

## Nonequilibrium Molecular Dynamics

### Theory, Algorithms and Applications

This book describes the growing field of nonequilibrium molecular dynamics (NEMD), written in a form that will appeal to the general practitioner in molecular simulation. It introduces the theory fundamental to the field, namely nonequilibrium statistical mechanics and nonequilibrium thermodynamics, provides state-of-the-art algorithms and advice for designing reliable NEMD code, and examines applications for both atomic and molecular fluids. It discusses homogenous and inhomogeneous flows and pays considerable attention to studies of highly confined fluids. In addition to statistical mechanics and thermodynamics, the book covers such themes as temperature, thermodynamic fluxes and their computation, the theory and algorithms for homogeneous shear and elongational flows, response theory and its applications, heat and mass transport algorithms, applications in molecular rheology, highly confined fluids (nanofluidics), the phenomenon of slip and generalised hydrodynamics.

**Billy D. Todd** undertook his bachelor and doctoral studies in physics at the University of Western Australia and Murdoch University in Perth, Australia. He then completed postdoctoral appointments at the University of Cambridge and the Australian National University, before moving to CSIRO in Melbourne in 1996. In 1999 he took up an academic appointment at Swinburne University of Technology, where he is currently Professor and Chair of the Department of Mathematics. His research focus is on statistical mechanics, nonequilibrium molecular dynamics and computational nanofluidics. He is a Fellow of the Australian Institute of Physics and a former President of the Australian Society of Rheology.

**Peter J. Daivis** holds Bachelor and Master's degrees in Applied Physics from Royal Melbourne Institute of Technology, a Graduate Diploma in Applied Colloid Science from Swinburne University of Technology, and a PhD from Massey University. After completing his PhD he worked on computational and theoretical investigations of transport processes at the Australian National University. He joined Royal Melbourne Institute of Technology in 1995 as a lecturer and has held the position of Professor since 2011. His research interests include applications of thermodynamics, statistical mechanics and computational physics to nonequilibrium phenomena. He is a member of the Australian Institute of Physics, the Institute of Physics UK and is currently President of the Australian Society of Rheology.

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Theory, Algorithms and Applications

BILLY D. TODD

Swinburne University of Technology

PETER J. DAIVIS

Royal Melbourne Institute of Technology



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# Contents

	<i>page</i>
<i>Preface</i>	<i>ix</i>
<b>1 Introduction</b>	<b>1</b>
<b>2 Nonequilibrium Thermodynamics and Continuum Mechanics</b>	<b>5</b>
2.1 Thermodynamics	5
2.2 Continuum Mechanics	7
2.3 Nonequilibrium Thermodynamics	9
2.4 Multicomponent Fluids and Coupled Transport Processes	19
2.5 Spin Angular Momentum	25
<b>3 Statistical Mechanical Foundations</b>	<b>31</b>
3.1 Fundamentals of Classical Mechanics	31
3.2 The Liouville Equation	34
3.3 Time Evolution	35
3.4 Response Theory	38
3.5 Green–Kubo Methods for Linear Transport	51
3.6 Fluctuation Theorems	54
<b>4 Temperature and Thermodynamic Fluxes</b>	<b>59</b>
4.1 Temperature	59
4.2 Pressure Tensor and Heat Flux Vector	62
4.3 Method of Planes Techniques for Inhomogeneous Fluids	76
4.4 Volume Averaged Form of the Local Pressure Tensor	91
4.5 Inclusion of Electrostatic Forces	92
<b>5 Homogeneous Flows for Atomic Fluids: Theory</b>	<b>104</b>
5.1 The SLLOD Equations of Motion	104
5.2 Dynamical Maps and the Relationship to Periodic Boundary Conditions	129

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5.3	Thermostats	136
5.4	Further Considerations of the SLLOD Equations of Motion	147
<b>6</b>	<b>Homogeneous Flows for Atomic Fluids: Applications</b>	<b>150</b>
6.1	Time-independent Flow	150
6.2	General Homogeneous Flows	163
6.3	Mixed Shear and Planar Elongational Flows	174
6.4	Thermodynamic, Rheological and Structural Results for Simple Fluids under Shear and Extensional Flows	177
6.5	TTCF Algorithms for Shear and Elongational Flows	190
<b>7</b>	<b>Homogeneous Heat and Mass Transport</b>	<b>203</b>
7.1	Single Component Heat Transport	204
7.2	Diffusion	210
7.3	Multicomponent Heat Transport	214
7.4	Evaluation of Thermodynamic Quantities	219
7.5	Heat Transport for Molecular Fluids	223
<b>8</b>	<b>Homogeneous Flows for Molecular Fluids</b>	<b>229</b>
8.1	Explicit and Coarse-grained Molecular Models	229
8.2	Molecular Representation of the Pressure Tensor	239
8.3	Molecular SLLOD	243
8.4	Momentum and Internal Energy Balance in the Presence of a Homogeneous Thermostat	245
8.5	Molecular Thermostats	247
8.6	Molecular SLLOD Algorithms for Shear Flow	251
8.7	Molecular SLLOD Algorithms for Elongational Flow	253
8.8	Results for Molecular Fluids	254
<b>9</b>	<b>Inhomogeneous Flows for Atomic Fluids</b>	<b>266</b>
9.1	Sinusoidal Transverse Field (STF) Method	267
9.2	Poiseuille Flow	277
9.3	Couette Flow	289
<b>10</b>	<b>Confined Molecular Fluids</b>	<b>294</b>
10.1	Molecular Fluids	294
10.2	Spin Coupling, Flow Reduction and Manipulation on the Nanoscale	302
10.3	Binary Mixtures	303

<b>11</b>	<b>Generalised Hydrodynamics and Slip</b>	306
	11.1 Generalised Hydrodynamics	306
	11.2 Predicting Slip	325
	<i>Bibliography</i>	335
	<i>Index</i>	355

## Preface

In 2007 we wrote a review, entitled ‘Homogeneous nonequilibrium molecular dynamics simulations of viscous flow: techniques and applications’ [1]. Our aim then was to write a comprehensive review of the current state of the field. Though limited only to homogeneous fluids, it was clear to us then that such a review was necessary because of the growing popularity of nonequilibrium molecular dynamics (NEMD) as a powerful tool to study the transport of molecular fluids far from equilibrium. While NEMD is powerful, it is also subtle and it is often quite easy to make fundamental errors in the design and implementation of algorithms and, hence, generate results that are not what the researcher actually intends.

There are several books that deal with NEMD methods, but only the one by Evans and Morriss is entirely devoted to the field [2]. However, this influential book concentrates more on the theoretical foundations of the field, rather than providing broad algorithmic guidance for those interested in writing NEMD programs. Furthermore, the mathematical depth of the treatment presents the subject in a way that may not be readily absorbed or implemented by graduate students or nonspecialist scientists or engineers who wish to make use of reliable NEMD algorithms in their research.

It is with this point central in our thoughts that we felt it timely to write a book that could appeal to the general practitioner in the broader field of molecular simulation: not only one which builds upon previous knowledge, but also one that provides a more general overview of the field – its motivations and theoretical foundations – introduces state-of-the-art algorithms, and provides guidance on how to design reliable NEMD code for both atomic and molecular fluids. Furthermore, this book now addresses the shortcoming of our 2007 review, in that we discuss techniques to simulate highly confined fluids, thus enabling researchers to apply these methods to the realm of nanofluidics. In this realm, traditional concepts of local transport coefficients must be questioned, and the principles of generalised hydrodynamics embraced. Not every NEMD method is discussed, and at the outset we acknowledge this limitation; time and space restrictions make it impossible to condense all methods into a single book. But we have hopefully discussed many of the important methods used to simulate liquids far from equilibrium, as well as their strengths and limitations.

The book is largely self-contained; however, it is assumed that readers have a basic knowledge of statistical mechanics, thermodynamics and are familiar with the underlying principles of molecular dynamics. The books by McQuarrie [3] and de Groot and Mazur [4] are excellent references for statistical mechanics and nonequilibrium

thermodynamics, respectively, while those of Allen and Tildesley [5], Rapaport [6], Frenkel and Smit [7] and Sadus [8] provide solid background for molecular dynamics methods implemented in Fortran, C or C++.

Additional resources including code examples in Fortran 90 are available under the Resources tab at <http://www.cambridge.org/9780521190091>.

The authors would like to thank Professor Denis Evans for introducing us to nonequilibrium molecular dynamics and nonequilibrium statistical mechanics while we were both postdoctoral researchers in the Research School of Chemistry, ANU. His inspiring leadership of the group at ANU has led to our enduring interest in this field of research.

Finally, we would like to thank our families for their patience, understanding and support over the years it has taken us to write this book, as well as a number of our colleagues and graduate students who have provided an enormous amount of intellectual stimulation, encouragement, good humour and advice over an extended period of time. In particular Jesper Hansen, Federico Frascoli, Adrian Menzel and Stephen Hannam are thanked for their careful reading of our manuscript and valuable suggestions for improvement.

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