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Molecular Modeling and  
Theory in Chemical  
Engineering

*Edited by*

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## PREFACE

The ultimate objective of the profession of chemical engineering is the manufacture of chemicals and products that improve societal and economic conditions. Achieving this goal often requires that chemical engineers understand and exploit many physical, chemical, and biological phenomena. In recent years, chemical engineers have increasingly been involved in the design, synthesis, and manufacture of high-value-added products and chemicals. These technologies often demand that product properties and processing methods be controlled with precision. Similar issues arise in research aimed toward developing more efficient processing of petroleum products and developing catalysts for synthesis of alternative fuels. In some cases, product properties must be precisely controlled at the macroscopic level, and in other cases, the properties that we seek are on much smaller scales (nanometers to micrometers). One way to confront this challenge with both classes of systems is to learn how to manipulate system characteristics at the molecular and/or mesoscopic scales so that we obtain the desired properties. Learning how molecular constitution and mesoscopic characteristics influence the properties of a system of interacting components can only be addressed by synergistic experimental and theoretical research. The pertinent experimental and theoretical methods must be able to interrogate systems on a wide range of length and time scales. Chemical engineers are playing an important role in the development and application of a number of such experimental and theoretical tools. These research efforts are taking steps toward developing the knowledge base required to relate structures to properties for both synthetic and biological systems. This volume of *Advances in Chemical Engineering* focuses on theoretical and computational efforts at the frontiers of a number of different application areas that benefit from such research.

The bedrocks of the theoretical and computational methods that allow study of relationships between molecular and mesoscopic scale events and system properties are quantum and statistical mechanics. Thus, this volume comprises chapters that describe the development and application of quantum and statistical mechanical methods to various problems of technological relevance. The application areas include catalysis and reaction engineering, processing of materials for microelectronic applications, polymer science and engineering, fluid phase equilibrium, and combinatorial methods for materials discovery. The theoretical methods that are discussed in the various

chapters include electronic structure calculations, *ab initio* molecular dynamics simulations, Monte-Carlo simulation methods, field-theoretic methods, and various theories of the liquid state. The diversity of application areas represented in this volume reflects the fact that methods based on quantum and statistical mechanics now play an important role in research that is relevant to a variety of technologies. The diversity of methods discussed in this volume reflects the fact that for complex problems no single method can serve as a panacea. In other words, studying properties influenced by phenomena at different length and time scales requires a hierarchy of methods.

This collection of articles is not a comprehensive compendium of the interesting work being done to study complex systems using quantum and statistical mechanical methods. It is hoped, however, that this representative sampling of work being carried out by chemical engineers in this broad area will provide the beginning graduate student and the experienced practitioner with a sense of the current state of the art and the challenges that need to be confronted in the future. My personal opinion is that future volumes dedicated to this broad topic will witness a greater emphasis on nonequilibrium phenomena, the coupling of quantum and statistical mechanical approaches, and more applications focused on biomedical problems.

My fellow editors of *Advances in Chemical Engineering*, the staff at Academic Press, and I thank the authors for taking time out of their busy schedules to contribute to this volume. The effort involved in writing good review articles is a selfless service to the profession and is truly appreciated. A personal note of thanks is also extended to the authors for their patience during the review and production process.

ARUP K. CHAKRABORTY

# CONTENTS

CONTRIBUTORS . . . . .	xi
PREFACE . . . . .	xiii

## Hyperparallel Tempering Monte Carlo and Its Applications

QILIANG YAN AND JUAN J. DE PABLO

I. Introduction . . . . .	1
II. Methodology . . . . .	3
III. Applications . . . . .	5
A. Lennard-Jones Fluid . . . . .	5
B. Primitive Model Electrolyte Solutions . . . . .	7
C. Homopolymer Solutions and Blends . . . . .	11
D. Semiflexible Polymers and Their Blends with Flexible Polymers . . . . .	15
E. Block Copolymers and Random Copolymers . . . . .	17
IV. Discussion and Conclusion . . . . .	18
References . . . . .	20

## Theory of Supercooled Liquids and Glasses: Energy Landscape and Statistical Geometry Perspectives

PABLO G. DEBENEDETTI, FRANK H. STILLINGER, THOMAS M. TRUSKETT,  
AND CATHERINE P. LEWIS

I. Introduction . . . . .	22
A. Phenomenology of Vitrification by Supercooling . . . . .	23
B. Open Questions . . . . .	29
C. Structure of This Article . . . . .	32
II. The Energy Landscape . . . . .	33
III. Statistical Geometry and Structure . . . . .	39
A. Void Geometry and Connections to the Energy Landscape . . . . .	40
B. Quantifying Molecular Disorder in Equilibrium and Glassy Systems . . . . .	45
IV. Landscape Dynamics and Relaxation Phenomena . . . . .	50
V. Thermodynamics . . . . .	60



VI. Conclusion . . . . .	70
References . . . . .	72

## A Statistical Mechanical Approach to Combinatorial Chemistry

MICHAEL W. DEEM

I. Introduction . . . . .	81
II. Materials Discovery . . . . .	83
A. The Space of Variables . . . . .	84
B. Library Design and Redesign . . . . .	85
C. Searching the Variable Space by Monte Carlo . . . . .	87
D. The Simplex of Allowed Compositions . . . . .	89
E. Significance of Sampling . . . . .	91
F. The Random Phase Volume Model . . . . .	92
G. Several Monte Carlo Protocols . . . . .	94
H. Effectiveness of the Monte Carlo Strategies . . . . .	95
I. Aspects of Further Development . . . . .	96
III. Protein Molecular Evolution . . . . .	97
A. What Is Protein Molecular Evolution? . . . . .	98
B. Background on Experimental Molecular Evolution . . . . .	100
C. The Generalized NK Model . . . . .	102
D. Experimental Conditions and Constraints . . . . .	104
E. Several Hierarchical Evolution Protocols . . . . .	105
F. Possible Experimental Implementations . . . . .	109
G. Life Has Evolved to Evolve . . . . .	111
H. Natural Analogs of These Protocols . . . . .	113
I. Concluding Remarks on Molecular Evolution . . . . .	115
IV. Summary . . . . .	117
References . . . . .	118

## Fluctuation Effects in Microemulsion Reaction Media

VENKAT GANESAN AND GLENN H. FREDRICKSON

I. Introduction . . . . .	123
II. Reactions in the Bicontinuous Phase . . . . .	127
A. Diffusion Equations . . . . .	127
B. Objectives . . . . .	128
C. Mean-Field Analysis . . . . .	129
D. Renormalization Group Theory . . . . .	132
E. Discussion . . . . .	134
F. Summary . . . . .	135
III. Reactions in the Droplet Phase . . . . .	136
A. Outline . . . . .	136

B. Fluctuations of the Droplet Phase . . . . .	137
C. Diffusion Equation and Perturbation Expansion . . . . .	139
D. Consideration of Temporal Regimes . . . . .	141
E. Intermediate Times . . . . .	143
F. Short Time Regime . . . . .	143
G. Effect of the Péclet Number . . . . .	144
H. Discussion . . . . .	145
I. Other Effects . . . . .	146
J. Summary . . . . .	146
References . . . . .	147

## Molecular Dynamics Simulations of Ion–Surface Interactions with Applications to Plasma Processing

DAVID B. GRAVES AND CAMERON F. ABRAMS

I. Introduction . . . . .	149
A. Plasma Processing . . . . .	149
B. Length Scales in Plasma Processing . . . . .	152
C. The Nature of Plasma–Surface Interactions . . . . .	153
D. Ion–Surface Interactions in Plasma Processing . . . . .	155
II. Use of Molecular Dynamics to Study Ion–Surface Interactions . . . . .	156
A. Simulation Procedure . . . . .	156
III. Mechanisms of Ion-Assisted Etching . . . . .	161
A. Experimental Studies of Ion-Assisted Etching Mechanisms . . . . .	161
B. Molecular Dynamics Studies of Ion-Assisted Etching Mechanisms . . . . .	164
C. Ion–Surface Scattering Dynamics . . . . .	172
D. Ion–Surface Interactions with both Deposition and Etching: $\text{CF}_3^+/\text{Si}$ . . . . .	180
IV. Concluding Remarks . . . . .	198
References . . . . .	199

## Characterization of Porous Materials Using Molecular Theory and Simulation

CHRISTIAN M. LASTOSKIE AND KEITH E. GUBBINS

I. Introduction . . . . .	203
II. Disordered Structure Models . . . . .	206
A. Porous Glasses . . . . .	206
B. Microporous Carbons . . . . .	209
C. Xerogels . . . . .	213
D. Templated Porous Materials . . . . .	216
III. Simple Geometric Pore Structure Models . . . . .	218
A. Molecular Simulation Adsorption Models . . . . .	222
B. Density Functional Theory Adsorption Models . . . . .	225

C. Semiempirical Adsorption Models . . . . .	231
D. Classical Adsorption Models . . . . .	239
IV. Conclusions . . . . .	244
References . . . . .	246

## Modeling of Radical–Surface Interactions in the Plasma-Enhanced Chemical Vapor Deposition of Silicon Thin Films

DIMITRIOS MAROUDAS

I. Introduction . . . . .	252
II. Computational Methodology . . . . .	254
A. The Hierarchical Approach . . . . .	255
B. Density-Functional Theory . . . . .	257
C. Empirical Description of Interatomic Interactions . . . . .	258
D. Methods of Surface Preparation . . . . .	260
E. Methods of Surface Characterization and Reaction Analysis . . . . .	263
III. Surface Chemical Reactivity with $\text{SiH}_x$ Radicals . . . . .	264
A. Structure of Crystalline and Amorphous Silicon Surfaces . . . . .	265
B. Interactions of $\text{SiH}_x$ Radicals with Crystalline Silicon Surfaces . . . . .	266
C. Interactions of $\text{SiH}_x$ Radicals with Surfaces of Amorphous Silicon Films . . . . .	270
IV. Plasma–Surface Interactions during Silicon Film Growth . . . . .	273
A. Surface Chemical Reactions during Film Growth . . . . .	274
B. Mechanism of Amorphous Silicon Film Growth . . . . .	280
C. Surface Evolution and Film Structural Characterization . . . . .	281
D. Film Surface Composition and Comparison with Experiment . . . . .	283
E. The Role of the Dominant Deposition Precursor . . . . .	284
F. The Role of Chemically Reactive Minority Species . . . . .	286
V. Summary . . . . .	290
References . . . . .	291

## Nanostructure Formation and Phase Separation in Surfactant Solutions

SANAT K. KUMAR, M. ANTONIO FLORIANO,  
AND ATHANASSIOS Z. PANAGIOTOPOULOS

I. Introduction . . . . .	298
II. Simulation Details . . . . .	300
A. Models and Methods . . . . .	300
B. Some Methodological Issues . . . . .	301
III. Results . . . . .	302
A. Homopolymer Chains . . . . .	302
B. Role of Different Interaction Sets . . . . .	304
IV. Discussion . . . . .	308

V. Conclusions . . . . .	310
References . . . . .	310

### Some Chemical Engineering Applications of Quantum Chemical Calculations

STANLEY I. SANDLER, AMADEU K. SUM, AND SHIANG-TAI LIN

I. Introduction . . . . .	314
II. <i>Ab Initio</i> Interaction Potentials and Molecular Simulations . . . . .	315
III. Infinite Dilution Activity Coefficients and Partition Coefficients from Quantum Mechanical Continuum Solvation Models . . . . .	325
IV. Use of Computational Quantum Mechanics to Improve Thermodynamic Property Predictions from Group Contribution Methods . . . . .	335
V. Use of <i>ab Initio</i> Energy Calculations for Phase Equilibrium Predictions . . . . .	341
VI. Conclusions . . . . .	347
References . . . . .	348

### Car–Parrinello Methods in Chemical Engineering: Their Scope and Potential

BERNHARDT L. TROUT

I. Introduction . . . . .	353
II. Objectives and Description of This Article . . . . .	355
III. Objectives of Car–Parrinello Methods and Classes of Problems to Which They Are Best Applicable . . . . .	356
IV. Methodology . . . . .	357
A. Classical Molecular Dynamics . . . . .	357
B. Density-Functional Theory . . . . .	358
C. Choice of Model and Solution of the Equations Using Plane-Wave Basis Sets and the Pseudopotential Method . . . . .	362
D. Car–Parrinello Molecular Dynamics . . . . .	368
V. Applications . . . . .	370
A. Gas-Phase Processes . . . . .	372
B. Processes in Bulk Materials . . . . .	376
C. Properties of Liquids, Solvation, and Reactions in Liquids . . . . .	378
D. Heterogeneous Reactions and Processes on Surfaces . . . . .	382
E. Phase Transitions . . . . .	386
F. Processes in Biological Systems . . . . .	389
VI. Advances in Methodology . . . . .	392
VII. Concluding Remarks . . . . .	393
Appendix A: Further Reading . . . . .	393
Appendix B: Codes with Capabilities to Perform Car–Parrinello Molecular Dynamics . . . . .	394
References . . . . .	394

## Theory of Zeolite Catalysis

R. A. VAN SANTEN AND X. ROZANSKA

I. Introduction . . . . .	400
II. The Rate of a Catalytic Reaction . . . . .	401
III. Zeolites as Solid Acid Catalysts . . . . .	403
IV. Theoretical Approaches Applied to Zeolite Catalysis . . . . .	407
A. Simulation of Alkane Adsorption and Diffusion . . . . .	407
B. Hydrocarbon Activation by Zeolitic Protons . . . . .	414
C. Kinetics . . . . .	427
V. Concluding Remarks . . . . .	432
References . . . . .	433

## Morphology, Fluctuation, Metastability, and Kinetics in Ordered Block Copolymers

ZHEN-GANG WANG

I. Introduction . . . . .	439
II. Anisotropic Fluctuations in Ordered Phases . . . . .	441
III. Kinetic Pathways of Order–Order and Order–Disorder Transitions . . . . .	445
IV. The Nature and Stability of Some Nonclassical Phases . . . . .	450
V. Long-Wavelength Fluctuations and Instabilities . . . . .	452
VI. Morphology and Metastability in ABC Triblock Copolymers . . . . .	456
VII. Conclusions . . . . .	460
References . . . . .	460
INDEX . . . . .	465
CONTENTS OF VOLUMES IN THIS SERIAL . . . . .	487

# HYPERPARALLEL TEMPERING MONTE CARLO AND ITS APPLICATIONS

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I. Introduction	1
II. Methodology	3
III. Applications	5
A. Lennard–Jones Fluid	5
B. Primitive Model Electrolyte Solutions	7
C. Homopolymer Solutions and Blends	11
D. Semiflexible Polymers and Their Blends with Flexible Polymers	15
E. Block Copolymers and Random Copolymers	17
IV. Discussion and Conclusion	18
References	20

*This review discusses a newly proposed class of tempering Monte Carlo methods and their application to the study of complex fluids. The methods are based on a combination of the expanded grand canonical ensemble formalism (or simple tempering) and the multi-dimensional parallel tempering technique. We first introduce the method in the framework of a general ensemble. We then discuss a few implementations for specific systems, including primitive models of electrolytes, vapor–liquid and liquid–liquid phase behavior for homopolymers, copolymers, and blends of flexible and semiflexible polymers. © 2001 Academic Press.*

## I. Introduction

Complex fluids such as electrolyte solutions, polymer solutions, and biological macromolecule solutions pose significant obstacles to molecular

simulation, particularly at low temperatures and elevated densities. Conventional molecular dynamics methods are unable to generate trajectories that are long enough to cover the inherently long characteristic relaxation times that characterize polymeric fluids, and naïve Monte Carlo techniques are unable to sample their configuration space efficiently. All of these systems, however, are of engineering importance. Unfortunately, these are also systems for which our theoretical understanding is far from complete. Predictive models for the equilibrium thermodynamic and structural properties of such fluids are required to design chemical and separation processes; to formulate new models, it would be useful to have access to the results of simulations.

When only the equilibrium properties of a complex fluid are of interest, it is possible to devise “nonphysical” simulation techniques that are sometimes able to circumvent the sampling problems that are usually associated with complex fluids. Examples of such techniques include configurational bias Monte Carlo methods, multicanonical ensemble simulations, J-walking,  $1/k$  sampling, simulated tempering, and parallel tempering [1–14]. In this review we discuss some of our recent experiences with parallel tempering. This method has a number of useful features, which make it attractive for the study of complex fluids. Interestingly, while the idea of parallel tempering is not new [8, 9], its application to the study of many-body fluids has been limited. We therefore present results for a variety of systems, and in each case we try to emphasize the advantages provided by tempering over more conventional techniques.

The basic idea of parallel tempering consists of simulating several copies of a system in parallel; each copy or “replica” is constructed to represent the same system in a different thermodynamic state. Conventional Monte Carlo methods are employed to sample the configuration of each distinct replica under the relevant thermodynamic conditions. In addition to the trial moves involved in such methods, however, attempts are made to interchange the configurations corresponding to any two replicas of the system. Such trial “swaps” are accepted according to probability criteria that ensure the appropriate ensembles are sampled. The benefit of swapping is that if one of the replicas relaxes much faster than the others (e.g., a replica at a high temperature), the fast-evolving configurations in that replica can be artificially “propagated” to other boxes via exchanges, thereby effectively accelerating the relaxation of all other copies of the system.

Depending on the system and the ensemble of choice, the thermodynamic state of a replica can be specified through the number of molecules of each species, the volume, the temperature, the pressure, and the chemical potential. Our experience (and that of others [15, 16]) suggests that, from the point of view of improving sampling, open ensembles offer a number

of advantages over closed systems. In open ensembles, molecules can be completely removed from a system and reinserted at a later point in completely different positions and configurations, thereby circumventing diffusional bottlenecks. Furthermore, for difficult systems, such as polymers, deletions, and insertions can be facilitated significantly by resorting to expanded ensemble methods [17, 18]. Most of the implementations of hyperparallel tempering Monte Carlo (HPTMC) reported here are carried out in open ensembles, and whenever possible we also capitalize on the benefits provided by configurational bias and expanded ensemble techniques. As discussed in this review, it turns out that in some cases HPTMC can provide striking efficiency increases over traditional methods for the simulation of complex fluids with minimal changes to existing simulation algorithms and codes.

## II. Methodology

Formally, we consider a generalized ensemble whose partition function is given by

$$Z(\mathbf{f}) = \sum_x \Omega(x)w(x, \mathbf{f}), \quad (1)$$

where  $\mathbf{f}$  denotes a set of specified generalized forces or potentials, which determine the thermodynamic state of the system. In Eq. (1),  $x$  is used to denote a microscopic state or an instantaneous configuration of the system,  $\Omega(x)$  is the density of states, and  $w(x, \mathbf{f})$  is an arbitrary weighting function for state  $x$ , at the given set of generalized potentials  $\mathbf{f}$ . The grand canonical ensemble is recovered by writing

$$\mathbf{f} = \{T, \mu\}, \quad w(x, \mathbf{f}) = \exp(-\beta U(x) + N(x)\beta\mu), \quad (2)$$

where  $\beta = 1/k_B T$ ,  $T$  is the temperature,  $k_B$  is Boltzmann's constant,  $\mu$  is the specified chemical potential,  $U(x)$  is the potential energy corresponding to configuration  $x$ , and  $N(x)$  is the number of particles in configuration  $x$ .

Hyperparallel tempering simulations are conducted on a composite ensemble, which consists of  $M$  noninteracting replicas of the above-mentioned generalized ensemble. Each replica can have a different set of generalized potentials. The complete state of the composite ensemble is specified through  $\mathbf{x} = (x_1, x_2, \dots, x_M)^T$ , where  $x_i$  denotes the state of the  $i$ th replica. The partition function  $Z_c$  of the composite ensemble is given by

$$Z_c = (\mathbf{f}_1, \mathbf{f}_2, \dots, \mathbf{f}_M) = \prod_{i=1}^M Z(\mathbf{f}_i). \quad (3)$$



The unnormalized probability density of the complete state  $\mathbf{x}$  is proportional to

$$p(\mathbf{x}) \prod_{i=1}^M \Omega(x_i) w(x_i, \mathbf{f}_i). \quad (4)$$

In expanded grand canonical ensemble simulations [18] (also called simple tempering simulations), the system can jump along a set of expanded states, in addition to the conventional  $(N, U)$  phase-space variables of a grand canonical ensemble. For the particular implementation to polymeric fluids, chain molecules are inserted or removed gradually, i.e., several segments at a time. In other words, a simulation box contains several “regular” chain molecules and a tagged chain, whose length  $n_y$  fluctuates during the simulation;  $n_y$  therefore serves as the expanded state variable. A preweighting factor  $\exp(\Psi(y))$  is assigned to each expanded state  $y$ . In the language of Eq. (1), the weighting function for the expanded grand canonical ensemble is

$$\mathbf{f} = \{T, \mu, \Psi\}, \quad w(x, \mathbf{f}) = \exp[-\beta U(x) + N(x)\beta\mu + \Psi(y)]. \quad (5)$$

If we assume that the segmental chemical potential is independent of chain length, we can set the preweighting function to be

$$\Psi(y) = \frac{n_y}{n} \beta \mu^r = \frac{n_y}{n} \left[ \beta \mu - \ln \left( \frac{N_y}{V} \right) \right], \quad (6)$$

where  $N_y = N + n_y/n$ ;  $n_y$  is the length of the tagged chain and  $n$  is the length of a full polymer chain. In Eq. (6),  $\mu^r$  denotes the residual chemical potential of a polymer chain.

Figure 1 illustrates schematically the implementation of HPTMC. Each box in the figure represents a replica of the simulation system; each replica has a different value of  $T$ ,  $\mu$ , and  $n_y$ . To implement a hyperparallel tempering algorithm, three types of trial moves are necessary. (1) Conventional canonical Monte Carlo moves are used to sample configurations in each replica of the system. These moves include translational or rotational displacements and configurational-bias or reptation moves for polymers. (2) Trial shrinking or growing moves are proposed to change the length of a tagged chain in each replica, thereby implementing the underlying expanded grand canonical formalism. (3) Configuration swaps or exchanges are attempted between any two randomly chosen replicas. The arrows in Fig. 1 correspond to different types of moves.

The acceptance criteria corresponding to trials moves of type 1 or 2 are fairly standard and have been reported in a number of texts and articles. We therefore limit the remainder of this section to a brief discussion of the acceptance criteria for trial swap moves. Consider a swap between two replicas,  $i$  and  $j$ . After the swap, the new state of replica  $i$  will be the current