### THE ART OF MOLECULAR DYNAMICS SIMULATION

The extremely powerful technique of molecular dynamics simulation involves solving the classical many-body problem in contexts relevant to the study of matter at the atomistic level. Since there is no alternative approach capable of handling this broad range of problems at the required level of detail, molecular dynamics methods have proved themselves indispensable in both pure and applied research. This book is a blend of tutorial and recipe collection, providing both an introduction to the subject for beginners and a reference manual for more experienced practitioners. It is organized as a series of case studies that take the reader through each of the steps from formulating the problem, developing the necessary software, and then using the programs to make actual measurements.

This second edition has been extensively revised and enlarged. It contains a substantial amount of new material and the software used in the case studies has been completely rewritten.

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Cambridge University Press 978-0-521-82568-9 - The Art of Molecular Dynamics Simulation: Second Edition D. C. Rapaport Frontmatter More information Cambridge University Press 978-0-521-82568-9 - The Art of Molecular Dynamics Simulation: Second Edition D. C. Rapaport Frontmatter More information

# THE ART OF MOLECULAR DYNAMICS SIMULATION

Second Edition

D. C. RAPAPORT



CAMBRIDGE UNIVERSITY PRESS Cambridge, New York, Melbourne, Madrid, Cape Town, Singapore, São Paulo, Delhi, Mexico City

Cambridge University Press The Edinburgh Building, Cambridge CB2 8RU, UK

Published in the United States of America by Cambridge University Press, New York

www.cambridge.org Information on this title: www.cambridge.org/9780521825689

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First published 1995 Reprinted 1998 First paperback edition 1997 Reprinted 1998, 2001, 2002 Second edition 2004 Fifth printing 2010

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

ISBN 978-0-521-82568-9 Hardback

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# Contents

	Preface to the first edition Preface to the second edition About the software		<i>page</i> ix
			xii
			xiii
1	Introduction		1
	1.1	Historical background	1
	1.2	Computer simulation	2
	1.3	Molecular dynamics	4
	1.4	Organization	8
	1.5	Further reading	10
2	Basic molecular dynamics		11
	2.1	Introduction	11
	2.2	Soft-disk fluid	11
	2.3	Methodology	18
	2.4	Programming	20
	2.5	Results	34
	2.6	Further study	43
3	Simulating simple systems		44
	3.1	Introduction	44
	3.2	Equations of motion	44
	3.3	Potential functions	46
	3.4	Interaction computations	49
	3.5	Integration methods	60
	3.6	Initial state	67
	3.7	Performance measurements	74
	3.8	Trajectory sensitivity	77
	3.9	Further study	82

vi		Contents	
4	Equil	ibrium properties of simple fluids	83
	4.1	Introduction	83
	4.2	Thermodynamic measurements	84
	4.3	Structure	90
	4.4	Packing studies	96
	4.5	Cluster analysis	112
	4.6	Further study	118
5	Dyna	mical properties of simple fluids	120
	5.1	Introduction	120
	5.2	Transport coefficients	120
	5.3	Measuring transport coefficients	124
	5.4	Space-time correlation functions	134
	5.5	Measurements	145
	5.6	Further study	152
6	Alter	native ensembles	153
	6.1	Introduction	153
	6.2	Feedback methods	154
	6.3	Constraint methods	165
	6.4	Further study	174
7	None	quilibrium dynamics	176
	7.1	Introduction	176
	7.2	Homogeneous and inhomogeneous systems	176
	7.3	Direct measurement	177
	7.4	Modified dynamics	188
	7.5	Further study	198
8	Rigid	molecules	199
	8.1	Introduction	199
	8.2	Dynamics	200
	8.3	Molecular construction	216
	8.4	Measurements	222
	8.5	Rotation matrix representation	232
	8.6	Further study	243
9	Flexil	ble molecules	245
	9.1	Introduction	245
	9.2	Description of molecule	245
	9.3	Implementation details	247
	9.4	Properties	251
	9.5	Modeling structure formation	256

		Contents	vii
	0.6	Surfactant models	257
	9.0 0.7	Surfactant hohevior	257
	9.7	Suffactant benavior	202
10	9.0 Case	rutulei study	200
10		Introduction	207
	10.1	Introduction Coometrie constraints	207
	10.2	Solving the constraint problem	207
	10.5	Internal forces	270
	10.4	Implementation details	276
	10.5	Measurements	200
	10.0	Further study	201
11	Intonn	a coordinates	204
11	11 1		290
	11.1	Chain coordinates	290
	11.2	Kinomatic and dynamic relations	290
	11.3	Recursive description of dynamics	298
	11.4	Solving the recursion equations	299
	11.5	Implementation details	317
	11.0	Measurements	317
	11.7	Further study	322
12	Many	-hody interactions	325
14	12 1	Introduction	326
	12.1	Three-body forces	326
	12.2	Embedded-atom approach	320
	12.3	Further study	343
13	Long-	range interactions	344
10	13.1	Introduction	344
	13.2	Ewald method	345
	13.3	Tree-code approach	359
	13.4	Fast-multipole method	365
	13.5	Implementing the fast-multipole method	373
	13.6	Results	386
	13.7	Further study	389
14	Step p	ootentials	391
	14.1	Introduction	391
	14.2	Computational approach	392
	14.3	Event management	403
	14.4	Properties	411
	14.5	Generalizations	414

	٠	٠	٠
v	1	1	1
•	-	1	1

	14.6	Further study	417
15	Time-	418	
	15.1	Introduction	418
	15.2	Open systems	418
	15.3	Thermal convection	420
	15.4	Obstructed flow	429
	15.5	Further study	435
16	Granu	ılar dynamics	436
	16.1	Introduction	436
	16.2	Granular models	436
	16.3	Vibrating granular layer	439
	16.4	Wave patterns	443
	16.5	Further study	445
17	Algori	ithms for supercomputers	446
	17.1	Introduction	446
	17.2	The quest for performance	446
	17.3	Techniques for parallel processing	447
	17.4	Distributed computation	450
	17.5	Shared-memory parallelism	467
	17.6	Techniques for vector processing	473
	17.7	Further study	480
18	More	about software	481
	18.1	Introduction	481
	18.2	Structures and macro definitions	481
	18.3	Allocating arrays	487
	18.4	Utility functions	488
	18.5	Organizing input data	495
	18.6	Configuration snapshot files	498
	18.7	Managing extensive computations	500
	18.8	Header files	504
19	The fu	iture	505
	19.1	Role of simulation	505
	19.2	Limits of growth	506
	19.3	Visualization and interactivity	507
	19.4	Coda	508
	Appendix		509
	References		519
	Function index		532
	Index		535
	Colophon		549

### Preface to the first edition

Molecular dynamics simulation provides the methodology for detailed microscopic modeling on the molecular scale. After all, the nature of matter is to be found in the structure and motion of its constituent building blocks, and the dynamics is contained in the solution to the N-body problem. Given that the classical N-body problem lacks a general analytical solution, the only path open is the numerical one. Scientists engaged in studying matter at this level require computational tools to allow them to follow the movement of individual molecules and it is this need that the molecular dynamics approach aims to fulfill.

The all-important question that arises repeatedly in numerous contexts is the relation between the bulk properties of matter – be it in the liquid, solid, or gaseous state – and the underlying interactions among the constituent atoms or molecules. Rather than attempting to deduce microscopic behavior directly from experiment, the molecular dynamics method – MD for short – follows the constructive approach in that it tries to reproduce the behavior using model systems. The continually increasing power of computers makes it possible to pose questions of greater complexity, with a realistic expectation of obtaining meaningful answers; the inescapable conclusion is that MD will – if it hasn't already – become an indispensable part of the theorist's toolbox. Applications of MD are to be found in physics, chemistry, biochemistry, materials science, and in branches of engineering.

This is a recipe book. More precisely, it is a combination of an introduction to MD for the beginner, and a cookbook and reference manual for the more experienced practitioner. The hope is that through the use of a series of case studies, in which real problems are studied, both goals can be achieved. The book can be read from cover to cover to explore the principles and capabilities of MD, or it can be used in cookbook style – with a certain amount of cross-referencing – to obtain the recipe for a particular kind of computation. Some familiarity with classical and statistical mechanics, numerical methods and computer programming is assumed.

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#### Preface to the first edition

The case studies take the reader through all the stages from initial problem statement to the presentation of the results of the calculation. The link between these endpoints is the computer program – the recipe. The results of the simulations are 'experimental' observations, in the sense that the simulation is an experiment conducted on an actual, albeit highly idealized, substance. Some of these observations amount to mere measurement, while others can include the discovery of qualitatively novel effects; the custom of referring to MD simulation as computer experimentation is most certainly justified.

Computer programs are an important part of any MD project and feature prominently among the recipes. The view that programs are best kept out of sight along with the plumbing is seriously outdated, and program listings are integrated into the text, with the same status as mathematical equations. After all, a computer program is merely the statement of an algorithm (supplemented by a myriad details to assist the computer in performing its task), and an algorithm is a mathematical procedure. Without the details of the programs, the recipe oriented goal would not have been met: there are many vital, but often subtle, details that only emerge when the program is actually written, so that the program text is an essential part of any recipe and is meant to be read.

Given the near ubiquity of MD, the choice of material had to be restricted to avoid a volume of encyclopedic size. The focus is on the simplest of models, since these form the basis of almost all later developments. Even what constitutes a simple model is open to debate, and here a modest bias on the part of the (physicist) author may be discerned. The emphasis is on showing that MD can reproduce known physical phenomena at a qualitative and semiquantitative level, but without fine-tuning potential functions, molecular structures, or other parameters, for precise quantitative agreement with experiment. Exercises such as demonstrating the solid–fluid phase transition in a system of soft-disk atoms, observing the local ordering in a simple model for water, and following the gyrations of a highly idealized polymer chain, are all far more rewarding experiences for the beginner than detailed computations of specific heats or viscosities across the entire state space of the system. Quantitative detail is not neglected, however, although here some aspects will obviously appeal to more limited segments of the audience.

The model systems to be introduced in these pages can be readily extended and adapted to problems of current interest; suggestions for further work of this kind accompany the case studies, and can serve as exercises (or even research projects) in courses devoted to simulation. The same holds true for the computational techniques. We cover a variety of methods, but not all combinations of methods and problems. In some cases all that is required is a simple modification or combination of the material covered, but in other cases more extensive efforts are called for – the literature continues to report such methodological developments. While

#### Preface to the first edition

MD can hardly be regarded as a new technique, neither can it be regarded as a fully matured method, and thus there are often several ways of approaching a particular problem, with little agreement on which is to be preferred. It is not our intent to pass judgment, and examples based on alternative methods are included.

The practical side of MD is no less important than the theoretical. A true appreciation of the capabilities and shortcomings of the various methods, an understanding of the assumptions used in the models, and a feeling for what kinds of problem are realistic candidates for MD treatment can only be obtained from experience. This is something that even users of commercial and other packaged software should be aware of. The bottom line is that the reader should be prepared to use this book like any other recipe book: off to the kitchen and start cooking!

January, 1995

Dennis C. Rapaport

xi

# Preface to the second edition

The second edition of The Art of Molecular Dynamics Simulation is an enlarged and updated version of the first. The principal differences between the two editions are the inclusion of a substantial amount of new material, both as additional chapters and within existing chapters, and a complete revision of all the software used in the case studies to reflect a more modern programming style. This style change is a consequence of the population shift in the research community. At the time the first edition was written older versions of the Fortran language were still in widespread use; despite this fact, C was chosen as the programming language for the book in preference to Fortran, but in a form that would appear familiar to Fortran programmers of the era. Now that C - and related languages - are in widespread use, and Fortran has even evolved to become more like C, the expressive capabilities of C can be employed to the full, resulting in software that is easier to follow. The power of desktop computers has also increased by a large factor since the case studies of the first edition were developed; in recognition of this fact some of the studies consider larger systems, reflecting a shifting view of what is considered a 'short' computation. Other minor changes and corrections have been incorporated throughout the text. The exhortation to employ this volume as a cookbook remains unchanged.

January, 2003

D.C.R.

## About the software

### Software availability

Readers interested in downloading the software described in this book in a computer-readable form for personal, noncommercial use should visit the Cambridge University Press web site at http://uk.cambridge.org, where the home page for this book and the software can be found; a listing of the programs included in the software package appears in the Appendix. Additional material related to the book, as well as contact information, can be found at the author's website – http://www.ph.biu.ac.il/~rapaport.

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