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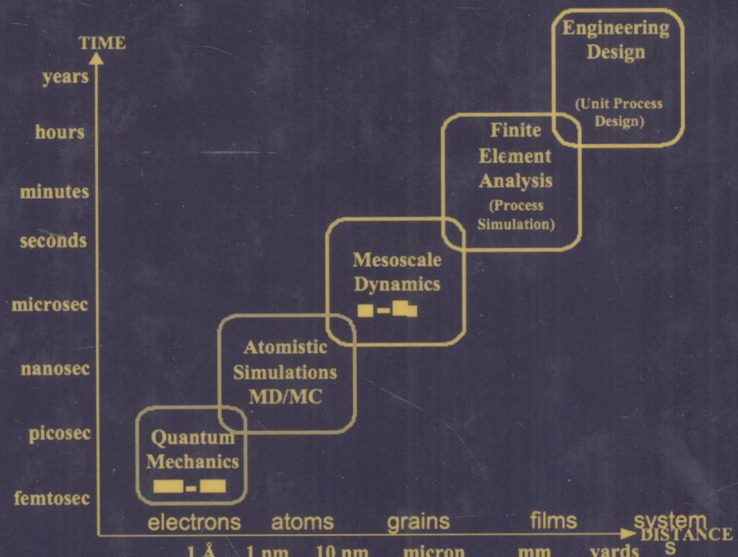
Multiscale Simulation Methods for Nanomaterials



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RICHARD B. ROSS
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PREFACE

This book is a result of a symposium, "Large Scale Molecular Dynamics, Nanoscale, and Mesoscale Modeling and Simulation: Bridging the Gap," which was held at the Fall 2005 National American Chemical Society Meeting in Washington, DC. The symposium featured 40 presentations in eight symposium sessions over four days. A broad range of cutting-edge large-scale time and/or length simulation papers were presented on topic areas spanning biological, inorganic, organic, polymer, nanomaterial, and hybrid materials. The chapters in this book are expanded contributions of 14 of the groups presenting material at the symposium.

This collection of studies does not exhaustively cover all the various methods—such an effort is impossible, owing to the breadth of methods and the ever-evolving approaches. However, it does present a breadth of useful methods that have been used to solve mesoscale problems. In addition, it presents a wide variety of examples where mesoscale phenomena are important. Most important, it presents strategies of tackling mesoscale problems.

It has been shown that mesoscale problems are each unique—it is difficult to develop a recipe and plug in parameters to solve them. Each problem has its own critical length and time scales—often, multiple sets of scales. Each problem may allow approximations in different regimes; and each problem demands different degrees of rigorousness: Thus, each problem requires different sets of strategies. This set of examples provides a broad set of strategies and suggests ways in which a researcher may design her or his simulations to attack the problem of interest while ensuring that critical information and knowledge is passed across the various scales.

Some of these contributions relate to tools that can help passage of knowledge across these scales or other tools that can help better approximations in these

processes. An example of one such strategy is presented in Chapter 5. The authors present an algorithm to fill in the detail when a coarse-grained representation of a molecular system is replaced by an atomistic representation. The methodology is demonstrated through implementation to liquid dodecane.

Another approach to passing knowledge across scales is described in Chapter 8. The authors describe the development of a coarse-grained methodology that incorporates current flow and Joule heating into a large-scale atomistic simulation. An example simulation is presented for an electrically "hot" and "cold" metal–metal contact that represents a contact in a microelectromechanical system device.

Another, easily visualized example is presented in Chapter 13. Although we understand decomposition reactions in simple gas-phase systems that can be described by elementary reactions, it is difficult to predict the thermal decomposition of nanostructures or of large molecules. Often, they break up into smaller aggregates and clusters, taking a number of different pathways. Certainly the characteristics of the individual atoms are important, but properties of the clusters also play an important role in their breakdown pathways. This study presents one way to incorporate these multiple scales in evolving our understanding of such processes.

Another example of critical mesoscale phenomena is presented in Chapter 6. What are the dynamics of proteins in a solvent (e.g., glycerol or trehalose)? The authors describe large-scale molecular dynamics simulations that probe and provide further insight into molecular mechanisms and the importance of dynamic coupling of the protein and solvent dynamics for lysozyme in pure glucose and trehalose. Understanding these dynamics on a pico- to nanosecond scale can help explicate longer-term phenomena such as denaturization.

Similarly, the effect of water and fatty acids on photosynthesis is explored in Chapter 2. The authors employ large-scale quantum mechanical and molecular mechanics methodologies to investigate self-assembly and the functioning of the photosynthetic process. They find that a critical role is played by the quantum effects associated with hydrogen bonds and van der Waals interactions resulting from increasing the number of water and fatty acid molecules. In both this case and Chapter 6, phenomena at atomistic scales and at scales including clusters of atoms (cells, aggregates) influence macroscopic properties of these materials and must be understood.

Examples of applications in nanomaterials can be seen in Chapter 3, whose authors discuss large-scale quantum electronic structure calculations coupled with a Green's function formulation for determining conductance as applied to carbon nanotubes doped with organic molecules. The studies are part of an effort to develop a framework for the design of nanotube-based electronic devices.

In an additional application to nanomaterials, multiscale and experimental studies on poly(*p*-phenylene vinylene) derivative nanostructures are discussed in Chapter 4, including the effects of high-level order and how these could also affect the creation of ordered domains in other polymer environments.

An industrial contribution applied to nanomaterials is described in Chapter 7, where multiscale methods to understand and simulate the effects of various solvents on silica nanoparticles with tethers of different chemistries are described. For these types of materials, important interactions to account for range from the molecular level between tethers and solvent molecules up to particle–particle interactions of entire tethered silica nanoparticles in a given solvent medium. Methodology developed for successive multiscaling from the molecular to the particle–particle interaction level is described and applied to several solvent and tether chemistry systems.

Continuing on a theme of method development and applications in Chapter 9, a fast variational fully analytical density functional method that has been developed for large molecules is covered in Chapter 9. The methodology has been applied to optimize the geometries of fullerines, fullerine-like cages, and nanotubes of more than 2000 atoms.

In an application to inorganic nanomaterials, the development of analytic potential energy functions and their use in for simulating aluminum nanoparticles are described in Chapter 10. Applications included simulations of liquid aluminum nanodroplets to study the size dependence of their densities, thermal expansivities, and particle shapes. Also investigated and reported are size-dependent effects on aluminum particle shape.

Multiscale modeling methodology development and application to biological-related reactions are described in Chapter 12. The authors describe a new quantum model based on a modified semiempirical AM1/d Hamiltonian that has been recently developed to model phosphoryl transfer reactions in solution, catalyzed by enzymes and ribozymes. The model has been integrated with a recently developed linear-scaling Ewald method to calculate long-range electrostatic interactions efficiently in combined quantum mechanical/molecular mechanical simulations. Applied studies to predict hydrolysis rates of dimethyl phosphate and ethylene phosphate in solution are discussed.

Several large-scale simulation applications are described in Chapter 11. Large-scale simulations employing transferable force fields are discussed for applications including retention in reversed-phase liquid chromatography, solubility of helium in *n*-hexadecane, entrainer effects on solubility in supercritical carbon dioxide, and segregation due to size effects for anions at aqueous vapor–liquid interfaces. In addition, first-principles Monte Carlo simulations are reported for water vapor–liquid coexistence curves.

In Chapter 14 current mathematical and molecular thermodynamical modeling techniques to predict thermodynamically stable surfactant mesoscale structures in solution are reviewed. The author then discusses the application of simulation-based approaches, dissipative particle dynamics in particular, which provide surfactant structure information and in addition provide predictions of dynamic behavior, nonequilibrium structures, and modeling of more concentrated systems, including mixtures of surfactants. Dissipative particle dynamics simulations for several surfactant systems, including ethoxylate, sodium dodecyl sulfate, and mixtures of the two, are then discussed.

Collectively, the fourteen chapters in this volume provide a snapshot of the broad range of mesoscale methodologies currently being developed and applied to a wide range of applications. The book should be very useful to current modeling experts seeking a more detailed understanding of current major mesoscale modeling approaches as well as to scientists and engineers new to the field who are seeking a rapid understanding of the current state-of-the-art approaches, their applications, and their scope: which types of material properties and structures are currently accessible via modeling and simulation and to what degree of accuracy.

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SANAT MOHANTY

CONTENTS

1

OVERVIEW OF MULTISCALE SIMULATION METHODS FOR MATERIALS

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Modeling has increasingly become a tool for better proactive design, besides being a method to explain phenomena. In these functions it must be validated with experimental observations before its results can be applied with confidence. Modeling at the continuum scale is well understood, and the accuracy, precision, and robustness of results using continuum methods have been analyzed. Numerous methods, including finite-element analysis, finite-difference methods, and boundary element methods, are now used routinely in a variety of areas, including flow visualization, design of materials and structures, and in industry for automotive design, construction and structure applications, and plant design.

Modeling at the atomistic scale has also begun to be accepted as part of routine research protocol. Results from such methods are now accepted with a reasonable understanding of their accuracy and robustness. Quantum mechanical calculations are now used to understand the properties of semiconductor materials. Atomistic calculations have been used to better understand phase behavior of components and mixtures for the chemical industry. Numerous process design tools used routinely in the chemical industry include information based on atomistic calculations. Increasingly, however, design of materials comes up against phenomena that are in the mesoscale: too large for atomistic simulations and too small for continuum analysis. This is the scale where one cannot use continuum-scale assumptions, yet the system is often larger than can be modeled tractably with atomistic methodologies. How do we study systems that are made of clusters of

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thousands of molecules that interact in specific ways? How do we take results from atomistic simulations and correlate them with parameters we need for continuum studies?

1. MESOSCALE MODELING

Examples of mesoscale phenomena include engineering of molecular clusters or of functionalized nanoparticles, crystals, and liquid-crystalline structures [such as clathrates[1] and micelles] that are used as templates for porous membranes,[2] materials with specific enzymatic,[3] or catalytic properties,[4] control of flow behavior,[5] nanocontainers with controlled release,[6] or materials with specific thermal, electromagnetic,[7] or mechanical properties.[8] Since a number of these materials are designed by self-assembly of atoms or molecules to form nano-sized clusters, modeling becomes a critical tool in engineering such materials. Modeling is also used to understand conditions to optimize processes to functionalize or engineer aspects of these structures, such as size of cluster, surface properties, or charges. Figure 1 shows some examples of nanoscale ordering and self-assemblies. Modeling mesoscale phenomena in materials design has thus become increasingly significant as mesoscale engineering of materials becomes critical in developing superior materials.

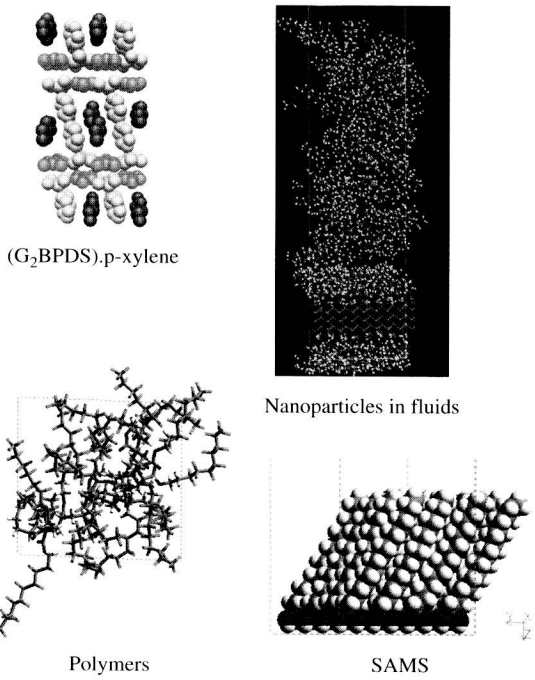

Figure 1 Mesoscale phenomena. (*See insert for color representation figure.*)

From a modeling perspective, there are a number of aspects to be addressed. Modeling helps to translate macroscopic observations based on nano- or mesoscale phenomena. Judicious use of simulations helps demonstrate why certain behavior is seen which is critical knowledge for engineering such behavior. For example, how can one predict the behavior of silicon nanoparticles whose surfaces have been modified with specific functional groups when they are in a polymer matrix;[9] or alternatively, how can one engineer the surfaces of nanoparticles so that polymer–particle composites may manifest a certain set of desired properties? Similarly, what types of structures do micelles made up of specific amphiphiles form, and how do they behave at different concentrations; or alternatively, what additives and amphiphiles could one use to engineer and design certain rheological properties in fluids, specific surface properties, or specific micellar structures?[10] How do molecules cluster in various environments,[11] and how does that affect their thermodynamic properties and mobility? Similar questions have been addressed for chromonic systems.[12] Another area with significant modeling effort is that of biomolecules.[13] Simulations have been used to understand the binding mechanisms of biomolecules on surfaces[14] and with each other, enzymatic pathways, mobility of molecules, and design of encapsulants—all with the aim of engineering drugs for specific action as well as methods of targeted delivery. Nano- and mesoscale models can be used not only to look at the equilibrium behavior of materials but also to study the mobility of particles and the rupture behavior of adhesives (essentially nonequilibrium phenomena).

Modeling mesosystems is difficult since the phenomena of interest are neither atomistic (so that solutions can be grasped by understanding the behavior of a few to hundreds of atoms or molecules) nor macroscopic (so that continuum properties of the material can be assumed without losing events occurring in the smaller-scale regime). Modeling phenomena that span different orders of length and time requires the use of multiscale models[15] (schematic in Figure 2). Yet mesoscale phenomena often define macromolecular properties (Figure 3). It is necessary to understand the mechanisms of the phenomena at these length scales

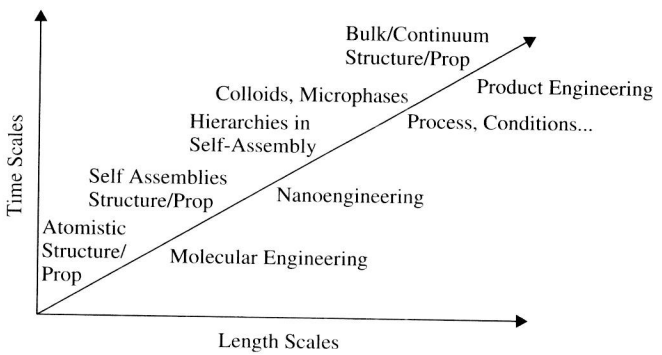

Figure 2 Modeling methods for various length and time scales.