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DARESBURY LABORATORY

# INFORMATION QUARTERLY
## for
# COMPUTER SIMULATION OF CONDENSED PHASES

An informal Newsletter associated with Collaborative Computational Project No. 5
on Molecular Dynamics, Monte Carlo and Lattice Simulations of Condensed Phases.

### Number 29                                    November 1988

## Contents

## Editorial

CCP5 has been involved in organising a NATO ASI which was held in Bath at the beginning of September. A brief report and reprint of the abstracts of the lectures is included in this issue of the newsletter.

Only three articles have been submitted for this newsletter. The secretarys would like to remind people that contributions for the newsletter are always welcome.

Contributors to the current issue.
Our thanks go to:

| | |
|---|---|
| D. R. Collins | Department of Chemistry, |
| C. R. A. Catlow | University of Keele, |
| | Keele, Staffs ST5 5BG. |
| | |
| M. J. Davies | School of Chemistry, |
| | University of Bath, |
| | Bath. |
| | |
| M. P. Allen | H. H. Wills Physics Laboratory |
| | Royal Fort, Tyndall Avenue |
| | Bristol BS8 1TL |

# COMPUTER MODELLING OF NEW MATERIALS
## UNIVERSITY OF BRISTOL
A joint CCP5 - CCP9 meeting

4 January - 6 January 1989

This conference will bring together experts in two areas of condensed matter research: atomistic computer simulation methods and electronic structure calculations. These two communities are supported in the UK through the SERC Collaborative Computational Projects CCP5 and CCP9 respectively. The aim of this joint meeting is to encourage cross-fertilization of ideas and techniques in a variety of applications.

The theme of the conference will be the modelling of materials of current technological interest. These include the new high-$T_c$ superconductors, semiconductors, polymers and liquid crystals. The following have agreed to give invited talks:

| | |
|---|---|
| E. A. Colbourne | (ICI Wilton) |
| A. N. Cormack | (Alfred University) |
| D. Dunmur | (Sheffield University) |
| M. Gillan | (Keele University) |
| B. L. Gyorffy | (Bristol University) |
| R. Jones | (Exeter University) |
| W. Mackrodt | (ICI Runcorn) |
| M. Payne | (Cambridge University) |
| A. Sutton | (Oxford University) |

Time will be available for contributed papers and poster sessions.

The meeting will be held in Bristol University's Clifton Hill House, a comfortable hall of residence with integral conference facilities. For further details contact:

Dr. M. P. Allen
H. H. Wills Physics Laboratory
Royal Fort
Tyndall Avenue
BRISTOL BS8 1TL
United Kingdom

Tel: (0272) 303030
JANET: MPA @ UK.AC.BRISTOL.CSA

Note that the electronic mail address given in the first announcement of this meeting (MPA @ UK.AC.BRISTOL.PVA ) is currently not available.

*Registration form overleaf*

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# COMPUTER MODELLING OF NEW MATERIALS
## UNIVERSITY OF BRISTOL
### 4 January - 6 January 1989
## REGISTRATION FORM

NAME          .................................................

ADDRESS       .................................................

                .................................................

                .................................................

                .................................................

                .................................................

Telephone     .................................

Electronic mail   ..................................

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## CONFERENCE CHARGES

Registration fee †                                £10   ...............
Accommodation                                     £32   ...............
Lunches, coffee and tea                           £14   ...............
Dinner on Wednesday 4 January                     £7    ...............
Conference dinner on Thursday 5 January           £12   ...............

TOTAL (Please make payable to 'University of Bristol')    ...............

†The registration fee will be waived for students: supervisor's letter of support is required.

The accommodation charge covers bed and breakfast for the nights of 4 and 5 January. Lunches, coffee and tea will be provided on all three days. Please indicate here any special dietary requirements: ......................

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## CONTRIBUTED PAPERS

I do / do not wish to contribute an oral / poster presentation entitled:

........................................................................

*Please enclose an abstract with this form.* Abstracts should be prepared on A4 paper with a 4 cm. right-hand margin. Slide and overhead projectors will be provided. Please indicate if you require any other audio-visual equipment (e.g. 16mm film, VHS video): ...........................................
It is intended to publish the proceedings of this meeting in a special issue of the journal *Molecular Simulation*. To ensure that this appears in reasonable time, only manuscripts which are given to the organizers at (or before) the meeting will be accepted. Both oral presentations and posters may appear in the proceedings, but all contributions will be subject to the usual refereeing process. Instructions for authors are enclosed.

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Please send this form, together with a cheque for the appropriate amount made out to 'University of Bristol', and an abstract of your contribution, if any, to the following address, to arrive no later than *18 November 1988*:

<div style="margin-left:4em">

Dr. M. P. Allen
H. H. Wills Physics Laboratory
Royal Fort
Tyndall Avenue
BRISTOL BS8 1TL
United Kingdom

</div>

# ADVANCE NOTICE OF A CCP5 SYMPOSIUM

"Novel Methods in Molecular Simulation"

at

Royal Holloway and Bedford New College,

Egham, Surrey, TW20 OEX.

3-4th July 1989

This is a symposium to discuss a number of new techniques that are becoming increasingly relevant to the field of *molecular simulation*. These include, for example, cellular automata, neural nets, percolation lattice-based simulations, aswell as novel methods in MD and MC.

A list of speakers so far includes:

- David Heyes (University of London), Continuum Percolation methods and applications.

- Jan Naudts (University of Anterp), Applications of percolation and lattice gas models.

- David Nicolaides (University of Bristol), Ising models and Mass Tensor MD.

If you are interested in attending or have comments, please contact:

Dr. D.M. Heyes, Department of Chemistry, Royal Holloway and Bedford New College, Egham, Surrey TW20 OEX, UK. Tel.: 0784-34455 ext. 3401; JANET: UHCA015@UK.AC.RHBNC.VAXA

or

Dr. W. Smith, Theory and Computation Section, SERC Daresbury Laboratory, Daresbury, Warrington WA4 4AD, UK. Tel.: 0925-603000 ext. 3257, JANET: WL@UK.AC.DARESBURY.DLGM

On 24th November 1988, Daresbury Laboratory is hosting a *Workshop on Parallel Computing.*

The aim of the workshop is threefold. Primarily it will serve as the inaugural meeting of the Parallel Computer User Group (see enclosed paper) which, as suggested by the Science Board Computing Committee, should coordinate and support university researchers who are interested in exploiting parallelism. Secondly it brings together members of the Collaborative Computational Project (CCP) community in technical matters of joint interest, with the backing of the CCP Steering Panel. Finally we aim to familiarise our visitors with some aspects of the Daresbury Laboratory's computing strategy, including the distributed-memory iPSC/2 and Meiko M10, shared-memory Convex C220 dual-processor vector minisuper and Ardent graphics workstation, and other transputer systems on site.

The experience we have of using this equipment may well be of interest to others. The facilities will be made available for evaluation purposes, and the main machines are accessible via JANET.

The rapid increase in parallel computing resources makes it vital to have regular discussions in order to quickly disseminate new algorithms and techniques, as well as to compare different computer architectures. Hopefully the meeting will encourage that process and stimulate activity in parallel computation in U.K. science.

PLEASE RETURN if you are interested in the Parallel Computer
User Group to                 *R.J.Allan (RJA@DL.DLGM)*
                    *ARCG*
                    *Daresbury Laboratory*
                    *SERC*
                    *Daresbury*
                    *Warrington, WA4 4AD*

Please tick appropriately:

1) I wish my name to be kept on the PCUG mailing list [ ]
2) I wish to attend the meeting at DL on 24/11/88     [ ]

Name ....
Address ....


e-mail address ....
principal interests in parallel computing ....

**A G E N D A**   PCUG meeting   24/11/88

Main Lecture Theatre, Daresbury Laboratory

10.30 C O F F E E

10.45 Opening remarks and background    B.T.Sutcliffe

11.00 Transputer arrays    D.Fincham
11.20 INTEL iPSC/2    M.F.Guest
11.40 Multitasking on shared–memory machines    V.R.Saunders

12.00 Molecular modelling within ICI    J.Kendrick
12.15 Parallel computation in materials science    P.J.Durham
12.30 Geometric parallelism    R.J.Blake
12.45 Concurrency in molecular simulation    W.Smith

1.00 L U N C H and informal discussion over coffee

2.00 FORTNET and FORTRAN programming    R.J.Allan
2.20 Mathematical Subroutine Libraries    L.M.Delves
2.40 Environment, Graphics and Support    J.F.L.Hopkinson

3.00 Reports of the Project Teams

4.00 Closing remarks and disperse    M.F.Guest

## General News

JOINT CCP4/CCP5 MEETING A study weekend on Molecular Simulation and Protein Crystallography will be held at Daresbury on 27th-28th January 1989. The study weekend will bring together workers in molecular simulation together with those involved in protein structure determination to discuss the background and application of molecular dynamics software (XPLOR and GROMOS) in the modelling of protein structures. The main techniques which will be discussed are molecular dynamics structure factor refinement and the inclusion of NMR NOE data in the refinement of macromolecular structures.

Invited speakers include

| | | | |
|---|---|---|---|
| L. Caves | (York) | W. G. J. Hol | (Groningen) |
| E. Dodson | (York) | J. Kuriyan | (New York) |
| W. van Gunsteren | (Groningen) | P. F. Lindley | (Birkbeck) |
| I. Haneef | (Leeds) | G. Taylor | (Oxford) |
| T. Harvey | (Oxford) | W. Weiss | (Yale) |

Further information will be available shortly.

The practical calculation of interionic potentials in solids A two day meeting to be held at the University of Keele on 3rd-4th April 1989. It is being organised by Dr. A. Harker (Harwell) and Dr. R. Grimes (Keele). Invited speakers include

| | | | |
|---|---|---|---|
| N. C. Pyper | S. C. Parker | R. A. Jackson | W. C. Mackrodt |
| M. Leslie | B. Vessal | J. H. Harding | D. L. Cooper |

A poster session will be held for which all delegates are invited to submit contributions. The proceedings will be published as an issue of Molecular Simulation. Further information may be obtained from Dr. R. Grimes, Department of Chemistry, University of Keele, Keele, Staffs. ST5 5BG.

Future meetings A CECAM workshop is being organised on the computer simulation of minerals. This will be held in London in Spring 1989. Further details may be obtained from Dr. G. D. Price, Department of Geological Sciences, University College, University of London, Gower Street, London WC1E 6BT.

Visitors Programme CCP5 uses some of its funds to support visitors to the U.K. from abroad. Readers are invited to suggest suitable names of foreign visitors. Please contact the CCP5 secretaries if you are interested.

Daresbury Daresbury have obtained an INTEL IPSC/2 as replacement for the FPS T20. There is an announcement in this newsletter

about a parallel computing workshop to be held at Daresbury on November 24th.

**UMRCC** UMRCC have announced that the Cyber 205 is to be replaced by an Amdahl VP1200. This will use the IBM MVS/XA operating system. The CYBER 205 will be withdrawn from service at the end of the year. At the same time the ROSCOE operating system will be withdrawn. Files written using ROSCOE (MVS) will no longer be able to be read by users who have no allocation on the VP system. Such files should be transferred to VM/CMS. The IMSL library will also be withdrawn and users should convert to use NAG.

**ULCC** ULCC have announced that the two CRAY-1S computers will be replaced by a single CRAY X-MP/28. It is expected to install the new computer at Christmas. COS 1.16 will be installed soon on the CRAY-1S computers. Users are advised to recompile their programs on the CRAY-1S using COS 1.16 and then recompile again once the XMP arrives. Work is also in progress at ULCC on the common user interface, VM/CMS will be used on the Amdahl and VAX/VMS will be available as an interface to the COS.

**CRAY TIME** CCP5 participants are reminded that CCP5 has an annual allocation of Cray time at Rutherford (Cray XMP-48), which is available for the development of simulation programs which are of general use to the CCP5 community. Readers who wish to use some of this allocation should write to the CCP5 Secretary, Dr. M. Leslie, TCS Division, SERC Daresbury Laboratory, Daresbury, Warrington WA4 4AD.

## The CCP5 Program Library.

We are pleased to report the addition of more programs to the library. We are grateful to Drs. Tildesley and Allen for their contributions.

These programs originally appeared on microfiche in the book "Computer Simulation of Liquids" by M. P. Allen and D. J. Tildesley, published by Oxford University Press, 1987. They are made freely available to members of CCP5, in the hope that they will be useful. The intention is to clarify points made in the text, rather than to provide a piece of code suitable for direct use in a research application. We ascribe no commercial value to the programs themselves. Although a few complete programs are provided, our aim has been to offer building blocks rather than black boxes. As far as we are aware, the programs work correctly, but we can accept no responsibility for the consequences of any errors, and would be grateful to hear from you if you find any. You should always check out a routine for your particular application. The programs contain some explanatory comments, and are written, in the main, in FORTRAN-77. One or two routines are written in BASIC, for use on microcomputers. In the absence of any universally agreed standard for BASIC, we have chosen a very rudimentary dialect. These programs have been run on an Acorn model B computers. Hopefully the translation of these programs into more sophisticated languages such as PASCAL or C should not be difficult.

The CCP5 Program Library provides programs and documentation free of charge to academic centres upon application to Dr. W. Smith, TCS Division, S.E.R.C. Daresbury Laboratory, Daresbury, Warrington WA4 4AD, U.K.. Listings of programs are available if required but it is recommended that magnetic tapes (to be supplied by the applicant) be used. It may also be possible to transfer a small number of programs over the JANET network to other computer centres in the U.K.. Please note that use of inappropriate packing for magnetic tapes (e.g. padded bags) may result in them being considered unusable by Daresbury Computing Division and returned without the required software. Please ensure that these forms of packaging are not used. A list of programs available is presented in the following pages. We should also like to remind our readers that we would welcome contributions to the Program Library. The Library exists to provide support for the research efforts of everyone active in computer simulation and to this end we are always pleased to extend the range of software available. If any of our readers have any programs they would like to make available, please would they contact Dr. Smith.

Table 1: INDEX

# THE CCP5 PROGRAM LIBRARY.

| | | |
|---|---|---|
| ADMIXT | [MD,LJA/MIX,LF,TH+MSD+RDF] | W. Smith |
| CARLOS | [MC,VS+Aquo,TH] | B. Jonsson |
| | | S. Romano |
| CARLAN | [DA,CARLOS structure analysis] | B. Jonsson |
| | | S. Romano |
| CASCADE | [LS,DIL,EM,TH+STR] | M. Leslie/ |
| | | W. Smith |
| CURDEN | [DA,Current Density Correlations] | W. Smith |
| DENCOR | [DA,Density Correlations] | W. Smith |
| EXAMPLES | [Book Examples] | D. Tildesley |
| | | M. P. Allen |
| HLJ1 | [MD,LJA,LF,TH+MSD+RDF] | D.M. Heyes |
| HLJ2 | [MD,LJA,LF,TH+MSD+RDF+VACF] | D.M. Heyes |
| HLJ3 | [MD,LJA,LF/LC,TH+MSD+RDF] | D.M. Heyes |
| HLJ4 | [MD,LJA,LF/CP+CT,TH+MSD+RDF] | D.M. Heyes |
| HLJ5 | [MD,LJA/SF,LF,TH+MSD+RDF] | D.M. Heyes |
| HLJ6 | [MD,LJA,TA,TH+MSD+RDF] | D.M. Heyes |
| HMDIAT | [MD,LJD,G5+Q4,TH+MSD+QC] | S.M. Thompson |
| HSTOCH | [MD/SD,VS+BA,LF+CA,TH] | W.F. van Gunsteren/ |
| | | D.M. Heyes |
| MCN | [MC,LJA,TH] | N. Corbin |
| MCLSU | [MC,LJA,TH] | C.P. Williams/ |
| | | S. Gupta |
| MCMOLDYN | [MD/MC,LJS+FC+AQ, | |
| | LF+QF/G5+QS,TH+RDF] | A. Laaksonen |
| MCRPM | [MC,RPE,TH+RDF] | D.M. Heyes |
| MDATOM | [MD,LJA,G5,TH+RDF+MSD+QC] | S.M. Thompson |
| MDATOM | [MD,LJA,LF,TH+MSD+RDF] | D. Fincham |
| MDDIAT | [MD,LJD,LF+CA,TH+MSD] | D. Fincham |
| MDDIATQ | [MD,LJD+PQ,LF+CA,TH+MSD] | D. Fincham |
| MDIONS | [MD,BHM,LF,TH+MSD+RDF+STF] | D. Fincham/ |
| | | N. Anastasiou |
| MDLIN | [MD,LJL,G5+Q4,TH+MSD+QC] | S.M. Thompson. |
| MDLINQ | [MD,LJL+PQ,G5+Q4,TH+MSD+QC] | S.M. Thompson |
| MDMANY | [MD,LJS+FC,LF+QF,TH] | D. Fincham/ |
| | | W. Smith |
| MDMIXT | [MD,LJS/MIX,LF+QF,TH] | W. Smith |
| MDMPOL | [MD,LJS+FC/MIX,LF+QF,TH] | W. Smith/ |
| | | D. Fincham |
| MDPOLY | [MD,LJS,G5+Q4,TH+MSD+QC] | S.M. Thompson |
| MDMULP | [MD,LJS+PD+PQ/MIX,LF+QF,TH] | W. Smith |
| MDSGWP | [MD,LJA/SGWP,LF,TH+VACF+RDF+QC] | W. Smith/ |
| | | K. Singer |
| MDTETRA | [MD,LJT,G5+Q4,TH+MSD+QC] | S.M. Thompson |
| MDZOID | [MD,GAU,LF+QF,TH+MSD+RDF+VACF] | W. Smith |

```
NAMELIST    [UT, Namelist emulation]                    K. Refson
SCN         [MC,LJA,RFD,TH]                             N. Corbin


SURF      [MD,BHM/TF/2D,LF,TH+RDF]                D.M. Heyes
SYMLAT    [LS,PIL,EM+SYM,TH+STR]                  Harwell
THBFIT    [LS,PIL,EM,Potential fitting]           Harwell
THBPHON[LS,PIL/3B,EM,Phonon dispersion]           Harwell
THBREL    [LS,PIL,EM,TH+STR]                       Harwell
```

Key:

| Program types: | MD | Molecular dynamics |
|---|---|---|
| | MC | Monte Carlo |
| | LS | Lattice simulations |
| | SD | Stochastic dynamics |
| | DA | Data analysis |
| | UT | Utility package |

| System models: | LJA | Lennard-Jones atoms |
|---|---|---|
| | LJD | Lennard-Jones diatomic molecules |
| | LJL | Lennard-Jones linear molecules |
| | LJT | Lennard-Jones tetrahedral molecules |
| | LJS | Lennard-Jones site molecules |
| | RPE | Restricted primitive electrolyte |
| | BHM | Born-Huggins-Meyer ionics |
| | SGWP | Spherical gaussian wavepackets |
| | TF | Tosi-Fumi ionics |
| | VS | Variable site-site model |
| | BA | Bond angle model |
| | PD | Point dipole model |
| | PQ | Point quadrupole model |
| | MIX | Mixtures of molecules |
| | GAU | Gaussian molecule model |
| | FC | Fractional charge model |
| | PIL | Perfect ionic lattice model |
| | DIL | Defective ionic lattice model |
| | 3B | 3-body force model |
| | 2D | Two dimensional simulation |
| | SF | Shifted force potential |
| | FC | Fractional charge model |
| | AQ | Aqueous solutions |

| Algorithm: | G5 | Gear 5th order predictor-corrector |
|---|---|---|
| | Q4 | Quaternion plus 4th. order Gear P-C. |
| | LF | Leapfrog (Verlet) |
| | QF | Fincham Quaternion algorithm |
| | QS | Sonnenschein Quaternion algorithm |

|      |                                    |
|------|------------------------------------|
| LC   | Link-cells MD algorithm            |
| CP   | Constant pressure                  |
| CT   | Constant temperature               |
| TA   | Toxvaerd MD algorithm              |
| CA   | Constraint algorithm               |
| EM   | Energy minimisation                |
| SYM  | Symmetry adapted algorithm         |
| RFD  | Rossky-Friedman-Doll algorithm     |

Properties:

|      |                                    |
|------|------------------------------------|
| TH   | Thermodynamic properties.          |
| MSD  | Mean-square-displacement           |
| RDF  | Radial distribution function       |
| STF  | Structure factor                   |
| VACF | Velocity autocorrelation function  |
| QC   | Quantum corrections                |
| STR  | Lattice stresses                   |

POSTDOCTORAL POSITION

## THEORETICAL CHEMISTRY

**LOCATION:** Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina.

**DURATION:** One year; can be extended.

**SALARY:** $18,000/year or more, depending on qualifications.

**STARTING DATE:** December 1988

**PREREQUISITE EXPERIENCE:** Strong background in theoretical chemistry and experience with computing.

**JOB DESCRIPTION:** Participation in research work on the structure and dynamics of aqueous solution in bulk and especially at interfaces, theoretical study of reactions in condensed phases. Recent examples of research can be found in J. Chem. Phys. 88, 7014 (1988), J. Chem. Phys. 87, 6682 (1987), J. Chem. Phys. 86, 376 (1987).

**FACILITIES:** Computational facilities include VAX 11/780, IBM 3081 and CONVEX 2 on campus. Computational time is available on CRAY XMP by access to Pittsburgh Supercomputer Center. In addition, starting Fall 1989 the North Carolina Supercomputer Center will host a CRAY Y-MP/432 supercomputer.

**APPLICATION:** Candidates should send a curriculum vitae and a statement of research interests to:

Professor Max Berkowitz
Department of Chemistry
University of North Carolina
CB# 3290, Venable Hall
Chapel Hill, NC 27599-3290

Telephone: (919) 962-1218

~ Please Post ~

UNIVERSITY OF MANCHESTER

Theoretical Chemistry Group

Postdoctoral Research Assistantship

There exist eighteen man-months worth of an SERC supported grant for a theoretical chemist or physicist to work on molecular theories and the computer simulation of nematic liquid crystals, the computing to be carried out on the VP1200 super-computer. The starting date, ideally, should be before 1st January, 1989.

Applicants should preferably have had experience of the computer simulation of fluids. Salary on the 1A Range for Research and Analogous Staff (£9305-£11,015). Scientific enquiries and applications with details of research experience and with the names and addresses of two referees to Dr. A.J. Masters, (061-275-4679), Department of Chemistry, University of Manchester, Manchester M13 9PL.

# Computer Simulation Studies of Micas and other layered Silicates

D. R. Collins and C. R. A. Catlow

Department of Chemistry,

University of Keele, Staffs. ST5 5BG.

Following the success of recent modelling studies of framework silicates, we have extended energy minimisation and more recently free-energy minimisation techniques to predict structural and elastic properties of layered structured compounds, concentrating initially on the mica, muscovite ($K\ Al_2\ AlSi_3\ O_{10}\ (OH)_2$). The structure of muscovite can be described in terms of the linking of edge sharing octahedra and corner sharing tetrahedra, which together form a rigid, negatively charged layer. These layers are relatively weakly held together by charge compensating potassium interlayer cations, resulting in a dominant cleavage parallel to the layers. Because of the marked differences between intra and interlayer bonding, the crystal also exhibits great anisotropy in its elastic properties.

Due to the structural complexity (3 cation sites, octahedral, tetrahedral and interlayer, and the presence of hydroxide groups) muscovite provides a rigorous test of the interatomic potentials employed in many earlier studies of metal oxides and simple silicates. As in our previous studies of framework structured silicates, the fully ionic model has been used, with 3 body bond bending terms included in the tetrahedral interactions.

The unit cell dimensions of both energy minimised and free energy minimised (at 300 K) simulations to constant pressure are all within 2%

(and frequently 1%) of those observed experimentally at room
temperature, as shown below:

| Cell dimension | Expt. room temp. | 0 K simulation | 300 K simulation |
|---|---|---|---|
| a | 5.204 | 5.246 | 5.254 |
| b | 9.018 | 9.129 | 9.195 |
| c | 20.073 | 19.780 | 20.009 |
| $\beta$ | 95.82 | 96.53 | 96.54 |

The free energy minimisation at 300K used the quasi-harmonic techniques
recently developed by Parker.

Of particular interest is the contrasting response in the two
simulations of the intra layer dimensions (a and b) and the inter layer
dimension (c). The former dimensions are rather invariant, unlike the
latter dimension which increases significantly in the free energy
simulation, agreeing extremely well with that observed at room
temperature. This clearly results from the weak interlayer bonding and
reveals the necessity to include the effects of thermal expansion in the
simulation of such a material.

The elastic stiffness modulii of both simulations also agree well with
experiment. The compressional modulii within the layers are rather
invariant to temperature ($C_{11}$ and $C_{22}$ ~ 23, cf expt 18), whereas that
perpendicular to the layers decreases with temperature, ($C_{33}$ 6.56 at 0k,
5.72 at 300K, cf expt 5.91). (Units for elastic modulii $10^{10}Nm^{-2}$). We also
correctly predict $C_{15}$ to be negative (-0.19 at 0k, -0.17 at 300k cf expt
-0.20).

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Simulations (at 0 K) were performed to investigate the effect of octahedral cation substitution on the stabilities and polyhedral distortions of the mica, phlogopite ($K Mg_3 AlSi_3 O_{10} (OH)_2$). Structures containing 100% octahedral occupancies of $Mg^{2+}$, $Co^{2+}$, $Ni^{2+}$ and $Fe^{2+}$ are stable, while those with cation radii larger than 0.78Å ($Mn^{2+}$, $Cd^{2+}$) are not. The lattice energies of relaxed structures containing these octahedral cations are given below:

| Octahedral Cation | Ionic Radii/Å | Lattice energy per formular unit/eV |
|---|---|---|
| $Ni^{2+}$ | 0.690 | -581.796 |
| $Mg^{2+}$ | 0.720 | -581.688 |
| $Co^{2+}$ | 0.745 | -580.156 |
| $Fe^{2+}$ | 0.780 | -578.684 |
| $Mn^{2+}$ | 0.830 | -575.216 |
| $Cd^{2+}$ | 0.950 | -569.188 |

We not only predict the experimentally unstable compositions to have the least favourable lattice energies, but the correct order of stability in the observed structures. We also reproduce the trends in the response of the unit cell dimensions and polyhedral distortions (tetrahedral rotation and octahedral flattening) to octahedral cation substitution.

These results together with the close agreement of bond lengths and and bond angles to experiment, give confidence in the use of our fully ionic potential model in the simulation of micas. We have also shown that when compared to experimental observations at room temperature, calculated properties can be significantly improved by using free energy

minimisation simulations, particularly in the case of crystals that exhibit weak interactions in one or more directions.

Despite the success of our potential model, we have not as yet been able to adequately simulate other phyllosilicates whose layers are uncharged and contain no interlayer cations. The hydrogen bonded layers of Kaolinite have proved the most difficult, with the simulation of pyrophyllite, whose interlayer attraction is dominantly a Van der Waals type, also being poor. The simulation of these structures, whose layers are more weakly bonded than micas, clearly require a more sophisticated potential model.

# Modelling Morphology of Ionic Crystals

Mark J. Davies

School of Chemistry, University of Bath, Bath

In this short note I shall describe a recently developed program for generating the crystal morphology and the important role that energy minimisation plays in calculating the morphology. Early work by Gibbs(1) and Wulff(2) established that evaluating the surface energies of each crystal face is sufficient to give the equilibrium morphology of small crystals. In this work the surface energies were determined using the MIDAS code developed by P.W. Tasker(4) where the crystal is divided into two regions; a surface region where the ions are allowed to relax to their minimum energy positions and a bulk region where the ions are held fixed. However, one limitaion of this technique is that dynamic and entropic effects are not included.

The approach for calculating the morphology follows the work of Dowty(4). This takes the spacegroup, lattice vectors and Miller indices with their corresponding surface energy $\gamma$ and goes through 4 stages.

1) Generating the vector plane equation for each input plane and all symmetry related planes.

The program requires a single Miller index which is a member of a group of symmetry related planes. Using the atomic positions in the spacegroup the symmetry matrices for the crystal and all their possible products can be generated. Thus the position y, y-x, -z gives the matrix

$$S_p = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

The symmetry related Miller indices are obtained by multiplying the Miller vector by the inverse of the $S_p$ matrices (inverse because the face indices are reciprocal of the axial intercepts). This gives us the set of all the symmetry planes in the crystals coordinate system. It is much easier to handle things in a cartesian system so these are converted by means of a conversion matrix M where

$$M = \begin{pmatrix} av_1 & 0 & 0 \\ av_2 & b\sin\alpha & 0 \\ a\cos\beta & b\cos\alpha & c \end{pmatrix}$$

$$v_1 = \frac{\sqrt{1-\cos^2\alpha - \cos^2\beta - \cos^2\gamma - 2\cos\alpha\cos\beta\cos\gamma}}{\sin\alpha}$$

$$v_2 = \frac{\cos\gamma - \cos\alpha\cos\beta}{\sin\alpha}$$

a, b, c, $\alpha$, $\beta$ and $\gamma$ are the unit cell dimensions obtained from the lattice vectors (5). The Miller indices for the planes are converted from crystal to cartesian coordinate systems by postmultiplying by the inverse matrix $M^{-1}$

This now gives the vector equation for each plane in the form

$$Ax + By + Cz = D$$

where A, B and C are the components of the normalised plane vector. D is the perpendicular distance from the plane to the origin and is proportional to the surface energy.

2) Generation of the vertices for the equilibrium crystal Morphology

The coordinates of the vertices are found by solving the three simultaneous plane equations for all planes generated in section 1. If a generated vertex is part of the crystal it must lie on or inside all the faces of the crystal. This is checked by calculating the perpendicular distance of the corner from each plane in the crystal. If any of these are greater than zero the vertex is beyond one of the faces of the crystal and is therefore discarded.

3) Generating edges of crystal from the vertices

A pictorial representation of the crystal requires the edges. These are obtained by considering all possible pairs of vertices, if the pair have two planes in common then an edge exits between them. In the program these edges are then grouped into faces.

4) Plot out the crystal morphology

The crystal morphology can now be plotted out, rotated to view the morphology from any angle.

Application: Hematite

This technique can be illustrated by application to hematite $\alpha$-$Fe_2O_3$ where a detailed experimental study is available(6) for comparison. The surface structure and energy were evaluated for each crystal face and after energy minimisation all surfaces show a high degree of relaxation but the amount of relaxation is unique to each individual surface. An important consequence of this is that the relative stability of the surfaces change on relaxation. Before relaxation the order of stability is

$$\{1012\} < \{1120\} < \{1011\} < \{0001\} < \{1010\}$$

and after it is

$$\{10\overline{1}2\} < \{10\overline{1}0\} < \{11\overline{2}0\} = \{0001\} < \{10\overline{1}1\}$$

The effect of this reordering has a dramatic effect on the predicted morphology (Figure 1). We go from a simple rhombohedral form for the unrelaxed structure to a complex habit for the relaxed structure. Comparing our predicted morphology with crystals grown by Bressières and Buro (6) yields good agreement although the basal plane is more prominent in the crystal that they quote. This shows the important effect relaxation has on surface energy and therefore morphology, the unrelaxed morphology being in complete disagreement with the experimental crystals. Thus this indicates that we cannot consider surfaces as simple bulk terminations as is common in most analytical methods of predicting morphology such as the periodic bond chain approach developed by Hartman and Perdok(7).

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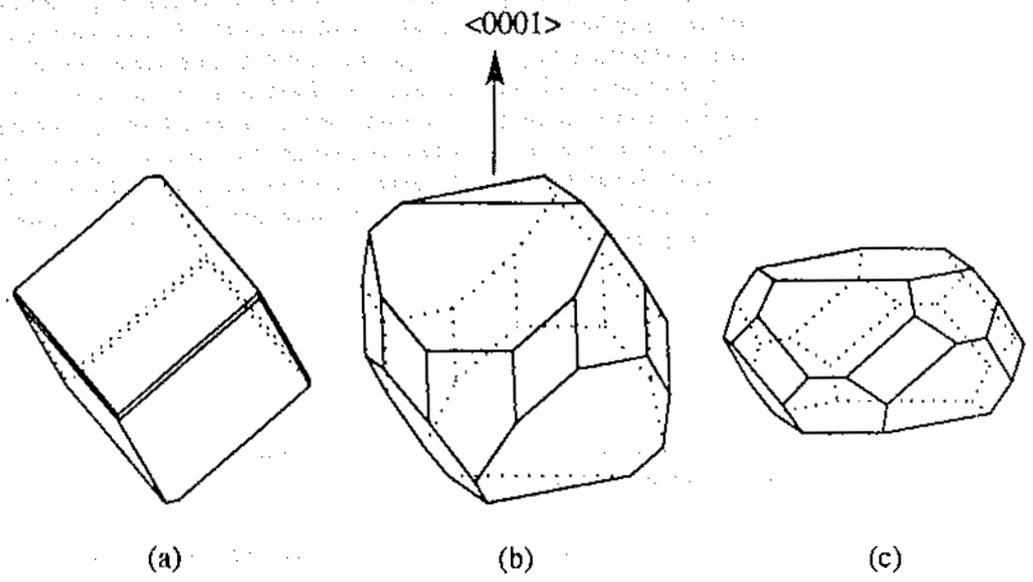7. Hartman P and Perdok W 1955 Acta Cryst. 8 49,521,525

Figure 1  Predicted morphologies for $Fe_2O_3$ a) unrelaxed b) relaxed
c) schematic of experimental morphology

# PATH INTEGRAL SIMULATION OF ROTORS

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This long-overdue article arose out of my participation in a 1987 CECAM workshop on 'Quantum Simulation of Condensed Matter'. That workshop was divided into two halves: one discussing the Car-Parrinello method, and the other looking mainly at the path-integral approach. I was involved with the path-integral simulation group, and was especially interested in discussing the treatment of molecules with rotational degrees of freedom. It turns out that some of the problems faced in the simulation of rotors are closely related to the treatment of exchange in atomic boson and fermion systems. In some ways, the one-dimensional rotor problem is simpler. I shall not review the basic formalism of path-integral Monte Carlo here: an introduction to the subject can be found elsewhere [1].

There has already been some work on quantum simulation of systems with rotational degrees of freedom, notably the simulation of water at ambient temperatures [2]. The basic formalism of the rotational problem, and differences from the translational case, have been dealt with in these papers. I wished to clarify (in my own mind at least!) points which become important at low temperature, specifically the effect of periodicity on the density matrix and the symmetry restrictions imposed on (for example) homonuclear diatomic molecules. A typical system of interest might be hydrogen or deuterium adsorbed at a graphite surface; similar points would apply to solid hydrogen or methane.

Consider a molecule constrained, perhaps by a strong surface field, to lie flat in a plane. It can rotate in the plane, in an external potential field. For a planar rotor such as this there is one angular coordinate. The free-rotor wave-functions and energy levels, of course, are

$$
\begin{aligned}
\psi_m(\phi) &= \frac{1}{\sqrt{2\pi}} \exp im\phi \\
E_m &= Bm^2
\end{aligned}
\tag{1}
$$

with $m = 0, \pm 1, \pm 2, \ldots$ and $B = \hbar^2/2I$, $I$ being the moment of inertia. The free-rotor density matrix $\rho(\phi_1, \phi_2; \beta)$ at temperature $T$ with $\beta = 1/k_B T$ is written as the usual sum over states:

$$
\rho(\phi_1, \phi_2; \beta) = \frac{1}{2\pi} \sum_{m=-\infty}^{\infty} \exp im\phi_{12} \exp -\beta B m^2
\tag{2}
$$

with $\phi_{12} = \phi_1 - \phi_2$. This expression is even in $\phi_{12}$, as the complex exponentials can always be combined to give cosine functions. More usefully, however, we can apply the Poisson sum formula for Fourier transforms, to re-write $\rho$ as

$$
\rho(\phi_1, \phi_2; \beta) = \frac{1}{\sqrt{\beta B}} \sum_{k=-\infty}^{\infty} \exp\{-(\phi_{12} + 2k\pi)^2/4\beta B\}.
\tag{3}
$$

This is a sum of an infinite number of overlapping Gaussians in $\phi_{12} = \phi_1 - \phi_2$,
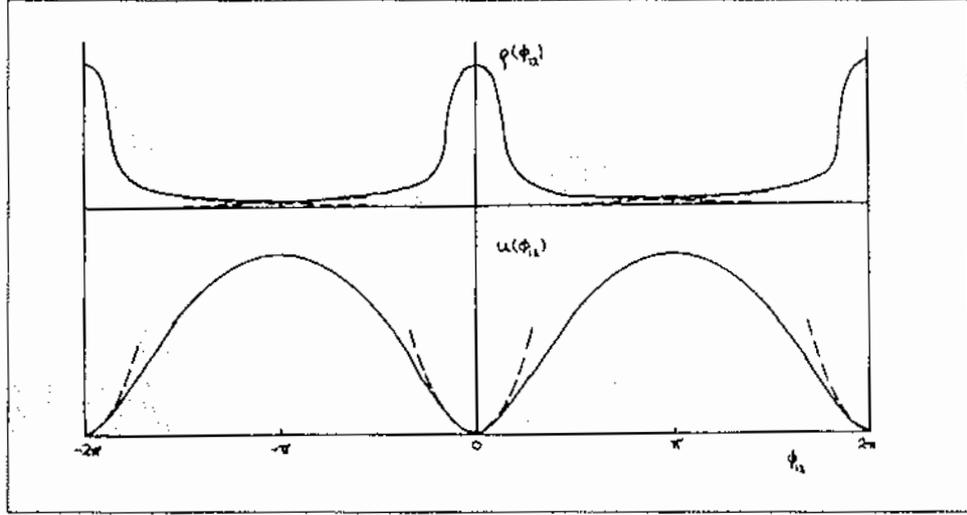
Figure 1: Sketch of the density matrix $\rho(\phi_{12})$ (solid line) as a sum of overlapping Gaussians (dashes), and the associated quantum potential $u(\phi_{12})$.

centred at $0, \pm 2\pi, \pm 4\pi$ etc. , and has period $2\pi$ (see Figure 1). The single Gaussian corresponding to $k = 0$ is just like the analogous translational free particle density matrix. Writing $\rho(\phi_{12}) = \exp -\beta u(\phi_{12})$ gives rise to the standard harmonic 'spring' potential $u(\phi_{12})$ between beads in the polymer of the classical isomorphism. In the rotor case, $u(\phi_{12})$ becomes a periodic potential with minima at $\phi_{12} = 0, \pm 2\pi \dots$, and maxima at $\phi_{12} = \pm \pi \dots$ . At high temperatures the potential is very strong, and the harmonic approximation is good. At lower temperatures, correction terms arise from the overlapping Gaussians in $\rho$. These correspond to paths between $\phi_1$ and $\phi_2$ which make one or more complete revolutions in angle between the end points. Drawing the paths on the surface of a cylinder, with motion along the axis representing imaginary time, and $\phi_{12}$ corresponding to rotation about the axis, is a useful visual aid (see Figure 2). Indeed, if one draws the molecular axes as diameters across the cylinder, the path resembles a section of a ribbon in three dimensions.

In the usual way, we write the partition function for a single quantum rotor as a classical configuration integral involving $P$ rotors:

$$Q = \int_{-\pi}^{\pi} d\phi_1 \int_{-\pi}^{\pi} d\phi_2 \dots \int_{-\pi}^{\pi} d\phi_P \quad \rho_{12}\rho_{23}\dots\rho_{P-1P}\rho_{P1} \tag{4}$$

where $\rho_{12}$ is shorthand for $\rho(\phi_1, \phi_2; \beta/P)$ etc. Note that each term now has inverse temperature $\beta/P$ instead of $\beta$. The polymer of linked beads is cyclic:
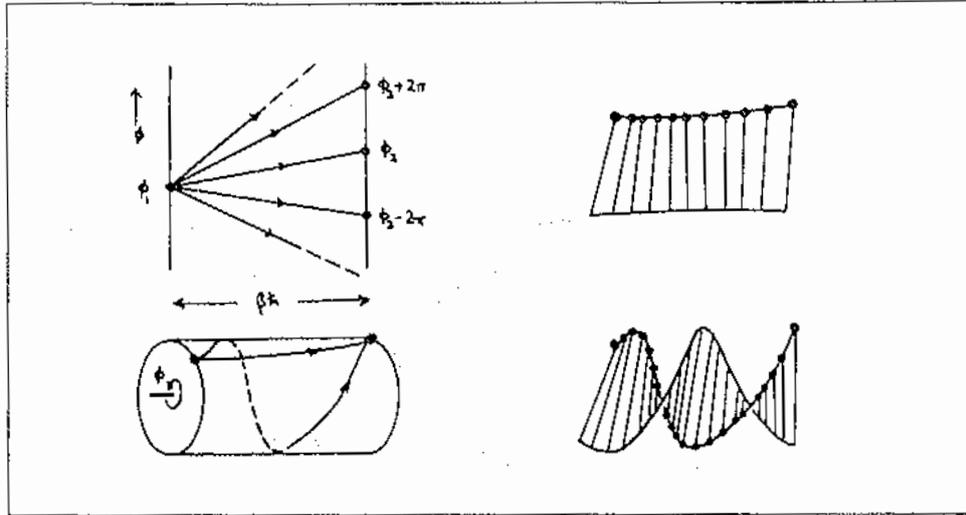
Figure 2: Paths $\phi$ over an imaginary time interval $\beta\hbar$ drawn in the plane, and on the surface of a cylinder. We also show the 'ribbon' picture for the untwisted and single-twist paths.

the classical isomorphism becomes a path drawn on the surface of a torus. It is essential to allow the whole trajectory to sample paths in which one or more angular turns are made during the circuit in imaginary time, i.e. to allow twisted ribbon forms as well as the obvious untwisted configuration. See Figure 3. Singly- and multiply-twisted configurations will be higher in energy, and hence less likely, because the 'springs' are more stretched in these cases. Clearly, however, this situation depends upon the temperature and the value of $P$: it is precisely these effects that become interesting in the quantum regime.

Let us quickly note a couple of points. An external potential energy term should have been included in the above equations; we are sticking to the free-rotor case for simplicity of notation. Similarly we could generalize to the case of many interacting rotors. Also, it should be noted that the quasi-topological classification of configurations by twist or winding number is not strict, since the links between beads are not unbreakable. There is a finite barrier to twisting/untwisting, that could, in principle, be traversed.

All these types of configuration should be sampled (with the appropriate Boltzmann weights) in a path-integral simulation. In principle, interconversion of twisted and untwisted forms could occur naturally during the simulation, but as a practical matter this is highly unlikely unless special efforts are made. Introducing a $2\pi$ twist involves crossing a high barrier and carrying out a mul-
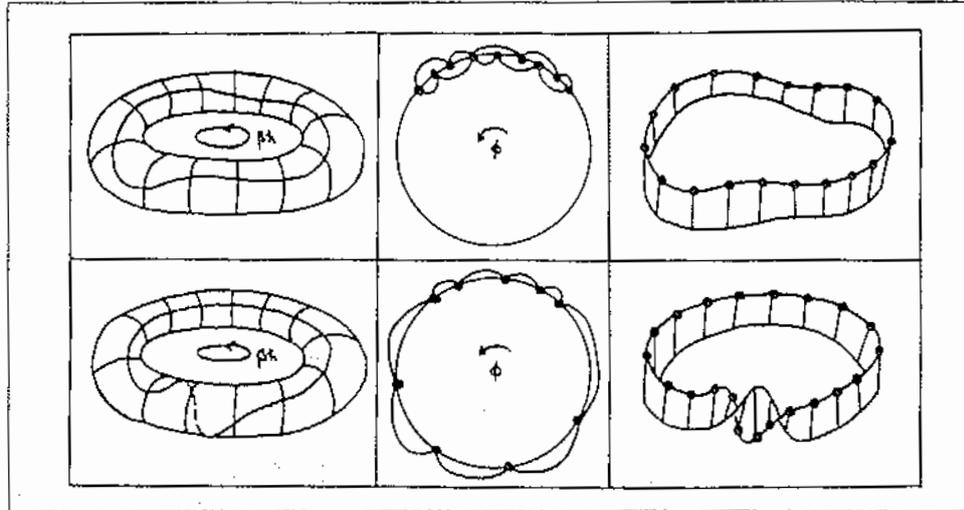
Figure 3: Cyclic paths $\phi$ over an imaginary time interval $\beta\hbar$ drawn on the surface of a torus, in the 'ribbon' form, and projected onto the angle plane. We show the untwisted and single-twist paths.

tiparticle move, with possible large changes in the external potential term.

The above observations apply to (say) heteronuclear diatomic molecules like HD. For homonuclear species, in well-defined nuclear spin states, symmetry restrictions apply to the density matrix: a change in angle $\phi_{12}$ by $\pi$ must lead to either no change (symmetric case) or a change of sign (antisymmetric case). This corresponds to restricting the sum in eqn (2) to even values of $m$ or odd values of $m$ respectively.

For the symmetric case, the density matrix $\rho^+$ has periodicity $\pi$ and is always positive. This can be seen in the Poisson sum expression analogous to eqn (3):

$$\rho^+(\phi_1, \phi_2; \beta) = \frac{1}{\sqrt{4\beta B}} \sum_{k=-\infty}^{\infty} \exp(-(\phi_{12} + k\pi)^2/4\beta B). \tag{5}$$

$\rho^+$ and the corresponding quantum spring potential are shown schematically in Figure 4. Half-twisted configurations of the classical ring polymer 'ribbon', i.e. Möbius strip configurations, are now allowed and must be sampled, but otherwise the technical problems are as for the heteronuclear case.

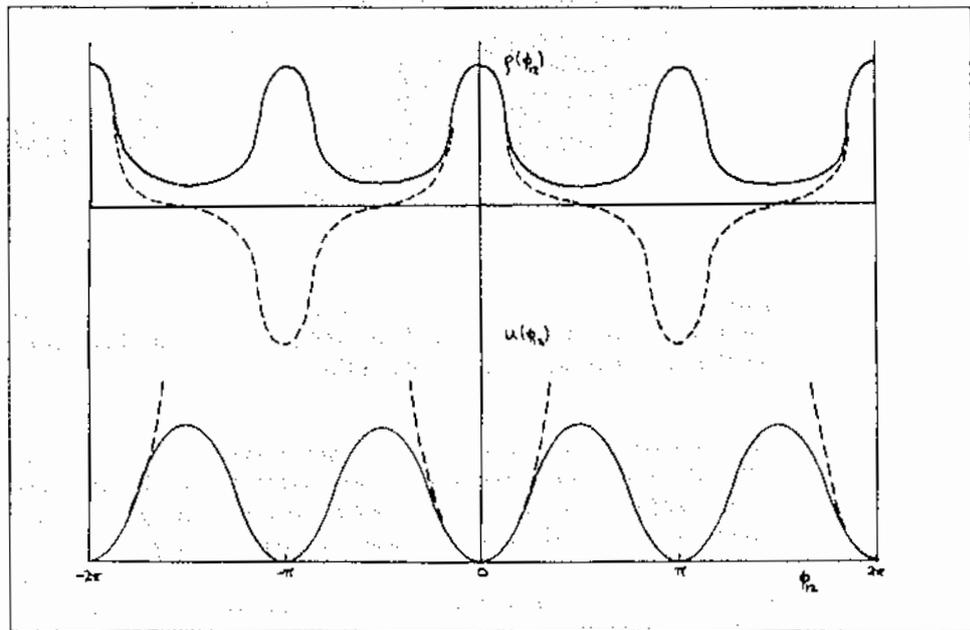For the antisymmetric case, the density matrix $\rho^-$ takes positive and nega-

Figure 4: Sketch of the density matrix $\rho^+$ and the associated quantum potential $u^+$ (solid lines). We also show $\rho^-$ and its potential $u^-$ (dashes).

tive values:

$$\rho^-(\phi_1, \phi_2; \beta) = \frac{1}{\sqrt{4\beta B}} \sum_{k=-\infty}^{\infty} (-1)^k \exp(-(\phi_{12} + k\pi)^2 / 4\beta B). \qquad (6)$$

This presents a problem: negative weights cannot be used directly in a Monte Carlo sampling program. Put another way, the quantum potential diverges at $\phi_{12} = \pm\pi/2$ and is undefined outside this range (see Figure 4). One way around this is to incorporate the changes of sign (a factor of -1 for each nearest-neighbour angle $\phi$ such that $|\phi| > \pi/2$) with the quantity to be averaged, and conduct the sampling with the absolute value distribution $\varrho = |\rho^-|$, which again has periodicity $\pi$. (This choice is not the only one. We could set $\varrho = \rho^+$, which has a roughly similar form, and follow through in the same way: this might have advantages.) The appropriate formulae for ensemble averages are exactly those used in umbrella sampling with a specified weight function. Explicitly,

$$< A > = \frac{\int \mathrm{d}\phi_1 \int \mathrm{d}\phi_2 \cdots (\rho_{12}^-/\varrho_{12})(\rho_{23}^-/\varrho_{23}) \cdots \varrho_{12}\varrho_{23} \cdots A}{\int \mathrm{d}\phi_1 \int \mathrm{d}\phi_2 \cdots (\rho_{12}^-/\varrho_{12})(\rho_{23}^-/\varrho_{23}) \cdots \varrho_{12}\varrho_{23} \cdots} \qquad (7)$$

We define a weighting function $W$ which is the product of all the ratios $(\rho_{12}^-/\varrho_{12})$, $(\rho_{23}^-/\varrho_{23}) \cdots$ i.e., in this case, of all the nearest-neighbour sign changes; hence $W$ takes values $\pm 1$. We conduct simulations using $\varrho$ as the sampling distribution, and denote averages in this ensemble by $< \ldots >_W$. Then eqn (7) becomes simply

$$< A > = < WA >_W / < W >_W . \qquad (8)$$

Unfortunately, the averages will involve positive and negative contributions which will substantially cancel at low temperature, giving poor statistics. Otherwise, the situation is very close to that described above for the symmetric case.

The key question that remains, in all the above cases, is how to introduce twists and half-twists into the configuration during the course of a simulation? This problem is particularly acute if there exists an external potential acting on the rotor, or if there are significant intermolecular interactions in a system of many rotors. We can take our lead here from quantum simulations of systems of identical atoms. The points made above are essentially identical with those faced in the simulation of atomic bosons and fermions, which is not really surprising. The relation between the unrestricted density matrix $\rho$ of eqn (3) and the symmetrized functions $\rho^\pm$ of eqns (5,6) may be written (apart from normalizing factors)

$$\rho^\pm(\phi_1, \phi_2; \beta) = \sum_P (\pm 1)^P \rho(\phi_1, \mathcal{P}\phi_2; \beta) \qquad (9)$$

where $\mathcal{P}$ is a symmetry operation (here $\mathcal{P}\phi = \phi$ or $\phi + \pi$), and the $(\pm 1)$ factor is the signature of the operation. The sum is over all such operations (here

just two). For the general bose/fermion case we sum over all (even and odd) permutations $\mathcal{P}$ of identical particles. The observation above, that there are unpleasant cancelling terms in the antisymmetric ensemble average, comes up again and again in the consideration of strongly-interacting fermion systems. There does not seem to be a quick and easy way out of this one. The other problem, of introducing drastic modifications of the polymer chain during the simulation, has received some attention [3,4,5]. Possible solutions involve direct sampling of the internal degrees of freedom of the polymer chain, using the external potential in a standard accept/reject prescription. This may entail complete or partial reconstruction of the ring polymer during a Monte Carlo move [5,6,7], rather than just undertaking single-bead moves. The rotor system seems to provide a simple test-bed for these methods.

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CCP5/NATO ASI : COMPUTER SIMULATION OF FLUIDS, POLYMERS AND
SOLIDS,

University of Bath,

4th - 17th September, 1988


The Summer School was attended by approximately a hundred lecturers and students from fifteen different countries. A wide range of topics were considered. Contemporary techniques for energy minimisation, molecular dynamics, Monte-Carlo and quantum simulations were reviewed. Lectures emphasised the exciting applications of modern simulation studies ranging from high temperature superconductors to protein dynamics. The School included problem classes and lively evening discussion sessions. Particularly notable were short contributions from participants which were of high quality and which again illustrated the diversity of the subject.

The organising Committee of the School are grateful to NATO for their sponsorship and to all the lecturers and participants who made the School such a success.

## Introduction to Computer Modelling of fluids, polymers and Solids

C. R. A. Catlow, Department of Chemistry, University of Keele, Staffs, ST5 5BG

### Abstract

This lecture will summarise the scope of contemporary modelling techniques, and will highlight some recent achievements of simulation methods. An introduction will be given to the key area of interatomic potentials. Limitations of present techniques will be discussed and the likely future directions of the field will be summarised.

## Energy Minimisation studies of Defects in Solids

C. R. A. Catlow, Department of Chemistry, University of Keele, Staffs, ST5 5BG

### Abstract

One of the most successful applications of modelling techniques in solid state has been the use of force balance procedures to obtain the structure and energies of defects and impurities in crystalline materials. In this lecture we will summarise the methodologies used in such calculations and will describe extension of the techniques to the calculation of defect entropies and free energies. Application of the methods will be reviewed, where we will pay special attention to work on ionic materials, for which simulation methods have had an impact on both our quantitative and qualitative understanding of defect processes.

## Parallel computers in the simulation of Solids and Fluids

David Fincham, Computer Centre, University of Keele, Staffs, ST5 5BG

### Abstract

These lectures will discuss the concept of parallelism in computing, explain the technological forces which make it an inevitable development. They will emphasize that parallel computing requires a completely different computational model from conventional computing. This makes it easier for novices than experts. In the real world, everything happens in

parallel, so it ought to be simple to simulate the world on a parallel computer. Unfortunately, the general tools to do this are not available. We have to do it separately for every problem and every parallel computer. The lectures describe in detail two classes of problem and two types of parallel computer. Crystalline solids have long-range order and comparatively short-range interactions. They can be simulated on massively parallel computers like the DAP. Examples are Monte-Carlo simulation of lattice spin models, and molecular dynamics of plastic crystals. Molecular liquids are less ordered: they can also be simulated on the DAP, but a better approach is to use systolic loop methods on multiple transputers.

### Non-Equilibrium methods

D. J. Evans, Research School of Chemistry, Australian National University, P.O. Box 4, Canberra, ACT 2600 Australia.

### Abstract

A review is presented of modern computer simulation techniques for computing the transport properties of fluids. Particular emphasis will be placed on the non-linear transport properties, for example rheological properties. The exact relationships between nonequilibrium computer simulations and nonequilibrium statistical mechanics will also be covered. This will include a brief discussion of the nonlinear generalisations of the famous Green-Kubo relations. The relationship between steady state and transient fluctuations and the derived properties of steady states will also be discussed.

### Energy Minimisation 1. Introduction to periodic systems

W. C. Mackrodt, I.C.I. Chemicals and Polymers Ltd., P.O. Box 8, The Heath, Runcorn, Cheshire, WA7 4QD, U.K.

### Abstract

This lecture introduces some of the basic ideas and approximations used in the real-space energy and free enegry minimisation of periodic systems. The topics covered will include the Born-Oppenheimer approximation, effective potentials, the shell-model, minimisation methods, energy minimisation at 0K, lattice dynamics in the harmonic approximation, thermal expansion and free energy minimisation. Anharmonic effects and the super-cell approach to the free energy of point defects will also be discussed.

### Atomistic simulation of ceramic oxides: the new high $T_c$ superconductors

W. C. Mackrodt, I.C.I. Chemicals and Polymers Ltd., P.O. Box 8, The Heath, Runcorn, Cheshire, WA7 4QD, U.K.

## Abstract

Over the past decade or so, atomistic lattice simulations have been used with much effect to investigate many of the properties of ceramic oxides. The recent discovery of high $T_c$ ceramic superconductors has presented a unique opportunity to extend the range of application of these techniques still further, at a time when there is almost unprecedented interest in these materials. This lecture will review recent lattice calculations of the structural, dynamic and point defect properties of $La_2CuO_4$ and other ternary cuprates related to high $T_c$ superconductivity.

## Computer Simulation of Inorganic Materials

R. A. Jackson, Department of Chemistry, University of Keele, Staffs, ST5 5BG

## Abstract

This lecture will present some recent applications of computer simulation techniques to inorganic materials. The techniques employed are lattice energy minimisation and defect energy minimisation. Examples of applications will include zeolites, electro-optic semiconductors and high-$T_c$ superconductors.

## Molecular dynamics

A. J. C. Ladd, Lawrence Livermore Laboratory, Livermore, California, U. S. A.

## Abstract

The basic methodology of equilibrium molecular dynamics is described. Examples from the literature are used to illustrate how molecular dynamics has been used to resolve theoretical controversies, provide data to test theories, and occasionally to discover new phenomena. The emphasis is on the application of molecular dynamics to an understanding of the microscopic physics underlying the transport properties of simple fluids.

# Path-Integral Quantum Simulation

M.J. GILLAN
Physics Department, University of Keele,
Keele, Staffordshire, U.K.

## Lecture 1

The first lecture will develop and explain Feynman's path-integral formalism of quantum-statistical mechanics, and show how it gives a natural way of simulating quantum systems in thermal equilibrium. I will begin by explaining the theory for a very simple system, consisting of a single particle in one dimension acted on by an external potential – a particular example of this is the simple harmonic oscillator. I will start from the standard basic expressions for the partition funtion and the thermal averages of observables, and show how a simple sequence of mathematical operations allows these to be brought into Feynman's path-integral form; in this form, the quantities of interest are expressed as an integral over cyclic paths of the particle. This integral can be integrated via a classical Monte Carlo simulation. This method, generalized to many particles in three dimensions, gives a simulation technique for quantum many-body systems. I will discuss how to calculate some important observables like the energy and pressure of the system and the radial distribution functions. I will also suggest some simple calculation exercises which allow one to appreciate the meaning of the technique for simple systems like the harmonic oscillator. In the application of path-integral techniques to systems like liquid helium, the inclusion of quantum exchange effects is crucial, and I plan to indicate how this can be done.

## Lecture 2

The second lecture will be concerned with applications of path-integral simulation, which will be taken from the published literature. Two classes of problem are of interest: (i) a single quantum particle dissolved in a system of other particles which can be treated classically; (ii) systems in which all the particles must be treated quantum-mechanically. As important examples of the first class, I will describe the work of Rahman and Parrinello on an electron dissolved in a molten salt, and my own work on hydrogen in metals. To illustrate the second class, I will talk about the work of Ceperley and Pollock on liquid helium.

Sarah L. Price, University Chemical Laboratory, Lensfield Road
Cambridge, CB2 1EW, England

The realism of computer simulations is usually limited because of
the inaccuracy of the model intermolecular potential, which forms the
fundamental scientific input into the calculation. We examine the reasons
for this highly unsatisfactory state of affairs by considering the
physical origins of intermolecular forces, highlighting the approximations
which are usually made in simulations, and discussing the problems in
quantifying intermolecular potentials by ab-initio methods, or by
fitting to experimental data. This emphasises the importance of
choosing a realistic functional form for the potential. The isotropic
atom-atom model potential, which is usually used for modelling polyatomic
molecules, is discussed in contrast with the recent anisotropic
site-site approach to designing model potentials. The electrostatic
interaction can be represented very accurately within this formalism by
the use of an ab-initio based distributed multipole model. Empirical
anisotropic site-site potentials have been used to great effect in a
Molecular Dynamics simulation of liquid chlorine and Monte Carlo
simulations of three phases of benzene. Therefore, we may hope to
perform more realistic simulations in the future, using accurate
model potentials which have a firmer theoretical basis.

MC 1,2,3

PT1 : Monte Carlo

Methods: D. Frenkel, Fysisck Laboratorium, Rijksuniversiteit,
Sorbonnelaan 4, Utrecht, The Netherlands.

Monte Carlo simulation techniques are discussed, with special emphasis on those technical aspects that are important for the simulation of dense liquids and solids.

In the first three lectures the Metropolis sampling scheme is introduced as a special case of importance sampling. Using simple example, the choice of the optimum trial move is discussed. Next we discuss the problems encountered when sampling orientational and internal degrees of freedom. After introducing the MC method as a technique to measure averages in the canonical ensemble, we briefly look at simulations in other ensembles, in particular: microcanonical, isobaric-isothermal and grand-canonical. The latter ensemble forms the starting point for a discussion of particle insertion techniques to measure chemical potential. Next we look at general acceptance-ratio and overlapping distribution schemes. As an example, we mention pressure measurements in cases where use of the virial expression is cumbersome. Finally, we describe thermodynamic integration techniques. We end our discussion of Monte Carlo simulations with an analysis of its relative advantages and disadvantages compared with the Molecular Dynamics method.

In a separate lecture we discuss the application of computer simulation techniques to the study of phase transitions. Although the emphasis will be on first-order transitions, some attention will be paid to the problems occurring in the vicinity of continuous phase transitions.

## MA 1: MD of chain molecules and constraint dynamics

J.P. Ryckaert, Pol de Physique, Faculte de Science, Universite Libre de Bruxelles, C.P. 223, Bruxelles, C.P. 223, B 1050 Belgium

Taking n-alkanes as an example, the Introduction will describe the models most commonly used in Molecular Dynamics to indicate in the practise the usefulness of models freezing specific degrees of freedom (fast vibrations) by geometrical constraints.

We will then consider a specific full atomic model of n-alkane which considers explicitly the CCC bendings and the torsional vibrations around C-C bonds but freeze all other intramolecular degrees of freedom by constraints. We will show that this model corresponds formally to a general model of masspoints particles in interaction subject to holonomic constraints.

The dynamics of such systems will be expressed in terms of the cartesian co-ordinates of the particles with explicit constraint forces in addition to the forces deriving from the potential. The constraint forces turn out to be expressed in terms of Lagrangian parameters. These parameters are obtained numerically by solving a set of algebraic equations which derive from the imposition of the constraint relations on the numerical trajectory at the next time step.

The procedure will be illustrated on a timer with two rigid bonds and flexible angle to show in particular the need of an iterative technique for systems with many (sometimes many hundreds) of constraints. The SHAKE iterative procedure will then be illustrated on the same example.

The lecture will end with some general comments on n-alkane MD simulations published in the last 10 years in order to introduce the specific applications of the next two lectures and more generally to appreciate the new perspectives offered by super-computers in the simulation of macromolecular systems.

SU 1,     Simulation of surfaces and interfaces of polar solids

Dr S.C. Parker

University of Bath

Surface properties play a vital role in many technologically important processes including catalysis and corrosion. However, detailed experimental studies of the structure and stability of interfaces, particularly in polar solids are often difficult and ambiguous. Computer simulation provides a complementary technique for probing the surface structure, stability and behaviour of defects.

The aim of this lecture is to desribe an approach for modelling surfaces and interfaces, the special problems they present to simulators, and the benefits derived by studying surfaces. The initial part of the lecture will focus on the static simulation of perfect surface structures and their corresponding energies. The principal difficulty arises from the electrostatic interaction between the charged planes of atoms. A second feature of surface simulations is that surfaces are not necessarily simple bulk termninations and may be modified considerably on relaxation. For example, those surfaces with a dipole moment perpendicular to the surface are only stabilised by large reconstructions, or adsorption of excess charge.

The second section will describe the extensions required for modelling the behaviour of defects and impurities of surfaces - again the major problem is from the long-range electrostatic interactions. The resolution to these problems will be discussed and the application of this approach to the segregation of impurities in binary and corundum structured oxides.

Finally, we will illustrate the scope of these techniques for modelling technologically relevant problems by describing work on the oxidation of nickel and the role of grain boundaries in enhancing the growth of the oxide scale.

## Simulation of the thermodynamic and structural properties of minerals

S.C. Parker

University of Bath

The aim of this lecture is to describe the developments in atomistic simulation techniques which enables us to predict the thermodynamic and structural properties of minerals found deep in the Earth and Mantle. The Mantle experiences temperatures from 500 to 4000K and pressures from 5000 to 105 atmospheres, and has convection currents which give rise to Plate Tectonics. These conditions prevent detailed experiments on the thermodynamic properties, thus computer simulation provides an ideal alternative.

The developments which allow such confident predictions have been 1) derivation of a potential model which can reliably simulate the interatomic forces of the mantle-forming magnesium silicate minerals and 2) application of lattice dynamics techniques. As the potential models will have been discussed in some detail earlier in the Summer School, I will attempt to highlight both the strengths and limitations of the lattice dynamics technique. The basis of this approach is energy minimisation except that free-energy is minimised, and the thermal component of the free-energy is obtained from the lattice vibrational frequencies. Its main advantage over molecular dynamics is that it is computationally quicker.

I am confident that the success in predicting the thermodynamic properties of magnesium silicate polymorphs demonstrates the potential for this technique for understanding phase stability of any group of samples of inorganic solids.

## Interatomic Potentials for Inorganic Materials

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This lecture has two aims. The first is to review the types of potential model used in the computer simulation of inorganic materials, and to discuss the various means of parameterising these models. The second is to show how computational difficulties arising from the use of certain models are overcome.

Inorganic materials are now widely and successfully modelled by simulation methods, but the success and relevance of this work is entirely dependent on the availability of reliable potential models. In many cases, good results may be obtained using a simple two body potential model description, with separate terms to describe the long range and short range interactions. Such models will be described in the lecture. Materials, however, such as silicates and aluminosilicates show a degree of covalency which may be described by a three body bond-bending term. Inclusion of this term has enabled these materials to be modelled accurately. The usual method of parameterising these potentials is by the empirical approach, where potentials are fitted to to the structure and crystal properties of representative materials, and transferred to other materials. In cases where such information is unavailable from experiment, various ab initio methods exist, ranging from electron gas methods to molecular orbital methods, which enable parameters to be calculated directly.

The ionic character of inorganic materials leads to the need to calculate electrostatic interactions which are slowly convergent in real space. The use of the Ewald method, which transforms a slowly converging sum in real space into two rapidly converging sums in real and reciprocal space, will be described.

## MA2: Short Chain Molecules

J.H.R. Clarke, Department of
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This lecture will be concerned with molecular dynamics studies of liquids and solids composed of short chain molecules.

We shall discuss the factors that need to be considered in choosing a set of interaction potentials for such systems. The Hamiltonian for such systems involves two three and four-body intramolecular terms which define the flexibility of the model. As we have seen one or more of these can, if necessary, be eliminated by using constraints but ultimately the choice of interaction potential depends on the system being studied and the properties that are of interest.

As examples we shall consider the cases of alkane crystals and alkane liquids. In the former case it is necessary to use a full atomic description for the intermolecular potential since the structure is very sensitive to details of the molecular interactions. In the case of fluids much can be still learned from studies using the "bead" model in which methylene groups, for instance, are treated as single interaction sites.

Topics to be discussed here include the chemical transformation rates between gauche and trans conformers, the evidence available regarding solvent effects on molecular conformations for small molecules and also the ways in which molecular flexibility can directly influence transport properties. The need to ensure the attainment of equilibrium in such systems where there are slowly relaxing degrees of freedom will be emphasised.

## HA 1    Hardware issues in molecular dynamics algorithm design

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The diversity of architectures on which modern supercomputers are based presents a serious obstacle for the designer of software that is to operate efficiently in a variety of enviroments. As case studies in how to live with processor hardware, two very different kinds of contemporary computer design are introduced, one being the familiar vector computer, the other an experimental loosely-coupled network of processors.

The basic concepts of each kind of computer that are relevant to algorithm development are discussed and the manner in which the machines have been harnessed to the task of large-scale molecular dynamics simulation are described.

Only by taking into account the specific features of each machine was it possible to carry out what are the most extensive simulations of this kind to date, involving as many as 200,000 particles.

These techniques apply to models based on differentiable potentials; an approach very different from direct numerical integration of the equations of motion is required for models that employ step potentials.

A method derived from concepts of event-driven simulation and list processing that proves to be highly effective for problems of this type is presented.

New results obtained by applying these techniques to the study of fluid dynamical problems at the microscopic level are briefly mentioned.

<u>PR1, 2</u>   Molecular Simulation of Protein Structure, Dynamics and
Thermodynamics

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A general overview of protein dynamics will be given. Progress from
1976, when the field first began, to the present will be discussed. The
field of protein simulation will be compared with other simulation
fields. The general form of the protein potential funtion will be
reviewed with a discussion of current force-field parameterization. A
molecular dynamics algorithm for proteins will be presented. Limits
in accuracy of parameterization of the force-field and some problems
associated with incomplete sampling in molecular dynamics will be
discussed. One of the outcomes of molecular simulations of protein
systems is the time-averaged structure; a discussion of how this
structure can be used in the interpretation of biochemical and physical
measurements will be presented. In addition, the mean-squared
amplitudes of atomic fluctuation are comparable to measured temperature
factors in crystallographic experiments. General features of this
comparison will be given, and the importance of atomic fluctuations for
the functioning of proteins will be detailed. Time-dependent
simulations also yield motional information, which in many cases can be
tied to biological function. The types of molecular motions occuring in
proteins will be categorized and discussed in terms of their amplitudes
and timescales. Correlation functions will be introduced to describe
the general features of this motion, and comparisons between calculated
molecular correlation functions and experimentally determined ones will
be given for the example of fluorescence depolarization decay. The
role of the solvent media in modulating and determining protein
behaviour will be presented. Several examples involving the calculation
of protein-ligand interactions and alterations of protein stability upon
introduction of site-directed mutations will be detailed. The general
utility of this type of calculation for understanding problems in drug
design and protein engineering will be discussed.

## PC1    Plastic Crystals

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### DEFINITION AND PROPERTIES

- High temperature phase (O.D.I.C.)
- Structure and mechanical behaviour
- Orientational disorder
- Molecular motion: vibrations, librations free rotations or rotational jumps

### SIMULATION TECHNIQUES

- Potentials: site-site, atom-atom, coulombic interactions (ionic systems)
- Algorithms: generalized coordinates, cartesian coordinates (constraints)
- Constant temperature, constant pressure

### APPLICATIONS

- Orientational disorder: structure factor, order-parameters, Debye-Waller factor, orientational probabilty density functions (symmetry adapted functions)
- Molecular rotations: direct evidence, time evolution of the order parameters
- Rotational jump frequencies: determination of the residence time, relaxtion of the order parameters.
- Collective modes.

### STRUCTURE OF THE ORDERED PHASES AND PHASE TRANSITIONS

- Constant pressure simulation of the ordered phases
- Transition between low temperature ordered phases and high temperature disordered ones, reverse transition.

## Free Energy Calculations For Defects In Solids

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Italy

The evaluation of Free Energies for point defects in solids is a particularly subtle task, because it involves the evaluation of a small quantity (of the order of one particle) as the difference between two very large quantitites (of the order of the total number, N, of particles).

The statistical error of separate estimates of the absolute free energies is then often larger than the difference itself, and methods to directly evaluate only the difference have to be used. The Monte Carlo Overlapping Distribution Method to perform this type of calculation will be reviewed in some detail, and applied as an example to calculate the formation and migration free energies for vacancies in a Lennard-Jones crystal.

Other ways to approximately estimate free energies for point defects in solids are however possible, due to the fact that in solids the atoms remain localized near lattice sites, exploring only low lying regions of the potential energy surface. The morphology of the potential energy surface near equilibrium configurations of the perfect and defective crystal, as well as close to saddle points for defect migration, is smooth and well defined. One can then approximate the potential energy surface, close to these equilibrium points, with many dimensional parabolas, and evaluate the free energy analytically, without statistical error, from the corresponding force constants.

By repeating the calculation at different volumes, one can then evaluate the pressure and all the thermodynamical quantities of interest, including constant volume and constant pressure free energies. Various aspects and intricacies of the quasi-harmonic approximation, will be discussed, in connection with its adequacy for defects in solids (rare gases, ionic solids, metals, semiconductors).

Finally, the dynamical effects in atomic motion, not included in the traditional rate theory approach, and therefore not evaluated in a free energy calculations will be discussed. The generalization of Rate Theory to include dynamical effects (SM-ART) will be presented, together with the most relevant results that have been recently obtained for the isotope effect. The predictions of these purely dynamical effects can only be evaluated by direct molecular dynamics simulation: its use in the present context will be reviewed.

# Molecular Dynamics Simulations of

## Aqueous Electrolyte Solutions

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The structural and dynamical properties of aqueous alkali halide
and alkaline earth chloride solutions are reported. The rigid ST2 and
the flexible BJH model for water are employed in the simulations. The
ion-water interactions are derived either by modelling the ions as
Lennard-Jones spheres with an elementary charge in the centre or from
ab initio calculations.

The structures of the solutions are described by radial distribution
functions, the orientation of the water molecules and their geometrical
arrangement in the hydration shells of the ions. The changes of the
hydration numbers with ion size are discussed. The dynamical
properties of ions and water molecules-e.g. self-diffusion coefficient,
spectral densities of hindered translations, librations and vibrations -
have been calculated from various autocorrelation functions. They are
reported separately for the three water subsystems - bulk water,
hydration water of the cation and of the anion - in order to investigate
the single ion effect.

The effect of pressure, temperature, and ionic concentrations on
various structural and dynamical properties of the solutions are
demonstrated by examples. In addition the changes in the structure of
water caused by Lennard-Jones and platinum walls are reported.

## MA3 Long Chain Molecules

### J.H.R. Clarke

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Much of our current understanding of the properties of polymers is based on the successful application of statistical dynamical theories to conceptually simple models which emphasise entropic effects and ignore the detailed structures of individual chains. In dense polymers however conformational fluctuations are greatly restricted by cross linking, excluded volume effects, entanglements and specific interactions. In order to understand the mechanical behaviour it is necessary to take specific account of monomer level interactions. A similar approach is necessary to provide a quantitative understanding of solvent effects on polymer conformation in solution.

In general polymers are characterised by a very wide range of relaxation times. Useful molecular dynamics simulations are only possible for single (short) chains or for the dense regime close to the glass transition where most of the slow processes (e.g. diffusion) have been frozen out and where mechanical properties are determined mainly by the high frequency motions in the system. Methods for preparing equilibrium samples of dense polymers will be discussed and the use of constant stress molecular dynamics for studying the deformation and relaxation of polymers will be outlined.

Examples will be described of computer simulation studies which have been used to study the effect of solvent on the conformation of single polymer chains and also the way in which the mechanical properties of both ordered and entangled chains are influenced by direct interactions.

# CCP5 Literature Survey 1987 - Addendum

The following references are to be added to the 1987 literature survey given in the last edition of this newsletter. Our thanks go to those who contributed them.

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