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.

Nonequilibrium Molecular Dynamics

Theory, Algorithms and Applications

BILLY D. TODD
Swinburne University of Technology

PETER J. DAIVIS
Royal Melbourne Institute of Technology

CAMBRIDGE
UNIVERSITY PRESS

CAMBRIDGE
UNIVERSITY PRESS

University Printing House, Cambridge CB2 8BS, United Kingdom

One Liberty Plaza, 20th Floor, New York, NY 10006, USA

477 Williamstown Road, Port Melbourne, VIC 3207, Australia

4843/24, 2nd Floor, Ansari Road, Daryaganj, Delhi - 110002, India

79 Anson Road, #06-04/06, Singapore 079906

Cambridge University Press is part of the University of Cambridge.

It furthers the University's mission by disseminating knowledge in the pursuit of education, learning, and research at the highest international levels of excellence.

www.cambridge.org
Information on this title: www.cambridge.org/9780521190091
10.1017/9781139017848

First published 2017

Printed in the United States of America by Sheridan Books, Inc.

A catalogue record for this publication is available from the British Library.

Library of Congress Cataloging in Publication Data
Names: Todd, Billy D., author. | Daivis, Peter J., author.
Title: Nonequilibrium molecular dynamics : theory, algorithms and applications / Billy D. Todd (Swinburne University of Technology), Peter J. Daivis (Royal Melbourne Institute of Technology).
Description: Cambridge, United Kingdom ; New York, NY : Cambridge University Press, 2017. | Includes bibliographical references and index.
Identifiers: LCCN 2016044167 | ISBN 9780521190091 (alk. paper) | ISBN 0521190096 (alk. paper)
Subjects: LCSH: Nonequilibrium statistical mechanics. | Nonequilibrium thermodynamics. | Molecular dynamics.
Classification: LCC QC174.86.N65 T63 2017 | DDC 541/.394 – dc23
LC record available at https://lccn.loc.gov/2016044167

ISBN 978-0-521-19009-1 Hardback

Contents

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.

Acknowledgement

This book contains extracts from two articles we published in Molecular Simulation http://dx.doi.org/10.1080/08927020412331332730 and http://dx.doi.org/10.1080/08927020601026629, reproduced here with the permission of the publisher, Taylor & Francis.