Advances in the Computer Simulations of Liquid Crystals

NATO Science Series

A Series presenting the results of activities sponsored by the NATO Science Committee. The Series is published by IOS Press and Kluwer Academic Publishers, in conjunction with the NATO Scientific Affairs Division.

A. Life Sciences	IOS Press
B. Physics	Kluwer Academic Publishers
C. Mathematical and Physical Sciences	Kluwer Academic Publishers
D. Behavioural and Social Sciences	Kluwer Academic Publishers
E. Applied Sciences	Kluwer Academic Publishers
F. Computer and Systems Sciences	IOS Press
1. Disarmament Technologies	Kluwer Academic Publishers
2. Environmental Security	Kluwer Academic Publishers
3. High Technology	Kluwer Academic Publishers
4. Science and Technology Policy	IOS Press
5. Computer Networking	IOS Press

NATO-PCO-DATA BASE

The NATO Science Series continues the series of books published formerly in the NATO ASI Series. An electronic index to the NATO ASI Series provides full bibliographical references (with keywords and/or abstracts) to more than 50000 contributions from international scientists published in all sections of the NATO ASI Series.

Access to the NATO-PCO-DATA BASE is possible via CD-ROM "NATO-PCO-DATA BASE" with user-friendly retrieval software in English, French and German (WTV GmbH and DATAWARE Technologies Inc. 1989).

The CD-ROM of the NATO ASI Series can be ordered from: PCO, Overijse, Belgium

Advances in the Computer Simulations of Liquid Crystals

edited by

Paolo Pasini

Istituto Nazionale di Fisica Nucleare,
Sezione di Bologna,
Bologna, Italy

and

Claudio Zannoni

Dipartimento di Chimica Fisica ed Inorganica,
Università di Bologna,
Bologna, Italy

Springer-Science+Business Media, B.V.

Proceedings of the NATO Advanced Study Institute on
Advances in the Computer Simulations of Liquid Crystals
Erice, Italy
11-21 June 1998

A C.I.P. Catalogue record for this book is available from the Library of Congress.

ISBN 978-0-7923-6099-5 ISBN 978-94-011-4225-0 (eBook)
DOI 10.1007/978-94-011-4225-0

Printed on acid-free paper

All Rights Reserved

© 2000 Springer Science+Business Media Dordrecht
Originally published by Kluwer Academic Publishers in 2000
Softcover reprint of the hardcover 1st edition 2000

No part of the material protected by this copyright notice may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying, recording or by any information storage and retrieval system, without written permission from the copyright owner.

CONTENTS

Preface	xiii
1 Introduction to simulations and statistical mechanics	1
<i>M.P. Allen</i>	
1 Introduction	1
1.1 Microscopic and macroscopic	2
1.2 Molecular dynamics and Monte Carlo	3
2 Statistical mechanics and why we need it	5
3 Ensembles and simulation	5
3.1 Thermodynamic quantities	6
3.2 Probability distributions	7
3.3 Time and length scales	7
3.4 Correlation functions and experiment	9
3.5 Transport coefficients	10
4 Sampling and summing over states	12
5 Molecular dynamics algorithms	15
2 Liquid crystal observables: static and dynamic properties	17
<i>C. Zannoni</i>	
1 Single particle properties	17
1.1 The singlet distribution and its expansion	18
2 Orientational order of cylindrical molecules in uniaxial phases	20
2.1 Expansion of the orientational distribution	20
2.2 Experimental determination of order parameters. An example	22
2.3 Getting order parameters from simulations	24
2.4 Second rank	24
2.5 Fourth rank	27
3 Biaxial order parameters	28
4 Pair properties	31
4.1 Pair distribution	31

4.2	Stone expansion of the pair distribution	32
4.3	Intermolecular vector correlation functions	33
5	Thermodynamic observables	36
5.1	Energy	36
5.2	Heat capacity	36
5.3	Pressure	37
5.4	Surface tension	38
6	Dynamic evolution of a molecular property	39
7	Contact with experiment. Linear response theory	41
8	Evolution in the presence of a perturbation	43
9	Theory of dielectric response	45
	Appendix	46
3	Phase behavior of lyotropic liquid crystals	51
	<i>D. Frenkel</i>	
1	Introduction	51
2	Phase transitions and free energy	52
2.1	Phase transitions in liquid crystals	54
2.2	Gibbs-Duhem integration	59
3	Simulations at infinite aspect ratio	61
3.1	Scaling	61
3.2	Mixtures	62
4	Chemical potential of flexible molecules	62
4.1	The particle insertion method	62
4.2	Chemical potential of macro-molecules with discrete conformations	64
4.3	Extension to continuously deformable molecules	67
5	Configurational bias Monte Carlo scheme	70
4	Modelling liquid crystal structure, phase behaviour and large-scale phenomena	73
	<i>M.P. Allen</i>	
1	Introduction	73
2	Onsager theory and hard-particle phase diagrams	74
2.1	Highly elongated molecules	75
2.2	Rod-plate mixtures	78
3	The Gay-Berne model	80
3.1	Varying the attractive anisotropy	81
3.2	Varying the elongation	81
4	Diffusion and rotation in smectic-A phases	84

5	Large-scale phenomena	87
5.1	Structure and dynamics near the I-N transition . . .	87
5.2	Structure of the S_A^* TGB phase	89
5.3	Bulk elastic constants	91
5.4	Surface anchoring strengths	93
5	Liquid crystal lattice models I. Bulk systems	99
	<i>P. Pasini, C. Chiccoli and C. Zannoni</i>	
1	Introduction	99
2	Periodic boundary conditions	100
3	The Lebwohl-Lasher model	101
3.1	Observables	102
3.2	Low dimensional systems	106
3.3	Cluster boundary conditions	109
3.4	Sample shape	110
4	Some other nematic lattice spin models	111
4.1	A P_2P_4 model	112
4.2	A P_1P_2 model	113
4.3	A biaxial model	114
5	Conclusions	117
6	Liquid crystal lattice models II. Confined systems	121
	<i>P. Pasini, C. Chiccoli and C. Zannoni</i>	
1	Introduction	121
2	Polymer dispersed liquid crystals	122
2.1	Molecular organization and deuterium NMR spectra	127
2.2	Polarized light textures	129
3	Liquid crystal displays	131
3.1	Twisted nematic display	131
3.2	In-plane switching effect display	134
4	Hybrid aligned nematic film	134
5	Conclusions	137
7	Computer simulation of lyotropic liquid crystals as models of biological membranes	139
	<i>O.G. Mouritsen</i>	
1	Introduction: membranes, lipid bilayers, and smectics	139
2	Computer simulations: molecular dynamics or Monte Carlo?	143
3	Phase transitions in lipid bilayers	144

4	Models of lipid bilayer phase transitions	145
4.1	The fundamental variables	146
4.2	Strategy (i): the multi-state Pink model	148
4.3	Strategy (iii): the Doniach model on a dynamic random lattice	153
5	Monte Carlo simulation techniques for phase transitions . .	156
5.1	Histogram and re-weighting techniques	157
5.2	Detection of phase equilibria by finite-size scaling .	158
6	Phase transition and lateral structure in lipid bilayers . . .	160
6.1	Nature of the main phase transition	160
6.2	Phase equilibria in binary lipid bilayers	165
6.3	Small-scale structure in lipid bilayers: fluctuations and lipid domains	166
6.4	Modulation of lipid domains by foreign compounds: cholesterol and drugs	171
7	Trans-bilayer structure	174
8	Organization and structure of lipid bilayers with proteins .	176
8.1	Single-protein effects	177
8.2	Lipid-mediated protein-protein interactions: aggregation and crystallization	177
8.3	Non-equilibrium organization of active proteins . . .	180
9	Lipid-membrane structure in relation to function	182
9.1	Passive bilayer permeability	183
9.2	Activity of membrane-bound enzymes	184
8	Flow properties and structure of anisotropic fluids studied by non-equilibrium molecular dynamics, and flow properties of other complex fluids: polymeric liquids, ferro-fluids and magneto-rheological fluids	189
	<i>S. Hess</i>	
1	Introduction	190
2	Description of the viscosity	191
2.1	General remarks, isotropic liquids	191
2.2	Viscosity of isotropic and liquid crystalline phases .	193
2.3	Alignment tensor, director and order parameter of nematics	193
2.4	The viscosity coefficients of nematic liquid crystals .	195
2.5	Effective viscosity and flow alignment	198
2.6	Applied orienting field	201
2.7	Normal pressure effects	202
3	NEMD for fluids of spherical particles	202

3.1	General remarks	202
3.2	Basics of molecular dynamics	203
3.3	Extraction of data from MD simulations	204
3.4	Interaction potential and scaling	204
3.5	Plane couette flow	205
3.6	Pressure tensor, viscosity	205
3.7	Structural changes	207
3.8	Generalized Stokes–Maxwell model	208
4	Nematic liquid crystals	210
4.1	Ellipsoids with perfect orientation	210
4.2	Discotic nematics	214
4.3	Biaxial nematics	214
4.4	Presmectic behavior	215
4.5	Soft spheres with P_2 -anisotropy	215
4.6	Gay–Berne fluids	219
5	Ferro-fluids and magneto-rheological fluids	222
6	Polymeric liquids	224
6.1	Polymer solutions	226
7	Concluding remarks	227

9 Self atom-atom empirical potentials for the static and dynamic simulation of condensed phases 235

A. Gavezzotti and G. Filippini

1	Introduction	235
2	Principles of intermolecular interactions	236
2.1	Long range interactions among non-overlapping electron densities	236
2.2	Short-range interactions among weakly overlapping electron densities	237
2.3	Attractive, short-range interactions	239
2.4	Non-additive terms: many-body interactions	239
3	Fitting intermolecular potentials with parametric equations	240
4	Analytical forms of empirical atom–atom potentials: an example	242
5	Applications to static simulations	245
6	Dynamic simulations	247
7	Modern force fields and their performance	247
8	Concluding remarks	248

10 Atomistic modelling of liquid crystal phases 251

M.R. Wilson, M.J. Cook and C. McBride

1	Introduction	251
2	Hybrid Gay-Berne/Lennard-Jones models	252
2.1	Introduction	252
2.2	Simulation results	253
3	Fully atomistic simulations	255
4	Improved force fields for liquid crystals	257
4.1	Nonbonded interactions	257
4.2	Dihedral angle parameters	257
5	Calculations of helical twisting power	258
5.1	Introduction	258
5.2	Theory	258
5.3	Statistical perturbation theory	259
5.4	Simulation results	260
6	Conclusions	261

11 Atomistic simulation and modeling of smectic liquid crystals 263

M.A. Glaser

1	Introduction	263
2	Model building	269
3	Methodology	275
3.1	The particle-mesh Ewald method	276
3.2	Why is molecular dynamics stable?	279
3.3	Multiple-timestep molecular dynamics	281
3.4	Hybrid Monte Carlo	282
4	Applications	296
4.1	Microscopic structure of a partial bilayer smectic	296
4.2	Photo-controlled nanophase segregation	303
4.3	Computer-aided design of ferroelectric liquid crystals	309
4.4	Microscopic organization of the smectic C phase	318
5	Conclusion	324

12 Multiple time steps algorithms for the atomistic simulations of complex molecular systems 333

P. Procacci and M. Marchi

1	Introduction	333
2	Symplectic and reversible integrators	338

2.1	Canonical transformation and symplectic conditions	338
2.2	Liouville formalism: a tool for building symplectic and reversible integrators	340
2.3	Potential subdivision and multiple time steps integrators for NVE simulations	343
2.4	Constraints and r-RESPA	347
2.5	Applications	348
3	Multiple time steps algorithm for the isothermal-isobaric ensemble	352
3.1	The Parrinello-Rahman-Nosé extended lagrangian	353
3.2	The Parrinello-Rahman-Nosé hamiltonian and the equations of motion	355
3.3	Equivalence of atomic and molecular pressure	358
3.4	Liouvillean split and multiple time step algorithm for the <i>NPT</i> ensemble	361
3.5	Group scaling and molecular scaling	365
3.6	Switching to other ensembles	366
4	Multiple time steps algorithms for large size flexible systems with strong electrostatic interactions	368
4.1	Subdivision of the “bonded” potential	368
4.2	The smooth particle mesh Ewald method	373
4.3	Subdivision the non bonded potential	377
4.4	Electrostatic corrections for the multiple time step simulation	381
5	Conclusion	384

13 Parallel molecular dynamics techniques for the simulation of anisotropic systems **389**

M.R. Wilson

1	Introduction to parallelisation	389
1.1	The need for parallelism	389
1.2	Types of parallel computer	390
1.3	Message passing for MIMD machines	390
1.4	MIMD methodologies	390
1.5	Parallel operations	393
1.6	Efficient parallel programming	393
2	Replicated data methods for parallel molecular dynamics	395
2.1	Introduction	395
2.2	Simulation of isotropic particles	396
2.3	Efficient load balancing	396
2.4	Simulation of anisotropic particles	398

2.5	Performance of the replicated data algorithm	400
2.6	Parallelisation of the integration loop	400
2.7	Extension to multi-site molecules	401
3	Systolic loop methods for parallel molecular dynamics . . .	403
3.1	Outline of the systolic loop method	403
3.2	Assessment of the systolic loop algorithm	403
4	Domain decomposition methods for molecular dynamics . .	404
4.1	Introduction	404
4.2	Calculation of forces using domain decomposition . .	405
4.3	Integration of equations of motion	407
4.4	Performance of the domain decomposition algorithm	407
4.5	Domain decomposition algorithm with twisted periodic boundary conditions	408
4.6	Extension to multi-site molecules	410
5	Other parallel approaches to molecular dynamics	412
6	Conclusions	412

PREFACE

Computer Simulations provide an essential set of tools for the understanding of the macroscopic properties of liquid crystals and of their phase transitions in terms of molecular models. While simulations of liquid crystals are based on the same general Monte Carlo and Molecular Dynamics techniques used for other fluids, they present a number of specific problems and peculiarities connected with the intrinsic properties of these mesophases. An example is the need to develop suitable algorithms to calculate anisotropic static properties such as order parameters and tensorial observables as well as dynamic quantities like diffusion tensors, viscosities, susceptivities etc. Another series of problems is connected with the need of predicting the properties of liquid crystals from molecular models. This involves the determination of phase transitions and their characteristics, and requires on one hand the development of intermolecular potentials for modelling the essential molecular features of mesogens, and on the other performing large scale simulations, with a number of particles often an order of magnitude greater than those used for simple fluids. Such large numbers require exploiting state of the art resources in computing, and particularly parallel techniques with the development of appropriate algorithms. Further peculiarities of liquid crystals, compared to ordinary isotropic fluids, are their topological defects and it is now becoming feasible to simulate their core structure and optical textures. Similar methods can even be used to perform direct microscopic level simulations of simple devices and displays.

The field of computer simulations of anisotropic fluids is clearly interdisciplinary and evolving very rapidly and this has brought us to organize the NATO Advanced School Institute (ASI) on Advances in the Computer Simulations of Liquid Crystals, held at the Ettore Majorana Centre of Scientific culture (CCSEM) in Erice, Sicily from June 11th to June 21st, 1998. The School, that has tried to cover all the above issues considering various techniques and model systems (from lattice to hard particle and Gay-Berne up to atomistic) for thermotropics, lyotropics and some liquid crystals of biological interest, has had an excellent panel of international Lecturers and has attracted over 70 very keen students and young researchers from different disciplines and 16 countries. The successful organization of the NATO ASI was only possible thanks to the help of many people and we would like

to mention particularly our collaborators R. Berardi, A. Porreca, S. Orlandi and the competent and helpful staff of CCSEM. A particular thought is due to the memory of Dr. Alberto Gabriele, in charge of organization at the Centre, whose efficiency together with kindness, courtesy and dedication to CCSEM we had the fortune to appreciate.

The present book contains a large part of the lectures given at the NATO ASI starting with some introductory papers followed by more applicative and technical chapters. We believe it provides a timely account of the techniques and problems in the field and we hope it will convey some of the stimulating atmosphere of the School.

We are particularly grateful to the Lecturers, the members of the Scientific Committee, Professors N.A. Clark, G.R. Luckhurst, D. Frenkel and to the CCSEM Director, Professor A. Zichichi. We wish to thank NATO and its Science Committee for their essential support which made the organization of the School and the production of this book possible. We also acknowledge financial contributions from Ente per le Nuove tecnologie, l'Energia e l'Ambiente (ENEA), Consorzio Interuniversitario per la Chimica dei Materiali (now INSTM), TECDIS S.p.A., Consiglio Nazionale delle Ricerche (CNR) and Quadrics Supercomputers World (QSW).

Paolo Pasini
INFN, Bologna

Claudio Zannoni
Università di Bologna