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
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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.

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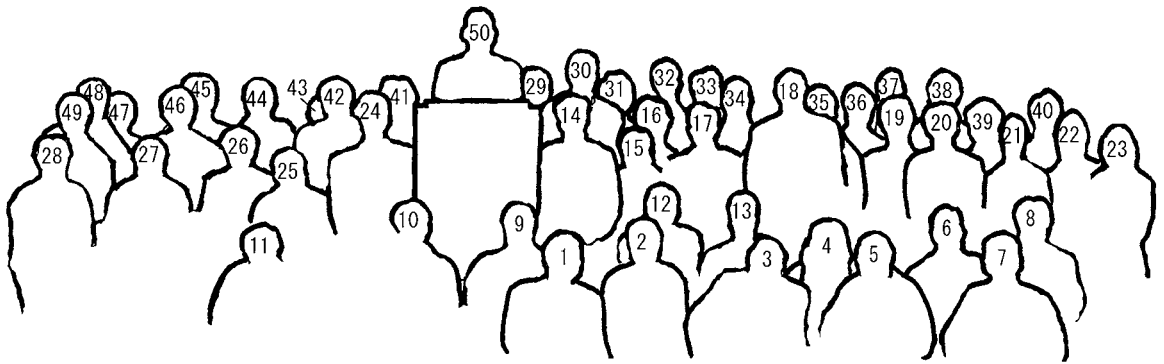

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PART I

PHASE-SPACE GEOMETRY OF MULTIDIMENSIONAL DYNAMICAL SYSTEMS AND REACTION PROCESSES