to saddles are structures in phase space. In order to formulate transition states as dividing surfaces, we have to resort to NHIMs and their stable and unstable manifolds. These phase space structures enable us to avoid the so-called recrossing problem. Moreover, Lie perturbation theory makes it possible to calculate the dividing surfaces at least locally near the NHIMs (see Ref. 6 for a review).

However, in systems with more than two degrees of freedom, the dividing surfaces do not generally exist globally in phase space [7,8]. Thus, the attempt to define the reaction rate based on dynamics has not been successful for systems with many degrees of freedom. Instead, global features of the phase space, such as the network of reaction paths, emerge as crucial ingredients in studying reactions from the dynamical point of view.

The reason why the dividing surfaces do not generally exist globally is because intersections between the stable and unstable manifolds of NHIMs sometimes involve tangency. This tangency reveals that branching structures exist in the network of reaction paths. Moreover, combining these branching structures with the Arnold web in the potential well, the global aspects of the phase space offer rich possibilities for nonergodic behavior for reactions in systems with many degrees of freedom. Implications of this possibility are to be sought in reactions under nonequilibrium conditions.

Thus, we shift our attention from quantities related to local equilibrium, notably reaction rate constants, to nonequilibrium aspects of reaction processes. In particular, we list the following three closely related questions as most important.

First, do dynamical correlations exist in processes involving multiple saddles, such as structural changes of macromolecules in clusters and proteins? In the conventional theory, it is supposed that consecutive processes of going over saddles take place independent of one another. In other words, the system loses its memory of the past immediately, since the vibrational relaxation within a well is assumed to be much faster than the escape from it and multistep processes are conventionally assumed to be Markov processes. To the contrary, when the characteristic time scale of IVR is comparable to that of the reaction, the system can keep dynamical correlations as it goes over successive saddles.

These correlations result in (a) acceleration of reactions for some initial conditions and (b) deceleration for others. This approach will shed new light on problems such as why reactions proceed on multibasin energy landscapes without being trapped in deep minima [9], why proteins fold so effectively, how enzymes help specific reactions to take place, and so on.

Second, how we can characterize nonequilibrium reactions using a dynamical viewpoint? Since the conventional concepts are not sufficient here, we need new ideas that relate measurable quantities to reaction dynamics. In particular, for reactions involving structural changes of macromolecules, collective variables will be necessary to describe processes, and the degrees of freedom that compose collective variables will change as the reaction proceeds over multiple saddles. Furthermore, dynamical correlations are likely to play important roles. Then, we need methods that answer the following questions: What degrees of freedom are necessary to describe reaction dynamics, in what way do they evolve and vary during the processes, and how we can extract information on their dynamics from measurements?

Third, what is the dynamical origin of Maxwell's demon? As is well known since the work of Maxwell, Szilard, and Brillouin, nonequilibrium conditions are necessary for systems to do information processing. Therefore, in studying biochemical reactions, we are interested in how nonequilibrium conditions are maintained at the molecular level. From the viewpoint of dynamics, in particular, the following problem stands out as crucial: Does any intrinsic mechanism of dynamics exist which helps to maintain nonequilibrium conditions in reaction processes? In other words, are there any reactions in which nonergodicity plays an essential role for systems to exhibit functional behavior?

Keeping these subjects in perspective, we organized a conference entitled "Geometrical Structures of Phase Space in Multidimensional Chaos—Applications to Chemical Reaction Dynamics in Complex Systems" from 26th October to 1st November, 2003, at the Yukawa Institute for Theoretical Physics, Kyoto University, Kyoto, Japan. A pre-conference was also held at Kobe University from 20th to 25th October.

This conference was interdisciplinary, where researchers from physics (including astrophysics), biophysics, physical chemistry, and nonlinear science gathered to discuss a wide range of problems in reaction dynamics with the common theme that chaos in dynamical systems plays a crucial role in studying chemical reactions. Furthermore, we argue that reactions involving macromolecules such as clusters, liquids, and proteins are important examples of dynamical systems with many degrees of freedom. Thus, we expect that studies of these reactions from a dynamics point of view will shed new light on phenomena such as phase transitions in clusters, slow relaxation in liquids, and

the efficiency of protein folding, as well as in seeking the possibility of manipulating these reactions.

In particular, in the Conference we focused our attention on the following topics.

1. Transition state theory revisited from the dynamical point of view, including a historical perspective of the study.
2. Phase-space structure of Hamiltonian systems with multiple degrees of freedom—in particular, normally hyperbolic invariant manifolds (NHIMs), intersections between their stable and unstable manifolds, and the Arnold web.
3. Analyses of reaction processes based on the phase space structure of the system.
4. Quantum aspects of chaos and how we can control them.
5. Nonstatistical properties, such as nonstationary behavior and multiple scales of time and distance for evolution, in systems of many degrees of freedom.
6. Dynamical understanding of reaction processes in macromolecules and liquids, such as phase transitions, fast alloying, energy redistribution, and structural changes in clusters and proteins.
7. Data mining to extract information on dynamics from time series data from experiments and simulations of molecular dynamics.
8. Dynamical insights into reactions at the macroscopic level, including chemical networks in cells and their evolution.

Here, in this volume, we have collected contributions from the invited speakers, from poster presentations that received the best poster awards (Yanao, Honjo, and Okushima), and from poster presentations chosen to cover topics that were not treated by the invited speakers. The best poster awards were decided based on a jury vote by the invited speakers and a popular vote by all the participants. Note, however, that there were many other posters that also deserved inclusion here.

In the following, we give a brief overview of the content of this volume. The volume consists of the following three parts:

- I. Phase-space geometry of multidimensional dynamical systems and reaction processes.
- II. Complex dynamical behavior in clusters and proteins, and data mining to extract information on dynamics.
- III. New directions in multidimensional chaos and evolutionary reactions.

In the first part, our aim is to discuss how we can apply concepts drawn from dynamical systems theory to reaction processes, especially unimolecular reactions of few-body systems. In conventional reaction rate theory, dynamical aspects are replaced by equilibrium statistical concepts. However, from the standpoint of chaos, the applicability of statistical concepts itself is problematic. The contribution of Rice's group gives us detailed analyses of this problem from the standpoint of chaos, and it presents a new approach toward unimolecular reaction rate theory.

In statistical reaction rate theory, the concept of transition state plays a key role. Transition states are supposed to be the boundaries between reactants and products. However, the precise formulation of the transition state as a dividing surface is only possible when we consider "transition states" in phase space. This is the place where the concepts of normally hyperbolic invariant manifolds (NHIMs) and their stable and unstable manifolds come into play.

The contributions of Komatsuzaki and Berry, and of Uzer's group, discuss these manifolds, and they present their calculations using Lie perturbation theory methods. The contribution of Wiesenfeld discusses these manifolds in reaction processes involving angular momenta, and the contribution by Joyeux et al. shows applications of the perturbation theory method to reactions involving Fermi resonance. The contribution of Sano discusses invariant manifolds in the Coulomb three-body problem.

The importance of NHIMs, and their stable and unstable manifolds is shared strikingly between chemical reactions and astrophysics. Therefore in the conference at Kyoto, Koon, from Caltech, discussed controlling an orbiter in astrophysics, and Uzer presented his study of asteroids near Jupiter, where analyses of these manifolds were essential.

In reaction processes for which there is no local equilibrium within the potential well, global aspects of the phase space structure become crucial. This is the topic treated in the contribution of Toda. This work stresses the consequences of a variety of intersections between the stable and unstable manifolds of NHIMs in systems with many degrees of freedom. In particular, "tangency" of intersections is a feature newly recognized in the phase space structure. It is a manifestation of the multidimensionality of the system, where reaction paths form a network with branches.

Here, we also include the contributions related to quantum mechanics: The chapter by Takami et al. discusses control of quantum chaos using coarse-grained laser fields, and the contribution of Takahashi and Ikeda deals with tunneling phenomena involving chaos. Both discuss how chaos in classical behavior manifests itself in the quantum counterpart, and what role it will play in reaction dynamics.

In the second part, we collect contributions concerning dynamical processes in complex systems such as clusters and proteins. Here, we also include those ideas related to data mining, since this topic is an indispensable part of the studies on dynamics of macromolecules.

The contribution of Berry presents an overview of the study of clusters as vehicles for investigating complex systems. The study of clusters has given birth to a variety of new ideas which turned out to be fruitful in other complex systems such as proteins. The contribution of Takatsuka discusses dynamical and statistical aspects of phase transitions in clusters, and the contribution of Yanao and Takatsuka studies the gauge structure arising from the dynamics of floppy molecules. Shida's contribution presents an important issue related to saddles of index of two or more, and shows their role in the phase transitions of clusters. Another interesting phenomenon of clusters is fast alloying, discussed in the contribution of Shimizu et al. from the standpoint of reaction dynamics.

Liquids and proteins are complex systems for which the study of dynamical systems has wide applicability. In the conference, relaxation in liquids (ϵ -entropy by Douglas at the National Institute of Standards and Technology, nonlinear optics by Saito, and energy bottlenecks by Shudo and Saito), energy redistribution in proteins (Leitner and Straub et al.), structural changes in proteins (Kidera at Yokohama City University), and a new formulation of the Nosé-Hoover chain (Ezra at Cornell University) were discussed. Kidera's talk discussed time series analyses in molecular dynamics, and it is closely related to the problem of data mining. In the second part of the volume, we collect the contributions by Leitner and by Straub's group, and the one by Shudo and Saito in the third part.

The contribution by Komatsuzaki's group bridges the two research fields—that is, dynamics in complex systems and data mining. They apply to a model of proteins the methods of embedding and Allan variance, both of which have been developed in dynamical system theory. Their results reveal, using the Allan variance, nonstationary behavior in protein dynamics, and they show, by embedding, how many degrees of freedom are necessary to describe this dynamics. Thus, this contribution indicates a crucial role for the methods of data mining in the study of processes involving macromolecules.

Therefore, contributions to methods of data mining are included here. It is uncommon to discuss this topic in the context of reaction processes. However, as we have already discussed, data mining becomes ever more important in analyzing experiments and simulations. In conventional data analyses, the concepts of equilibrium statistical physics have been routinely applied. To the contrary, in situations in which local equilibrium breaks down, established methods do not exist to analyze experiments and simulations. Thus, data mining

to extract information on dynamics is crucial here. In the conference, several methods were discussed (Broomhead at Manchester University on embedding, Vulpiani on finite-size Lyapunov exponents, Taguchi on nonmetric methods, and Hasegawa on inductive thermodynamics approach from time series). Here we include the contributions by Taguchi and Oono and by Hasegawa and Ohtaki.

In the third part, those contributions are collected which discuss nonergodic and nonstationary behavior in systems with many degrees of freedom, and seek new possibilities to describe complex reactions, including even the evolution of living cells.

Conventional theory supposes that statistical ideas would be more applicable to systems of many degrees of freedom than to few-body systems. To the contrary, in these systems, new kinds of behavior such as multiergodicity, nonstationarity, and an anomalous approach to equilibrium can emerge. Consequently, their implications for reaction dynamics should be explored, especially in those cases where biological functions are involved.

Thus, the contribution of Shudo and Saito starts by presenting the problem concerning the relation between nonergodicity and $1/f$ noise. For systems with two degrees of freedom, the dynamical origin of $1/f$ noise is attributed to the hierarchical structures of resonant tori (Aizawa). However, for systems with many degrees of freedom, this relationship is not well understood. This discussion goes on to systems with a gap in the spectrum of characteristic time scales and nonergodic behavior, based on the studies of the Italian group (Benettin et al.). The contributions of Aizawa and of Yamaguchi also discuss these problems in the context of cluster formation (Aizawa) and of an approach to equilibrium (Yamaguchi). These features will become important in understanding reaction processes in complex systems such as protein folding and slow relaxation in complex liquids.

Nonlinear resonances are important factors in reaction processes of systems with many degrees of freedom. The contributions of Konishi and of Honjo and Kaneko discuss this problem. Konishi analyzes, by elaborate numerical calculations, the so-called Arnold diffusion, a slow movement along a single resonance under the influence of other resonances. Here, he casts doubt on the usage of the term “diffusion.” In other words, “Arnold diffusion” is a dynamics completely different from random behavior in fully chaotic regions where most of the invariant structures are lost. Hence, understanding “Arnold diffusion” is essential when we go beyond the conventional statistical theory of reaction dynamics. The contribution of Honjo and Kaneko discusses dynamics on the network of nonlinear resonances (i.e., the Arnold web), and stresses the importance of resonance intersections since they play the role of the hub there.

Here we also include the contribution of Okushima, in which the concept of the Lyapunov exponents is extended to orbits of finite duration. The mathematical definition of the Lyapunov exponents requires ergodicity to ensure convergence of the definition. On the other hand, various attempts have been made to extend this concept to finite time and space, to make it applicable to nonergodic systems. Okushima's idea is one of them, and it will find applications in nonstationary reaction processes.

The contributions of Vulpiani's group and of Kaneko deal with reactions at the macroscopic level. The contribution of Vulpiani's group discusses asymptotic analyses to macroscopic reactions involving flows, by presenting the mechanism of front formation in reactive systems. The contribution of Kaneko deals with the network of reactions within a cell, and it discusses the possibility of evolution and differentiation in terms of that network. In particular, he points out that molecules that exist only in small numbers can play the role of a switch in the network, and that these molecules control evolutionary processes of the network. This point demonstrates a limitation of the conventional statistical quantities such as density, which are obtained by coarse-graining microscopic quantities. In other words, new concepts will be required which go beyond the hierarchy in the levels of description such as micro and macro.

We hope that the contributions collected in this volume convey the stimulating and interdisciplinary atmosphere of the conference. We also expect that the results and discussions in these contributions form a first and decisive step toward understanding reaction processes from the standpoint of dynamics.

The conference was supported by the following grants and institute. We greatly appreciate these organizations for their financial support.

- Japan Society for Promotion of Science, Japan–U.S. Cooperative Science Program.
- The Inoue Foundation for Science.
- Yukawa Institute for Fundamental Physics, Kyoto University.
- Grant-in-Aid for Scientific Research on Priority Areas “Control of Molecules in Intense Laser Fields” from the Ministry of Education, Science, Sports, and Culture.

References

1. M. Toda, *Adv. Chem. Phys.* **123**, 3643 (2000).
2. K. Yamanouchi, N. Ikeda, S. Tsuchiya, D. M. Jonas, J. K. Lundberg, G. W. Adamson, and R. W. Field, *J. Chem. Phys.* **95**, 6330 (1991).
3. T. Shibata, H. Lai, H. Katayanagi, and T. Suzuki, *J. Phys. Chem.* **A102**, 3643 (1998).

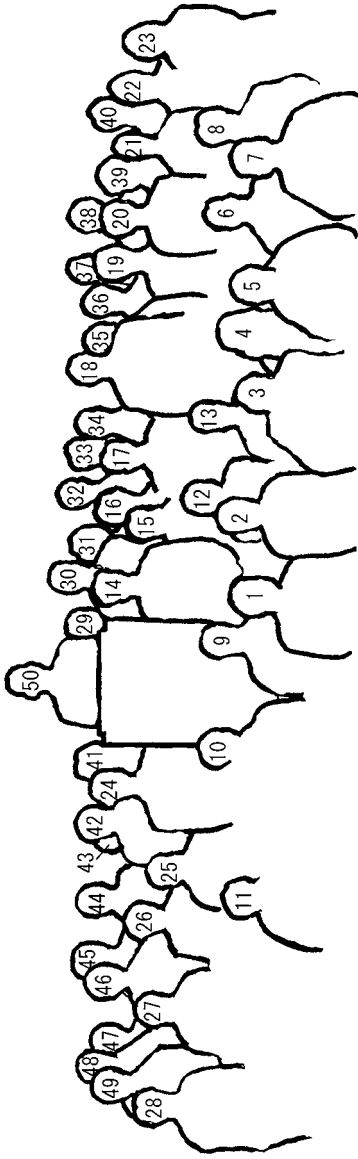
4. S. L. Schultz, J. Qian, and J. M. Jean, *J. Phys. Chem.* **A101**, 1000 (1997).
5. M. J. Davis and S. K. Gray, *J. Chem. Phys.* **84**, 5389 (1986).
6. T. Komatsuzaki and R. S. Berry, *Adv. Chem. Phys.* **123**, 79 (2002).
7. R. E. Gillilan and G. S. Ezra, *J. Chem. Phys.* **94**, 2648 (1991).
8. S. Wiggins, *Physica* **D44**, 471 (1990).
9. L. Sun, K. Song, and W. L. Hase, *Science* **296**, 875 (2002).

Spring 2004

M. TODA
T. KOMATSUZAKI
T. KONISHI
R. S. BERRY
S. A. RICE



YTP International Symposium on Geometrical Structures of Phase Space in Multidimensional Chaos—Applications to Chemical Reaction Dynamics in Complex System, October 26–November 1, 2003, at the Yukawa Institute for Theoretical Physics, Kyoto University, Kyoto, Japan.



- (1) Tamiki Komatsuzaki (2) Gregory Ezra (3) R. Stephen Berry (4) Charles Jaffé (5) Angelo Vulpiani (6) Yoji Aizawa (7) Mikito Toda (8) Masanori Shimono (9) Dave F. Broomhead (10) Shinichiro Goto (11) Yoshihiro Taguchi (12) Shinji Saito (13) David M. Leitner (14) Laurent Wiesenfeld (15) Koji Hotta (16) Seiichiro Honjo (17) Wang Sang Koon (18) Stuart A. Rice (19) Akinori Kidera (20) Toshiya Takami (21) Kyoko Hoshino (22) Ayako Nozaki (23) Yoko K. Ueno (24) Kazuo Takatsuka (25) Yasushi Shimizu (26) Kin'ya Takahashi (27) Mitsuada M. Sano (28) Hiroshi H. Hasegawa (29) Koichi Fujimoto (30) Turgay Uzer (31) Tetsuro Konishi (32) Hidetoshi Morita (33) Yoshiyuki Y. Yamaguchi (34) John E. Straub (35) Hiroshi Fujisaki (36) Mitsuori Takano (37) Sotaro Fuchigami (38) Jack F. Douglas (39) Kazuo Kuwata (40) Taku Mizukami (41) Teruaki Okushima (42) Kim Kyeon-deuk (43) Norihiro Shida (44) Akira Shudo (45) Takefumi Yamashita (46) Kunihiko Kaneko (47) Youhei Koyama (48) Marc Joyeux (49) Lintao Bu (50) Statue of Hideki Yukawa (Nobel Prize Laureate (Physics) 1949)

CONTENTS PART A

PART I PHASE-SPACE GEOMETRY OF MULTIDIMENSIONAL DYNAMICAL SYSTEMS AND REACTION PROCESSES	1
CHAPTER 1 CLASSICAL, SEMICLASSICAL, AND QUANTUM MECHANICAL UNIMOLECULAR REACTION RATE THEORY <i>By Meishan Zhao, Jiangbin Gong, and Stuart A. Rice</i>	3
CHAPTER 2 REGULARITY IN CHAOTIC TRANSITIONS ON TWO-BASIN LANDSCAPES <i>By Tamiki Komatsuzaki and R. Stephen Berry</i>	143
CHAPTER 3 A NEW LOOK AT THE TRANSITION STATE: WIGNER'S DYNAMICAL PERSPECTIVE REVISITED <i>By Charles Jaffé, Shinnosuke Kawai, Jesús Palacián, Patricia Yanguas, and Turgay Uzer</i>	171
CHAPTER 4 GEOMETRY OF PHASE-SPACE TRANSITION STATES: MANY DIMENSIONS, ANGULAR MOMENTUM <i>By Laurent Wiesenfeld</i>	217
CHAPTER 5 INTRAMOLECULAR DYNAMICS ALONG ISOMERIZATION AND DISSOCIATION PATHWAYS <i>By Marc Joyeux, Sergy Yu. Grebenshchikov, Jens Bredenbeck, Reinhard Schinke, and Stavros C. Farantos</i>	267
CHAPTER 6 CLASSICAL COULOMB THREE-BODY PROBLEM <i>By Mitsusada M. Sano</i>	305
CHAPTER 7 GLOBAL ASPECTS OF CHEMICAL REACTIONS IN MULTIDIMENSIONAL PHASE SPACE <i>By Mikito Toda</i>	337
CHAPTER 8 CLASSICAL MECHANISM OF MULTIDIMENSIONAL BARRIER TUNNELING <i>By Kin'ya Takahashi and Kensuke S. Ikeda</i>	401

CHAPTER 9 COARSE-GRAINED PICTURE FOR CONTROLLING QUANTUM CHAOS	435
<i>By Toshiya Takami, Hiroshi Fujisaki, and Takayuki Miyadera</i>	
AUTHOR INDEX	459
SUBJECT INDEX	487

CONTENTS PART B

PART II COMPLEX DYNAMICAL BEHAVIOR IN CLUSTERS AND PROTEINS, AND DATA MINING TO EXTRACT INFORMATION ON DYNAMICS	1
CHAPTER 10 ATOMIC CLUSTERS: POWERFUL TOOLS TO PROBE COMPLEX DYNAMICS <i>By R. Stephen Berry</i>	3
CHAPTER 11 TEMPERATURE, GEOMETRY, AND VARIATIONAL STRUCTURE IN MICROCANONICAL ENSEMBLE FOR STRUCTURAL ISOMERIZATION DYNAMICS OF CLUSTERS: A MULTICHANNEL CHEMICAL REACTION BEYOND THE TRANSITION-STATE CONCEPT <i>By Kazuo Takatsuka</i>	25
CHAPTER 12 EFFECTS OF AN INTRINSIC METRIC OF MOLECULAR INTERNAL SPACE ON CHEMICAL REACTION DYNAMICS <i>By Tomohiro Yanao and Kazuo Takatsuka</i>	87
CHAPTER 13 ONSET DYNAMICS OF PHASE TRANSITION IN Ar ₇ <i>By Norihiro Shida</i>	129
CHAPTER 14 RAPID ALLOYING IN BINARY CLUSTERS: MICROCLUSTER AS A DYNAMIC MATERIAL <i>By Yasushi Shimizu, Taizo Kobayashi, Kensuke S. Ikeda, and Shin'ichi Sawada</i>	155
CHAPTER 15 VIBRATIONAL ENERGY RELAXATION (VER) OF A CD STRETCHING MODE IN CYTOCHROME c <i>By Hiroshi Fujisaki, Lintao Bu, and John E. Straub</i>	179
CHAPTER 16 HEAT TRANSPORT IN MOLECULES AND REACTION KINETICS: THE ROLE OF QUANTUM ENERGY FLOW AND LOCALIZATION <i>By David M. Leitner</i>	205
CHAPTER 17 REGULARITY IN CHAOTIC TRANSITIONS ON MULTIBASIN LANDSCAPES <i>By Tamiki Komatsuzaki, Kyoko Hoshino, and Yasuhiro Matsunaga</i>	257

CHAPTER 18	NONMETRIC MULTIDIMENSIONAL SCALING AS A DATA-MINING TOOL: NEW ALGORITHM AND NEW TARGETS	315
	<i>By Y-H. Taguchi and Yoshitsugu Oono</i>	
CHAPTER 19	GENERALIZATION OF THE FLUCTUATION-DISSIPATION THEOREM FOR EXCESS HEAT PRODUCTION	353
	<i>By Hiroshi H. Hasegawa and Yoshikazu Ohtaki</i>	
PART III	NEW DIRECTIONS IN MULTIDIMENSIONAL CHAOS AND EVOLUTIONARY REACTIONS	373
CHAPTER 20	SLOW RELAXATION IN HAMILTONIAN SYSTEMS WITH INTERNAL DEGREES OF FREEDOM	375
	<i>By Akira Shudo and Shinji Saito</i>	
CHAPTER 21	SLOW DYNAMICS IN MULTIDIMENSIONAL PHASE SPACE: ARNOLD MODEL REVISITED	423
	<i>By Tetsuro Konishi</i>	
CHAPTER 22	STRUCTURE OF RESONANCES AND TRANSPORT IN MULTIDIMENSIONAL HAMILTONIAN DYNAMICAL SYSTEMS	437
	<i>By Seiichiro Honjo and Kunihiko Kaneko</i>	
CHAPTER 23	MULTIERGODICITY AND NONSTATIONARITY IN GENERIC HAMILTONIAN DYNAMICS	465
	<i>By Yoji Aizawa</i>	
CHAPTER 24	RELAXATION AND DIFFUSION IN A GLOBALLY COUPLED HAMILTONIAN SYSTEM	477
	<i>By Yoshiyuki Y. Yamaguchi</i>	
CHAPTER 25	FINITE-TIME LYAPUNOV EXPONENTS IN MANY-DIMENSIONAL DYNAMICAL SYSTEMS	501
	<i>By Teruaki Okushima</i>	
CHAPTER 26	THE ROLE OF CHAOS FOR INERT AND REACTING TRANSPORT	519
	<i>By Massimo Cencini, Angelo Vulpiani, and Davide Vergni</i>	
CHAPTER 27	ON RECURSIVE PRODUCTION AND EVOLVABILITY OF CELLS: CATALYTIC REACTION NETWORK APPROACH	543
	<i>By Kunihiko Kaneko</i>	
AUTHOR INDEX		599
SUBJECT INDEX		627

PART I

PHASE-SPACE GEOMETRY OF MULTIDIMENSIONAL DYNAMICAL SYSTEMS AND REACTION PROCESSES

