

## PREFACE

The present volume of the Advanced Series in Physical Chemistry serves to expose an emerging frontier for physical chemists: the elucidation of chemical dynamics in natural and technical environments that are identified as extreme. With the steady increase in affordable computational power, a growing number of macroscopic phenomena are modeled at the molecular level, exerting new demands on the understanding of detailed molecular dynamics in exotic conditions. The development of computational environmental models depends on bidirectional cross-disciplinary collaboration between chemists and technical experts of a number of fields including geophysics, plasma and fluid physics, materials science, and engineering. Not only must researchers attempting to model an extreme environmental system be acquainted with physical chemical expertise and information, but the physical chemist must also be intimately familiar with the parameters of the investigated system in order to identify the relevant processes, and propose a chemical model having a complexity commensurate with the fidelity of the ultimate environmental model. Unfortunately, despite a consensus that the breakthroughs of the future will come from multidisciplinary efforts, interdisciplinary communication has faced considerable resistance. This is mainly attributable to the division of most universities into disciplinary departments, an organizational form that is also reflected in many federal funding agencies. This division ultimately results in a peer structure that is based on disciplinary excellence.<sup>a</sup>

There have been, however, concerted efforts in breaching the barriers between disciplines, a noteworthy example of which is the US Department of Defense Multidisciplinary Research Program of the University Research Initiative that funds cross-departmental efforts to address specific technological objectives, many of which involve exploiting or mitigating the forces

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<sup>a</sup>N. Metzger and R. N. Zare, *Science* **283**, 642 (1999).

released in systems under extreme conditions. As an additional step in this direction, the present volume attempts to highlight chemical dynamics studies tied to unraveling the mysteries of extreme environments.

This book identifies a number of examples where knowledge of the detailed chemical dynamics is a vital component of the description of a respective extreme environment. A rigid definition of what constitutes an extreme environment does not exist. In selecting the topics, I have chosen environments where the fundamental chemical processes are generally far from thermal and chemical equilibrium, either on short transient time scales, or continuously. At conditions where the energy associated with the various degrees of freedom is not equilibrated, knowledge of the state-to-state dynamics becomes important, and given the limited database on excited state processes, modelers are frequently forced to speculate on the pertinent kinetics. Extreme environments, however, can refer to any condition far from room temperature and atmospheric pressure, a definition adopted by Berman in Chap. 1. In an overview, Berman reverses the general theme of this volume by pointing out how various instances of physical chemical innovation have resulted from the need to understand chemical dynamics under extreme conditions.

Each of the following chapters addresses one or more extreme environments, outlines the associated chemical mechanisms of relevance, and then covers the leading edge science that elucidates the chemical coupling. The chapter topics have been chosen to create a balance between theory and experiment; between gas-phase, solid state, plasma, and interface dynamics; and natural and technical environments. What has resulted is a collection of reviews with overlapping but also highly variable chemical dynamics including timescales ranging from femtoseconds to a billion years. While in one chapter (Chap. 10), the research has not reached the stage at which the molecular structural information is sufficient to commence theoretical dynamical studies, another environment is examined at the level of hyperfine-level transitions (Chap. 4).

In Chap. 2, Raz and Levine investigate a regime of dynamics where the motion along intermolecular coordinates is comparable or faster than that of intramolecular vibrational modes. These conditions exist momentarily when a large cluster impacts a surface at hyperthermal velocities ( $\sim 10 \text{ km s}^{-1}$ ). In Chap. 3, Boyd describes the challenges facing a direct simulation Monte Carlo modeler of hypersonic flows in a regime intermediate to the continuum and free molecular flow limits. Many of the lessons

learned in Chap. 2 find application in this work. In Chap. 4, Heaven takes a close look at the energy transfer and reaction kinetics of chemical laser media. This review is a nice example of how the drive for new technology has fostered new physical chemical techniques as well as the acquisition of kinetic data of fundamental scientific interest. In Chap. 5, Schulz, Volpp and Wolfrum present selected laboratory experiments on gas-phase and surface reactions of importance in combustion systems. The reader is lead through a remarkable progression from the detailed investigation of the  $\text{H} + \text{O}_2$  reaction dynamics to  $\text{NO}_x$  formation mechanisms in flames, unsteady methanol oxidation under laminar flow conditions, laser diagnostics of surface reactions on a platinum catalyst, to, finally, quantitative laser spectroscopic diagnostics in actual combustion engines. Dressler and Murad describe the phenomenology of meteors in Chap. 6 and review the current understanding of the hyperthermal gas-phase chemical dynamics that are at the origin of various observations. In Chap. 7, Jacobs links the results from detailed studies of the dynamics of hypervelocity surface scattering to physical properties of spacecraft, such as space vehicle drag and charging. Johnson reviews the current understanding of the solid state radiation chemistry of the Galilean moons of Jupiter in Chap. 8. The bombardment by energetic ions and electrons trapped in Jupiter's giant magnetosphere directly affect the appearance of the satellites, and generate volatiles that form the atmosphere and local plasma. In Chap. 9, Minton and Garton review the mechanisms behind atomic oxygen induced degradation of polymers used in low earth orbit. This chapter demonstrates that studies of the appropriate surface interactions are shedding important light on the origin of materials erosion in space. The understanding of the durability of ceramic thermal barrier coatings (TBCs) on the molecular level is the subject of Chap. 10 by Christensen, Jarvis and Carter. TBCs are used to protect turbine blades of aircraft engines, thereby allowing them to run more efficiently at higher temperatures. While Chap. 10 is focused on the structure of ceramic-metal interfaces with the eventual goal of understanding solid state kinetics on a long time scale (years), Chap. 11 by White, Swanson and Robertson examines the ultrafast molecular dynamics associated with shock-induced phase transitions and detonations in solids. The results reported in Chap. 11 show that molecular simulations using reactive potentials provide a powerful probe of the interplay between the continuum properties of shock waves and the atomic scale chemistry.

A better understanding of this interplay is key to the design of safer, more reliable explosives.

Given the broad readership that this volume is intended to address, the authors have taken great care in presenting the material with as general a terminology as possible. Nevertheless, expressions appear that may not be familiar to all readers and would interrupt the flow of the text if explained at the first occurrence. A number of expressions are, therefore, defined in a Glossary at the end of this book.

I thank all of the authors for taking a step outside of their current peer structures and contributing to this volume. I have thoroughly enjoyed interacting with you during the course of the past year. I am particularly grateful to M. Berman for his enthusiastic support of this endeavor and for assisting me in assembling the list of distinguished authors. I am also indebted to C. Kolb, P. Armentrout, E. Murad, G. Pachioni, M. Tagawa, R. Coombe, S. Davis, T. Madden, G. Manke, D. Setser and R. Hardy for donating their precious time in reviewing one or more chapters.

Rainer A. Dressler  
Air Force Research Laboratory  
Space Vehicles Directorate  
AFRL/VSBX, 29 Randolph Rd.  
Hanscom AFB, MA 01731-3010