# Daresbury Laboratory INFORMATION NEWSLETTER FOR COMPUTER SIMULATION OF CONDENSED PHASES

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

### Number 47

February 2000

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Editor: Dr. M. Leslie

CLRC Daresbury Laboratory Daresbury, Warrington WA4 4AD UK



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# **General News**

### MEMBERSHIP OF EXECUTIVE COMMITTEE

Following a ballot by Email of UK members of CCP5 in September, two new executive committee members have been elected. The executive committee members who have retired are

Dr. J. Harding	Condensed Matter & Materials Physics University College London
Email: j.harding@ucl.ac.uk	
Prof. G.S. Pawley	Dept. of Physics & Astronomy University of Edinburgh
Email: g.s.pawley@ed.ac.uk	

The current executive committee members are

Professor D. Heyes (Chairman)	Department of Chemistry University of Surrey	
Email: d.heyes@surrey.ac.uk		
Dr. J. Anwar	Department of Pharmacy Kings College London	
Email: jamshed.anwar@kcl.ac.uk		
Dr. M. Dove	Department of Earth Sciences University of Cambridge	
Email: martin@esc.cam.ac.uk		
Dr. J. Gale	Dept. of Chemistry Imperial College	
Email: j.gale@ic.ac.uk		
Dr. R.L. Johnston	School of Chemistry University of Birmingham	
Email: roy@tc.bham.ac.uk		
Dr. J. Melrose	Polymer and Colloid Group, Cavendish Lab University of Cambridge	
Email: jrm23@phy.cam.ac.uk		

Prof. A.P. Sutton	Department of Materials University of Oxford
Email: adrian.sutton@materials.ox.ac.uk	

# An index of current meetings in the area of computer simulation of condensed phases.

A summary table is given, further details may be found by following the links.

♦ CCP5 Annual General Meeting 2000

Molecular Simulation in the 21st Century. University of Surrey Guildford, UK. UK 2nd-5th July 2000

Modelling Biomolecular Mechanism: From States to Processes at the Atomic Level

http://www.mgms.org/diary.htm

A meeting of the Molecular Graphics and Modelling Society

University of York, April 5-8, 2000

#### Psi-k2000 Conference

http://psi-k.dl.ac.uk/psi-k2000
Schwäbisch Gmünd, Germany, August 22 - 26, 2000

 Theory and Simulation of Clusters and Nanoparticles http://www.tc.bham.ac.uk/~roy/Summer2000.html
 Royal Society of Chemistry - Theoretical Chemistry Group
 University of Birmingham 27 August - 6 September 2000

 6th Granada Seminar on Computational Physics http://ergodic.ugr.es/cp/
 Granada, Spain, 4-9 September 2000

### Funds for workshops, visitor proposals and collaborations.

Applications for funding can now be processed using a WWW form. Copies of these forms may be found on the CCP5 WWW pages. There are copies of the forms on the following pages, these are intended to show the information needed. If you wish to use them please fill in the WWW version.

# WORKSHOP PROPOSAL FORM

CCP5 organises a programme of workshops on focussed research topics in addition to the annual meeting. It is intended that these should be for a smaller group of people (20 - 30) and concentrate on a specific topic. Speakers may be invited to attend. CCP5 workshops usually last for one to two days (i.e., possibly with an overnight stay). If you have any suggestions for future workshops please fill in the form below, and it will be considered for funding.

Please make every attempt to fill in all of the boxes. If you do not have the requisite information, please leave the box blank.

### Workshop proposal

Workshop name	
Proposed dates	
Proposed organiser (Optional)	
Where workshop is to be held	
Suggested speakers	

Enter a brief description of the proposal in the box below

# VISITOR PROPOSAL FORM

CCP5 organises a visitors program which funds the visit to the UK of overseas collaborators. We would normally expect a visitor to visit three sites in the UK and give a lecture at each site. These lectures would be open to all members of CCP5 as well as members of the host university. The visit would normally last between one or two weeks. CCP5 would pay for the cost of travel to the UK (up to a limit of an APEX air fare) and within the UK between universities. CCP5 would expect some contribution towards accommodation expenses at the host university to be met by the university.

If you would like to suggest a visitor, please complete as much of the form below as possible. Additional information may be submitted at a later date. When you have a detailed itinerary, please fill in the details in the visitor itinerary form.

### Visitor proposal

Your name	
Visitor name	
Visitor address	
Proposed dates	

Please give a brief summary of the research area and the timeliness of the visit for UK Science.

I would like CCP5 to ask for suggestions from the members  $\Box$ 

#### Funding

I expect to be able receive part of the cost of the visit from another source. (If this is the case, please send Email to m.leslie@dl.ac.uk giving details)  $\Box$ 

# VISITOR ITINERARY

Please fill in a suggested itinerary below, after consultation with the local organisers. If you would like CCP5 to ask for suggestions from the members please check the box at the end. There is space for 5 locations, however CCP5 does not expect visitors to visit more than 3 locations.

Please make every attempt to fill in all of the boxes. If you do not have the requisite information, please leave the box blank.

Host department and Institution	Local organiser (Name and Email address)	Proposed Dates (From - To)
}		

I would like CCP5 to ask for suggestions from the members

#### Lecture schedule

Please fill in available information below

Location	Time and Date	Proposed title of lecture
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	····	

#### Funding

I have asked the local organisers if their host universities can pay for the cost of overnight accommodation and other local expenses.

# COLLABORATION PROPOSAL FORM

CCP5 can make available funds of up to £200 per annum for groups of two or more UK researchers wishing to undertake a collaborative project within the scientific area covered by CCP5. The funds are intended to cover travel and subsistence costs.

Researchers who wish to apply for funds are requested to fill in the form below, and it will be considered for funding.

### Collaboration proposal

Name and Address of First Collaborator	
Name and Address of Second Collaborator	

Enter a brief description of the proposal in the box below

### Electronic Distribution of CCP5 Newsletters and World Wide Web

All newsletters starting from issue 39 (October 1993) are now available on line, together with some articles from earlier newsletters. An index of recent newsletter articles can be found on the World Wide Web server; readers can access the individual articles by this means or by anonymous ftp. (Anonymous ftp will not access the index).

Starting with this issue, the format that is used to distribute the newsletter has changed. The newsletter is still available as a postscript file for downloading as before, also separate copies of the articles. There is also a RTF version for use with MSWORD. The CCP5 WWW pages now point to a HTML version of the newsletter to be viewed online.

### Distribution of Information by Email

CCP5 will distribute by Email to the members on the mailing list (about 850 world wide) information which is of interest to our members. Three lists are maintained, for UK members, members in other European countries and all other members. If you have information which you would like sent out in this way please send it by Email to M. Leslie, indicating whether it would be appropriate to restrict its distribution. We also send out post-graduate, post-doctorate and lectureship positions notified to us. Normally the Email messages for post-graduate positions within the UK are restricted to UK members, however if the position is open to non-UK students then Email may be sent to the rest of Europe or the complete mailing list. Messages sent out may be batched together in which case there may be a short delay between the receipt of the message at Daresbury and its transmission. CCP5 no longer places the positions on the WWW or ftp servers but a link will be placed from CCP5's page to a page at a University advertising the position.

### THE CCP5 PROGRAM LIBRARY

Copies of the newsletter no longer include a complete description of the program library. If readers wish to obtain a copy of the documentation it is available by anonymous ftp or through the World Wide Web page. The program library description is in ccp5.newsletters/library directory (postscript and ASCII text versions).

### **Request for Contributions**

Readers are reminded that contributions are always welcome. Contributions may be sent by Email in LaTeX. WORD documents should preferably be sent in rtf format. Documents for inclusion in the next newsletter can now be sent as HTML.

# MOLECULAR SIMULATION IN THE 21st CENTURY.

University of Surrey

## Guildford, UK. UK 2nd-5th July 2000

The Annual Meeting of CCP5 in the year 2000 happens to be the 21st in the series and also the first in the 21st century. As befits this auspicious coincidence, we plan this meeting to be a rather special occasion, consisting of invited keynote lectures covering a diversity of topics in rapidly moving branches of condensed matter molecular and mesoscale simulation. There will also be opportunities for contributed talks and posters.

An important theme of this meeting is to review the progress made in various branches of what is loosely referred to as 'molecular simulation', and to discuss prospects for and to identify areas that are likely to become of central importance in the not too distant future. The particle-based simulation of liquids, solids and granular materials will be included in the programme. Special attention will be given to methods for expanding the scope of molecular simulation techniques to shorter/longer time and length scales, e.g. biased sampling schemes in Molecular Dynamics and Monte Carlo, and coarse-graining procedures. In the latter case a desire is to retain important aspects of, for example, chemical discernment at the coarse-grained level of description.

Jean-Louis Barrat	Département de Physique des matériaux Université Claude Bernard Lyon 1	Simulating Non-equilibrium Dynamics in Glassy Systems: Aging, Effective Temperature and Behaviour under Shear.
William G. Hoover	Department of Applied Science University of California, Davis	From Atoms to Continua, using Smooth Particles.
Benedict Leimkuhler	Department of Mathematics and Computer Science University of Leicester	Multiple timescale integrators for Molecular Dynamics Simulation.
Ruth M. Lynden-Bell	Atomistic Simulation Group School of Mathematics and Physics The Queen's University of Belfast	Simulation: How to do things that experimentalists can't do and wish they could.

### Plenary Lecturers will include:

Paul Madden	Physical & Theoretical Chemistry Laboratory University of Oxford	Many-body interaction effects on the properties of molten ionic mixtures.
Ugur Tüzün	Dept Chemical & Process Engineering School of Engineering in the Environment University of Surrey	Macromolecular Product Engineering using a Simulation Toolkit.

There are opportunities to give contributed talks and posters (see below).

## Local organisers:

Prof. David Heyes Department of Chemistry University of Surrey Guildford GU2 5XH, UK.	Tel: Fax: Email:	(+44) 1483 259580 (+44) 1483 876851 d.heyes@surrey.ac.uk
Dr. Sebastian Reich, Department of Mathematics and Statistics, University of Surrey, Guildford GU2 5XH, UK.	Tel: Fax: Email:	(+44) 1483 259000 ext. 2638 (+44) 1483 876071 s.reich@surrey.ac.uk

# Other members of the organising committee:

Dr. J. Anwar,	
Department of Pharmacy,	
King's College London,	
Franklin Wilkins Building	
150 Stamford Street	
Waterloo Campus	
London SE1 8WA.	
Dr. W. Smith,	
CLRC Daresbury Laboratory	
Daresbury,	
Warrington,	
Cheshire WA4 4AD.	

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Prof. Adrian P. Sutton, University of Oxford Department of Materials Parks Road Oxford OX1 3PH.

### Conference timetable:

The meeting will start at 09.00 on Monday 3rd July and finish at 13:00 on Wednesday 5th July. For residential delegates, accommodation is provided for the nights of Sunday 2th July, Monday 3rd July and Tuesday 4th July. All accommodation is on the University Campus, a few minutes walk from the lecture theatre.

### **Registration and Accommodation:**

A registration form is available at the CCP5 website (details given below).

The full conference cost (including accommodation, refreshments, meals and conference dinner) is in the range  $\pounds 195-240$  per person (depending on the type of accommodation), reduced to  $\pounds 175$  for students. For those not requiring accommodation, there is also a reduced conference fee.

There is a £20 supplement for those registering after 1st June.

#### **Presentations and abstracts**

An abstract should be sent (preferably at the time of registration and definitely before June 1st) by electronic mail, preferably in LATEX or simply as a text file. If you use MS WORD, please send the abstract as a rtf document. Oral contributions and posters are welcome.

The final date for submitting an abstract for an oral or poster presentation is June 1st.

The abstracts of the talks and posters will be published as part of the conference booklet and also in an issue of the CCP5 quarterly newsletter. Delegates are also encouraged to submit a longer account of their work for publication in the newsletter. Postscript diagrams are acceptable.

### **Registration Form:**

We must have a paper version of the registration form sent in the post to David Heyes, for all methods of payment.

### WWW information

Up-to-date information about the meeting can be found at

http://www.dl.ac.uk/CCP/CCP5/meetings/ann2000.html

where there is also a postscript version of this information http://www.dl.ac.uk/CCP/CCP5/meetings/ann2000.ps and registration form. Postscript http://www.dl.ac.uk/CCP/CCP5/meetings/registration2000.ps

**Rtf** http://www.dl.ac.uk/CCP/CCP5/meetings/registration2000.rtf

The University of Surrey at Guildford is close to London and is conveniently situated for two of London's major airports, Heathrow and Gatwick. It is readily reached by public transportation from within the UK. A train from central London takes about 35 minutes. Details of how to travel to the University of Surrey may be found at the WWW address:

http://www.surrey.ac.uk/Where/directions.html

David Heyes February 2000

# **REGISTRATION FORM**

## CCP5 ANNUAL MEETING 2000

## MOLECULAR SIMULATION IN THE 21st CENTURY

at

### University of Surrey, Guildford, UK.

2nd-5th July 2000

SURNAME: (Prof , Dr , Mr , Mrs , Ms *) (BLOCK letters please). (*) Please delete as appropriate	MALE 🖵
INITIALS:	FEMALE 🖵

BADGE: Please indicate how you wish your name to appear on your badge (e.g. David HEYES).

L		i
Address		
City:	County/State:	
Postcode:	Country	
Tel:	Fax:	
Email		

Please indicate if you have any special dietary requirements

To help us advertise our events more effectively in the future, we would appreciate, as an optional question, to discover where you learnt about this conference

Please send this form, together with any payment details to:

Prof. D.M. Heyes, Department of Chemistry, University of Surrey, Guildford GU2 5XH United Kingdom.

# CONFERENCE COSTS (Prices are in Pounds Sterling $(\pounds)$ .)

WE OFFER THREE POSSIBLE PACKAGES.

#### PACKAGE A

RESIDENTIAL DELEGATE (includes accommodation on the nights of Sunday, Monday and Tuesday 2nd-4th July, teas, coffees, lunches on 3-5th July, evening meal on Monday 3rd July and the conference dinner on Tuesday 4th July.)

full	(standard University room)	£195.00	
full	(Room with En-suite bathroom)	£240.00	
student	(standard University room)	£175.00	

En-suite rooms have washbasin, shower and we. Standard rooms have a washbasin.

#### PACKAGE B

NON-RESIDENTIAL DELEGATE WITHOUT CONFERENCE DINNER (includes teas, coffees, and lunches on 3-5th July)

full	£95.00	
student	£85.00	

#### PACKAGE C

NON-RESIDENTIAL DELEGATE WITH CONFERENCE DINNER (includes teas, coffees, and lunches on 3-5th July, and conference dinner on Tuesday 4th July.)

full	£130.00	
student	£120.00	

Late registration, for all categories (after 1st June 2000)	£20.00	
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TOTAL PAYMENT:	L £	
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Payment method (in Pounds Sterling (£) only):

#### Cheque:

I enclose a cheque for  $\pounds$ 

payable to 'University of Surrey' and crossed. The reference: "DHS25B/CCP5/NAME", where NAME is your family name in capital letters, should be mentioned in any accompanying letter with the cheque.

Cheques from outside the UK must be made out in Pounds Sterling  $(\pounds)$  and drawn on a UK branch of a British Bank.

#### Credit Card:

We can ONLY accept Mastercard, Visa or American Express credit cards.

#### **Credit Card Payment Details**

I authorise the University of Surrey to debit my Mastercard/Visa/American Express (delete as appropriate)

the sum of £			•····	
Account Number:	<u> </u>			···· · ····
Expiry Date:	/	Date:		
Name on card:				
Signature:				
Credit Card Billing Address:				
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## CONFERENCE PRESENTATIONS

I would like to submit a presentation	YES		
	NO		
I would prefer a presentation which is	ORAL		
	POSTER		
Please tick as appropriate			
TITLE	<u> </u>	- 10-10-10	
Load author (presenter):			
All	,		
Address:			
Co-author(s):			
Address:			

Special visual aids required (overhead projector is available).

35mm Slide projector:	YES	NO	
Data projector:	YES	NO	
VHS video playback PAL: (UK)	YES	NO	
VHS video playback NTSC: (USA)	YES	NO	

An abstract should be sent at the time of registration by electronic mail in LATEX, HTML or as a text file to David Heyes, (d.heyes@surrey.ac.uk).

The abstracts will be published in the conference booklet and also as part of an issue of the CCP5 quarterly newsletter. Delegates are also encouraged to submit a longer account of their work for publication in the newsletter. Postscript diagrams are acceptable.

Closing date for receipt of contributed papers is 1st June 2000. The registration cost after 1st June is increased by £20.

# DL POLY on the Manchester Cray T3E

### Introduction

The following is an account of the performance of the DL\_POLY program (Version 2.11) on the CSAR

*http://www.csar.cfs.ac.uk* Cray T3e service at Manchester Computing Centre (June-July 1999). The evaluation is based on example simulations from the standard DL\_POLY benchmark suite, which is available from the CCP5 Program Library at Daresbury Laboratory:

Preliminary remarks

Benchmark 1: Metallic aluminium

Benchmark 2: A peptide in water

Benchmark 3: Transferrin in water

Benchmark 4: Sodium chloride

Benchmark 5: Sodium potassium disilicate glass

Benchmark 6: Potassium-valinomycin complex in water

Benchmark 7: Gramicidin in water

Benchmark 8: Magnesium oxide microcrystal

Benchmark 9: Model membrane/valinomycin system

Summary

Acknowledgements

### **Preliminary Remarks**

The simulation program DL\_POLY is a distributed memory parallel program based on the Replicated Data (RD) strategy for parallelisation. It was designed initially for machines with up to 64 processors and systems of up to 30,000 atoms, but has since found use on much larger architectures, where memory-memory (i.e. low overhead) message passing is possible. Implicit in the RD approach is a dependence on fast global summations, which are not available on all machines. For this reason the performance may suffer markedly with increasing processor numbers. Also, the performance scaling (i.e. speed up with number of processors used) will vary according to the kind of simulation being undertaken - algorithms that require the most communication will scale less well than ones which require fewest. In practice systems possessing complex molecular topologies scale less well than ones requiring simple atomic descriptions, as they require a higher communication overhead.

The reported test give an honest indication of the capabilities of DL\_POLY in realistic applications. Each benchmark is described separately and the performance of the code on 8,16,32,64,128 and 256

processors of the T3E is given. The times quoted are wall-clock times (in sec.) to complete the described job. The plots shown are for the log (base 10) of the job times vs. log (base 2) of the number of processors.

### Benchmark 1: Metallic Aluminium



Benchmark 1

This system consists of 19,652 aluminium atoms on an FCC lattice at 300 K. The potential model is a Sutton-Chen many body potential with a cutoff at 8.6 Angtroms (A). No electrostatic forces are present in the system. The time step is 5 fs and the simulation is for 1000 time steps in the

NVE ensemble. The time quoted includes initial data input and writing restart files at the end.

The performance scaling with processor number is very good up to 64 processors, where it achieves a maximum. There is an increase in simulation time thereafter. This is probably a reflection of the fact that the Sutton-Chen potential requires a density calculation in addition to the normal pair force terms, which demands an additional global sum during the forces calculations. Global sums generally are detrimental to performance scaling.

### Benchmark 2: A Peptide in Water

This simulation is of a peptide comprised of 15 amino acids in a solvent of 1247 TIP3P water molecules. The water is treated as a rigid body and the peptide bonds are handled using the SHAKE algorithm. The total number of atoms is 3,993 The electrostatics in this simulation are handled using a neutral group scheme with a reaction field. The potential cutoff, for both electrostatic and Van der Waals interactions, is set at 8 A. The description of the peptide includes valence angle, and dihedral potentials. The simulation is for 2000 time steps with a time step of 1 fs in the NVT ensemble due to Berendsen. The time quoted includes all data input and output.

The performance plot in this case shows a gradual reduction in simulation time, without an obvious linear regime. Scaling at high processor numbers is poor and probably reflects the difficulty in apportioning the neutral group calculations across processors at this extreme. Similarly, the use of SHAKE for the bond constraints is likely to be another contributor to poor scaling, on account of its communication overheads. Gains in performance for smaller node numbers (up to 32) are much better. Nevertheless this is a rather small simulation and the result implies that better scaling is possible for larger systems.



Benchmark 3: Transferrin in Water

This simulation is of the enzyme transferrin in a solution comprised of 8102 TIP3P water molecules. A total of 27,593 atoms are in the system. The electrostatic forces are handled by a combination of neutral groups with the coulombic potential. All forces cutoffs are set at 8 A. The simulation is for 250 steps with a time step of .1 fs, in the NVE ensemble. The water molecules are treated as rigid bodies and the transferrin is maintained by bond constraints using





Benchmark 3

The performance scaling resembles Benchmark 2 in that is shows no obvious linear regime, though the scaling at large processor numbers is significantly better, probably due to the better apportioning of the neutral groups in this larger system. Note that this simulation is too large to be run on less than 16 processors of the Manchester T3E.

### Benchmark 4: Sodium chloride

This represents a straightforward simulation of sodium chloride at 500K, using the standard Ewald summation method to handle the electrostatic forces. A multiple timestep algorithm is used to increase performance, which requires recalculating the reciprocal space forces only twice in every five time steps. The electrostatic cutoff is set at 24 A in real space, with a primary cutoff of 12 A for the multiple timestep algorithm. The Van der Waals terms are calculated with a cutoff of 12 A. The simulation is for 200 steps with a time step of 1 fs in the Berendsen NVT ensemble. The system size is 27,000 ions. Timings include data input and output.



Performance scaling in this case is extremely good and is (almost) linear over the entire range of

processor numbers. This reflects the high parallel efficiency of the Ewald sum implementation.

### Benchmark 5: Sodium Potassium Disilicate Glass

This simulation is of 8,640 atoms of an alkali disilicate glass at 1000 K. The electrostatics are handled by the Ewald sum and the interaction potential includes a three-body valence angle term, which requires a link-cell scheme to locate atom triplets.



Benchmark 5

The electrostatic cutoff is 12 A and the Van der Waals cutoff is 7.6 A Three body forces are cut

off at 3.45 A. The simulation is for 300 steps in the Hoover NVT ensemble, with a timestep of 1 fs. Timings include data input and output.

The performance scaling in this case resembles Benchmark 4, though being a smaller system, it shows a slight tendency to deviate from ideal behaviour as it approaches 256 processors. Nevertheless, performance overall is extremely good.

#### Benchmark 6: Potassium-Valinomycin Complex in Water

Valinomycin is a naturally occuring cyclic molecule that forms a hexadentate complex with potassium. This simulation models the stability of the complex in water at 310 K, the simulation is for 500 steps with a timestep of 1 fs in the Hoover NVT ensemble. The valinomycin is modelled by a modified AMBER potential and structurally maintained by constraints with SHAKE. The water consists of 1223 SPC water molecules held rigid by bond constraints with SHAKE. The whole system is relatively small at 3838 atoms and is defined with truncated octahedral boundary conditions. The ewald sum is used to calculate the electrostatic interactions, with a real space cutoff of 16 A. A multiple timestep is used with two reciprocal space calculations every 4 time steps. The primary cutoff is 10 A. The Van der Waals interactions are truncated at 10 A. Valence angle and dihedral angle potentials are present in the valinomycin model. Timings include data input and output.

The performance scaling in this case is good up to 64 processors, but shows no improvement thereafter. The source of this difficulty lies in the use of SHAKE for the constraint bonds, which has a high communications overhead, particularly in instances where the program cannot assign complete molecules to processors and bond constraints interact across processors as is believed to be the case here. No result was obtained for 128 processors, as the program was unable to find a convenient apportioning of the constraints to each processor.



### Benchmark 7: Gramicidin in Water

This system is comprised of 13,390 atoms, including 4012 TIP3P water molecules solvating the gramicidin A protein molecule at 300K. Both the protein and water molecules are defined with rigid bonds and maintained by the SHAKE algorithm. The water is held completely rigid, while the protein has angular and dihedral potential terms. Electrostatic interactions are handled by the neutral group method with a coulombic potential truncated at 12 A. The Van der Waals interactions are truncated at 8 A. The simulation is for 500 time steps in the NVE ensemble with a 1 fs time step.

Timings include data input and output.



Benchmark 7

The performance scaling resembles Benchmarks 2 and 3, in showing a reduction in job time with increasing numbers of processors, but not following an obviously linear trend. The scaling is better overall than the previous examples however. The main cause of this improvement, given that the simulations are otherwise similar, is that Benchmark 7 uses a larger cutoff in the electrostatic calculations and therefore has a lower communication/computation ratio, making for better scaling properties.

### Benchmark 8: Magnesium Oxide Microcrystal

This simulation is a roughly cubic microcrystal of 5,416 atoms of magnesium oxide in vacuo without periodic boundary conditions at 2000 K. The electrostatics are calculated directly with a cutoff of 50 A, corresponding to an all-pairs calculation. The Van der Waals terms are truncated at 10 A. The simulation is for 100 steps in the Hoover NVT ensemble with a timestep of 1 fs. Timings include data input and output.



Benchmark 8

The performance scaling is almost linear for this case, except for a slight deviation at 256 processors. This simulation is heavily compute dominated and so the communication overheads have relatively little impact until large numbers of processors are used. The comparison with Benchmarks 4 and 5

is interesting, in view of the different electrostatic calculation methods.

### Benchmark 9: Model Membrane/Valinomycin System

This simulation is a model of the biological activity of valuomycin in the cell membrane and is comprised of 8 valinomycin molecules (including 4 potassium complexes), 196 hydrocarbon chains each 41 units in length, 25 molecules of potassium chloride and 3144 molecules of SPC water - making 18866 atoms in all. The electrostatics are handled by Ewald sum.



### Benchmark 9

The simulation uses the multiple timestep algorithm and evaluates the reciprocal space terms twice in every 4 steps. The real space electrostatic cutoff is 14 A, with a primary cutoff of 10.7 A. The Van der Waals cutoff os 10 A. The simulation is for 500 steps, with time step of 1 fs, at a temperature of 310 K in the Berendsen NPT ensemble. Timings include data input and output.

The performance scaling is similar to Benchmark 6, with good scaling up to 64 processors and no improvement afterwards. This is ascribed to the same problem, seen earlier, in being unable to assign complete molecules to individual processors in SHAKE, leading to high communication overheads.

### **Benchmark Summary**

The benchmarks reported here show some distinct features of running DL\_POLY on a parallel computer. Firstly it is clear that performance scaling is generally good if the simulated system does not possess constraint bonds. Secondly, if constraint bonds are present, as they usually are in bio-molecular or polymer systems, then deviations from ideal behaviour are to be expected, and the user must always be aware that using excessive numbers of nodes may be counterproductive. Of course the user is not obliged to use constraint bonds (though this is often the most sensible option) and where extensible bonds can be used, optimal scaling can be recovered. Thirdly, it is generally true that increasing the size of the problem makes for a more efficient parallel implementation, so large simulations can be expected to scale best. The corollary of this is that small systems run best on small numbers of processors.

Procs	B1	B2	<b>B</b> 3	B4	B5	B6	B7	<b>B</b> 8	B9
8	572.0	337.7		1385.1	1009.3	635.9	1258.9	326.2	3053.4
16	354.9	203.5	200.2	777.9	523.9	334.9	693.7	171.7	1516.4
32	224.5	141.6	141.7	362.8	248.6	192.7	388.4	88.6	840.0
64	163.5	130.2	119.3	183.1	134.4	133.4	242.7	46.6	532.9
128	176.8	127.8	105.2	94.4	75.4	-	165.9	25.8	583.0
256	178.1	119.9	102.0	62.9	56.3	134.2	139.7	17.9	618.9

Table: Summary of simulations (Job Times in Sec)

#### Acknowledgements

The Manchester Computing Centre is thanked for providing access to the CSAR

http://www.csar.efs.ac.uk Cray T3E Service. EPSRC is thanked for continuing support of DL\_POLY.

# Finding of the smallest enclosing cube to improve molecular modeling

#### Mihaly Mezei

Department of Physiology and Biophysics Mount Sinai School of Medicine, CUNY, New York, NY 10029, USA.

KEY WORDS: cubic grid, Delphi.

Abstract

It is argued that by optimizing the orientation of a molecule in a cube can improve the efficiency of certain molecular modeling procedures.

#### INTRODUCTION

Molecular modeling involving large molecules frequently involves the overlay of a cubic grid around the molecule and the region around it. Examples for the use of such grid includes (but is not limited to) the calculation of the electrostatic energy of the solute with the surrounding dielectric (e.g., with the program Delphi [1,2]), calculation of volume elements in various proximal regions around solute atoms [3], calculating solvent density from a simulation trajectory. Since the total number of gridpoints is inversely proportional to the cube of the gridsize, reduction of the gridsize to increase numerical precision soon reaches computational limitations. However, by optimizing the orientation of the molecule to be modeled the enclosing cube can be reduced, resulting in a reduction of the gridsize without increasing the number of gridpoints.

#### METHOD

The orientational optimization has been implemented into the program Simulaid [4], using the simplex method for nonlinear optimization as described and programmed in Numerical Recipes [5]. For each orientation with Euler angles [6]  $(\phi, \theta, \psi)$  the program calculates the minimum and maximum of the x, y, and z coordinates,  $x_{\min}, x_{\max}, y_{\min}, y_{\max}, z_{\min}, z_{\max}$ . The corresponding enclosing cube's edge is  $max(x_{\max} - x_{\min}, y_{\max} - y_{\min}, z_{\max} - z_{\min})$  Thus the calculation of a single cube's size is linear in the number of atoms.

#### RESULT AND DISCUSSION

The program Simulaid already incorporates the optimization of orientation in various periodic cells and optimal centering [7]. Figure 1 (prepared by Simulaid on an SGI O2 workstation) shows the protein p53 in the orientation obtained from the PDB and after optimizing its orientation as described above. The edge of the original enclosing cube was 84.40 Å, the edge of the optimized cube was 71.48 Å, a reduction of 12.92 Å. The minimization was performed from 10 different (randomly generated) orientations and half of the runs resulted in an edge shorter than 72 Å.

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Figure: The protein p53 before and after optimization with their smallest enclosing cube.

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### іяталу Мелей

Department of Physiology and Biophysics, Nount Sinai School of Medicine, CUNY, New York, NY 10029, USA.

Periodic boundary conditions have been proven to be extremely useful in the simulation of fluid phase systems. They can, however, give rise to an interesting artifact under some rare circumstances, as described in this note.

The question posed in the title actually has two possible answers. The first answer refers to the finite precision of the floating-point representation of real numbers used in present-day computers. This finite precision makes the result of all computations dependent on the order of operations, albeit generally to a small degree.

The second answer is more interesting. In general, a rectangular cell is defined by

(1) 
$$\delta_{\mathbf{k}}/2 < x_{\mathbf{k}} \leq b_{\mathbf{k}}/2, \quad \mathbf{k} = 1, 2, 3$$

Applying the periodic boundary conditions under the minimum image convention to the interaction of particle *i* with particle *j* requires the selection of the image of *j* nearest to *i*. In the special (and rare) case when  $|x_k^{\rm L} - x_k^{\rm J}| = L_k/2$ , due to the difference between "<" and "<" in Eq.(1), the translation giving the image of *j* nearest to *j*. In the special (and rare) case when  $|x^{\rm L} - x_k^{\rm J}| = L_k/2$ , due to the difference between "<" and "<" in Eq.(1), the translation giving the image of *j* nearest to *j*. In the translation giving the image of *j* nearest to *i* will *not* be the negative of the translation giving the image of *j* nearest to *i* will *not* be the negative of the translation giving the image of *j* nearest to *j*.

When can this be a problem? Since potentials in general depend on the absolute value of interatomic distances, the energy of atomic fluids are not affected since this discrepancy in the images does not affect  $|\mathbf{r}^i - \mathbf{r}^j|$ , but it does change the corresponding force component. When molecular systems are simulated using group based cutoff, the energy between molecules (or groups/residues) i and j will differ nontrivially since the different translation of the molecule will result in a different set of interatomic distances.

Even in this case, the argument can be made that the switch from one translation to the other is occurring anyway when molecule j actually crosses the boundary of the box around i, so it is of little importance. However, in a Monte Carlo simulation where the self-tests suggested in [1] are periodically executed, it can show up as a discrepancy between the energy calculated freshly from the coordinates and the energy "carried" during the calculation. In fact, the observation about this artifact started as a lengthy debugging effort when, after several hundred million steps of simulating lipid bilayers with the MMC program [2] a discrepancy popped up between the carried and recalculated energy of one of the lipid molecules. This event thus serves as a demonstration of the facts that (a) the artifact discussed here can occur, but (b) very ravely.

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## FREE ENERGY CALCULATIONS

DARESBURY LABORATORY JULY 12 1999

• Programme organiser: Prof. M. Finnis (m.finnis@qub.ac.uk)

Local Organiser: Dr. W. Smith (w.smith@dl.ac.uk)

#### Introduction

In materials science, many important processes such as phase transformations, diffusion, fracture, segregation, the growth of surface layers, surface reconstruction, are sensitive to temperature. There is strong motivation for calculating the free energy changes involved in such processes, since calculations and understanding of the driving forces based on zero Kelvin total energies may be inaccurate or totally inappropriate. Methods for calculating free energy changes include thermodynamic integration, Monte Carlo simulation, quasiharmonic phonons, and others. The aim of this workshop is to bring together people who are interested in such methods and their application, to pool ideas and results. There will be relatively few talks and time will be specifically allocated for discussions between them. It is hoped to strike a balance between methodologies and applications.

#### Abstracts

#### Free Energy Evaluation via Quasiharmonic Lattice Dynamics

Neil L. Allan

School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS

In principle, lattice dynamics is an attractive route for the calculation of the thermodynamic propertics of crystals with periodic symmetry. Quantum effects are readily taken into account and the method does not rely on long runs for high precision. Unstable vibrational modes provide a sensitive test for interionic potentials and interpretation of the normal modes is straightforward, revealing, for example, the mechanisms of phase transitions or thermal expansion. The kinetic barriers and critical slowing-down effects suffered by Monte Carlo and molecular dynamics techniques are avoided. The bulk of the computational effort is usually expended in the optimisation problem of finding the equilibrium geometry at a given temperature and pressure; given this, calculation of the free energy, heat capacity, thermal expansion etc. is rapid and accurate. We have recently developed a new code, SHELL [1], for three- dimensional ionic crystals and slabs which calculates the full set of free-energy first derivatives analytically and so for the first time a full minimisation of the quasiharmonic free energy with respect to all internal and external variables is possible for large unit cells. Currently short-range interactions are via two and three-body potentials. In this talk the theory [2,3] will be outlined and recent applications discussed, including (i) negative thermal expansion ceramics (ii) surface [3] and defect [4] free energies. Lattice dynamics is also the basis of a recently proposed methodology [5] for obtaining the free energy of disordered solids and solid

solutions, which is quite different from standard approaches. Results for MnO/MgO and CaO/MgO will be presented.

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#### Ab Initio Thermodynamics of Matter under Extreme Conditions.

The QUASI Project.

Paul Sherwood Computational Science and Engineering Dept. CLRC, Daresbury Laboratory, Daresbury, Warrington. WA4 4AD

The talk will describe the QUASI project (Quantum Simulation in Industry), a European funded collaboration developing simulation techniques based on QM/MM (coupled Quantum Mechanical / Molecular Mechanical) schemes and application to industrial problems. The QM/MM method will be reviewed, and the software development aspects of the project described. The functionality of the MD module, currently under development based on elements of the DL\_POLY package) will be discussed. Particular emphasis will be given to the use of a Tcl interpreter to control the simulation protocol, statistics collection and constraint terms in free-energy simulations. The target applications for QUASI, spanning biological, zeolitic and surface catalytic systems, will be summarised.

#### Efficient Calculation of Free Energy from Computer Simulation.

#### Jeff Rickman

Lehigh University, Dept. of Mat. Sci. and Eng., #5 Whitaker Lab, 5 E Packer Avenue, Bethlehem PA 18105-3195, USA

In the last few years a number of complementary approaches have been devised to obtain free energies from simulation. In this talk I will discuss several such methods including: histogram techniques, cumulant expansions, harmonic approximation schemes and so-called "mechanical" calculations wherein the entropy of a system is determined directly from its region of motion in phase

space. For the purposes of illustration, the results of the application of these methods to various model systems will also be presented. Finally, I will outline some recent progress in the application of stereological techniques to the determination of entropy.

#### Interfacial and Surface Free Energies in Polymeric Systems.

#### Dr. Marcus Mueller,

Institut fuer Physik, WA331 (Theorie der Kondensierten Materie), Johannes Gutenberg-Universitaet, Staudingerweg 7, D55099 Mainz, Germany.

Surface free energies and interfacial tensions are important for many practical applications (e.g. wetting, coatings, adhesion). We study wetting phenomena and interfacial properties in a binary polymer blend by Monte Carlo simulation of a coarse grained polymer model (bond fluctuation model). Two methods for calculating the interfacial tension shall be discussed: reweighting techniques and the analysis of interfacial fluctuations. Employing an expanded ensemble where the monomer wall interaction is a stochastic variable we are able to accurately measure the surface free energy difference of the two species of the blend at a wall. Both free energies allow a localisation of the wetting transition via the Young equation. For our model of a binary polymer blend we find strongly first order wetting transitions. The consequences for the phase diagram of a mixture confined into a film are discussed.

# Free Energy calculations in Molecular Dynamics simulations: Surfaces and Solvation.

#### R.M.Lynden-Bell

Atomistic Simulation Group, School of Maths and Physics, The Queen's University, Belfast BT7 1NN

There are a number of methods for calculating changes in Free Energy in Molecular Dynamics simulations. I shall describe three recent rather different calculations which illustrate some of the methods and technical problems involved.

- 1. Measuring surface free energies of solids with surface melting/disorder [1]. This we did by thermodynamic integration. The technical problem was to find a suitable path to turn off the interaction between slices of a bulk (infinite) crystal to generate slabs with surfaces.
- Measuring free energy profiles for small molecules passing through the liquid-vapour interface [2]. This was done by measuring average forces in a constrained simulation, and then integrating. The main technical problem were long relaxation times.
- 3. Measuring ion solvation free energies [3]. We were concerned to find the solvation free energy as a function of charge and size of a spherical solute in water. This was done by a method in which the system with given charge and solute size was embedded in a higher dimensional space

with charge and/or size as additional variables. The variation of free energies in this higher dimensional system with extended dynamics was found from both integrating the forces on the new variables and using the histogram method in a molecular dynamics simulation with extended dynamics.

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#### Lattice Switch Monte Carlo

Graeme Ackland, University of Edinburgh.

Lattice Switch Monte Carlo is a technique for obtaining free energy differences directly without calculating the absolute free energies. As such, it offers considerable computational advantages over methods which attempt to evaluate the exact free energy. The method requires construction of a bipartite phase space describing the two systems to be compared, and incorporating a Monte Carlo move which switches between regions of space.

A practical application of the method, involving biassed sampling techniques, will be illustrated with an example of the free energy difference between the fcc and hcp structures of hard spheres. Further applications of the method will be discussed, including switching between different models for the total energy of a system.

#### Free Energy Calculations for Defect Processes in the Dilute Limit.

John Harding,

Materials Research Centre, Department of Physics and Astronomy, University College London, Gower St., London WC1E 6BT

Point defects in solids affect the vibrational spectrum of the crystal; producing both a general perturbation of the form of the density of states and individual, strongly localised modes ('true' local modes, gap modes and resonances). These effects are an important contribution to the entropy of defect processes and also offer a sensitive test of the model of crystal forces used.

We discuss methods for obtaining free energies of defect processes in ceramics within the quasiharmonic approximation and the problems of comparison with the (rather limited) experimental data available.

# EPSRC CCP5 Workshop on Particle Simulation Techniques for Colloids, Pastes and Powders.

Cavendish Laboratory, Mandingley Road, University of Cambridge Thursday 1st April 1999 David Heyes

CCP5 held a workshop on mesoscale particle modelling of colloidal liquids, pastes and granular systems at the Cavendish Laboratory, Cambridge on the 1st of April 1999. The meeting, which was the first of its kind for CCP5, was well-attended with in excess of 40 participants. The purpose of the workshop was to bring together theoreticians and simulators involved in modelling these materials at the microstructural particulate level. The focus was on calculating properties of practical/materials science relevance such as rheology.

There are still many technical challenges associated with the particle modelling of these systems. These are primarily ones of establishing the most relevant length and timescales to include in the computer model. Modelling these systems from the atomistic level (a sort of 'bottom up' approach) is not feasible and moreover, even if it were, would not be effective procedure for identifying the key physical and dynamical processes that are responsible for the material's behaviour. (There is not much you can easily do with the co-ordinates and positions of millions of atoms!) The important dynamical processes and interactions that govern the physical behaviour (mechanical, rheological and structural) take place on the mesoscale. The atomistic approaches, Molecular Dynamics and Monte Carlo would completely miss these because of the quantity of information they would provide. To make progress and minimise the number of particles that need to be followed in a simulation, it is necessary to identify the key distance and lengthscales operating in the material that determine its physical properties. To a certain extent, the starting point for this is physical intuition, but this has to be justified by the success of model in reproducing a range of experimentally verifiable phenomena. Inevitably, a series of iterations and refinements to the model will then be required.

With this prologue in mind, this workshop was concerned with particle modelling of (a) colloidal liquids, in which solid particles are suspended in a liquid 'host' medium (b) dry powders, in which a gas fills the interstities between the granules, and (c) pastes, which are like very high concentration colloidal liquids that are so viscous that they have solid-like characteristics on 'short' timescales. The scientific and technical issues, which are actually to a large extent the same, were discussed for all of these systems. The morning session commenced with Tony Ladd (Chemical Engineering, University of Florida at Gainesville) who gave a talk outlining the technical challenges associated with Lattice Boltzmann simulations of colloidal liquids. In this technique the solvent is represented by a distribution of 'particles' on a lattice. The boundaries of the colloidal particles have to map on to this fluid lattice, the methodology for achieving this most realistically is still an active area of debate.

Eric Dickinson (Department of Food Science, University of Leeds) talked about particle modelling of particle gels such as are found in foods. In these systems the interactions between the particles

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are quite strong and 'sticky' at short range, so the particles can form irreversible 'bonds' between them when they approach and which then have a significant orientational dependency. These strong interactions dominate the physical properties, and consequently a relatively simple model for the solvent was considered to be sufficient to a first approximation (the Brownian Dynamics method). A full treatment of the solvent hydrodynamics was not deemed so important for this class of systems.

I gave a talk on algorithms at the Brownian Dynamics level. The Brownian Dynamics, BD, simulation technique invented by Ermak in 1975 was the first to provide a numerical scheme for integrating the Smoluchowski (position Langevin) equation. This is a basic model for colloidal liquids that ignores many-body hydrodynamic effects. Each colloidal particle is assumed to be 'hydrodynamically' isolated and subject only to a Stokes drag and uncorrelated Brownian Forces. The original Ermak BD algorithm is still widely used. I showed the results of BD simulations carried out with alternative algorithms which offer significant improvements in numerical efficiency. These were developed in collaboration with A.C. Branka (Polish Academy of Sciences, Poznan, Poland). These were based on, for example, Runge-Kutta and Smart Monte Carlo. These modifications are quite simple to implement and can lead to factors of two or three at least increase in timestep while at the same time giving more accurate thermodynamic and static properties.

The morning session was concluded with a lively open discussion, led by John Melrose (Cavendish Laboratory, Cambridge). One of the main discussion topics in this part of the first session was: what elements of the hydrodynamics in the system is it necessary to incorporate in the model? For concentrated dispersions, and especially at high shear rates, so-called lubrication forces between the colloidal particles are probably the most important terms. These are essentially pair-wise additive and therefore can be incorporated in a particle simulation code relatively efficiently. The physical origin of this term is when two colloidal particles approach closely the liquid between them gets 'squeezed out' but with great reluctance, so there is an effective repulsive force between the particles, which is proportional to their relative velocity of approach. This interaction diverges at sphere contact (assuming them to be hard spheres) which means that, in this continuum level description, the two spheres can never touch! When the particles attempt to move apart, there is an effective attraction force.

The afternoon session was commenced with Ugur Tüzün (Chemical Engineering, University of Surrey) who talked about Granular Dynamics simulations and tomographic imaging of granular beds. One of the problems holding back theoretical developments of granular materials has been, until recently, that there were no effective non-intrusive probes that could investigate the state of the inside of a bed of granular material as it is conveyed or simply standing in a heap, for example. Our understanding of granular materials was confined to their behaviour at the surface (e.g., wall pressures on silos) and macroscopic properties such as flow rates. This has made particle simulation techniques particularly valuable. Granular Dynamics, an extension of Molecular Dynamics has proved effective in its relatively short history. One of the recurrent themes of discussion was again the appropriate lengthscale and timescale for the interparticle interactions to include in the model. Granular particles can be said to be in 'contact' over a wide range of distance scales. Two typical granules are rough and therefore are in 'contact' at the asperity micron level at numerous points where the two mountainous surface profiles touch. It was argued that this, however, was not the appropriate scale upon which to base the computer model. Rather, the particle scale was the appropriate scale

to describe the assembly. The particle 'contact' is assumed to occur over a reasonable fraction of the particle's surface. It is assembly dynamics and statics that are most appropriately followed, rather than asperity micromechanics which are on a much finer and therefore more poorly defined surface topography. John Baxter (Chemical Engineering, University of Surrey) gave a presentation showing a movie of particles discharging from a model silo, work carried out in collaboration with Ugur Tüzün. Various engineering conditions were changed and the discharge characteristics were shown to depend on these variables. Paul Langston (Chemical Engineering, University of Nottingham) discussed the simulation procedures for modelling pastes, using a continuum finite element level description of the interstitial fluid.

This was a very successful workshop in my opinion. There was much lively and informed discussion from the participants and the attendees. The local arrangements were admirably organised by John Melrose and Meg Staff of the Cavendish Laboratory.

# Simulating Clusters and Interfaces CCP5 Annual Meeting 1999 Birmingham

6-8th September 1999

## INVITED TALKS

## Energy Landscapes of Clusters, Biomolecules and Solids

Dr. David J. Wales

The University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK

The energy landscape approach to structure, dynamics and thermodynamics appears to hold the key to resolving both the Levinthal and Kauzmann paradoxes. For small clusters it is possible to find all the important minima and the pathways that link them. Hence for water clusters one can determine the appropriate molecular symmetry group with which to characterise the energy levels of these non-rigid systems.

To treat larger systems the superposition approximation may be used to calculate approximate thermodynamics and the master equation may be used to study relaxation dynamics. Clusters provide examples of both efficient relaxation to the global minimum and of trapping.

Disconnectivity graphs enable us to visualise a high dimensionality potential energy surface. To some extent the dynamics and thermodynamics of the system can be deduced simply by inspecting its disconnectivity graph. Examples are provided by the annealing of C60 to buckminsterfullerene, the folding of a model polypeptide and the freezing of a "nanodroplet" of water.

The insight gained from studies of clusters and abstract energy landscapes led to the "basinhopping" approach to global optimisation. This algorithm produced the best results in the literature for Lennard-Jones clusters and has since been applied to a range of atomic and molecular clusters.

# Metal Clusters: Structures, Mixing, Phases, Reactivity, and all that \*

Julius Jellinek

Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439 USA

Results of dynamical and statistical simulation studies of metal clusters of different materials and sizes will be reviewed and discussed. The simulations are based on either first principles or semiempirical many-body potentials. The discussion will encompass structural issues, mixing vs.

segregation in two-component alloy clusters, thermal properties (including composition-dependent peculiarities), electronic features, and interactions of clusters with molecules.

·	Work	supported	by	$_{\rm the}$	Office	$^{\rm of}$	Basic	Energy	Sciences,	Division
of	Chemic	al Scienc	es,	US-DOE	unde	9 <b>r</b>	Contract	No.	W-31-109-EN	íG-38.

## **Extending Atomistic Simulation time scales**

Arthur F. Voter

Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

A significant problem in the atomistic simulation of materials is the time scale limitation of the molecular dynamics method. While molecular dynamics can easily access nanoseconds with empirical potentials, many of the most interesting diffusive events occur on time scales of microseconds and longer. If the transition state (i.e., the saddle point) for a given reaction pathway is known, transition state theory can be applied to compute a rate constant directly. If all possible events are known for a given system, these rate constants can be employed in a kinetic Monte Carlo algorithm to evolve the system from state to state over long time scales. Unfortunately, for realistic systems, the transition states are often hard to find. Moreover, it is often the case that our intuition about how the system will behave breaks down, so that key events are missing from the kinetic Monte Carlo treatment. This situation is typical in metallic surface growth, where complicated exchange events prevail, and in many other physically important processes, such as annealing after radiation damage, or diffusion at a grain boundary.

I will discuss some new methods for treating this problem of complex, infrequent-event processes. The idea is to directly accelerate the molecular dynamics simulation to achieve longer times, rather than trying to specify in advance what the available mechanisms are. These new methods, hyperdynamics, parallel replica dynamics, and temperature extrapolated dynamics, can be used individually, or in combination, to extend the molecular dynamics simulation time by orders of magnitude, thus making much closer contact with experimental conditions. I will discuss the relative merits of the different methods and present results demonstrating the power of this general type of approach. Examples will include growth of a copper surface from vapor deposition and from ionized physical vapor deposition.

#### Theory modelling and simulation of surfactant self-assembly processes

Professor P.V. Coveney Department of Chemistry, Queen Mary and Westfield College, University of London

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One major challenge for modelling and simulation is linking microscopic to macroscopic properties, particularly in non-equilibrium situations. Amphiphilic fluids provide an example of the general problem: the macroscopic behaviour is determined by microscopic and mesoscopic features, yet the timescales for most micellar and interfacial self-assembly processes are too long to be accessible by conventional molecular dynamics methods. In this talk, we shall describe some recent very large scale (massively) parallel MD simulations of amphiphilic self-assembly, and compare and contrast the information available from such atomistic approaches with more coarse-grained but much faster mesoscale (lattice gas, lattice-Boltzmann and dissipative particle dynamics) methods, as well as kinetic theories based on the Becker-Doering cluster aggregation/fragmentation equations.

## CONTRIBUTED TALKS The Dynamics of Protonated Rare Gas Clusters: Quantum and Classical ab initio Simulation

F.A. Gianturco

Department of Chemistry, University of Rome, Cittá Universitaria, 00185 Rome, Italy

The presence of the "naked" proton or, more realistically, the presence of protonated molecular species has always played a major role in the understanding of a large class of chemical processes. The possible understanding of the microscopic mechanisms which preside over the formation of such species, therefore, is of marked importance in many areas of chemical physics. In the last few years we have undertaken a systematic study of the possible stable structures of  $H^+$  inserted in small He and Ar clusters by analysing the ionic cromophores in both systems using *ab initio* quantum methods [1,2,3]. We have further extended the study to the possible dynamics of cluster growth and cluster break up by using *ab initio* molecular dynamics simulations and simulated annealing methods [4,5,6].

Finally, we have investigated the role of quantum effects by constructing the smaller clusters using stochastic methods and quantum diffusion Montecarlo techniques [7]. The combination of all the above methods turns out to provide a rather detailed picture of the microscopic phenomena and to yield specific, and realistic answers for the many questions related to the modelling of microsolvation with small rare gas clusters.

The most recent results will therefore be reported at the meeting and discussed under the above global analysis of our simulations.

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## Optimisation of cluster geometries for single and multi-component systems using a genetic algorithm

Roger Smith and Steven Hobday

School of Mathematics and Physics, Loughborough University, Loughborough, Leicestershire LE11 3TU, UK

Applications of Genetic Algorithms for optimisation of atomic and molecular clusters are reported. It is shown that the genetic algorithms are very useful tools for determining the minimum energy structures of clusters of atoms described by many-body interatomic potential functions containing up to a few hundred atoms. The algorithm generally outperforms other optimisation methods for this task. A number of applications are given including covalent carbon and silicon clusters, close-packed structures such as argon and silver and the two-component C-H system.

#### Large Structural and Electronic Properties of Small Gold Clusters

Alvaro Posada Amarillas <sup>1</sup> <sup>1</sup> I, Ignacio L. Garzón <sup>2</sup> , Donald H. Galván <sup>3</sup> <sup>1</sup> Departamento de Investigación en Física, Universidad de Sonora, Mexico <sup>2</sup> Instituto de Física-UNAM, Mexico <sup>3</sup> Centro de Ciencias de la Materia Condensada-UNAM, Mexico

We have investigated the structural properties of several small ordered and disordered gold clusters by computer simulation molecular dynamics using a Gupta n-body model potential. A commonneighbour analysis was implemented in order to characterize the degree of order. Distorted multilayer icosahedral order was found to be most representative of the disordered clusters with the lowest energies. At higher energies the amorphous structures are characterized by the presence of distorted local icosahedral order. We discuss the origin of the stability in both ordered and disordered gold clusters, and present the total density of states (TDOS) calculated by the extended Hückel method for both ordered and disordered gold clusters.

Current address: Centro de Ciencias de la Materia Condensada-UNAM, Mexico.

## From Clusters to Colloids: Modelling the Structures of Gold Nanoparticles

Nicholas T. Wilson and Roy L. Johnston

School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, U.K.

Metal nanoclusters promise to be of significant technological importance. There is particular interest in clusters and colloids of gold (indeed colloidal gold has been known since Egyptian times). Unfortunately, it is often difficult to determine the structures of these nanoparticles directly, which is why theory continues to play an important role in cluster science. This presentation will describe the application of a many-body potential to predict structural motifs and stabilities of gold clusters in the nanometer size range.

#### Theory of the Island and Capture Zone Size Distributions in Thin Film Growth

P.A. Mulheran and D.A. Robbie

Department of Physics, University of Reading, Whiteknights, Reading RG6 6AF, U.K.

A striking characteristic of the early stages of thin film deposition, where the deposited monomers cluster together into islands, is the scaling property of the island size distribution observed both experimentally and in simulations. The origin of this phenomenon has recently been explained through identifying Voronoi-type capture zones with the island growth rates for the broad range of systems where island development is controlled by the surface diffusion of the monomers. However a gap in the full understanding of the islands' scaling properties remains, because the ongoing nucleation of islands during the deposition process continually changes the network of capture zones and leads to non-trivial broadening of the island sizes. In this presentation we show how this gap is closed by modelling the evolution of the joint probability distribution of island and capture zone sizes, taking into account both island nucleation and growth throughout the film deposition. Furthermore our analysis reveals that the joint probability has robust scaling for spontaneous nucleation (e.g. islands nucleating through the interaction of monomers with the substrate) and a weak coverage- dependence only for systems where it takes two monomers to nucleate an island. The solutions to our model equations correspond well to the joint probability distributions found in thin film deposition simulations. We also find quantitative predictions for the island size distributions that agree well with simulations and experiments for the first time. The work is of importance for many technological systems where the understanding and control of the island sizes and their spatial arrangements is crucial.

## Simulation of Colloidal Particles at Fluid Interfaces

Fernando Bresme and Nicholas Quirke

Department of Chemistry, Imperial College of Science, Technology and Medicine, Exhibition Road, London. SW7 2AY, UK

Colloidal particles are relevant in different areas of practical interest such as the petrochemical industry, foam science and also, more recently, in the synthesis and characterisation of nanomaterials. These nanomaterials are often prepared as thin films at fluid interfaces. In this talk we will describe the behaviour of a single colloidal particle, with size of a few nanometers, at liquid-vapour and liquid-liquid interfaces. Molecular dynamics simulations of this model allows us to study the factors that influence the stability of spherical substrates at interfaces. In particular our work has provided information on the role and size of the line tension in determining the contact angle the fluid makes with the colloidal particle.

We also consider a monolayer of colloidal particles at a liquid-liquid interface. This monolayer is compressed emulating a real Langmuir-trough experiment. These studies give insight into the response of the monolayer to compression and are also helpful to asses the validity of thermodynamic analyses, which are the basis for interpretation of the Langmuir-trough experiments.

During this talk we will discuss also the validity of macroscopic approaches such as Young's equation. We consider wetting in systems involving nanometer curved surfaces, such as the colloidal particle considered above, and also liquid lenses at interfaces, which exhibit the interesting phenomena of spreading.

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# Car-Parrinello Simulation of H<sub>2</sub>O on Rutile

W. Langel

Institut für Chemie und Biochemie, Universität Greifswald, Soldmannstraße 23, D-17489 Greifswald, Germany langel@mail.uni-greifswald.de

Titanium implants are widely used because they exhibit both high biocompatibility and favorable mechanical properties. In practice the surface of metallic titanium reacts with ambient oxygen to form an  $\text{TiO}_2$  layer which is covered by physi- and chemisorbed water. The adhesion of amino acids on this hydroxylated titanium oxide governs the biocompatibility, but only a few studies are dealing

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with the mechanism of this process, reporting both physisorption [1] and bonding of the carbonyl group to dehydroxylated surface Ti [2].

Progress in this field at first affords a good understanding of the hydroxylation of  $\text{TiO}_2$ . It was shown by thermal desorption that the (110) surface is not very reactive as compared to (100) [3]. Recently a complicated mechanism for the dissociation of water on oxygen vacancies in the (110) surface was proposed [4]. First principles molecular dynamics gives direct access to reactions mechanisms on oxides [5]. A CASTEP simulation [6] resulted in spontaneous dissociation of adsorbed  $H_2O$  on rutile (110). A more detailed study by the same authors [7] revealed that at higher coverages molecular rather than dissociative adsorption occurs and that the energy gain of the dissociation process itself is only 0.04 eV which is well below kT.

Here first results of a calculation using the Car Parrinello method with ultrasoft Vanderbilt pseudopotentials and gradient correction are presented. Simulation cells for both (110) and (100) consist of three layers with four Ti and eight O atoms each. During short molecular dynamics runs the temperature was stepwise increased by rescaling velocities. Then the trajectories for free dynamics were recorded for some thousand time steps (0.17 fs). Neither on (110) nor on (100) clean surfaces spontaneous dissociation of adsorbed water was observed. As this could be due to an unfavourable starting position of the water molecule, the dynamics of dissociated water molecules was simulated. This resulted in recombination within less than one ps implying that hydroxylation does not occur via water adsorption on regular surfaces. In contrast to that water molecules readily dissociated after insertion into an oxygen vacancy on the (100) surface.

Addition of further hydrogen resulted in a very stable fully hydroxylated (100) surface, which is used as basis for the adsorption of amino acids. In a first calculation the carboxyl group of a cystein molecule formed hydrogen bonds with the surface hydroxyl groups indicating that their structure is essential for the adsorption process. Work in this field is in progress.

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### Modelling the Effect of Inhibitors on the Growth of Wax Crystals

D.M.Duffy <sup>1</sup> and P.M.Rodger <sup>2</sup>

<sup>4</sup> Dept. of Chemistry, Reading University, Whiteknights, Reading, RG6 6AD
<sup>2</sup> Dept. of Chemistry, Warwick University, Coventry, CV4 7AL

The deposition of wax from hydrocarbons is a significant problem for the oil industry, as the deposited wax tends to block pipelines and restricts the flow of oil. Research into effective inhibitors, which reduce the deposition rate to an acceptable level, is in progress. Such inhibitors generally have a dramatic effect on the morphology of deposited wax crystals.

We have used computer modelling techniques to study the interaction between inhibitor molecules and a number of wax crystal surfaces. It was found that the polymer tails of the inhibitor tend to align with the C chains and the inhibitor molecules interact strongly with the wax surface. Two low energy configurations were found, one with the polymer tails pointing in the same direction (closed) and the other with the polymer tails pointing in opposite directions (open). The strong interaction between the molecule and the wax crystal is suggestive of an inhibitor mechanism that involves the incorporation of the additive into the growing crystal, resulting in a weaker, defective crystal.

A model of crystal growth has been developed in which the wax molecules are deposited in a low energy configuration on a surface, using a molecular dynamics technique. The resulting surface is annealed to reduce the density of defects. Three different growth simulations were performed for the (010) surface: one using a clean surface, one with an adsorbed inhibitor molecule in the closed configuration and one with an adsorbed inhibitor molecule in the open configuration. The same number of molecules was deposited in each case. The configuration and energy of the deposited molecules were examined and compared for the three cases. The inhibitor molecules were found to be a source of defects in the growing crystal. These defects weaken the crystal structure and modify the surface energy, and consequently the shape, of the crystal.

### The effect of corrosion inhibitor films on deposition of wax to metal oxide surfaces

M.A. San-Miguel and P.M. Rodger Department of Chemistry, University of Warwick, Coventry, CV4 7AL

There are some processes such as corrosion, scale deposition, wax deposition and clathrate hydrate formation which reduce the efficiency of the transport processes in the oil and gas pipelines. The interaction between these effects is significant. There have been some theoretical and experimental studies in order to understand the separate processes and develop inhibitors to protect the pipelines from them, however there is little information about the interplay between the different processes. The pipelines made of mild steel lead to an oxide film on the iron surface, which mostly presents a hematite structure. To protect this surface from the corrosion it is common to add specific molecules that form protective films and thereby inhibit the process [1,2] Nevertheless, it has been observed that the use of these compounds can induce the wax deposition. In this work, by using molecular dynamics techniques we have studied the deposition processes of the most common alkane chains and their crystal growth on the hematite surface. Adsorption of oleic imidazoline molecules used as corrosion inhibitors has also been modelled. Finally, we have simulated the behaviour of wax molecules in presence of the adsorbed corrosion inhibitor. It has been observed according to the experimental evidences that the inhibitor favours the wax deposition.

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## Molecular Dynamics Studies of Nucleation and Critical Nuclei in the Freezing of Molecular Liquids

L. S. Bartell and Y. Chushak

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109, USA

We report the behavior of large liquid clusters subjected to deep supercooling. Several features distinguish our work from that of virtually all prior MD studies of nucleation. First, we investigate clusters instead of bulk-like systems to avoid effects of periodic boundary conditions, and our subjects are polyatomic molecules, not atoms. In addition, we observe spontaneous nucleation (i.e., nucleation unaided by biasing potentials or the implantation into the liquid of preformed nuclei). Our critical nuclei do not much resemble the idealized nuclei often envisaged by theorists. Our most striking result is that the nucleation rate decreases with increasing cluster size even after the effect of Laplace pressure is taken into account. This is because nuclei preferentially form at or near the surface.

# The Riddle of Resorcinol Crystal Growth Revisited: Molecular Dynamics Simulations of $\alpha$ -Resorcinol Crystal - Water Interface

Mumtaz Hussain and Jamshed Anwar

Computational Pharmaceutical Sciences, Department of Pharmacy, King's College London, Franklin-Wilkins Building, 150 Stamford Street, London SE1 8WA, United Kingdom Email: jamshed.anwar@kcl.ac.uk

The mechanism by which solvent exerts its effect during the process of crystallisation is poorly understood. An important and ongoing problem is the uneven growth of the faces  $\{0, 1, 1\}$  and  $\{0 \ \overline{1} \ \overline{1}\}$  of  $\alpha$ -resorcinol in water. Growth occurs mainly at the  $\{0 \ \overline{1} \ \overline{1}\}$  surface. In an attempt to determine the mechanism, molecular-dynamics simulations have been carried out of the two surfaces in contact with water. The dynamical properties of the water close to the surface as well as the overall interaction energies of the water with the respective faces have been calculated. The strongest water-binding sites have also been determined and energetically characterised. The data indicate that the adsorption of water molecules is stronger at the slower growing  $\{0 \ 1 \ 1\}$  face, with the strongest binding occurring at specific sites on this face. The motion of the water molecules in the surface layer at this face is also more localised and restricted compared with that at the faster growing  $\{0 \ \overline{1} \ \overline{1}\}$  face. The binding sites at the  $\{0 \ 1 \ 1\}$  surface are not within the grooves that are present at this surface but are located above the outermost part of the crystal surface. The water molecules form strong hydrogen bonds with the limited number of hydroxyl oxygens of the resorcinol molecules protruding from the surface. The overall inference is that the stronger binding of the water molecules at the  $\{0, 1, 1\}$  surface serves to retard crystal growth, rather than enhancing it as predicted by the surface roughening theory.

## The Simulation of Osmosis and Semi-Permeable Membranes.

#### Jack G.Powles

The Physics Laboratory, University of Kent, Canterbury, Kent, CT2 7NR, UK

The first computer simulation of osmosis using tolerably realistic semi-permeable membranes was performed in 1993 [1]. This topic has developed rapidly and there are now some twenty papers treating both statics and dynamics of osmosis, reverse osmosis and electro-osmosis. The "experiments", the membranes and the mixtures are becoming rapidly even more realistic and more useful. This has led to a better understanding of the osmosis mechanism especially as regards the dynamics of the process and will surely lead to better, and better-designed, membranes.

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## Modelling Meso-Scale Diffusion Processes in Stochastic Fluid Bio-membranes

H. Rafii-Tabar <sup>1</sup> H.R. Sepangi <sup>2</sup>

<sup>1</sup> Computational Nano-Science Research Group, Centre for Numerical Modelling and Process Analysis, School of Computing and Mathematical Sciences, University of Greenwich, Woolwich Campus, Wellington Street, London SE18 6PF, UK

<sup>2</sup> Department of Physics, Shahid Beheshti University, Evin, Tehran 19834, Iran

The space-time dynamics of rigid inhomogeneities (inclusions) free to move in a randomly fluctuating fluid bio-membrane is derived and numerically simulated as a function of the membrane shape changes. Both vertically placed (embedded) inclusions and horizontally placed (surface) inclusions are considered. The energetics of the membrane, as a two-dimensional (2D) meso-scale continuum sheet, is described by the Canham-Helfrich Hamiltonian, with the membrane height function treated as a stochastic process. The diffusion parameter of this process acts as the link coupling the membrane shape fluctuations to the kinematics of the inclusions. The latter is described via Ito stochastic differential equation. In addition to stochastic forces, the inclusions also experience membrane-induced deterministic forces. Our aim is to simulate the diffusion-driven aggregation of inclusions and show how the external inclusions arrive at the sites of the embedded inclusions. The model has potential use in such emerging fields as designing a targeted drug delivery system.

## Growth mechanisms in calcite

 J.H. Harding, <sup>1</sup> N.H. de Leeuw and S.C. Parker <sup>2</sup>
<sup>1</sup> Dept. of Physics & Astronomy, University College London <sup>2</sup> School of Chemistry, University of Bath

Molecular dynamics simulations were used to model two stepped  $\{10\bar{1}4\}$  surfaces of the calcium carbonate polymorph, calcite. The acute monatomic steps were found to be more stable than the obtuse monatomic steps. Using potential parameters which reproduce the experimental enthalpies of growth of the calcite crystal, the formation of the double kinks on the obtuse step is shown to cost less energy than growth onto the acute step, probably due to the lower stability of the obtuse surface. The simulations suggest that formation of the kink sites on the growing edge of the obtuse step of calcite is the rate-determining step and this edge is predicted to grow preferentially, which is in agreement with experimental findings of calcite growth under aqueous conditions.

Growth of magnesium ions onto the growing calcite steps is an exothermic process on both acute and obtuse edges, indicating that incorporation of magnesium into the calcite crystal is a straightforward process on energetic grounds. These results agree with the fact that large amounts of magnesium are found in calcite crystals. Subsequent growth of calcium ions onto the magnesium terminated edges is endo-thermic which indicates that precipitation of magnesium onto the edges inhibits calcite growth, again in agreement with experimental findings.

## Methane Hydrate: Memory and Melting

Dr P.M. Rodger

Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK

We present the results of a long timescale molecular dynamics simulation of a methane hydrate / methane gas interface formed along the  $[0\ 0\ 1]$  hydrate surface. The simulations were performed at 15 - 20°C above the stable hydrate temperature so that we were able to observe melting under conditions that were sufficiently gentle to allow any residual order associated with the memory effect for hydrate nucleation to be identified. The simulations have been analysed using a set of novel order parameters designed specifically to quantify the microscopic molecular structure associated with the different phases of water. The simulations do show an enhanced level of ice- and clathrate-structure in the liquid water that forms when the hydrate decomposes, but there is no evidence of significant clusters of the ordered water.

## Monopoles, Dipoles and Quadrupoles, A Chemist's Perspective

Dr. Martin Grayson

Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK

The usefulness of the partial atomic charge approximation and its definitions are discussed. This leads on to the definition and use of the higher moments. In the world of modern computational density functional theory is any of this any use by comparison with the full density?

Notwithstanding that for a thousand pounds one can buy as much computing power in a supermarket as was in the national computer centre 20 years ago some calculations which can be done on the back of an envelope are presented. Such calculations often make use of the archaic concept of electronegativity, used continually in chemical discussion, but not so useful where Delta-chi is small. Concepts such as the chemical potential of a single molecule are however fully and precisely definable in density functional theory.

Very often in the real world we have an inverse problem of the problem we can really answer. "Give me a molecular system which has properties A, B, C, and not D, which costs less than

E dollars per kilogram and can be safely buried in the garden when we have done with it." Often our only answer is: "give me the geometry of a candidate and I will give you the values of A-D to within a fifth of an order of magnitude". The crude way to invert this problem is to generate and screen all plausibilities with a fast algorithm. Regrettably it appears to be desirable that the same person must be able to do both supercomputer and back of the envelope calculations in order to be able to interpret, explain and predict the properties of matter, tough!

### Large Molecular Dynamics Simulations of Nanocolloidal Liquids

D. M. Heyes, <sup>1</sup> M. J. Nuevo and J. J. Morales, <sup>2</sup> A. C. Branka <sup>3</sup>

 Department of Chemistry, School of Physical Sciences, University of Surrey, Guildford GU2 5XH UK

<sup>2</sup> Departamento de Física, Facultad de Ciencias, Universidad de Extremadura, 06071 Badajoz, Spain.

<sup>a</sup> Institute of Molecular Physics, Polish Academy of Sciences, Smoluchowskiego 17/19, 60-179 Poznan, Poland.

Nanocolloids are at the forefront of technology as small-scale devices are starting to feature nanocolloids and nanocolloidal technology *e.g.*, in the area of data storage and 'defect-free' ceramics. Nanoparticles are also 'primary' particles that are the initial stages of precipitation of inorganic and polymers from solution. Overbased detergent (surfactant-coated calcium carbonate particles) are nanoparticles added to automotive and marine engine lubricants to neutralise the acidic by-products of combustion which would otherwise corrode the engine.

In this talk I will review our ongoing simulation studies of nanocolloids and nanocolloidal liquids [1]-[11]. Molecular Dynamics, MD, simulations have been used to calculate the translational and rotational relaxation dynamics of model atomistically rough spherical nanocolloidal particles in solution at infinite dilution by immersing a single Lennard-Jones cluster in a molecularly discrete solvent. The effects of the relative solvent and colloidal particle mass density, and colloid size on the translational and rotational self-diffusion coefficients were investigated. At liquid-like number densities (  $\rho_s = N\sigma_s^3/V \simeq 0.9$ ) the translational, D, and rotational,  $D_{\rm rot}$ , self-diffusion coefficients for the nanocolloids of all sizes were statistically independent of the ratio of colloidal to solvent particle mass density up to the value of ca. 20.0 explored.

Key timescales characterising colloidal particle dynamical relaxation were computed from time correlation functions. For translational motion these were  $\tau_v$ , the colloidal velocity relaxation time,  $\tau_f$ , the hydrodynamic relaxation time and the timescale for significant particle displacement,  $\tau_d$ . We show that  $\tau_v \simeq \tau_f$  when the relative mass density of the colloidal particle divided by the bulk density of the solvent is ca.  $\rho^* = 20$ , in agreement with theoretical predictions. Preliminary evidence from the velocity autocorrelation functions, VACF, of the nanocolloidal particle also supports the theoretical treatments that the transition from the Liouville to Fokker-Planck description (evident by exponential decay in the VACF) is determined by both the colloidal particle mass and size.

We calculated the relaxation times for angular velocity relaxation,  $\tau_{\omega}$  and reorientation,  $\tau_u$  and found them to scale reasonably well with the relaxation time for the free rotor, for size dependence but not so well for mass dependence. The angular velocity correlation function of 13 atom clusters departed from Langevin (exponential) relaxation also for  $\rho^* < 20$ . The rotational self-diffusion coefficient was also non-classical in this range.

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#### POSTER ABSTRACTS

## Ab initio density-functional calculations of the geometries, electronic structures and magnetic moments of Ni-Al clusters

M. M. G. Alemany, M. Calleja, C. Rey and L. J. Gallego, <sup>1</sup> P. Ordejón, <sup>2</sup> D. Sánchez-Portal, E. Artacho and J. M. Soler <sup>3</sup>

<sup>1</sup> Departamento de Física de la Materia Condensada, Facultad de Física, Universidad de Santiago de Compostela, Santiago de Compostela E-15706, Spain

<sup>2</sup> Departamento de Física, Universidad de Oviedo, E-33007 Oviedo, Spain

<sup>\*</sup> Departamento de Física de la Materia Condensada C-III, Universidad Autónoma de Madrid,

E-28049 Madrid, Spain

We report *ab initio* molecular dynamics simulations of  $Nl_2$ ,  $Al_2$ ,  $Nl_{13}$ ,  $Al_{13}$  and  $Nl_{12}Al$  clusters using SIESTA [1], a fully self-consistent density-functional method that employs linear combinations of atomic orbitals as basis sets, standard norm-conserving pseudopotentials and a generalized-gradient approximation to exchange and correlation (see Ref. [2]). Our results for the pure Ni and Al clusters, which are compared with those obtained by other recent *ab initio* calculations [3,4], are in good agreement with available experimental data. For the binary cluster  $Nl_{12}Al$  our calculations show that a distorted icosahedral configuration with the Al atom at the cluster surface is more stable than that with the Al atom located at the central site, a result which clarifies discrepancies between the results of different semiempirical treatments [5,6].

This work was supported by the DGICYT, Spain (Project Nos. PB95-0720-C02-02 and PB95-0202) and the Xunta de Galicia (Project No. XUGA20606B96). P. Ordejón was partially supported by a Sponsored Research Project funded by Motorola Phoenix Corporate Research Laboratories.

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## **Computer Modelling of Metal Carboxylates**

L. S. Barreto, <sup>1,2</sup> K. A. Mort, <sup>1</sup> R. A. Jackson <sup>1</sup> and O. L. Alves <sup>2</sup>

<sup>1</sup> Chemistry Department, Keele University, Keele, Staffs ST5 5BG, UK

<sup>2</sup> Instituto de Química, Universidade Estadual de Campinas, Campinas, SP, Brazil

A key feature of this work has been the development of a working potential model for metal carboxylates, and an assessment of its transferability to related molecular systems. The structures of these organic salts depend on a combination of strong iouic forces and weak van der Waals forces. This system exhibits mixtures of bonded and non-bonded interactions which need to be considered in the potential model.

The aim of this work was to establish a set of potentials that could describe the structure and properties of the short chain metal carboxylates, sodium and lithium acetate.

Empirical potential fitting was used to obtain potentials for lithium acetate dihydrate and anhydrous sodium acetate. The results showed good agreement with the experimental crystal structure.

## **Computer Modelling of Crystal Morphology**

A. L. Braybrook, B. R. Heywood and R. A. Jackson School of Chemistry & Physics, University of Keele, Staffs, ST5 5BG

During the last 10 years the growth in computer power, both hardware and software has meant that computers are no longer used solely for the reproduction and analysis of experimental data, but can be used as a predictive tool in the determination of crystal morphology.

The technique of lattice energy minimisation, using the GULP (General Utility Lattice Program) code has been used to model the calcite phase of calcium carbonate. The original potential model [1] has been modified in light of recent work carried out on modelling solids containing molecular ions [2,3]. Results are presented of the calculated bulk structure.

The next stage of the project has involved the use of the MARVIN program to calculate surface and attachment energies, and hence predict the morphology of calcite. Results are presented of the calculated surface and attachment energies of calcite.

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# The effect of ion localization on cluster size. MD simulations of $CI(H_2O)_n$ (n=10, 25, 50, 100, 200, 400, 800) clusters

Steve Brdarski and Gunnar Karlström <sup>1</sup> Per Linse <sup>2</sup> <sup>1</sup> Department of Theoretical Chemistry <sup>2</sup> Physical Chemistry

\* r uysicar Giennistry

Chemical Centre, P.O. Box 124, University of Lund, S-22100 Lund (Sweden)

MD simulations on  $\operatorname{Cl}(\operatorname{H}_2\operatorname{O})_{\mathfrak{g}}(\mathfrak{n}=10, 25, 50, 100, 200, 400, 800)$  clusters have been performed in order to study the effect of the location of the Cl<sup>-</sup> ion in the water clusters. A new augmented NEMO potential has been used for the H<sub>2</sub>O-Fl<sub>2</sub>O and H<sub>2</sub>O-Cl<sup>-</sup> interactions. It was found that the ion prefers to locate at the surface of the cluster for all the cluster sizes above. It was also found that the ratio polarizability/size of the ion plays an important role for the location of the ion in the clusters. An energy transfer from the internal degrees of freedom to the total rotation and translation degrees of freedom was observed during the simulation. The problem is related to the velocity rescaling in order to keep the temperature constant. The internal motion will slow down and the cluster will be internally cooled. To get rid of this phenomena one has to periodically remove the net translation and rotation of the center of mass of the clusters.

#### Structural and dynamical properties of fulleren - rare gas clusters

A. Dawid and Z. Gburski

Institute of Physics, University of Silesia, Universytecka 4, 40-007, Katowice, Poland

Using molecular dynamics (MD) simulation technique we have studied the fullerene - argon mixture cluster  $C_{60}Ar_{46}$ . The temperature evolution of the radial distribution function, mean square displacement, velocity correlation function and diffusion coefficient were calculated for argon. The substantial differences between the dynamics of argon in pure  $Ar_{46}$  and mixture  $C_{60}Ar_{46}$  clusters have been observed, both in solid and liquid state.

## Embedded atom model calculations of the ground-state configurations of Fe and Fe-Al clusters

O. Diéguez, R.C. Longo, C. Rey and L.J. Gallego Departamento de Física de la Materia Condensada, Facultad de Física, Universidad de Santiago

de Compostela, E-15706 Santiago de Compostela, Spain

Using the noncentral embedded atom model potential recently proposed by Besson and Morillo [1] for  $\operatorname{Fe}_{1-y}\operatorname{Al}_{y}$  bulk alloys ( $y \leq 0.5$ ), we performed computer simulations to predict the ground-state configurations of  $\operatorname{Fe}_{n}$  and  $\operatorname{Fe}_{n-x}\operatorname{Al}_{x}$  clusters ( $n \leq 19$ ) [2]. The computed structures of  $\operatorname{Fe}_{n}$  clusters are in general agreement with such theoretical results as have been obtained by density functional calculations (i.e. for  $n \leq 7$ ; [3,4]). The results for Fe-rich  $\operatorname{Fe}_{n-x}\operatorname{Al}_{x}$  clusters show surface segregation of Al, which is in keeping with the findings of a previous study of  $\operatorname{Ni}_{n-x}\operatorname{Al}_{x}$  clusters [5].

This work was supported by the DGICYT, Spain (Project No. PB95-0720-C02-02) and the Xunta de Galicia (Project No. XUGA20606B96).

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# Depolarized light scattering from $C_{60}Ar_{46}$ cluster - MD study

Z. Gburski and A. Dawid

Institute of Physics, University of Silesia, Universytecka 4, 40-007, Katowice, Poland

We have calculated (MD simulation) the interaction-induced polarizability correlation functions and spectra of the depolarized light scattering from argon atmosphere surrounded fullerene. The solid and liquid phases of  $C_{50}Ar_{46}$  have been studied.

## Molecular Dynamics Simulations of Overbased Detergent Particles

C.A. Bearchell, and D.M. Heyes

Department of Chemistry, School of Physical Sciences, University of Surrey, Guildford GU2 5XH.

Overbased detergents, OD, are sold commercially as additives for automotive and marine engine base oils. They are mixed in with the base oil to neutralise the acidic by-products of fuel combustion and oil degradation, which would otherwise corrode the engine. Chemically the OD are typically a mixture of calcium carbonate (the neutralising agent) closely bound to the calcium salt of a surfactant. Experimental work (e.g., Low angle neutron and X-ray scattering, and surface pressure determination by Langmuir trough measurements) suggests that the overbased detergent exists in the oil in an inverse micellar state, with the detergent 'coat' surrounding the calcium carbonate core thereby making it oil-soluble (see refs. [1] - [4]).

The results will be described of Molecular Dynamics simulations we have carried out over the last few years with the objective of elucidating the atomistic structure of the OD particles. We have been particularly interested in the effects of surfactant type on the shape and structure of these micellar particles.

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## A Highly Vectorized "Link-Cell" FORTRAN Code for DL\_POLY Molecular Dynamics Simulation Package

Kholmirzo Kholmurodov, <sup>1</sup> <sup>\*</sup> William Smith, <sup>2</sup> Kenji Yasuoka <sup>4</sup> and Toshikazu Ebisuzaki <sup>4</sup>

<sup>1</sup> Computational Science Division, Advanced Computing Center, The Institute of Physical and

Chemical Research (RIKEN), Hirosawa 2-1, Wako, Saitama 351-0198, Japan

tel: +81-48-467-9415, fax: +81-48-467-4078

e-mail: mirzo@atlas.riken.go.jp

<sup>a</sup> CLRC Daresbury Laboratory, Daresbury, Warrington WA4 4AD, UK

Permanent address: Laboratory of Computing Techniques and Automation, Joint Institute for

Nuclear Research, Dubna, Moscow region, 141980, Russia

The highly vectorized fortran subroutines based on the link-cell algorithm for DL\_POLY molecular dynamics simulation package are developed. For several specific benchmark systems the efficiency of the proposed codes on Fujitsu VPP700/128E vector computer has been tested. It is shown that in the constructing of neighbour list and calculating of atomic forces our link-cell method is more faster than the original code.

## Modelling aluminium clusters with an empirical many-body potential

#### L.D. Lloyd.

#### School of Chemistry, University of Birmingham, Birmingham B15 2TT, UK.

An empirical two-plus-three-body atomistic potential, derived by fitting experimental data pertaining to bulk aluminium, has been applied to the study of structures and growth patterns of small aluminium clusters. The high dimensionality of the nuclear configuration space for clusters results in an extremely large number of isomers and local minima on the potential energy hypersurface. Global optimisation (i.e. searching for the lowest energy structure) was carried out using Random Search and Monte Carlo Simulated Annealing methods, for  $Al_2$  to  $Al_{20}$ . The results of random searching have been used to put lower bounds on the number of minima for these nuclearities, and the efficiency of the Monte Carlo Simulated Annealing approach has been demonstrated. Comparisons have generally been in good agreement with results of previous calculations using electronic structure and empirical potential methods. While many of the global minima were also global minima for Lennard-Jones or Morse clusters, a number of new structures have been identified for  $Al_{N}$  clusters, notably for N = 9, 16, 17, 18 and 20.

#### Structure and melting of small Ni clusters on Ni surfaces

R.C. Longo, C. Rey and L.J. Gallego

Departamento de Física de la Materia Condensada, Facultad de Física, Universidad de Santiago de Compostela, E-15706 Santiago de Compostela, Spain

Using the Voter and Chen (VC) version of the embedded atom model (EAM) [1], we performed computer simulations to obtain the structures and binding energies of small Ni clusters on Ni(001), Ni(110) and Ni(111) surfaces [2]. The predicted Ni cluster structures on Ni(001) and Ni(111) generally agree with the results obtained by Liu and Adams [3] using the Foiles, Baskes and Daw (FBD) version of the EAM [4] (the only exception is one structure formed on the Ni(001) surface), but the corresponding binding energies differ significantly. The temperature-dependence of the behaviour of the seven-atom Ni cluster on the Ni(111) surface shows that the predicted cluster melting temperature also depends significantly on which version of the EAM is used. Hence EAM predictions of the properties of supported metal clusters depend crucially on the parameterization of the model, i.e. on the kind of data used in optimizing the embedding function and pair interaction. Although *ab initio* results for Ni clusters on Ni surfaces are not available for comparison, it seems plausible that the EAM description of supported transition metal clusters, like the EAM description of free transition metal clusters, may in general be more accurate if the VC version of the model is used rather than the FBD version since the former uses diatomic data as well as bulk properties in

optimizing the EAM functions, and its parameterization should therefore be more appropriate for the cluster level.

This work was supported by the DGICYT, Spain (Project No. PB95-0720-C02-02) and the Xunta de Galicia (Project No. XUGA20606B96).

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## Molecular Dynamics Simulation of Molecular Ionic Materials

K.A. Mort and R.A. Jackson

Chemistry Department, Keele University, Keele, Staffs ST5 5BG, UK

Molecular ionic materials such as ammonium nitrate play an important role in industry and are challenging materials to model. We present continuing work on ammonium nitrate, showing the simulation of thermal expansion in phase V and a solid/solid phase transformation to phase IV. We also present recent results of work on the thermal expansion of sodium nitrate, and potassium dihydrogen phosphate.

## Enthalpies of mixing of solid oxides

B.K. Pongsai and N.L Allan

School of Chemistry, University of Bristol, Bristol BS8 1TS

We propose a simple method for the calculation of the enthalpy of mixing of binary oxides, based on the use of quasiharmonic lattice dynamics for the efficient evaluation of the free energy of individual configurations. Results are presented for MnO/MgO, CaO/MgO and ZrO<sub>2</sub>/CaO.

### The effects of oblique incidence and surface steps on energetic silver cluster impacts with graphite

C. Sanz-Navarro and R. Smith

School of Mathematics and Physics, Loughborough University, LE11 3TU, UK

The energetic impact of Ag clusters on graphite is investigated using classical molecular dynamics simulations with pair interatomic potentials to describe the Ag - C interactions and and semiempirical many-body potentials for Ag - Ag and C - C. The impact of normally incident sizeselected silver cluster ions on graphite over the energy range 15-1500 eV has been previously studied [1] by a combination of scanning tunnelling microscopy and molecular dynamics simulations. Here we consider the effects of oblique incidence with silver clusters over the energy range 1 - 3 keV, investigating the dependence on the incidence angle of the cluster penetration into the graphite crystal, the area of the footprint which the cluster creates on the surface and the effect of surface steps. The initial stable configuration of silver clusters of various sizes is obtained by a genetic algorithm. We implement a long-range interatomic potential to model the interaction between different layers of graphite to improve the elastic properties of the material and to enable the modelling of steps on the surface. The simulations show that the clusters reflect from the surface at incidence angles  $\theta$  in excess of  $\approx 75^{\circ}$  and that up to the reflection angle the depth of the cluster penetration is proportional to  $\cos\theta$ .

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## Clusters and adlayers on NaCl(100) and MgO(100)

Ola Engkvist and Anthony J. Stone

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

Adsorbed water on ionic crystal surfaces have been extensively studied experimentally and theoretically. The conclusions from these studies are not always in agreement. We have explored structures of small clusters and adlayers of water molecules adsorbed on NaCl(100) and MgO(100). On NaCl there is a conflict between the optimum  $O \cdots O$  distance of about 3Åin hydrogen-bonded water and the Na<sup>+</sup> ···Na<sup>+</sup> distance of 4Å, with the consequence that there are several monolayer structures with similar energies. In the case of MgO the Mg<sup>2</sup> + ···Mg<sup>2</sup> + distance is 3Å, so which matches the optimum  $O \cdots O$  distance, but the square structure of the crystal surface is still in conflict with the preferred hexagonal structure of ice. Monte Carlo calculations suggest that there is considerable disorder in water adlayers on NaCl. Experimental infrared spectroscopy of the adsorbed water at ambient temperatures suggests that two phases coexist on the surface at low

coverage, and our calculations suggest that one of them comprises a relatively ordered monolayer structure and the other, which appears at higher vapour pressure, a more disordered liquid-like phase involving 3 or more water molecules per NaCl unit. The distribution function g(z) of water molecules with respect to height above the surface shows a distinct division into three layers.

#### Computational investigation into the morphology of solvated crystalline urea

G. W. Turner, K. D. M. Harris and R. L. Johnston, <sup>4</sup> B. Slater and C. R. A. Catlow <sup>2</sup>
<sup>4</sup> School of Chemistry, University of Birmingham
<sup>2</sup> The Royal Institution of Great Britain

The prediction of crystal morphology is important for industrial processes. The morphology is controlled by the relative growth rates of the crystal faces. An ability to make valid predictions of the influence impurities and inhibitor molecules have is crucial to understanding how crystal morphologies may be tailored to suit specific requirements. Urea is chosen as a model system for such a study and in particular its morphology is investigated with respect to the influence solvent interactions have on determining morphology. The attachment energies of (001), (110), (101) and (200) faces are considered and morphologies are predicted for urea in vacuo, urea with static solvent interactions and urea with explicit treatment of solvent and solute dynamics, using MARVIN.

## Modification of Lattice Phonon Absorption at the Interface Between Diamond and Graphite Nanoclusters.

Sergey Yastrebov ' and Roger Smith

School of Mathematics and Physics, Loughborough University, Loughborough LE11 3TU, UK. on leave from A.F.Ioffe Physical-Technical Inst, St.Petersburg, 194021,Russia

The effect of giant enhancement of two-phonon lattice absorption at the interface between a diamond nanocluster and graphite is observed experimentally and is modelled by considering a heterostructure consisting of a semi-infinitive conductive media and a semi-infinitive dielectric medium. The dielectric medium consists of a material which possesses the phonon lattice absorption. This enhancement of the absorption is considered in terms of excitation of collective electronic oscillations at the interface. It is suggested that the oscillations can be induced by the dynamical dipole momentum of the material. This effect appears when the absorption coefficient of the material exhibits its maximal value. The Born approach is used to derive an analytical expression for the enhancement factor of the absorption. The effect of the influence of spatial confinement of the heterostructures on the enhancement of the absorption is investigated in terms of the effective medium approximation

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(EMA) theory. For this purpose the EMA theory is mödified to obtain the dielectrical response of a medium constructed with a set of nanoclusters of two different types. The dielectric (diamond) and metallic (doped graphite) clusters are assumed to have the shape of flat ellipsoidal disks and the model takes into account the dielectrical permittivities of both materials from which the clusters are constructed. The conditions for a large increase in the absorption coefficient are given. A comparison between theoretical and experimental data on the giant enhancement of two-phonon absorption of diamond-graphite nanosize heterostructures is presented.

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## NEW HPC SUPPORT MECHANISMS

Daresbury Laboratory and University of Edinburgh are collaborating with University of Manchester to provide future HPC support.

#### Future Mechanisms for HPC Support from EPSRC

The current funding for the three UK HPCI Centres ended at the end of October 1999. The future HPC support mechanisms which were approved by EPSRC's High Performance Computing Strategy Committee (HSC) in June 1999 are now in place following the response to calls for proposals from centres for both Dedicated Consortium Support and Core Activities.

The Dedicated Support funding from EPSRC now contains two strands:

- Ongoing Dedicated Support for research groups and HPCI Consortia with existing grants at the Daresbury and EPCC HPCI Centres until the end of that grant;
- Dedicated Support for individual research groups applying for new grants either within the research group or at a high-end computing centre (e.g. Daresbury, EPCC or CSAR) of the research group's choice. This will be peer-reviewed via the normal programme lines.

Support for the existing scientific consortia is continuing at Daresbury and EPCC until their current research grants end. In addition to this consortia previously mapped to Southampton have been re-assigned to either Daresbury or EPCC as follows:

- Daresbury: Materials Chemistry (Prof. Catlow, RI), DNS of Fluids (Prof. Sandham, Southampton), Liquid Crystals (Prof. Allen, Bristol)
- EPCC: UGAMP (Prof. O'Neill, Reading) OCCAM (Dr. Webb, Southampton), Geophysics (Prof. Price, Birkbeck).

Future requests to EPSRC for Dedicated Support for individual research groups should be made to the appropriate Research Council. Other Research Councils are currently making their own arrangements.

### **Core Support Activity**

EPSRC provided separate funding, via a call for proposals, for a Core Activity to track and disseminate information on developing standards in software and tools and to promote good programming practice. This is to be provided

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by the "UKHEC Collaboration", a collaboration between Daresbury, EPCC and the Manchester Research Centre for Computational Science (MRCCS).

2

The UKHEC Collaboration will investigate underlying HPC issues relating to hardware and software technology which might enhance the effective use of HPC resources in the UK. This includes programming languages (e.g. C, Java, Fortran95), software engineering and QA, data management, visualisation and VR, and meta-computing. Technical reports will be produced and short courses and workshops held in key areas. Information will be announced via HPCProfile and the Web pages (see below).

#### New HPCI Web pages

EPCC and Daresbury Laboratory are collaborating to provide a new Web pages with appropriate URL for their diverse HPC activities. Links to all the supported consortia and related activities will be provided via these pages which will complement those at CSAR. The draft pages can be found at http://www.cse.clrc.ac.uk/ListActivities/CLASS=5;CLASSTYPE=43; Please note that the URL will be simplified shortly. We have applied to UKERNA for DNS addresses www.hpci.ac.uk and www.ukhec.ac.uk . We invite your comments on the kind of material you would like to see here.

#### HPCProfile

The last issue of HPCProfile in its current form appeared in December 1999. As a part of the UKHEC collaboration we shall be producing two issues a year starting in 2000 devoted to HPC programming techniques and underlying computing issues. This will be supplemented by other material which will provide information on the Dedicated Consortium Support, CCPs and Distributed Computing Programme (DisCo).

### Further Information

In addition to looking at the existing Web pages you can contact:

Robert Allan

Department for Computational Science and Engineering Daresbury Laboratory Daresbury Warrington WA4 4AD *r.j.allan@dl.ac.uk* 01925 603207 *http://www.cse.clrc.ac.uk/Activity/HPCI* 

David Henty Edinburgh Parallel Computing Centre JCMB, Maxwell Buildings University of Edinburgh

February 2000

Mayfield Road Edinburgh EH9 3JZ Scotland d.s.henty@epcc.ed.ac.uk 0131 650 5960 http://www.epcc.ed.ac.uk/t3e/hpci

Terry Hewitt Manchester Computing University of Manchester Oxford Road Manchester M60 9PL w.t.hewitt@mcc.ac.uk 0161 275 6095 http://www.man.ac.uk/mrccs http://www.csar.cfs.ac.uk

> e Alexandria Alexandria Alexandria

## CLUSTER-COMPUTING DEVELOPMENTS IN THE UK

Computational Science and Engineering Department,

Daresbury Laboratory, Warrington, WA4 4AD

#### Introduction

A "cluster" is a collection of complete computers (nodes) that are physically interconnected by a high-performance "local area network" (LAN). Typically each node is a workstation or personal computer (PC). Clusters permit running parallel jobs using PVM or MPI implemented over the network as well as permitting independent use of the nodes for task farming.

The advantages of cluster computing derive from the fact that off-the-shelf commodity components are used. This offers a cost-effective solution to medium-scale computing requirements.

For a good introduction to the concepts of cluster computing and architectures available see "Scalable Parallel Computing" by K. Hwang and Z. Xu (WCB/McGraw-Hill, 1998, ISBN 0-07-031798-4).

Cluster computing solutions in the USA are becoming mainstream and may become the dominant system of the future for computational science. A 64x2-way Alpha-based system built by Alta Technology and installed at the University of New Mexico has been accepted into the USA Alliance computational meta-computing grid. A similar system, the CPlant

*http://www.cs.sandia.gov/cplant*, is supported by Compaq under a 4-year agreement with the US DoE and is now being used at Sandia National Laboratory with a Myrinet high-performance switch for enhanced communications. This system forms part of the Accelerated Strategic Computing Initiative (ASCI) Path Forward programme.

#### One of the first projects, the Beowulf

http://www.beowulf.org, was started at NASA in 1994. This Web page also contains links to many related sites worldwide. Commodity cluster systems are now often known as Beowulf-class computers.

It is important for UK scientists to be able to evaluate this kind of equipment for parallel computing, as has been noted by EPSRC in recent surveys. Daresbury Laboratory therefore, as part of the Distributed Computing (DisCo) Programme, has built a 32-processor Beowulf cluster using 450 MHz Pentium III processors. Currently the processors, which are in the form of off-the-shelf PCs, each with memory and disk but no keyboard or monitor, are connected by dual fast Ethernet switches - 2x Extreme Summit48, one network for IP traffic (e.g. nfs) and the other for MPI message passing. Additional 8-port KVM switches are used to attach a keyboard and monitor to any one of the nodes for administrative purposes. The whole cluster has a single master node (with a backup spare) for compilation and resource management. All nodes are currently running RedHat Linux v6.0.

Applications, such as GAMESS-UK, DL\_POLY, ANGUS, CRYSTAL, POL-ERSEM, REALC and CASTEP are being ported to the system for evaluation. Results showing their performance will be
#### posted on the DisCo Web site

http://www.cse.clrc.ac.uk/Activity/DisCo as they become available.

Over the coming months we also plan to evaluate a variety of networking and software options for the system. Some of the options are summarised below. Prices vary, as does performance and robustness, and it is not yet clear what will be the preferred solution for building a large-scale compute server.

## **Network Options**

network	latency $(\mu s)$	bandwidth (MB/s)
fast Ethernet	50	12.5
Gigabit Ethernet †	9.6	93
Myrinet	20	62
QSW QsNet ‡	5	210

† Gamma project with Packet Engines NIC.

‡ MPI short message protocol.

Figures in the table are subject to confirmation and depend on what driver hardware and software is used.

## Message-passing Options

Message passing options include implementations of MPI and PVM, but there are others too.

## MPICH

http://www-unix.mcs.anl.gov/mpi/mpich/index.html - Argonne National Laboratory's implementation of MPI

## LAM/MPI

http://www.mpi.nd.edu/lam - Local Area Multicomputer MPI, developed at the Ohio Supercomputer Center and Univ. of Notre Dame

#### Globus

http://www.globus.org/ - Metacomputing Environment

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# Compilers

Widely-used compilers include the Gnu family, Portland Group, KAI, Fujitsu, Absoft, NAG etc.. Compaq is about to beta test AlphaLinux compilers which are reputedly excellent. Some people already compile their applications under Digital Unix and run them on Alpha Linux, although this is not permitted under the license conditions.

## Absoft Corp.

http://www.absoft.com - FORTRAN77 (f77) and Fortran 90 (f90)

## The Portland Group

http://www.pgroup.com (PGI) - High Performance Fortran (pghpf), FORTRAN77 (pgf77), C and C++ (pgcc)

### Numerical Algorithms Group http://www.nag.com (NAG) - FORTRAN 90 (f90), Fortran 95 (f95)

## Gnu CC/egcs

http://egcs.cygnus.com - free FORTRAN77, C, Pascal, and C++ compilers

## Pentium gcc

http://goof.com/pcg , aka PGCC - from the Pentium Compiler Group uses Pentium-specific optimisations to produce 5%-30% speedups from regular gcc

## BERT 77

http://www.plogic.com/bert.html - described as "an automatic and efficient Fortran paralleliser"

## Lahey/Fujitsu

http://www.lahey.com - LF95 Linux Express fully optimising Fortran 95 compiler

## Numerical Libraries

## **ASCI** Option Red software

http://www.cs.utk.edu/~ghenry/distrib/archive.htm - BLAS, fast-Fourier transform, hardware performance-monitoring utilities, extended-precision and maths primitives are all available free under restricted licenses

## Fast Maths library

http://www.lsc-group.phys.uwm.edu/~www/docs/beowulf/os\_updates/fastMath.html and Free Fast Maths library - makes standard mathematical functions much faster

## NAG

http://www.nag.co.ukParallel Library - a version tuned for Beowulf systems is available commercially

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## **Resource Management and Job Scheduling Options**

#### LSF

http://www.platform.com - Load Sharing Facility from Platform Computing

#### LobosQ

http://www.lobos.nih.gov - queuing system from NIH, Bethesda USA

#### PBS

http://pbs.mrj.com - Portable Batch System developed at NASA Ames Research Center now commercially available from MRJ Inc.

#### Virtual Private Server

*http://www.sychron.com* - new software infrastructure for scalable internet services and enterprise services from Sychron Ltd. Oxford.

#### DQS

http://www.scri.fsu.edu/~pasko/dqs.html - Distributed Queueing System. A free batch queueing system

#### BVIEW

http://w272.gsfc.nasa.gov/~udaya/Public/software/bview/bview.html - monitoring software

#### bWatch

http://www.sci.usq.edu.au/staff/jacek/bWatch - monitoring software

#### BPROC

*http://www.beowulf.org/software/bproc.html* - making processes visible across nodes, allowing fork()s to happen across nodes, allowing process migration, allowing kill()s to work across nodes, currently pre-alpha release

#### Cluster patches for procps

http://www.sc.cs.tu-bs.de/pare/results/procps.html - lets you compile /proc-based programs like ps so they report on all processes on the cluster, not just the ones on the machine you're logged into

#### SMILE

http://smile.cpe.ku.ac.th/software/scms/index.html Cluster Management System - Run commands on all nodes, shut down individual nodes and sets of nodes, monitor health of nodes. Makes clusters easier to administer.

## Parallel Virtual Filesystem

*http://ece.clemson.edu/parl/pvfs* - LD\_PRELOAD-based filesystem modification to let you transparently stripe big files across many disks. Allows high-performance access to big datasets.

#### Scripts for configuring 'clone' worker nodes

ftp://ftp.sci.usq.edu.au/pub/jacek/beowulf-utils/disk-tess - makes adding nodes to a Beowulf painless

#### Scripts

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*ftp://ftp.sci.usq.edu.au/pub/jacek/beowulf-utils/misc\_scripts* for doing various things on a cluster, backups, shutdowns, reboots, running a command on every node

### Software

http://www.beowulf-underground.org is being added to the public domain on a daily basis, see for instance "The Beowulf Underground" URL

## Other Beowulf Clusters in the UK

There are a number of other Beowulf systems being built in the UK. We list just a few of them on the DisCo Web page at **URL** 

http://www.cse.clrc.ac.uk/Activity/DisCo. These include: Enterprise and Voyager (Cambridge), The Borg (Cranfield), University of Glasgow, Stac Follaidh (Lancaster), HPCI (Southampton), MadDog (UMIST).

## Some Commercially available Systems

## WorkstationsUK

http://www.workstationsuk.dcmon.co.uk

InSiliCo http://www.insilico.co.uk

SALT http://www.suse.de - Commercial Hardware Vendor in Germany

Sybrandt Open Systems http://www.sybrandt.com provides a commercial Beowulf solution

## Paralline

http://www.paralline.com distributes Linux clusters, high-speed networks and services

## ParTec

*http://www.par-tec.com* supports the ParaStation project and sells clusters and services See also the NASA Web site mentioned above.

## An Example

 $\{X_{i}\}_{i=1}^{n} \in \{1, \dots, n\}$ 

As an example of our initial experiences using the Daresbury Beowulf we show the performance obtained from DL\_POLY. The test cases were NaCl MTS Ewald 27000 ions, NaK disilicate glass 8640 ions and Gramicidin in water, SHAKE, 13390 atoms. Results from the 450 MHz Pentium III system are compared with an earlier 260 MHz Pentium II system and Cray T3Es. Clearly the single-node performance of the Pentium III is good compared to the Cray T3E-1200E, but the latter offers superior scalability for parallel programs needing a large number of processors.





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