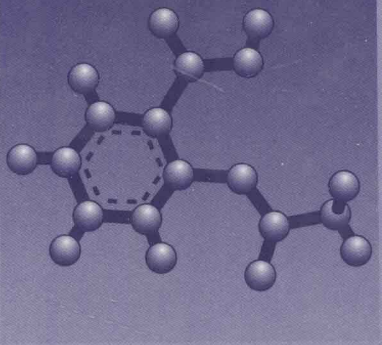
SPECIALIST PERIODICAL REPORTS

RSC
ROYAL SOCIETY OF CHEMISTRY



Chemical *Modelling*

APPLICATIONS AND THEORY

Volume 2

senior reporter A. HINCHLIFFE

A Specialist Periodical Report

Chemical Modelling
Applications and Theory
Volume 2

A Review of the Literature Published between June 1999 and May 2001

Senior Reporter
A. Hinchliffe, *Department of Chemistry, UMIST, Manchester, UK*

Reporters
D. Babić, *Rudjer Bošković University, Zagreb, Croatia*
D.M. Heyes, *University of Surrey, Guildford, UK*
D.J. Klein, *Texas A & M University at Galveston, Galveston, Texas, USA*
R.A. Lewis, *Lilly Research Centre, Windlesham, Surrey, UK*
P.L.A. Popelier, *UMIST, Manchester, UK*
D. Pugh, *University of Strathclyde, Glasgow, UK*
T. Simos, *Democritus University of Thrace, Kanthi, Greece*
P.J. Smith, *UMIST, Manchester, UK*
M. Springborg, *University of Saarland, Saarbrücken, Germany*
N. Trinajstić, *Rudjer Bošković University, Zagreb, Croatia*
S. Wilson, *Rutherford Appleton Laboratory, Chilton, Oxfordshire, UK*

RS•C
ROYAL SOCIETY OF CHEMISTRY

ISBN 0-85404-259-8

ISSN 1472-0965

Published by The Royal Society of Chemistry
Thomas Graham House, Science Park, Milton Road, Cambridge CB4 0WF, UK

Registered Charity Number 207890

For further information see our web site at www.rsc.org

Typeset by Keytec Typesetting Ltd
Printed by Athenaeum Press Ltd, Gateshead, Tyne and Wear, UK

Chemical Modelling
Applications and Theory

Volume 2

SPECIALIST PERIODICAL REPORTS

RS•C
ROYAL SOCIETY OF CHEMISTRY

Systematic and detailed review coverage in major areas of chemical research.

A unique service for the active research chemist with annual or biennial, in-depth accounts of progress in particular fields of chemistry, in print and online.

NOW AVAILABLE ELECTRONICALLY - chapters from volumes published 1998 onwards are now available online, fully searchable by key word, on a pay-to-view basis.

Contents pages can be viewed free of charge.

Now available online:

- Amino Acids, Peptides & Proteins *Vol.29 - 32*
- Carbohydrate Chemistry *Vol.30 - 32*
- Catalysis *Vol.14 - 15*
- Chemical Modelling *Vol.1*
- Electron Paramagnetic Resonance *Vol.16 - 17*
- Nuclear Magnetic Resonance *Vol.27 - 30*
- Organometallic Chemistry *Vol.26 - 29*
- Organophosphorus Chemistry *Vol.29 - 31*
- Photochemistry *Vol.29 - 32*
- Spectroscopic Properties of Inorganic and Organometallic Compounds *Vol.31 - 34*

Titles for 2002:

- Amino Acids, Peptides & Proteins *Vol.33*
- Carbohydrate Chemistry *Vol.33*
- Catalysis *Vol.16*
- Chemical Modelling *Vol.2*
- Electron Paramagnetic Resonance *Vol.18*
- Nuclear Magnetic Resonance *Vol.31*
- Organometallic Chemistry *Vol.30*
- Organophosphorus Chemistry *Vol.32*
- Photochemistry *Vol.33*
- Spectroscopic Properties of Inorganic and Organometallic Compounds *Vol.35*

RSCADS/16110109-MONO

Or visit our web pages today:
www.rsc.org/spr

Orders & further details Sales & Customer Care Dept · Royal Society of Chemistry
Thomas Graham House · Science Park · Milton Road · Cambridge · CB4 0WF · UK
T +44(0)1223 432360 · F +44(0)1223 426017 · E sales@rsc.org
Or visit our websites: **www.rsc.org** and **www.chemsoc.org**
Registered Charity No. 207890

ROYAL SOCIETY OF CHEMISTRY *Investing in Chemical Science*

此为试读，需要完整PDF请访问：www.ertongbook.com

Preface

I laid the foundations for this Series in Volume 1.

The ground rules are very simple: colleagues reporting on new topics are asked to give the rest of us an easily understandable historical perspective together with their own critical comments on the literature for the period under review. Colleagues reporting on continuing topics are simply expected to give a critical review of the literature for the period. The period under consideration for this volume is June 1999 to May 2001, and subsequent volumes will give biennial coverage of the literature to May 2003 + n, where $n = 0, 2, 4, 6, \ldots$

Note my repeated use of the word 'critical'. When the RSC and I market researched this new SPR title, it quickly became apparent that colleagues were not interested in a dull and uncritical compilation of literature references. Several of them remarked (rather unkindly, I thought) that they could ask their PhD students to sit at a networked PC, dial up Web of Science, and produce such a comprehensive list by the end of a single afternoon. What they wanted was critical insight into the recent literature.

That is what we are trying to give. There are still many gaps in coverage, and I'm sure you will have your own ideas as to what is good and bad with this very new title. Rather than grumbling to your colleagues and writing acidic book reviews, why not volunteer your own expertise? I am always willing to listen to constructive suggestions, and can be reached at

alan.Hinchliffe@umist.ac.uk

Volume 2 consists of eight contributions. Several are continuations from the topics treated in Volume 1, some are new. A couple of existing Reporters in Volume 1 asked to be excused for Volume 2, but will reappear in Volume 3. The contributions are not in any particular order, other than the 'new' topics are towards the start of the volume.

The molecular simulation of liquids is now a vast field of human endeavour, and we open with a contribution on 'Simulation of the Liquid State' by David Heyes. David captures the spirit of the SPR exactly when he writes '...The ready availability of fast computers has meant that there are many more researchers working in this ever expanding field ...[and] ...I have restricted my discussion to ... areas that have interested me'.

Several people pointed out a gap in the coverage of Volume 1, namely the field of enumeration. Nenad Trinajstić and his co-workers have written our first chapter in this field, which strikes a nice balance between historical perspective and up-to-the-minute literature.

Michael Springborg continues to report on the growth of density functional theory.

Theodore Simos reported on the current status of atomic structure calculations in Volume 1. He has broadened the scope a little for Volume 2, and reports on progress in the solution of 1D, 2D and 3D differential equations in chemistry.

It was always my intention to include industrial applications. Much of this kind of work never reaches the primary journals because of confidentiality restrictions and commercial forces. I am very pleased to tell you that Richard Lewis has been able to give us a fascinating glimpse into the world of commercial computer-aided drug design, without apparently breaching a single one of his employer's trade secrets.

David Pugh continues his coverage of electric and magnetic properties. David also gives us a historical insight into those rare beasts magnetizability and hypermagnetizability.

Steven Wilson continues his coverage of many body perturbation theory, whilst Paul Popelier and Paul Smith continue the story of recent advances in the theory of quantum topological atoms.

Alan Hinchliffe
Manchester, 2001

Contents

Chemical Modelling: Applications and Theory, Volume 2

1

Simulation of the Liquid State

BY D.M. HEYES

1 Introduction

The molecular simulation of liquids is a now vast field of research, and as with many others in recent years it is becoming increasingly difficult to keep abreast of all of the significant developments that are taking place. The ready availability of fast computers has meant that there are many more researchers working in this ever expanding field of applications, producing ever larger amounts of work to assimilate! This poses something of a problem when it comes to writing a review, especially one with the rather ambitious title of ‘Computer Simulation of Liquids’. I am not going to attempt to cover all the branches of this field. Rather, in my review of the developments between 1999 and 2001 I have restricted my discussion to a few areas that have interested me. The choice is inevitably somewhat subjective, but hopefully by adopting this approach I will have a better chance of producing a useful document, rather than a gallop through many topics with only the briefest of discussion about each, which I am sure would be of little use to the scientific community. There are a number of molecular simulation books that describe the standard techniques, and these are recommended as background material for the present article, *e.g.* refs. 1–7.

I am therefore not going to discuss the ‘nuts and bolts’ of molecular simulation, except to mention an often overlooked fact, which is the reason for much of the success of these approaches. Most simulations are carried out still typically for less than a thousand molecules, and if it was not for the use of periodic boundary conditions (PBC) it would not be possible to simulate bulk systems with this number of molecules. These systems would have such a high surface to volume ratio that the results would be dominated by surface effects. The PBC procedure is illustrated in Figure 1, which shows a two-dimensional square cell in which the molecules are surrounded by image cells. A molecule near the cell boundary interacts with the ‘real’ molecules in the central cell and with image cell molecules. Molecules leaving the cell re-enter through the opposite face with the same velocity.

Chemical Modelling: Applications and Theory, Volume 2

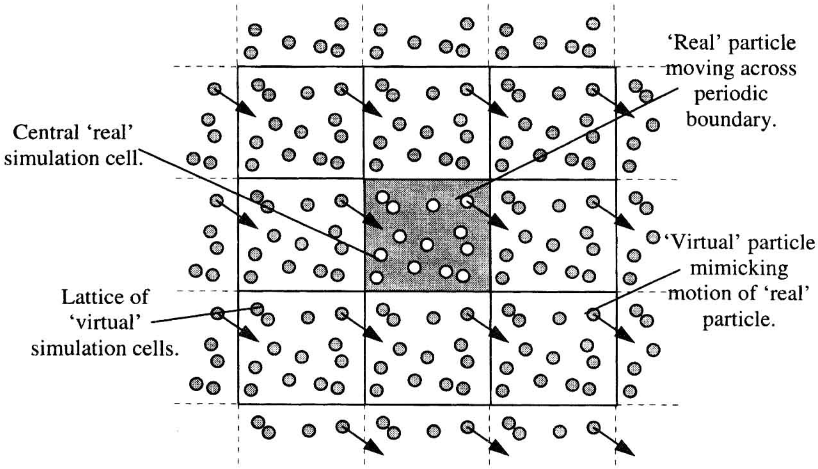


Figure 1 *Schematic representation of the Periodic Boundaries construction in two dimensions. A particle from the central cell moves across a boundary (defined by the arrow) and is replaced by an image of itself. The image then becomes a 'real' particle and the simulation continues uninterrupted*
(Courtesy of Dr. C.A. Bearchell, Department of Chemistry, University of Surrey)

2 Simple Liquids

The study of simple liquids can be said to be the beginning of Molecular Dynamics and Monte Carlo in the 1950s and 60s. Although the scope of molecular simulation, as a field or discipline, has widened dramatically since then, there is nevertheless a continual interest in simple liquids. In fact, this is partly due to the fact that the so-called 'simple' liquids are far from simple! One of the motivations for the continual interest in the simple liquids is that, because of the basic nature of the interparticle interactions, an improved understanding of these systems should lead to better theoretical models, which can be extended to more complex molecular liquids. Also, the rapid growth of interest in colloids and polymers (so-called 'complex' liquids) in recent years has provided new areas where the theories of simple liquids can be applied, especially those associated with local structure and thermodynamics. In the latter case, phase equilibria and the location of phase boundaries feature prominently. In this section, some of the recent advances in our understanding of simple liquids are covered.

2.1 Dynamics. – Of course, within the category of 'simple liquids' studied by statistical mechanics and molecular simulation, there are model liquids that are, strictly speaking, not found in nature. For example, the ubiquitous hard sphere fluid, where the pair potential has the form

$$\begin{aligned}\phi(r) &= \infty, \qquad r \leqslant \sigma \\ &= 0, \qquad r > \sigma \end{aligned} \tag{2.1}$$

is a case in point. The energy is infinite on contact of the spheres (at σ) and zero for larger separations. This is the energy of interaction which would approximate that of two macroscopically sized elastic spheres with high elastic modulus, say two snooker or billiard balls. In these cases the length-scale of the particle interactions is many orders of magnitude smaller than the particle diameter. One of the main features of hard spheres is the co-ordination number. It has been shown recently that for spheres at random close packing, the mean number of particle contacts is 4.8, which is somewhat lower than has often been assumed before (6, and even 12, have been used).[8] Interestingly these authors also performed a computer 'simulation' in which they took a random test sphere, and placed immobile point contacts on its surface. They determined the mean number of points required on the surface of the sphere to eradicate the possibility of translation of the test particle, which was found to be 2D + 1, where D is the space dimension. Therefore, in 3D this 'co-ordination number' is 7, which is lower than the value of 4.8, indicating that in states where the contacts are 'correlated' (*i.e.* in a dense liquid or glassy state) translational diffusion can be removed by fewer contacts. The procedure for carrying out Metropolis Monte Carlo of hard spheres is particularly simple, as the Boltzmann factor does not require specific evaluation – just overlap detection. Jater proposed an improved Metropolis Monte Carlo algorithm to simulate hard core systems, in which they replaced the usual sequence of single particle trial displacements by a collective trial 'move' of a chain of particles.[9]

The hard-sphere system is widely used in statistical mechanics as a reference state in theories of liquids and solids. Its uses have traditionally been quite broad, extending from equations of state, the structure of molecular liquids and dynamical properties. As mentioned already, it has also found a new lease of life as a model reference system for some colloids and granular materials. Simple molecules (*e.g.* water) interact with an appreciable attractive tail extending beyond the hard core, and which usually has more or less the same range as the core. It is not possible to find a simple molecule that does not have an appreciable attractive or van der Waals region as well as a hard repulsive core. In contrast, on the micron and larger scale, for these systems, the hard-sphere can be an even more realistic representation of the effective pair potential, which can be steeply repulsive and have a negligible attractive component. It must be borne in mind, however, that the hard-sphere particle potential is fundamentally unrealistic in that its pair potential is discontinuous and non-differentiable unlike those for *all* real systems. Considerable care is therefore required in extrapolating from any steeply repulsive potential, made progessively steeper, to the hard-sphere potential. This is because many quantities diverge either to zero or infinity according to the order in which the limit is made, of potential steepness and number of particles *etc.*, any of which factors may be significant. Non-physical results such as purely exponential and delta function time correlation functions may be generated. These