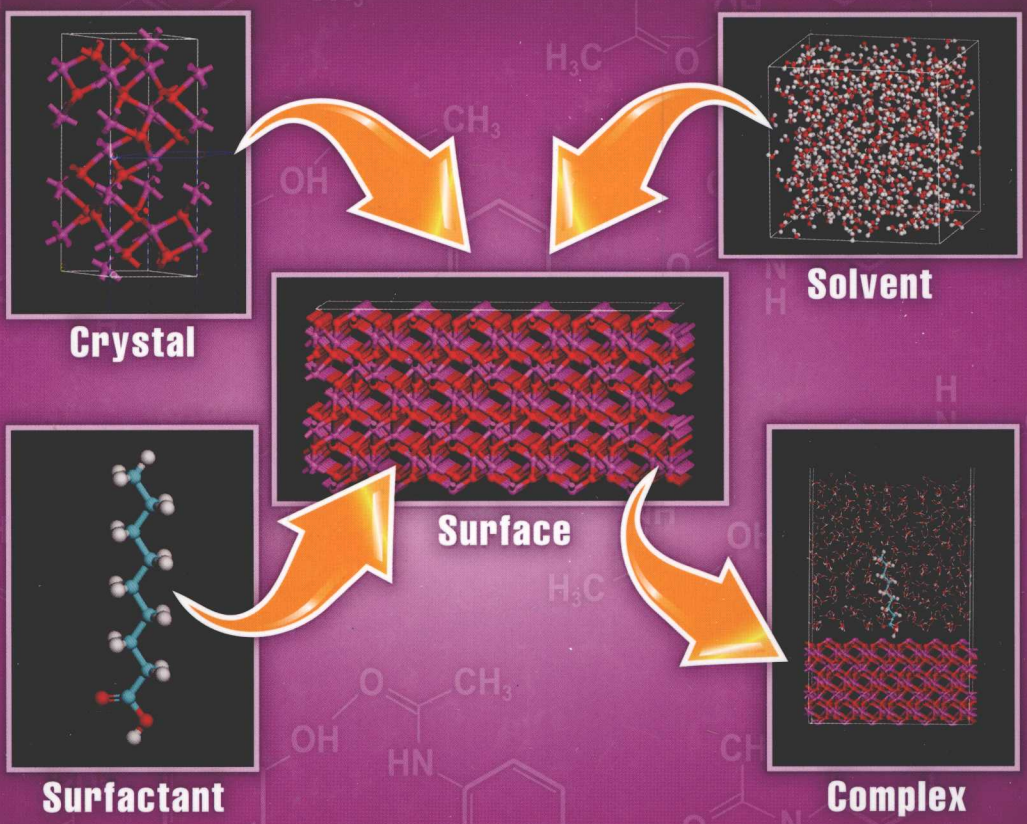
# Molecular Modeling *for the* Design *of* Novel Performance Chemicals *and* Materials

Edited By
**Beena Rai**

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# Molecular Modeling *for the* Design *of* Novel Performance Chemicals *and* Materials

*Anor aniyan mahaan mahiyan*
*[The greatest of the great is hidden in the smallest of the small like atomic energy.]*

*The Vedic dictum*

# Foreword

I am extremely pleased to write the Foreword for *Molecular Modeling for the Design of Novel Performance Chemicals and Materials*, edited by Dr. Beena Rai. The techniques of modeling and simulation have been developed extensively over the last few years. The approximations involving *ab initio* and density functional theory at quantum length scales, as well as the classical atomistic simulation and coarse-grained simulation at larger length scales, have made the computational tools potent in the modeling of materials. I expect the multiscale approach to simulation of materials to be further refined in future years, such that the modeling of designer materials may be attempted in a serious manner. At the same time, there has been tremendous growth in computational hardware in terms of speed, architecture, and affordability. This has been coupled with developments in numerical algorithms and efficient strategies of coding. All these together make the future of materials modeling extremely promising.

It is thus fitting that at this stage it is necessary to take stock of the current status of the modeling of materials and the applications of such techniques to meaningful problems. This book brings together topics on various facets of such modeling techniques and applications in diverse ranges from pharmaceuticals to cement. The interesting point to note is that even though the case studies presented are very diverse, the chapters are organized according to certain underlying themes. The book starts with a review of molecular modeling tools in Chapter 1, subsequently describing several applications in succeeding chapters. Chapters 2 to 4 deal with the modeling of mineral–reagent interactions. The adsorption of surfactants at air–liquid and solid–liquid interfaces, as studied through various molecular modeling techniques, and their effect on the macroscopic behavior of the system under study has been illustrated with various case studies drawn from the work of the authors. Chapter 5 deals with the application of molecular modeling tools in the crystallization and design of pharmaceutical products of desired properties. Chapters 6 and 7 deal with studies on the microstructure in water—surfactant systems using atomistic and mesoscale applications. Chapter 8 emphasizes the study of phase transitions in porous media and their role in the design of novel porous materials for improved industrial processes. The study of wettability on solid surfaces is examined in detail in Chapter 9, with a focus on the advantages and disadvantages of various methodologies and relevant case studies. Chapter 10 illustrates applications in the area of transport properties of materials, with a special focus on zeolite and nanofluids—novel heat-transfer liquids that possess higher thermal conductivity. Chapters 11 to 14 describe the use of density functional theory in hydrogen storage materials, semiconductor alloys, cement clinker compounds, and catalysis, each of which is an important area. The authors are all accomplished in their areas, and the book brings together a suite of competencies on molecular modeling in different parts of material research.

I think it is an extremely important addition to the growing field and will serve as an important reference book.

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# Preface

Beginning with the 1980s, molecular modeling (MM) has become an important tool in many academic institutions and industrial laboratories. Although the role of MM in biological fields—especially in the design and development of novel drug molecules or formulations—is well established and acknowledged, its direct role in the design and development of performance chemicals and novel materials is still not well known. Questions such as which new products have resulted from an MM-based approach are often still asked. Although MM may be playing an important role in product development, quite often it becomes difficult to predict its direct impact because most of the time the problem being addressed involves a multidisciplinary approach. Further, the assumption that the fundamental phenomena being modeled through MM will have direct impact on the macroscopic and functional properties of a product makes the situation more complicated. In most cases, MM actually works as an enabler toward the development of novel products and materials rather than directly coming up with these new products and materials, such as novel drug molecules in biological application. This is precisely the reason that, despite seeing value in MM tools, most engineers and practitioners often focus on the question of how to leverage these tools to design and develop novel materials or chemicals for the industry the person is working in? Unfortunately, there is no simple answer to this question. Excellent books and research publications highlight the most intricate, fundamental, and theoretical details about MM techniques and tools. However, the use of highly specialized terminologies and a lack of practical case studies make it almost impossible for those who do not specialize in MM to assimilate the knowledge and use it for their benefit. What is required from the user's perspective is a simple guide that highlights the utility and power of MM tools.

The goal in editing this book is to provide answers to these important questions. The attempt here is to provide a simple and practical approach to the MM paradigm. The focus of this book is to highlight the importance and usability of MM tools and techniques in various industrial applications as illustrated by several case studies. The contributing authors have provided numerous examples in which MM tools have been used to understand the properties of the materials and rationally design novel chemicals and materials.

The book is divided into 14 chapters that cover a diverse range of industrial applications from pharmaceuticals to cement. The interesting point to note is that even though the case studies presented are wide ranging, the chapters are organized according to certain underlying themes. Chapter 1 provides a brief overview of MM techniques and tools as may be appropriate for a beginner. Adequate references are provided for more expert learning.

Chapters 2 to 4 deal with the modeling of mineral–reagent interactions. The adsorption of surfactants at air–liquid and solid–liquid interfaces and its effect on their macroscopic behavior is illustrated through various case studies. The applications range from mineral processing to pharmaceuticals. Concepts like the wetting of bare mineral surfaces and those coated with a monolayer of surfactants are also addressed. These chapters clearly provide an insight into the utility and power of MM in the design and development of performance chemicals.

The application of MM tools in the crystallization and design of pharmaceutical products is described in Chapter 5.

Chapters 6 deals with some of the fundamental aspects of surfactant assembly, while in Chapter 7 the behavior of liquid in confinement and its implications in industrial applications are described. Phase transitions in porous media and their role in the design of novel porous materials for improved industrial processes are illustrated in Chapter 8. Chapter 9 deals with the advantages and disadvantages of various methodologies employed in the studies of wettability on solid surfaces, as illustrated

through relevant case studies. The application of MM in the study of transport properties of materials—with a special focus on zeolite and nanofluids—is described in Chapter 10.

Chapters 11 to 14 demonstrate applications of density functional theory and simulations in the design and development of novel materials for hydrogen storage, new semiconductor alloys, cement, and catalysis.

This book has been compiled with two types of audiences in mind—practicing engineers and practicing chemists, each approaching MM from different perspectives but sharing a common desire to solve the practical problems in the most effective manner. I hope that this book serves both communities and provides a fresh perspective on the application of MM tools and techniques in various industries. I am sure that researchers entering the fascinating field of MM will find it useful as a reference guide.

I thank all the authors for their contributions and encouragement in the creation of this book. I also thank all the reviewers for their valuable comments and suggestions. My thanks to the members of the technical communication team at Tata Research Development and Design Centre Pune and to Deenaz Bulsara for their editorial help. I thank all my previous and present colleagues for their direct or indirect contributions to the work presented here. I am extremely thankful to Dr. Sourav Pal, Director, National Chemical Laboratory, Pune, India for writing a befitting Foreword for the book. Special thanks are due to Dr. Pradip, who has been a constant source of encouragement and a guide throughout the compilation of this book. I also thank K. Ananth Krishnan, Corporate Technology Officer, Tata Consultancy Services, Ltd., for his encouragement and support. Finally, my sincere thanks are due to my family—Kulbhushan, Kritika, and Kaustubh—who have silently supported me in this endeavor.

**Beena Rai**
*Pune, India*

# Editor

**Beena Rai** earned her PhD in 1995 from the National Chemical Laboratory, Pune, India. Currently, she is working as senior scientist at the Process Engineering Innovation Lab, Tata Research Development & Design Centre (TRDDC) (a division of Tata Consultancy Services Ltd.), Pune, India. At TRDDC, she leads the research program on the rational design of industrial performance chemicals using molecular modeling techniques. She, along with her coworkers, has successfully applied these techniques to the design and development of performance chemicals for various industrial applications. Her research interests include mineral processing, rational design, synthesis and testing of performance chemicals, colloids and interfacial science, ultrafine grinding, waste recycling, cements, nanofluids, drug delivery, and biosensors. She has several industrial projects to her credit and has authored 50 research publications, 7 patents, and several reports. She has been a visiting scientist at Laboratoire Environnment et Mineralogie, INPL-CNRS, Nancy, France.

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# Contents

# 1 Basic Concepts in Molecular Modeling

*Beena Rai*

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## 1.1 INTRODUCTION

With ever-changing needs for innovative materials and improved performance chemicals that exhibit unique functional properties, researchers and engineers have become increasingly involved in designing materials at the molecular level. The study of substances at the molecular level is not new, but using the knowledge about the interactions between atoms and molecules to design materials and chemicals with the desired functional properties is new. A computational chemistry approach leading to a rigorous systematic scientific approach toward the design and development of novel products seems to be the most logical option. In fact, with the high costs associated with experiments, computational chemistry definitely offers a relatively less expensive alternative for the purpose of design of materials. The popularity of using the computational approach to investigate structure–property relationships for both macroscopic and nanoscaled systems is reflected by the increasing number of computational chemistry software vendors at various chemical engineering conferences worldwide.

*Molecular modeling* can be defined as the application of computational techniques, grounded in theory, to predict or explain observable biological, physical, or chemical properties of molecules. The most accepted definition, as stated by Pensak (1989), is "Molecular modeling (MM) is anything that requires the use of a computer to paint, describe, or evaluate any aspect of the properties of the structure of a molecule." Most of the methods applied in MM can be broadly classified as computational methods based on energetic models of the systems and other concepts such as structure matching, chemical similarity, quantitative structure–activity relationships (QSAR), molecular shape compatibility, and materials informatics. Among the energetic models, techniques based on electronic structure calculation (molecular orbital, density functional, semiempirical methods, *ab initio*) can be differentiated from the empirical energy function (force field) methods. Force field methods do not treat electrons explicitly but model their effects in terms of analytical functions expressing energy contributions from bond stretching, angle bending, torsion and nonbonded interactions. As compared with the energy-based methods, the nonenergy-based methods are generally much more qualitative in nature, deriving benefits from some of the well-known concepts in statistics, mathematics, and computer science. In the following sections, a brief summary of these

molecular modeling concepts is presented. The objective here is to introduce the reader to different paradigms without exploring the theoretical details.

## 1.2 MOLECULAR MECHANICS OR ATOMISTIC SIMULATIONS

*Molecular mechanics* or *atomistic simulations,* consider the atomic composition of a molecule to be a collection of masses that interact with each other through harmonic forces. Because of this simplification, it is a relatively faster method applicable to large systems, as compared with quantum chemical methods. Furthermore, with the recent developments of accurate force field parameters for diverse kinds of molecules, it is possible to treat almost all types of molecular systems, including transition metals. Atomistic simulation provides a set of tools for predicting many useful functional properties of systems of industrial relevance. These properties include thermodynamic properties (e.g., equations of state, phase equilibria, and critical constants), mechanical properties (e.g., stress–strain relationships and elastic moduli), transport properties (e.g., viscosity, diffusion, and thermal conductivity), and morphological information (e.g., location and shape of binding sites on a biomolecule and crystal structure). This list is by no means exhaustive and continues to grow as algorithmic and computer hardware advances make it possible to access additional properties. Some of the most relevant textbooks of molecular simulation provide excellent reviews (Allen and Tildesley 1987; Frenkel and Smit 1996; Sadus 1999).

In the framework of molecular mechanics, the atoms in molecules are treated as rubber balls of different sizes (atom types) joined by springs of varying length (bonds). The potential energy of a system can be expressed as a sum of valence (or bond), cross-term, and nonbond interactions, which together are commonly referred to as force fields:

$$E_{\text{total}} = E_{\text{valence}} + E_{\text{crossterm}} + E_{\text{nonbond}} \tag{1.1}$$

### 1.2.1 Valence Interactions

The energy of *valence interactions* is generally accounted for by diagonal terms such as bond-stretching, angle-bending, dihedral-angle torsion, and inversion or out-of-plane interactions. Generally, the interatomic forces are assumed to be harmonic and the bond-stretch term is represented by a simple quadratic function:

$$E_{\text{str}} = \frac{1}{2} k_b (b - b_0)^2 \tag{1.2}$$

where $k_b$ is the stretching force constant, $b_0$ is the equilibrium bond length, and $b$ is the actual bond length. For angle bending, a simple harmonic expression is used:

$$E_{\text{bend}} = \frac{1}{2} k_\theta (\theta - \theta_0)^2 \tag{1.3}$$

where $k_\theta$ is the angle-bending force constant, $\theta_0$ is the equilibrium bond angle, and $\theta$ is the actual bond angle. A cosine expression is commonly used for the dihedral potential energy, as represented in Equation 1.4:

$$E_{\text{tors}} = \frac{1}{2} k_\varphi (1 + \cos(n\varphi - \varphi_0)) \tag{1.4}$$

where $k_\varphi$ is the torsional barrier, $\varphi$ is the actual torsion angle, $n$ is the periodicity, and $\varphi_0$ is the reference torsional angle.

### 1.2.2 Valence Cross-Terms

Some of the modern force fields also include *cross-terms* to account for bond or angle distortions caused by nearby atoms. These terms are required to accurately reproduce experimental vibrational frequencies of molecules. Cross-terms may include stretch–stretch, stretch–bend–stretch, bend–bend, torsion–stretch, torsion–bend–bend, bend–torsion–bend, stretch–torsion–stretch terms.

### 1.2.3 Nonbond Interactions

The energy of interactions between nonbonded atoms is accounted for by the following:

- van der Waals interactions between nonbonded atoms that are usually represented by Lennard–Jones potential:

$$E_{\text{vdw}} = \sum \frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}} \tag{1.5}$$

  where $A_{ij}$ and $B_{ij}$ are the repulsive and attractive term coefficients, respectively, and $r_{ij}$ is the distance between the two atoms.
- Electrostatic interactions are described by a coulomb term:

$$E_{\text{elec}} = \frac{1}{\varepsilon} \frac{Q_1 Q_2}{r_{ij}} \tag{1.6}$$

  where $Q_1$ and $Q_2$ are the charges on the interacting atoms, $\varepsilon$ is the dielectric constant, and $r_{ij}$ is the interatomic distance.

### 1.2.4 Constraints

*Constraints* that can be added to an energy expression include distance, angle, torsion, and inversion constraints. Constraints are useful for examining only part of a structure.

The equilibrium values of bond lengths, angles, torsional angles, and various constants associated with the functions used to describe the potential energy surface in a force field are referred to as *force field parameters*. These parameters are derived empirically from various experimental techniques or from more accurate quantum chemical calculations. The purpose of a force field is to describe the potential energy surface of entire classes of molecules with reasonable accuracy. Accordingly, there are some generic force fields offering broadest possible coverage of the periodic table, with necessarily lower accuracy (Casewit et al. 1992a, 1992b; Mayo et al. 1990; Rappe' et al. 1992, 1993). However, there are also some force fields that aim for high accuracy for a limited set of elements, thus enabling good predictions of many molecular properties (Sun 1998).

A typical force field contains all the necessary elements for calculations of energy and force for a given molecular system, and these elements include

- A list of force field types
- A list of partial charges
- Force field–typing rules
- Functional forms for the components of the energy expression
- Parameters for the function terms
- If applicable, rules for generating parameters that have not been explicitly defined
- In some cases, a way of assigning functional forms and parameters

In general, many experimental properties such as vibrational frequencies, sublimation energies, and crystal structures can be reproduced with a force field, even though it includes most of the