

DARESBUY LABORATORY

# INFORMATION QUARTERLY for COMPUTER SIMULATION OF CONDENSED PHASES

An informal Newsletter associated with Collaborative Computational Project No. 5  
on Molecular Dynamics, Monte Carlo and Lattice Simulations of Condensed Phases.  
Number 32 February 1990

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## Editorial

At the time of writing, CCP5 is undergoing the all too frequent exercise of renewal. Past experiences of this procedure have been somewhat dispiriting since the funding arrangements have been somewhat complicated; involving CCP5 bidding in hard currency terms for the support of the staff at Daresbury. Against this background it has always been difficult to get funding for a postdoctoral research assistant (PDRA) to work in an area designated by CCP5. However the current renewal proposal, which is being prepared by the CCP5 Executive Committee, does not need to include the costing of the Daresbury staff and should not therefore place such a burden on the grant resources of the (surprisingly many) SERC Committees it is to be considered by. We therefore have high (well, higher) hopes of funding a PDRA this time. For the record, our intention is to put the PDRA to work in the area of macromolecular simulations, where hopefully he or she can provide the CCP5 program library with some much needed programs in this area, to counteract the diminishing availability of such programs on account of their adoption by commercial ventures. The CCPs, after all, were established to make good scientific software readily available to all. Let us hope that our ambitions are realised in this renewal round.

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## General News.

1) At the last meeting of the CCP5 Steering Committee at Cambridge in December 1989, Professor Richard Catlow stepped down as Chairman of CCP5 and was replaced by Professor Dominic Tildesley of Southampton University. While welcoming Dominic to the rôle of chairman, it is appropriate to recall the excellent work Richard Catlow did as Chairman of CCP5; his enthusiasm for promoting the aims of CCP5 resulted in a very high degree of activity within the project, the pinnacle of which was probably the NATO ASI at Bath in September 1988, which was immensely successful. In addition the project continued the sequence of workshops in specific areas, which have helped considerably towards solving difficulties in the areas concerned. Richard was also enthusiastic about sponsoring visitors from overseas to the U.K. and several eminent practitioners of computer simulation have come to share their expertise with us. Lastly one should perhaps recall Richard's interest in the industrial applications of simulation, which has resulted in some interesting conferences and collaborations within CCP5. Undoubtedly Richard will continue his interests in CCP5 from the Royal Institution, but his rôle as Chairman deserves special mention and thanks.

2) Also at the same Steering Committee meeting, new appointments to the Executive Committee were made. The current composition of the Committee is now:

- Prof. D. Tildesley, Chairman (Southampton)
- Dr. M. Roger (Reading)
- Dr. E. Colbourn (ICI)
- Dr. N. Quirke (BP)
- Dr. N. Allan (Bristol)
- Dr. D. Fincham (Keele and Daresbury)
- Dr. M. Leslie (Daresbury)
- Dr. W. Smith (Daresbury)

Our thanks go to the outgoing members: Dr. R.M. Lynden-Bell and Dr. S.C. Parker (Bath).

3) The organisation of the CCP5 Conference on "Architectures and Algorithms in Condensed Phase Simulation", which is due to take place at St. Andrews from 2 to 5 July 1990, is now well advanced. An excellent line up of speakers has been arranged and the whole meeting promises to be an excellent first venture by CCP5 into Scotland (may it be the first of many!). More details are provided in a circular included with this newsletter. An early application to attend is recommended.

4) During 1990 CCP5 will be inviting a number of overseas scientists to the U.K.. We have reasonably firm confirmations on the following:

- Dr. G. Malenkov (Moscow), to visit London, Oxford, Daresbury and St. Andrews in May (date to be arranged).

- Dr. R Cohen (Naval Research Lab.), to visit London March 31-April 8.

5) A workshop on the subject "Simulation of Adsorbed Monolayers and Multilayers" is being organised by R.M. Lynden-Bell for CCP5. It will take place at New Hall, Cambridge on Friday July 13th. The principal speaker will be Professor W.A. Steele (Pennsylvania). Accommodation will be available on Thursday night (and probably on Friday night for those who need it). As well as a lecture by Professor Steele, it is planned to have sessions on potentials, experimental problems, and results from simulations. All participants are requested to contribute to the discussion and it is hoped that most will be prepared to talk for 5-10 minutes in a rather informal way.

An application form appears with this newsletter.

6) Our thanks are owed to Dr. M. Leslie and Dr. R.M. Lynden-Bell, who organised the CCP5 Annual Meeting in Cambridge entitled "Grand Challenges in Molecular Simulation", which took place from 17-19 December at Downing College. Also, somewhat late, (for which we apologise) we wish to thank Dr. D.M. Heyes for organising the meeting last July on "Novel Methods in Molecular Simulation" at Royal Holloway and Bedford new College.

7) The Theory and Computational Science Division (TCS) at Daresbury Laboratory is to receive a 32 node INTEL iPSC/860 parallel computer. This represents a substantial upgrade of current INTEL iPSC/2, in that it incorporates the legendary INTEL i860 microprocessor, the "Cray on a chip". The upgrade will strengthen the interests of the division in applying parallel processing to scientific problems. Currently TCS employs the iPSC/2 in molecular dynamics simulations of polymers, band structure calculations and quantum chemistry. It is believed that the original 64 node iPSC/2 will be retained as a down-graded machine with 32 nodes and will function as a development machine.

8) The Second International Europhysics Conference on Computational Science takes place at Amsterdam on 10-13 September 1990. The scientific programme covers special and general purpose hardware and software, and the connections between physical applications. Speakers from physics, chemical physics and astrophysics are invited. Neural networks, parallel computing and software design methods will be covered. Contributions to the *poster session* are invited before 1st. July. For details write to Mw. Rita van der Sluijs, Secretariat CP90 Conference, NIKHEF-H, PO Box 41882, 1009DB Amsterdam, The Netherlands. (E-Mail: cp90@nikhef.nl).

## Program Libraries

### The CCP5 Program Library.

#### IMPORTANT ANNOUNCEMENT

There is to be a change in the policy of distribution of the CCP5 Program Library. Up to now the programs have been released only to academic institutions and on the condition that the recipient does not re-distribute the programs or attempt to exploit them for commercial gain. The purpose of these restrictions was to protect the commercial rights of the program authors. These restrictions automatically excluded commercial companies from receiving the CCP5 programs. The CCP5 Steering Committee is negotiating with SERC so that the distribution of the programs to commercial companies can take place, though the following constraints will apply.

1. Academic institutions will still receive programs free of charge and with the same restrictions on re-distribution and commercial exploitation as before.
2. Commercial companies will receive programs at the discretion of the CCP5 Program Library and on payment of a £100 handling fee.
3. Commercial companies will not be permitted to re-distribute or market the programs in any way.
4. Neither SERC nor the authors of the programs can be held accountable for any loss arising from the use of the programs, even if the loss occurs through programming error or erroneous documentation.
5. Programs will not be sent to commercial companies over any kind of network or telephone link.
6. The programs owned by Harwell and the programs CASCADE, SYMLAT, THBFIT, THBPHON and THBREL, will not be released to commercial companies. The named programs are available free of charge to UK academic institutions only.

These constraints are provisional only and will be subject to review.

Programmers who have donated programs to the CCP5 Program Library who object to the programs being distributed in this way are invited to withdraw the programs, or to stipulate their wishes with regard to the release of the programs to commercial companies. CCP5 will not act as agents for sale of programs. Authors who wish to restrict programs to academic institutions may request that this be done. However, CCP5 will not accept any liability for programs erroneously released. Authors of programs are requested to communicate their wishes to the program librarian before March 31st 1990, after which time it will be assumed that the authors have no objection to the new regime.

The CCP5 Program Library may be obtained upon application to Dr. W. Smith, TCS Division, S.E.R.C. Daresbury Laboratory, Daresbury, Warrington WA4 4AD, U.K.. Listings of programs are available if required but it is recommended that magnetic tapes be used. It may also be possible to transfer a small number of programs over the JANET network to other academic centres in the U.K.. A list of programs available is presented in the following pages.

Readers should also note that we are authorised to supply the example programs originally published in the book "Computer Simulation of Liquids", by M.P. Allen and D.J. Tildesley (Clarendon Press, Oxford 1987). These are supplied in the same manner and under the same conditions as the resident CCP5 programs. We are grateful to Mike Allen and Dominic Tildesley for their permission.

We should also like to remind our readers that we would welcome further contributions to the Program Library. The Library exists to provide support for the research efforts of everyone active in computer simulation and to this end we are always pleased to extend the range of software available. If any of our readers have any programs they would like to make available, please would they contact Dr. Smith.

W. Smith

### **Program from the Book: "Computer Simulation of Liquids" by M.P. Allen and D. Tildesley, Clarendon Press, Oxford 1987.**

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

M.P.Allen

## THE CCP5 PROGRAM LIBRARY.

ADMIXT	[MD,LJA/MIX,LF,TH+MSD+RDF]	W. Smith
CARLOS	[MC,VS+Aquo,TH]	B. Jonsson S. Romano
CARLAN	[DA,CARLOS structure analysis]	B. Jonsson S. Romano
CASCADE	[LS,DIL,EM,TH+STR]	M. Leslie/ W. Smith
CURDEN	[DA,Current Density Correlations]	W. Smith
DENCOR	[DA,Density Correlations]	W. Smith
HLJ1	[MD,LJA,LF,TH+MSD+RDF]	D.M. Heyes
HLJ2	[MD,LJA,LF,TH+MSD+RDF+VACF]	D.M. Heyes
HLJ3	[MD,LJA,LF/LC,TH+MSD+RDF]	D.M. Heyes
HLJ4	[MD,LJA,LF/CP+CT,TH+MSD+RDF]	D.M. Heyes
HLJ5	[MD,LJA/SF,LF,TH+MSD+RDF]	D.M. Heyes
HLJ6	[MD,LJA,TA,TH+MSD+RDF]	D.M. Heyes
HMDIAT	[MD,LJD,G5+Q4,TH+MSD+QC]	S.M. Thompson
HSTOCH	[MD/SD,VS+BA,LF+CA,TH]	W.F. van Gunsteren/ D.M. Heyes
MCN	[MC,LJA,TH]	N. Corbin
MCLSU	[MC,LJA,TH]	C.P. Williams/ S. Gupta
MCMOLDYN	[MD/MC,LJS+FC+AQ, LF+QF/G5+QS,TH+RDF]	A. Laaksonen
MCRPM	[MC,RPE,TH+RDF]	D.M. Heyes
MDATOM	[MD,LJA,G5,TH+RDF+MSD+QC]	S.M. Thompson
MDATOM	[MD,LJA,LF,TH+MSD+RDF]	D. Fincham
MDCSPC4B	[PRMD,BHM+FC,G5+G4,TH+STF+RDF]	W. Smith
MDDIAT	[MD,LJD,LF+CA,TH+MSD]	D. Fincham
MDDIATQ	[MD,LJD+PQ,LF+CA,TH+MSD]	D. Fincham
MDIONS	[MD,BHM,LF,TH+MSD+RDF+STF]	D. Fincham/ N. Anastasiou
MDLIN	[MD,LJL,G5+Q4,TH+MSD+QC]	S.M. Thompson.
MDLINQ	[MD,LJL+PQ,G5+Q4,TH+MSD+QC]	S.M. Thompson
MDMANY	[MD,LJS+FC,LF+QF,TH]	D. Fincham/ W. Smith
MDMIXT	[MD,LJS/MIX,LF+QF,TH]	W. Smith
MDMPOL	[MD,LJS+FC/MIX,LF+QF,TH]	W. Smith/ D. Fincham
MDNACL	[MD,BHM,LF,TH+MSD+RDF]	W. Smith
MDPOLY	[MD,LJS,G5+Q4,TH+MSD+QC]	S.M. Thompson
MDMULP	[MD,LJS+PD+PQ/MIX,LF+QF,TH]	W. Smith
MDSGWP	[MD,LJA/SGWP,LF,TH+VACF+RDF+QC]	W. Smith/ K. Singer
MDTETRA	[MD,LJT,G5+Q4,TH+MSD+QC]	S.M. Thompson
MDZOID	[MD,GAU,LF+QF,TH+MSD+RDF+VACF]	W. Smith

NAMELIST	[UT, Namelist emulation]	K. Refson
PIMCLJ	[PIMC,LJA,MC,TH+RDF+QC]	K. Singer
		W. Smith
SCN	[MC,LJA,RFD,TH]	N. Corbin
SURF	[MD,BHM/TF/2D,LF,TH+RDF]	D.M. Heyes
SYMLAT	[LS,PIL,EM+SYM,TH+STR]	Harwell
THBFIT	[LS,PIL,EM,Potential fitting]	Harwell
THBPHON	[LS,PIL/3B,EM,Phonon dispersion]	Harwell
THBREL	[LS,PIL,EM,TH+STR]	Harwell

### Key:

Program types:	MD	Molecular dynamics
	MC	Monte Carlo
	PRMD	Parrinello-Rahman MD
	LS	Lattice simulations
	SD	Stochastic dynamics
	DA	Data analysis
	UT	Utility package
	PIMC	Path Integral Monte Carlo
System models:	LJA	Lennard-Jones atoms
	LJD	Lennard-Jones diatomic molecules
	LJL	Lennard-Jones linear molecules
	LJT	Lennard-Jones tetrahedral molecules
	LJS	Lennard-Jones site molecules
	RPE	Restricted primitive electrolyte
	BHM	Born-Huggins-Meyer ionics
	SGWP	Spherical gaussian wavepackets
	TF	Tosi-Fumi ionics
	VS	Variable site-site model
	BA	Bond angle model
	PD	Point dipole model
	PQ	Point quadrupole model
	MIX	Mixtures of molecules
	GAU	Gaussian molecule model
	FC	Fractional charge model
	PIL	Perfect ionic lattice model
	DIL	Defective ionic lattice model
	3B	3-body force model
	2D	Two dimensional simulation
	SF	Shifted force potential
	FC	Fractional charge model
	AQ	Aqueous solutions
Algorithm:	G5	Gear 5th order predictor-corrector
	Q4	Quaternion plus 4th. order Gear P-C.

	LF	Leapfrog (Verlet)
	QF	Fincham Quaternion algorithm
	QS	Sonnenschein Quaternion algorithm
	LC	Link-cells MD algorithm
	CP	Constant pressure
	CT	Constant temperature
	TA	Toxvaerd MD algorithm
	CA	Constraint algorithm
	EM	Energy minimisation
	SYM	Symmetry adapted algorithm
	RFD	Rosky-Friedman-Doll algorithm
Properties:	TH	Thermodynamic properties.
	MSD	Mean-square-displacement
	RDF	Radial distribution function
	STF	Structure factor
	VACF	Velocity autocorrelation function
	QC	Quantum corrections
	STR	Lattice stresses

## Programs from the Book "Computer Simulation of Liquids"

- F.1 Periodic boundary conditions in various geometries
- F.2 5-value Gear predictor-corrector algorithm
- F.3 Low-storage MD programs using leapfrog Verlet algorithm
- F.4 Velocity version of Verlet algorithm
- F.5 Quaternion parameter predictor-corrector algorithm
- F.6 Leapfrog algorithms for rotational motion
- F.7 Constraint dynamics for a nonlinear triatomic molecule
- F.8 Shake algorithm for constraint dynamics of a chain molecule
- F.9 Rattle algorithm for constraint dynamics of a chain molecule
- F.10 Hard sphere molecular dynamics program
- F.11 Constant-NVT Monte Carlo for Lennard-Jones atoms
- F.12 Constant-NPT Monte Carlo algorithm
- F.13 The heart of a constant  $\mu$ VT Monte Carlo program
- F.14 Algorithm to handle indices in constant  $\mu$ VT Monte Carlo
- F.15 Routines to randomly rotate molecules
- F.16 Hard dumb-bell Monte Carlo program
- F.17 A simple Lennard-Jones force routine
- F.18 Algorithm for avoiding the square root operation
- F.19 The Verlet neighbour list
- F.20 Routines to construct and use cell linked-list method
- F.21 Multiple timestep molecular dynamics
- F.22 Routines to perform the Ewald sum
- F.23 Routine to set up alpha fcc lattice of linear molecules
- F.24 Initial velocity distribution
- F.25 Routine to calculate translational order parameter
- F.26 Routines to fold/unfold trajectories in periodic boundaries
- F.27 Program to compute time correlation functions
- F.28 Constant-NVT molecular dynamics - extended system method
- F.29 Constant-NVT molecular dynamics - constraint method
- F.30 Constant-NPH molecular dynamics - extended system method
- F.31 Constant-NPT molecular dynamics - constraint method
- F.32 Cell linked-lists in sheared boundaries
- F.33 Brownian dynamics for a Lennard-Jones fluid
- F.34 An efficient clustering routine
- F.35 The Voronoi construction in 2d and 3d
- F.36 Monte Carlo simulation of hard lines in 2d
- F.37 Routines to calculate Fourier transforms

# ARCHITECTURE AND ALGORITHMS IN CONDENSED PHASE SIMULATION

2 July to 5 July

Plans for the meeting to be held at St. Andrews in Scotland from the 2nd to 5th July 1990 are now well advanced.

We begin after lunch on the Monday with a session covering simulation on single-instruction-multiple-data computers such as the DAP and the connection machine. On Tuesday morning we will cover simulation on multiple-instruction- multiple-data machines such as the Meiko computing surface, the Intel hypercube, and the Alliant. On Tuesday afternoon we focus on purpose-built machine such as the Delft and Bell Lab. MD machines. The second session on Tuesday afternoon will cover mainframe pipeline processors such as the CRAY, the IBM VF, and the VP. In each of these sessions we will focus on the advantages and disadvantages of the architectures for condensed phase simulations, the algorithms for Monte Carlo, molecular mechanics, molecular and Brownian dynamics and highlight some of the scientific advances achieved with these machines. Wednesday morning is free and Wednesday afternoon has been set aside for demonstrations of hardware and software by research groups and computer companies as well as a large poster session. Thursday morning will consist of three invited speakers presenting a detailed account of recent research and looking to the future of condensed phase simulation.

Speakers for the meeting include:

F.F. Abraham, (IBM San Jose)	A.F. Baaker, (Delft )
H.J.C. Berendsen, (Groningen)	B. Boghosian, (Thinking Machines)
E. Clementi, (IBM York Town)	D. Fincham, (Keele)
M.F. Guest, (Daresbury)	A.R. Larrabee, (Boeing)
D.P. Landau, (Atlanta)	B.M. Pettitt, (Houston)
K. Wilson, (San Diego)	

St. Andrews itself is a beautiful seaside town, close to Edinburgh and easily reached by road, rail and air. It is the home of Golf and the public can play on all the courses including the Old Course. There are marvellous walks along the shore and inland and there is plenty of bird and marine life for the nature lover. The city boasts a history which is as rich as neighbouring Edinburgh. The hall of residence chosen for the conference is 50 yards from the Old Course and the sea front.

The time has now arrived to register for this meeting and to submit an abstract for consideration as an oral or poster presentation. Please give this meeting your full support.



ARCHITECTURE AND ALGORITHMS IN CONDENSED PHASE SIMULATION

NAME: ..... TITLE: .....

ADDRESS: .....

.....

..... GENDER: .....

SPECIAL DIETARY REQUIREMENTS (e.g. Vegetarian) .....

Please tick the appropriate boxes:-

Lunch, Monday 2nd July	£ 4.10	<input type="checkbox"/>
Dinner, Monday 2nd July	£ 5.30	<input type="checkbox"/>
Bed and Breakfast, 2nd/3rd July	£15.50	<input type="checkbox"/>
Lunch, Tuesday 3rd July	£4.10	<input type="checkbox"/>
Dinner, 3rd July	£5.30	<input type="checkbox"/>
Bed and Breakfast, 3rd/4th July	£15.50	<input type="checkbox"/>
Lunch, Wednesday 4th July	£4.10	<input type="checkbox"/>
Conference Dinner	£14.50	<input type="checkbox"/>
Bed and Breakfast, 5th July	£15.50	<input type="checkbox"/>
Conference Fee	£25.00	<input type="checkbox"/>
TOTAL INCLUDING CONFERENCE DINNER	£108.90	<input type="checkbox"/>
Optional, Lunch Thursday 5th July	£4.10	<input type="checkbox"/>
Additional Bed and Breakfast for Sunday 1st July	£15.50	<input type="checkbox"/>

Cheques should be made payable to:

CCPS: ST. ANDREWS MEETING

and returned with this form to:

Professor D. J. Tildesley  
Department of Chemistry  
The University  
SOUTHAMPTON SO9 5NH.

POSTERS AND PAPERS

ARCHITECTURE AND ALGORITHMS IN CONDENSED PHASE SIMULATION

The organising committee is planning a large poster session and there is space in the programme for a number of contributed papers of twenty minutes length. If you would like to present your work at this meeting please complete the form and return it with an abstract of not more than 250 words to:

Professor D. J. Tildesley  
Department of Chemistry  
The University  
SOUTHAMPTON SO9 5NH.

CONTRIBUTED PAPER

POSTER

TITLE .....

AUTHORS .....



**CCP5 Workshop**  
**“Simulation of Adsorbed Monolayers and  
Multilayers”**

Cambridge

13 July 1990

A workshop on this subject being organised by R.M. Lynden-Bell for CCP5. It will take place at New Hall, Cambridge on Friday July 13th. The principal speaker will be Professor W.A. Steele (Pennsylvania). Accommodation will be available on Thursday night (and probably on Friday night for those who need it). As well as a lecture by Professor Steele, it is planned to have sessions on potentials, experimental problems, and results from simulations. All participants are requested to contribute to the discussion and it is hoped that most will be prepared to talk for 5-10 minutes in a rather informal way.

Please return the following application if you wish to attend



# Simulation of Adsorbed Monolayers and Multilayers

Name: \_\_\_\_\_ Title: \_\_\_\_\_

Address: \_\_\_\_\_

\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

Tel: \_\_\_\_\_

I wish to attend the workshop on Simulation of Adsorbed Monolayers and Multilayers and require accommodation for the nights of (delete as appropriate):

		Cost (Pounds)
Thursday 12 July	..... YES/NO	41.00 Dinner(12th)+B&B+Lunch(13th)
Friday 13 July	..... YES/NO	17.50 B&B

Special dietary requirements:

\_\_\_\_\_

I will give a seminar..... YES/NO

The title of the seminar will be:

\_\_\_\_\_  
\_\_\_\_\_

Please return this form plus cheque for accommodation (made out to CCP5 Surfaces Workshop) to:

Dr. R.M. Lynden-Bell  
The Chemical Laboratory,  
The University of Cambridge,  
Lensfield Road,  
CAMBRIDGE CB2 1EW



# CCP5/ARCG Workshop on Parallel Algorithms in Molecular Simulation.

W. Smith

Daresbury Laboratory, 8 th. November 1989

This workshop was jointly organised by CCP5 and the Daresbury Laboratory Advanced Research Computing Group (ARCG). The purpose of the meeting was to assess the state of the activity in the U.K. with regard to the implementation of parallel algorithms in molecular simulation; raise awareness of what is being done; broadcast news of effective algorithms and strategies and initiate contacts between the groups with common interests and methodologies. The meeting was well attended, with 30 participants (including some industrial scientists) and 18 speakers.

The first speaker of the meeting was Mr. M. Pinches (Southampton University) who described a parallel implementation of the well-known link-cells MD algorithm. Mr. Pinches has adapted this algorithm for the Cray XMP/48 and the Intel iPSC/2 ("hypercube"). The implementation on the Cray XMP, he reported, is not strictly parallel since the user usually has limited control over the allocation of the processors to a given task. Thus while it is easy to couch the algorithm in terms of largely independent processes it is not guaranteed that these will execute on independent processors. Thus it is common for processes to "double up" on the same processor. Much more control is afforded to the user of the Intel hypercube, where the allocation of processes to nodes is straightforward.

The essence of Mr. Pinches' algorithm is the geometric partition of the MD cell into equal cubic regions (or slabs - the method works for many partitioning schemes), each of which is assigned to a processing node. The region assigned to each node is then further subdivided into cubic subcells, which match the linear size of the cutoff, as in the standard link-cells scheme. To establish the physical contact between the regions treated by each node, the subcells that lie on the edges of the regions are passed to directly neighbouring nodes, where their coordinates are appended to the list of particle coordinates for those regions. The forces are then calculated in the standard link-cell way. The integration of the equations of motion is followed by a reallocation of those particles that have moved out of the regions allotted to the processors, after which the MD cycle continues. The algorithm has excellent scaling properties, since communication costs are low. Simulations of the order of 1 million particles are now within practical reach and the performance of the 64 node program is similar to a single processor Cray XMP.

S. Liem (UMIST) also described the implementation of the link-cells algorithm, this time on a 16 node Meiko Transputer system and with the intention of performing simulation studies of fluid flow. Mr. Liem described the mapping of the 2-D link-cells algorithm onto the "square mesh" network of Transputers in some detail. The algorithm inevitably had much in common with that of the previous speaker, but differed in the detail regarding the maintenance of continuity of the sample across node boundaries.

The Pinches implementation passed particle coordinates in both directions along links between neighbouring nodes, while the Liem implementation passed the coordinates in one direction only and later passed force accumulators in the reverse direction. Mr. Liem showed several graphs indicating the performance of the implementation. The high efficiency and good scaling properties were apparent.

J. Perram (Odense) provided an overview of the parallel hardware and software currently being exploited and enhanced at Odense. The hardware currently consists of a 10 Transputer system with an Apollo DN 3500 workstation, two 64 Transputer Meiko Computing Surfaces and a further requirement for a 162 Transputer Meiko. The institute has examined several strategies for parallel processing, such as "coarse graining", which leads to the idea of a "task farm", where a control processor apportions work to subordinate processors as the need arises. This strategy however is not especially suited to MD work. More useful in simulation is the idea of "domain decomposition" in which the data to be processed is shared amongst processors under a scheme which takes into account the physical disposition of the data. Professor Perram illustrated this concept with the example of a recently published algorithm in which a 3D system of molecules is partitioned in the XY plane in a manner resembling the link-cells method, but in the Z direction is partitioned into sub-regions within the potential cut-off. The resulting algorithm resembles in some respects, a systolic loop algorithm, but the number of data passes is now a function of the number of sub-divisions of the cutoff. Thus overall the algorithm avoids the need to consider all pairs of molecules in the system and can be expected to be more efficient than systolic loops in simulations where the cut-off range is substantially less than the size of the MD cell.

A.D. Smith (Canterbury) described the Transputer system that is being used by the Canterbury Physics department for liquid simulations. This is a Perihelion system running the Helios operating system. The hardware consists of several Transputer "quad" boards which are software reconfigurable and with 1 M byte of memory per Transputer. There is an additional "host" board with 4 M bytes of memory. The system is interfaced with several Atari microcomputers, which handle i/o and interface to the printers and hard discs. Mr. Smith also described the software for reconfiguration and program harnessing. The system is a multi-user system, though there is not much by way of software protection and consequently requires experienced multi-users for safe operation! The programming languages available are Pascal, FORTRAN, C and Occam. Overall, the Canterbury group are well satisfied with their experience of the system.

The current MD algorithm the Canterbury group are using is a systolic loop algorithm. The program is controlled by a master process, which runs on the host Transputer and the systolic cycle runs on the network of Transputers. The algorithm passes coordinate and force arrays around a ring of Transputers until all pair forces have been calculated. A potentially expensive rewind of the data to the home Transputer (for integration of the equations of motion) is avoided by passing data directly across the ring of Transputers.

D.J.N. White (University of Glasgow) described the COMMET system built by his group at Glasgow. This system is a high performance graphics system consisting of 32 Transputers and is used for several aspects of molecular modelling. It is currently used mostly for parameter optimisation, where the main part of the code executes on the host Transputer and tasks are delegated to the network of transputers. The system is also capable of MD simulations and is currently being used to model the tertiary

structure of proteins by the process of "mutation" from the known structure of a related protein. Dr. White showed several slides which indicated the graphical capabilities of the COMMET system. Various representations of protein structures, depicted as ribbons, space-filling spheres, stick models and columns, were shown. The overall performance of the COMMET system was reported to be Cray-like.

D.M. Jones (Birkbeck) described the work currently in progress at Birkbeck to design efficient Monte Carlo algorithms for Transputer arrays. A typical simulation undertaken by the Birkbeck group is of a solute molecule suspended in a solvent (e.g. one ethanol molecule surrounded by 216 water molecules). The object of interest is usually the solute, but the bulk of the computational effort is expended on the solvent. Parallelism was seen as a means to remove this bottleneck. The initial work was done on a 5-Transputer Meiko (one "quad" board and a "host"), programs were written in FORTRAN and communications between Transputers were written in Occam. Mr. Jones described the methods undertaken to implement the basic Monte Carlo algorithm, beginning with a "process farm" in which the solvent molecule moves were handled by the "slave" processors. This arrangement was characterised by very high communications costs and further improvements were sought. Buffering the communications and changing the configuration of the network to binary and tertiary trees did not result in great improvements. A new strategy involved the construction of a distributed random number generator so that several MC trajectories could be generated in parallel, with ensemble properties communicated to the host process. The algorithm was verified on the Edinburgh Concurrent Supercomputer. Further improvements have been obtained by overlapping the random number generation and host-node communications.

D. Fincham (University of Keele and Daresbury) began his talk by overviewing the work on parallel algorithms being undertaken at the University of Keele KOSMOS Project. This project covers a wide range of simulation projects in solid state, liquid state and biological systems and requires the development of software for simulation and graphics and incorporating parallel processing. Keele is a Unix site, with a Sequent mainframe, Sun workstations and Meiko inSun hardware for parallel programming. The latter employs Meiko ctools to provide parallelism within the FORTRAN language, and a multi-user environment.

Dr. Fincham went on to describe the systolic loop methods that are finding their way into the mainstream of parallel simulation work. The methods have their origins in the "Tractor Tread" algorithm devised by the Waterloo group in 1982, and have since been extended to include the SLS, SLD and SLB algorithms (with grouping and overlapping communications modifications) by Dr. Fincham and his colleagues. Dr. Fincham described the SLS-G algorithm (deemed to be the most efficient variant) in some detail, including its load balancing and communication aspects. The extension of the variant known as SLD to deal with three-body forces (named SLT) was presented and shown to be feasible for certain "magic numbers" of processors. An appeal for a more general theorem dealing with this problem was made! The talk was concluded with an observation regarding the MD algorithm of Perram *et al*, which he suggested was also a systolic loop algorithm, but with spatial ordering to reduce the amount of data passing.

S. Miller (University of Keele) described his work on the inclusion of long range forces within the systolic loop framework. The ability of the systolic loop methods to model many-particle systems was well known, however little work has been done to incorporate

standard techniques for long-range (Coulombic) forces. Mr. Miller has looked at two possible methods: the Ewald sum and the approximations introduced by Adams. Many levels of approximation are available, the first three of which are spherically symmetric and higher orders are anisotropic. The anisotropic forms are continuations of the same algebraic series, which may be truncated at different stages according to the desired level of accuracy. Tests of the relative accuracy of these approximations, measured against the Ewald sum, for the  $CsCl$  lattice showed that the spherical approximations were quick, but not accurate. However some speed was still gained, and the desired accuracy obtained, for a higher order of the anisotropic sum.

The parallelisation of the Ewald sum was described. Basically, the real space part is dealt with by the conventional SLS-G algorithm. The reciprocal space part is partitioned into sub-sums over the groups of ions present on each node, each of which calculates the full range of k-vectors. The sub-sums are then passed to the "head" node of the SLS chain for summation, and the result broadcast to the other nodes for completion of the forces.

A. McDonald (University of Keele) described a distributed visualisation system for simulations running on the Keele parallel computers, which runs on the Sun workstations at Keele and uses standard Unix pipelined channels to provide the interface between the simulation programs and the graphics packages. The latter uses Sunview windows to display the results. The system is interactive: while a simulation is running it is possible for the user to intervene and change the conditions of the simulation e.g. temperature, timestep etc. The graphical output provides running plots of the thermodynamic variables, RDFs etc, and a 2D plot of the particle positions. The Keele group would welcome any suggestions for later inclusion in the package.

A. Raine (University of Cambridge) described his implementation of the systolic loop algorithms for simulations of biopolymers on Transputer systems. The central difficulty he reported, was the adaptation of the SLS-G algorithm to incorporate the multi-body forces present in the biopolymers. Such forces include the bond angle forces (3-body) and torsional forces (4-body). These contributions come within the capabilities of the SLS-G algorithm because they are "bonded" terms that are defined by a "fixed" polymer backbone. Simple rules may be employed to help with the partitioning of the atoms into the groups required by the SLS-G algorithm. If these are obeyed (and in very many cases they can be made so) the method becomes possible. The rules ensure that the atoms involved in a particular 3-body or a 4-body interaction are not separated into more than two groups.

Dr. Raine also discussed the implementation of the "SHAKE" algorithm for rigid bonds, in a parallel environment. The main problem is the interdependence of the bonds over the whole molecule, which is necessarily distributed over many processors. A parallel implementation therefore implies a computationally expensive systolic approach. Possible exceptions are the  $C - H$  bonds, which are not highly interdependent and can in principle be processed in parallel. There appeared to be no universal principles to assist in the general case and several strategies were suggested. An Occam biopolymer program has been written by Dr. Raine to run on Transputer systems. Further news of availability etc. will be made through CCP5.

M.T. Dove (Cambridge) discussed the implementation of lattice simulations on the DAP parallel processor, which he has exploited in studies of quartz. He began with a brief description of the DAP hardware, mentioning the 4096 processing elements and the

availability of special shift functions to permit communication between nearest neighbour elements. He outlined the basis of the MD algorithm he uses for simulations of minerals, which employs a special mapping of the 3D system onto the 2D processing array of the DAP. The implementation of a full Ewald sum has not yet been completed, but he was considering using only the Bragg vectors in calculating the reciprocal space terms in order to speed up the program.

A. Kara (University of Liverpool) described the planned development of a parallel MD program for the simulation of gas-surface interactions on the Intel Hypercube. The physical problem he described was the collision of a rare gas atom with the surface of a metal. A number of phenomena can occur, including scattering and trapping of the incoming atom. In the first approximate model the treatment involved the construction of concentric regions of the surface and underlying layers. The innermost regions were dealt with most explicitly, while the outer regions give way to a rigid lattice model. The parallel implementation involved a master-slave algorithm, with the master process running on the host computer and the slaves on the Intel nodes. Each slave was allocated a specific "slab" of the concentric regions. The dynamics of the slabs were calculated by the nodes, while the host calculated the dynamics of the incoming atom. The communication between the nodes was minimal in the first approximate model, where the lattice forces were harmonic (Einstein solid). The bulk of the communication was between the host and the nodes, which after the initialisation of the system consisted of the passing of the incoming atom coordinates to the nodes and the returning of the forces acting on the particle to the host. The program has been designed to adapt to node availability in the multi-user environment of the Intel.

C. Care (Sheffield Polytechnic) described the theory and lattice simulation of amphiphilic systems. The objective of this work was to discover the simplest model manifesting micellar behaviour and to study it in detail. The system exhibits a rich phenomenology including: micelles, inverse micells, surfactant crystals, lamellar micelles and various packings of these basic structures. The lattice model employed in the Monte Carlo simulations was described. It consisted of  $N$  chains of fixed length, with a distinct "head" unit distributed on a 3D ( $32 \times 32 \times 32$  site) lattice. Interactions were confined between nearest neighbours and included only head-solvent and tail-solvent parameters. Moves of the chains were by reptation Monte Carlo and a multispin coding technique was employed for more efficient memory usage.

The current hardware available for these simulations consist of an IBM PC AT with B004 and B012 transputer boards. A 50 Transputer system is planned. In parallelising the simulations, geometric parallelism was ruled out because of difficulties with boundaries when extended chains are used and also because clustering prevents good load balancing. The first strategy tried was that of a "processor farm" with a control processor and a special processor to manage the lattice. Unfortunately, the lattice manager proved to be a bottleneck in the algorithm and seriously delayed the simulations. Consequently Dr. Care opted for a "naive" parallelisation - running several independent simulations simultaneously on each pair of Transputers. This was found to be very efficient and cost effective. Each Transputer pair was capable of  $100 \mu s$  per MC move and the whole network  $700 \mu s$  per MC move. Dr. Care concluded with a brief outline of some of the scientific results, showing some of the structures obtained.

D. Nicolaidis (Bristol) described a new approach to molecular dynamics simulations, which he hoped would remove one of the limitations encountered in MD, namely the

inability to simulate long lived phenomena. In a dynamical systems the method requires the introduction of a "mass matrix"; the elements of which are dependent on the interaction terms ("susceptibility matrix"). Normally it is understood that when the density of eigenvalues of the susceptibility matrix is nonzero at zero eigenvalue, long lived phenomena are present. The purpose of coupling the susceptibility matrix to the mass matrix, is to obtain equations of motion in which the modes evolve on a reasonable timescale. Dr. Nicolaides is currently exploring the insight gained from this approach, by attempting other heuristic scalings of the mass matrix to achieve the same effect (e.g. scaling as a function of the correlation length). Dr. Nicolaides has plans to implement this approach on the Bristol DAP array processor.

J. Craven (Edinburgh) gave a short, unscheduled account of his implementation of a parallel MD algorithm on the Edinburgh Concurrent Supercomputer. The algorithm he described is currently being used to simulate systems of rigid molecules. Initially the atoms are divided into even sized groups and each group allocated to a "home" processor. While the forces within the home group are evaluated, the groups are also concurrently sent round the ring of processors, so that every node can construct a replica of the system. Then the forces calculations within the home groups are temporarily suspended, while the interactions between groups are evaluated. These are resolved into (incomplete) molecular forces and torques, which are circulated around the ring, while the home group forces calculation continues. The overlapping of forces calculations and passing of the data is designed to reduce the major part of the communications costs. When the complete forces have been obtained on each node (i.e. for the home groups), the molecular force and torques are obtained and the equations of motion integrated. The MD cycle then continues. The algorithm is used in conjunction with a link-cells strategy to reduce the number of interactions between groups and thus the number of forces and torques to be transferred.

Dr Craven described the performance of the algorithm for increasing numbers of processors (the algorithm deteriorated in performance as the process number increased, but the deterioration was less in larger simulations). For a system of 4224 12-site benzene molecules, a computation rate approaching 80 Mflops was obtained on 132 Transputers.

W. Smith (Daresbury) gave a cautionary tale of an implementation of a parallel MD algorithm on the Daresbury Intel iPSC/2. The "Replicated Data" (RD) algorithm described retains copies of the coordinates and velocities of all the particles in the system on every node of the parallel computer and each node integrates the equations of motion independently. The nodes however share the work of calculating the pair forces and a global pass-and-sum algorithm is required to provide each node with a full description of the forces between the particles. Dr. Smith described the workings of the pass-and-sum algorithm and indicated how round-off errors, if unattended, can lead to divergence of the trajectories on each node. A simple cure was prescribed. Dr. Smith also gave empirical formulae describing the efficiency the RD algorithm and showed the circumstances under which the algorithm was most and least efficient.

R.J. Allan (Daresbury) described the Occam harness FORTNET, which was developed at Daresbury. The harness is designed to support parallel FORTRAN programs on Transputer networks. The user is freed from the need to write scientific code in Occam, since the communication between Transputers is controlled by the Occam harness and is invoked by calls to a library of communication routines. Dr. Allan described the function of the routines available. The harness is currently in use at many academic

sites and is continually being upgraded. For example the current version is capable of supporting programs designed initially for the Intel hypercube. (Readers interested in obtaining the harness should contact Dr. Allan at Daresbury.)

M. Leslie (Daresbury) concluded the presentations with a description of distributed matrix inversion on parallel computers. His current strategy involves the decomposition of the matrix into lower (L) and upper (U) triangular matrices. He described the difficulties of implementing this particular decomposition on the Daresbury Intel iPSC/2.

The final event of the day was a discussion of different approaches to parallel processing. It was proposed that in molecular simulation (by either MD or Monte Carlo methods) it is possible to use parallel processing simply to simulate many different systems at the same time, or possibly the same system at many different state points simultaneously. There were a number of advantages to this approach. Firstly, a full study of a system could be speeded up by a factor equal to the number of processors. Secondly, questions about load balancing, communication overheads and scaling of the algorithm with the number of processors were redundant. Thirdly the design of the programs did not require a knowledge of parallel processing as such, provided a suitable communication harness was available.

The arguments put forward in favour of developing truly parallel programs were as follows. Firstly, that parallel processing offered a way of making new scientific enquiries, such as could only be achieved by enhanced computational power. The microscale hydrodynamics study of Rapaport was put forward as an example. Secondly, there were clearly occasions when an investigation of many state points of a system were not required and a single simulation of a large system (e.g. a protein) was needed. There are also other branches of computational science where multiple calculations in parallel are not the most suitable way of proceeding e.g. lattice simulations. Thirdly, questions were raised about the control of many simultaneous simulations, where user intervention was required. Finally, there were hardware considerations, such as the output of data from many concurrent simulations requiring sophisticated processing in its own right, including expensive distributed disc systems.

What remained clear from the discussion was that the two opinions could exist side-by-side. Parallel processors could satisfy both approaches, a point which underlines their versatility.

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# 'Kosmos - An aid to Scientific Visualisation'.

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## Abstract

A method of linking a standard molecular dynamics simulation program to a remotely located graphics workstation (a Sun in this case) is outlined. A brief description of the method using a simple Lennard-Jones system as the host molecular dynamics program is presented.

## Introduction

With the currently increasing performance/price ratio of computer systems, workers now find themselves in the enviable position of having more computer power available and at lower cost than ever before. This leads to the question of how to use this (relatively cheap) computer power to enhance the productivity of (relatively expensive) research staff. The traditional way of using greater computer power is to soak it up in simulating larger and/or more complex systems and analyzing the (voluminous) data produced at a later time, ie in batch form. Many current users of research computer systems will be familiar with this method of working. There is at least one other way of working however, and this is to use some of the computer power to perform complex data analysis in real time, ie as the simulation is progressing. Ideally the data should be presented to the person running the simulation in visual form as the combination of the human eye and brain is capable of processing vast amounts of data and drawing conclusions about the underlying patterns in the data much quicker than a computer.

## Description of KOSMOS (the Initiative)

The KOSMOS project (Keele Open Software for MOlecular Simulation) is a project to develop a new generation of software for molecular simulation. The software will be robust and well-documented, since a primary aim is to bring the techniques into routine use by non-experts, particularly within industry (financial support from ICI Chemicals and Polymers is gratefully acknowledged). It will exploit the power and cost-effectiveness of parallel computing; it will make much greater use of graphics and interaction than is possible using traditional super-computer batch-processing.

## Description of KOSMOS (the program)

Under the auspices of the KOSMOS project here at Keele, a small demonstration system has been constructed. The KOSMOS program (named after the initiative) runs under the UNIX operating system. This is necessary as the UNIX concepts of 'pipes' and 'standard input and output' are crucial to the operation of the program. The KOSMOS program runs on standard Sun hardware (Sun 3/60's) and is programmed in the C language, this being preferential for systems/graphics type programs. The host program can be programmed in almost any computer language, but as most research workers are familiar with FORTRAN, the host program used as the test case was programmed in this language:

A simple two-dimensional Lennard-Jones system has been programmed as the host program, this program performs all the usual static and dynamic numerical calculations such as the Radial Distribution Function and the Velocity Auto-Correlation Functions. Thermodynamic parameters are also calculated.

The KOSMOS program controls the host Lennard-Jones program using the standard input/output concepts of UNIX and a simple 'control language' to command the host program to perform functions such as switching off voluminous outputs of data, changing the pressure or temperature of the system or anything else that the user has programmed into the host program.

Using standard input/output in this way means that the host program can be tested on it's own, entirely independent of the KOSMOS program, ie through an ordinary terminal and in some circumstances this can be very useful.

A two-way communication of data occurs between the KOSMOS and host program, KOSMOS sends commands to the host program, which the host program acts upon and sends back data in the form of numbers (integers or floating point), and textual information (such as warnings about the Hamiltonian straying outside defined ranges). This information is not coded in binary or any other form, ie the data is human-readable.

The advantage of using the UNIX system and the method used in executing the host program is that theoretically any machine that can be remotely logged into (ie any machine that responds to 'rlogin') can be used as the host machine running the simulation. Here at Keele, we run the same simulation program on a Sequent mainframe, and a Melko in-Sun computing surface using Transputers (and gratifyingly the latter simulation runs several times faster than the Sequent - which is already recognised as a fast mainframe).

### **What KOSMOS can do...**

To make the control of the host program as simple as possible several useful devices are installed into the KOSMOS program 'as standard', these include the ability to control the simulation using the 'point-and-click' user-interface known as Sunview, which allows the user to use a mouse to control the entire simulation (ie it isn't necessary to use the keyboard at all). The data analysis powers of the KOSMOS program include the ability to display the data in a familiar two-dimensional graph, and 'read' values off the graph using the mouse, or to have an electronic 'chart-recorder' continuously record the value of certain parameters (in the demonstration program, the temperature of the system, along with the kinetic, virial and total energies of the system are recorded). There also exists an 'animation' display that in the demonstration version shows idealised images of the atoms 'bouncing around' in their computational box.

There is currently no way of users installing their own routines for handling the data from the host program without coding in C and recompiling the program.

### **How KOSMOS does It...**

Central to the idea of how KOSMOS operates is the UNIX facilities of 'rsh' (remote shell) and 'pipes'. A remote shell is a command interpreter for another UNIX machine that is invoked from a machine that may be in the same room as, or on the other side of a campus from the host machine. Pipes allow the output of one program to be used as the input to another program, for example the command `who | wc` will count the number of users on the machine (who is a command that details what all the users on a machine are doing - one per line, whilst wc is a word

and line counting program). KOSMOS does not use pipes in this way, rather using them as 'communication channels' between the host program and the KOSMOS controlling program.

The KOSMOS program uses a configuration file that allows the user to change parameters that the KOSMOS program will use. When the KOSMOS program is invoked with this configuration file, it uses the `rsh` command to start up the simulation program on the host machine. The configuration file contains the name of the remote host program, which machine it resides on and how many 'windows' the user wants ('windows' used in this context includes the graphical devices that the user uses to display data on the screen as well as the definitions for the graphical controls that drive the host program - for example, the control that tells the host to change its time step).

Once the host program has started up, KOSMOS waits for one of two things to happen - the user selecting a control on the graphics screen, or data to become available on the 'pipe' from the host program. In the first case, a control string is constructed consisting of the command to execute, and any arguments that may be necessary (eg the command to change the time step is `dtee0.000001`). This control string is then kept waiting until the second action occurs - data appearing on the pipe. When this occurs, the KOSMOS program starts interpreting the data according to the configuration file provided by the user. Typically this will consist of the host program telling KOSMOS how many 'updates' are about to occur, and the data associated with these updates. Once all the data has been read in by KOSMOS (and various windows have been updated), the command string is sent to the host program telling it what the users request is. Typically this will be the string 'none', implying that no action is necessary and that the host program can continue with its processing. If an action is required however, the host program will decode the command string, and call one of several subroutines to perform the action (change the temperature, density, time step etc.).

These actions are continually performed by the two programs, until the user tells the host program to halt.

This method of working means that there can only be one command sent to the host program per time step (time step here means the interval between successive updates from the host program), this can be changed relatively easily however, to allow the user to set several parameters at once and have them all acted upon by the host program (ie interpreted).

### **Why this way?**

There are a number of possible ways in which a simulation program can running on one machine can connect to a graphics program running on another, and we would like eventually to consider all these possibilities.

The X-windows approach is becoming the standard method for doing this kind of thing. This is based on the concept of servers and clients. The user program acts as the client and contains the graphics calls; these control the server program running on the workstation, all communications between the two being handled by the underlying protocols, transparently to the user. However one relies on the server program provided by the workstation manufacturer to utilise its graphics facilities efficiently, and in the current state of development there can be performance problems.

There are low-level methods within Unix by which different processes, possibly on different machines, may communicate with each other. In Berkeley Unix they are called sockets ; in System V they are known as IPC facilities. These methods are rather complex for the average scientific user, though no doubt they are very powerful.

Another approach is possible using the Meiko ctools software which provides the message-passing between processors which we use in writing parallel programs on our Transputer system. In their latest version of this software Meiko have provided a facility to use the same message-passing routines between Suns on a network, and between Suns and Transputers. This is obviously an attractive approach for us as it means there is only one set of software for us to learn. However, there are snags: Suns and Transputers have different internal data representations and messages sent between them must be converted into appropriate form. Furthermore this is a proprietary rather than portable approach.

At the moment the use of two-way pipes seems the most suitable method for us. The simulation program can be written in Fortran, developed independently of the graphical interface, and will be completely portable. The only limitation is that it should read instructions and data from standard input, and produce results on standard output. The graphical interface can be written in C, and can make use of all the graphics facilities and software available on the workstation. The two programs are coupled together by a facility which is very easy to use and is completely standard in all versions of Unix.

## **Limitations**

The KOSMOS program as written at the present time is limited mainly by its mode of communication. Two-way pipes are a quick and easy method of passing data around between the two programs, but may not be the most efficient way. There exist other methods of data transfer (specifically Berkeley style sockets, and shared memory), but these are all more complex than the method chosen.

Because (relatively) slow pipes are used to transfer the data, applications that output vast amounts of data (imaging systems coming to mind initially) are not suitable for the method of visualisation used in KOSMOS.

## **Future Directions/Requests for Input**

The KOSMOS program is still very new and although more powerful systems do exist for scientific visualisation, the ease with which a standard molecular dynamics program can be converted to run under the KOSMOS system and thereby enjoy the benefits of graphical interaction/real-time data analysis is definitely useful - it is even theoretically possible to take a current MD program and with the addition of the parsing routine to decode commands from the Sun workstation, have it run under a graphical shell.

However, this writer is inexperienced in the molecular dynamics field and would very much appreciate further guidelines/input on how to make the KOSMOS program more useful in general and to the molecular dynamics community in particular.

I wish to extend my grateful thanks to Professor Mike Gillan and Dr. David Fincham for their invaluable help in implementing this system.

# Report on the CCP5 Workshop on the Computer Simulation of Polymers

W. Smith

Daresbury Laboratory, 15 November 1989

The inspiration for this workshop was the CCP5 sponsored visit to Daresbury Laboratory by Professor Kurt Binder of the University of Mainz and was one of the scheduled events in Professor Binder's short lecture tour of the United Kingdom. Nearly 20 scientists took part in the actual workshop and a much larger number attended the lecture given by Professor Binder, who began the meeting.

Professor Binder's lecture was entitled "Monte Carlo Simulation in Polymer Physics" and covered three areas of polymer simulation: polymer mixtures; mesophase formation in block copolymers and adsorption of polymers at a wall, the first topic forming the bulk of the lecture. At the beginning of his lecture Professor Binder emphasised the need to simulate longer polymer chains and cited the cheap computational power afforded by modern parallel processors. In Mainz they currently have an 80 Transputer Meiko system, which with optimal programming achieves approximate Cray XMP (single processor) performance.

He began the description of the work of the Mainz group on polymer mixtures by describing the phenomenon of phase separation of a binary mixture. The thermodynamics of this process has been described for a long while in terms of the Flory-Huggins model (1941) in which the enthalpy parameter  $\chi$  is of central importance in accounting for the capacity of two polymers to mix.  $\chi$  can be derived from scattering experiments, from which the dependence on the temperature and the fractional composition of the mixture is clear. The Flory-Huggins model is a lattice model in which the polymer chains (A and B) are regarded as self-avoiding random walks and the free lattice sites are regarded either as "free volume" or solvent molecules. The chains have lengths  $N_A$  and  $N_B$  and the enthalpy parameter  $\chi$  is related to the molecular interactions ( $\epsilon_{AA}, \epsilon_{BB}, \epsilon_{AB}$ ) through the formulae:

$$\epsilon = \epsilon_{AB} - (\epsilon_{AA} + \epsilon_{BB})/2$$

$$\chi = Z\epsilon/k_B T$$

with  $Z$  as the coordination number. Using this model the free energy of mixing can be calculated and it has been used to study the coexistence curves and critical mixing of polymers.

Professor Binder stressed the approximate nature of both entropy and enthalpy expressions in this model, in particular the neglect of the correlation in site occupancy in the enthalpy. In several important respects the model fails: the critical temperature can be incorrect by an order of magnitude; the model displays an incorrect dependence on polymer concentrations; the functional dependence of  $\chi$  on the interaction parameters is incorrect, and the predictions of the model appear to worsen as the polymer sizes are

increased. For these reasons Monte Carlo simulations have been used to explore the system to highlight the reasons for the failure of the model.

The MC simulations were also performed on a grid, though the system was simulated at different chemical potentials (assuming a reservoir of polymer chains) rather than with two kinds of chain. Chains were equilibrated using "kink jumps" and "end rotations" etc. In principle mixing can be seen as the collapse of a suitable order parameter to zero at the critical temperature. However, complete collapse is hindered by finite size effects and an extrapolation to zero in the order parameter. Finite size effects are also seen in the collective structure factor at zero wave vector, where the developing peak at the critical temperature is affected. Resorting to finite size scaling theory, Professor Binder explained importance of the ratio of the system linear dimension to the correlation length and how this can be used to obtain the precise critical temperature.

Comparison of the coexistence curves produced by the Monte Carlo simulations with those obtained from the Flory-Huggins model and the more sophisticated Guggenheim model showed that while the MC curves possessed a "plateau", the FH curves were parabolic and the Guggenheim results were intermediate between the two. A possible cause for this behaviour was the collapse of the A and B chains at different rates near the critical point in the FH model, but this was shown to be incorrect by the MC simulations. It was shown that the principal cause was the failure of the FH model to account adequately for the numbers of nearest neighbours. For example, for 32-bead polymer chains at the critical point the FH model implied of the order of 77 nearest neighbours, the Guggenheim model 54 and the MC simulations 30. This weakness in the FH model is the most important source of error.

Professor Binder also discussed the calculation of the equation of state, which is important because it allows the calculation of an effective  $\chi$  which may then be compared with experiment. He also touched on the phenomenon of spinodal decomposition and Cahn's theory. The evidence obtained suggests that the polymer chains contract somewhat in the early stages of spinodal decomposition.

He concluded his lecture with a brief description of two current investigations. The first was the mesophase formation in block copolymers, in which specific isomorphic blocks of the polymer chains form ordered "lamella" structures while other blocks remain amorphous. Liebler's theory for this phenomenon is currently being investigated. The second investigation was the adsorption of polymers on walls, where a detail investigation of the formation of points of contact as a function of the interaction parameters was under way.

The first speaker in the following workshop was Dr. J.H.R. Clarke of U.M.I.S.T. whose talk on the subject of "Polymer Simulations: Why Bother with Dynamics" provided an overview of the recent molecular dynamics simulation undertaken by his group in the Department of Chemistry. Their studies of dense polymers, where slow motions of polymer chains are not of interest, have shed light on the phenomenology of elastic strain, yield in plastic flow and the glass transition. The polymer model they have used is a linear "united atom" chain, with published interatomic parameters. They have developed their own method of creating *in situ* a pseudo periodic amorphous polymer system, by a growth process with Boltzmann weighting. A constant stress MD algorithm, based on Berendsen's approach, is used to relieve the stresses in the system.

Dr Clarke described some results obtained when the model polymer is subjected to an uni-axial stress. Initial work used step-wise increments in stress, but latterly a

continuous stress model has been used. The gradual extension of the sample gives rise eventually to plastic flow at the yield point, which is only partially reversed when the stress is removed. The removal of the stress prior to reaching the yield point results in elastic recovery. There is a reduction in density up to the point where yield occurs, and an increase thereafter and the chains become more ordered when stretched. A comparison of affine and non-affine displacements in the chains show that the non-affine displacements are much the smaller during yielding. Comparison of atomic positions before and after yielding, using scaled coordinates, shows that yield results from large movements of relatively small parts of the chains.

Dr. M. Bishop, also of U.M.I.S.T., gave a talk entitled "Computer Simulations of Polymers at a Surface". The model examined was a simple "bead" polymer with a "head" bead anchored to the surface (by an "infinite" mass). The inter-bead interactions consisted of harmonic springs ("bonds") and Lennard-Jones nonbonded forces. Bead polymer models are favoured by Dr. Bishop, since they provide a simple model for investigation, while at the same time possessing the required scaling properties for the macroscopic case. The surface was modelled as a flat plane, with a 9-3 surface-bead potential. The density of the polymer molecules at the surface was set very low ( $\rho \sim 0.00001$ ) to prevent chain interactions between periodic images. Brownian dynamics were used to incorporate solvent effects.

The basic model chains have been used in studies of structural properties of isolated polymers, where parameters of the polymer shape (such as RMS radius of gyration  $\langle s^2 \rangle$ ) have been related to chain length in scaling laws of the form:

$$\langle s^2 \rangle = A(N - 1)^P$$

in which P represents a universal exponent. Different "regimes" of behaviour have been observed, with different exponents, depending on the LJ potential parameters used and the dimensionality of the system. Both "excluded volume" (EV) and "non-excluded volume" (NEV) chains have been studied and compared with statistical mechanical predictions. Dr. Bishop also described the collapse transition where polymer chains become dominated by intramolecular forces and consequently shrink to a globular structure.

With regard to polymers at a surface, it was shown that increasing the surface-bead attraction causes the chain to reside closer to the surface, up to the point where it lies entirely on the surface and behaves statistically like a 2D system. However, increasing the intra-chain attraction causes the polymer to coalesce into a 3D globule with radial distribution functions resembling the bulk crystalline material. Competition between the surface and intramolecular forces is expected to show interesting phenomena, such as tilting of the globule at the surface at a characteristic angle.

Dr. S.R. Euston of the Procter Department of Food Science, Leeds University described his research into competitive adsorption at a surface, in his talk "Simulation of Competitive Adsorption between Polymers and Small Displacer Molecules at a Surface". The subject is of interest to food scientists because of the competitive adsorption effects between protein stabilizers and low molecular weight emulsifiers in food colloids. The model studied by Dr. Euston was a Monte Carlo simulation of a 3D tetrahedral lattice with both polymer and displacer molecules. The initial system consisted of pure polymer, which was allowed to equilibrate, with some segments lying in an interfacial region. The displacer molecules were then added to this equilibrated system.

The polymer surface interaction energy was fixed at a constant value and the effects of changes in the displacer-surface and polymer-displacer interactions and displacer con-

centration were investigated. The assessment of the changes in the adsorption of the polymer was obtained in terms of the fractions of "loops", "tails" and "trains" in the adsorbed polymer (Figure 1).

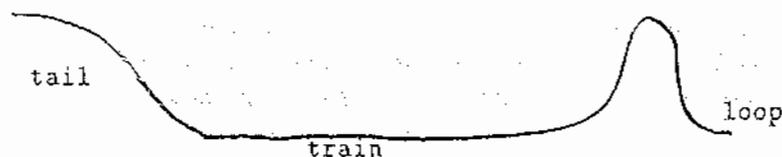


Figure 1. Loops, tails and trains

The results showed that the primary cause of polymer displacement was the surface concentration of the displacer molecules. Varying the displacer-surface attraction appeared to be less important than the surface coverage. However, for low surface-displacer attraction, a higher concentration of displacer was required to achieve the same coverage. This higher concentration appeared to retard the displacement. Changing the displacer-polymer interaction at fixed concentration had little effect when it was repulsive, but when attractive increased the polymer adsorption. Dr Euston concluded his talk with a brief survey of analytical theories of the effect of displacer molecules.

Dr. M. Saqi of the Department of Crystallography, Birkbeck College, gave a talk entitled "Monte Carlo Free Energy Simulation of Amino Acids". Free energy calculations are relevant in many areas of biomolecular simulations, including drug design. The techniques currently being used at Birkbeck are concerned with the effects of substituting an amino acid unit in a protein sequence with an alternative amino acid (i.e. a substitution of the type  $A-B-C-D \rightarrow A-B'-C-D$ ); in aqueous solution.

The free energy method employed is based on thermodynamic perturbation theory, in which the system hamiltonian contains a perturbing term, with a coupling parameter (say  $\lambda$ ). Evaluation of the equilibrium energy of the system with different values of the coupling parameter enables the free energy difference between the original, unperturbed system and the final, fully perturbed system, to be calculated by integration over the coupling parameter. In applications to protein problems the perturbation takes the form of a substitution of one amino acid residue for another. Many queries are raised by this technique, such as: adequacy of sampling; choice of suitable values of  $\lambda$  (i.e. "windows"); reproducibility of the results; effects of neighbouring residues (local environment), and how to deal with long range effects.

Dr. Saqi described the nature of these difficulties with reference to some example perturbation calculations: the substitution of  $-OH$  for  $-CH_3$  in methanol; the substitution of threonine (THR) for valine (VAL) in a tripeptide, and THR for VAL in a pentapeptide. The BOSS program of Jorgensen (Purdue) was used for this work and the water model was TIP4P. Many important points were made by Dr. Saqi, arising from these simulations. The main lesson appeared to be the need for adequate error estimation. There is a tendency in modern work to judge the merit of the results obtained on a basis of the absence of apparent hysteresis on reversing the substitution process to the starting point. However, examination of hysteresis over each individual window, reveals that underestimates of the errors can arise from this. Dr. saqi recommended this approach in the interests of better error estimation. Longer simulations, better sampling algorithms and careful choice of windows may be required in future.

The final talk of the workshop was given by I. Siepmann of Cambridge University and was entitled "A New Method for the Calculation of Chemical Potentials of Dense Chain Systems". He began by describing the "particle insertion" method of Widom, which requires the attempted insertion of "ghost" particles at intervals into a simulated system in order to obtain an estimate of the chemical potential. The method been used successfully, but is impractical for dense systems and difficult to implement for molecules. Mr. Siepmann has implemented a method for performing the insertion of moderately long polymer chains, which entails the initial insertion of a "head" particle, followed by the insertion of the following chain by a Self Avoiding random Walk (SAW).

The method has been tested in simulations of polymer molecules adsorbed at a surface and compared with Widom's method and the "grid insertion" method. The results clearly showed that, in this application, the SAW method converged the most rapidly and very long simulations (240 million MC moves !) were required to produce agreement between the methods. The Widom method appeared to be much the worst of the three methods.

The final event of the day was an informal talk by Dr. A. Masters of Manchester University, who outlined some of the scaling problems encountered in lattice studies of the system comprised of a polymer in a solvent. A summary of this contribution has been kindly provided by Dr. Masters in the following article.

## Acknowledgements

The organisers wish to thank Professor Binder, whose visit to Daresbury was the inspiration for this workshop, and the speakers who agreed to take part.

## List of Participants

K. Binder (Mainz) M. Bishop (UMIST)  
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# A SINGLE POLYMER CHAIN ON A LATTICE - SOME QUERIES

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Towards the end of the CCP5 workshop of polymer simulation (15th November, 1989), there was granted an opportunity for the participants to raise queries and questions about polymers and I duly displayed my ignorance about lattice chains. Many comments were made by the audience, so now that I have been asked to reveal my confusions to even more people, I hope I can incorporate some of the points made then. At the outset, though, I would like to make the disclaimer that I am fairly new to the polymer field, so many of my problems and arguments will doubtless either be old chestnuts or, as likely as not, just simply wrong! In any case, I would like to learn more about the subject, so any suggestions, references, etc., would be most welcome.

In this article I would like to consider single lattice chains in good solvent conditions. I thus begin with a rapid outline of two-parameter theory, then give a brief account of self-avoiding walks on a lattice (SAW's) and finally consider SAW's but with nearest neighbour attractions. Finally I try to summarize what I do not understand.

## 1 Two-Parameter Theory

It is commonly assumed [1] that the behaviour of sufficiently long chains in good solvents is predicted by a Hamiltonian,  $\mathcal{H}$ , given by

$$\mathcal{H} = -\frac{3}{2l^2} \int_0^N dn \left( \frac{\partial \mathbf{r}(n)}{\partial n} \right)^2 - \frac{v}{2} \int_0^N dn_1 \int_0^N dn_2 \delta(\mathbf{r}(n_1) - \mathbf{r}(n_2)), \quad (1)$$
$$|n_1 - n_2| > a$$

where the chain is represented by a continuous curve of contour length  $Nl$  and  $\mathbf{r}(n)$  is a point a contour length  $nl$  along the chain. The excluded volume parameter is  $v$ ,  $l$  is the Kuhn persistence length and  $a$  is a cut-off to rule out segments interacting with themselves. In the limit  $a \rightarrow 0$  one obtains the result

$$\frac{\langle R^2 \rangle}{Nl^2} = F(z); \quad F(0) = 1, \quad (2)$$

where  $\langle R^2 \rangle$  is the mean squared end-to-end distance and

$$z = \left( \frac{3}{2\pi} \right)^{3/2} \frac{v}{l^3} N^{1/2}. \quad (3)$$

Similarly,  $\langle S^2 \rangle / Nl^2$ , where  $\langle S^2 \rangle$  is the mean squared radius of gyration, is also simply a function of the single variable,  $z$ .

The most recent calculation I know of  $F(z)$  is due to Muthukumar and Nickel [2], and their results are fitted extremely well by

$$F(z) = (1 + 7.524z + 11.06z^2)^{0.1772} \quad (4)$$

Another recent formula due to Douglas and Freed [3] is

$$F(z) = 1.732z^{0.1772} \quad (z > 0.75) \quad (5)$$

and many other formulae have been proposed.

We can now ask whether lattice chains obey two parameter theory, and, if so, how we get values for  $v$ ,  $l$ , and  $N$ ? Then one could attempt to verify the various approximate formulae for  $F(z)$ . We first consider the most studied lattice model of SAW's without attractions.

## 2 Potted History of SAW's

For a walk of  $N$  steps, each of length  $l$ , Domb and Barrett [4] noted that

$$\lim_{N \rightarrow \infty} \frac{\langle R \rangle^2}{Nl^2} \sim 1.64z_{DB}^{0.4} \quad (6)$$

for many types of three dimensional lattices, where

$$z_{DB} = \frac{\sqrt{N}}{3} \left( \frac{3}{2\pi} \right)^{3/2} v_{cell} \quad (7)$$

$v_{cell}$  being the volume per lattice point of the unit cell (for a diamond lattice  $v_{cell} = 1.54l^3$ ). The denominator in eq. (6),  $Nl^2$ , is the mean square end-to-end distance for a random walk with immediate reversals allowed.

Some theoretical basis for this form for  $z$  came from studies of the Domb-Joyce model [5], where intersections of the chain are permitted with a non-zero probability, a configuration being weighted by the factor  $\prod_{i,j} (1 - w\delta_{ij})$ .  $w = 0$  corresponds to a random walk without reversals and  $w = 1$  corresponds to a SAW.

It was found by carrying out an expansion in  $w$  that

$$\frac{\langle R \rangle^2}{Nl^2} = 1 + A_1w + A_2w^2 + \dots, \quad (8)$$

where  $A_1 = (4/3)z_{DB}(1 + O(N^{-0.5}))$  and so on. Thus if, in each term, one kept only the leading power of  $N$ , one regains the two-parameter theory with  $z = z_{DB}$ ,  $N$  and  $l$  being simply the number of steps and the step length respectively i.e.

$$\frac{\langle R \rangle^2}{Nl^2} = F(wz_{DB}) \quad (9)$$

Yamakawa [6] compared this prediction against computer simulation, finding plots of  $\langle R \rangle^2 / Nl^2$  vs.  $z_{DB}$  gave a smooth curve for results from many different lattices. On the diamond lattice, with  $42 < N < 240$  Yuan [7] found  $\langle R \rangle^2 / Nl^2$  fitted eq. (5) very well with  $z = z_{DB}$  but agreed very poorly with eq. (4).

Not all lattices fitted this picture, though, but Tanaka [8] showed that if  $v$  was treated as a parameter to be fixed empirically for each type of lattice, a smooth master

curve could be obtained for  $\langle R^2 \rangle / \langle R^2 \rangle_0$  where  $\langle R^2 \rangle_0$  is the value of  $\langle R^2 \rangle$  for a random walk in which immediate reversals were forbidden (e.g. for large  $N$  on a diamond lattice,  $\langle R^2 \rangle_0 = 2Nl^2$ ). Furthermore, having now determined  $z$ , Tanaka showed a plot of  $\langle S^2 \rangle / \langle S^2 \rangle_0$  vs.  $z$  (where again  $\langle S^2 \rangle_0$  corresponds to a random walk without immediate reversals) gave a smooth curve for all the lattices considered.

The questions now arise as to whether one can calculate the value of  $v$  theoretically and as to why the Yamakawa and Domb-Barrett form of two-parameter theory, obtained from consideration of eq. (8), seems to fail. We now pursue these points a little further in the course of considering attractive potentials.

### 3 Attractive Potentials

A typical simulation might take the pair potential,  $v(r)$ , between two segments to be

$$v(r) = \begin{cases} \infty, & r = 0 \\ \frac{\epsilon}{kT}, & r = 1 \\ 0 & r > 1 \end{cases} \quad (10)$$

At  $\epsilon = 0$  we regain the SAW, but there is a theta point, where  $\epsilon = \epsilon_0$ , when

$$\lim_{N \rightarrow \infty} \langle R^2 \rangle = C_\infty Nl^2 \quad (11)$$

i.e. the random walk without immediate reversals result.

Two-parameter theory would suggest an  $\epsilon$ -dependent volume,  $v(\epsilon)$ , should exist, where  $v(\epsilon_0) = 0$ . Within the Domb-Barrett approach, one would presumably use eq. (7) replacing  $v_{cell}$  by  $v(\epsilon)$  and having  $v(0) = v_{cell}$ . This fails, though, at the theta-point, for eq. (8) would then incorrectly predict  $\langle R^2 \rangle_0 = Nl^2$  instead of the result given by eq. (11). Thus modifications must be made to the Domb-Joyce model if it is to have any hope of describing the variation of  $\langle R^2 \rangle$  with  $\epsilon$ .

The obvious approach is simply to forbid immediate reversals in the original model, in which case one finds

$$\frac{\langle R^2 \rangle}{\langle R^2 \rangle_0} = B_0 + B_1 w + B_2 w^2 + \dots \quad (12)$$

where  $B_0 = 1 + O(N^{-1})$  and  $B_1 = (4/3)z'_{DB}(1 + O(N^{-1/2}))$ , etc. with  $z'_{DB}$  containing an excluded volume different from  $v_{cell}$ . If one is permitted to keep only the leading powers of  $N$  in each term (as before in the original model), one obtains

$$\frac{\langle R^2 \rangle}{\langle R^2 \rangle_0} = F(wz'_{DB}) \quad (13)$$

with the same function  $F$  as in eqs. (2) and (9).

As  $w \rightarrow 1$ , however, both models reduce to the same SAW and then eqs. (9) and (13) are clearly incompatible. Evidently the problems have arisen from dropping the lower order powers of  $N$  in the expansion coefficients - in a way that I do not see, the sum of these neglected terms must be of the same order of magnitude as the terms retained. In

fact, looking at the problem this way, I find it hard to see how, in the  $w = 1$  limit, the series in eqs. (8) and (12) can agree and still obey two parameter theory!

On the more practical side, preliminary studies suggest that eq. (13) also fails. It appears that a plot of  $\langle R^2 \rangle / \langle R^2 \rangle_0$  vs.  $z'_{DB}$  gives anything but a smooth curve for all the different lattices, and, for the diamond lattice, the results disagree strongly both with eqs. (4) and (5).

I also attempted, for the diamond lattice, to determine directly  $v(\epsilon)/v(0)$  by requiring a plot of  $\langle R^2 \rangle / \langle R^2 \rangle_0$  vs.  $(v(\epsilon)/v(0))N^{1/2}$  to yield as smooth a curve as possible ( $42 < N < 220$ ). The results are shown in fig. (1). The full curve is the best fit to the data from eq. (4), using  $v(0)$  as the fitting parameter. Close inspection reveals that points for a given  $\epsilon$  cross the master curve, and clearly eq. (4) fits the data poorly. Furthermore a plot of  $\langle S^2 \rangle / \langle S^2 \rangle_0$  vs.  $(v(\epsilon)/v(0))N^{1/2}$ , with  $v(\epsilon)/v(0)$  determined from the  $\langle R^2 \rangle$  data, shows no smooth curve. Evidently, for this range of chain lengths on a diamond lattice, two parameter theory is not working too well.

## 4 Final Comments

Ideally one would like to use the computer simulation of lattice chains to test theories, such as two parameter theory. The work of Tanaka suggests that if the excluded volume parameter is fitted empirically, then  $\langle R^2 \rangle / \langle R^2 \rangle_0$  and  $\langle S^2 \rangle / \langle S^2 \rangle_0$  for SAW's for many different lattices fall onto a single master curve when plotted against  $z$ . So far our attempts to extend this analysis to include walks with attractive potentials have failed - studies on chains much longer than  $N = 210$  would probably be needed.

The problem in testing theories such as the one given by eq. (4) lies in determining  $v$ . The original and modified Domb-Joyce models give different predictions for  $v$ , and indeed, in the SAW limit and for large  $N$ , it is hard to see how the two expansions contrive to sum to the same result, which they evidently must do.

These, then, are my difficulties. The theoretical ones being a failure to properly understand the relationship between two parameter theory and the Domb-Joyce models and the practical ones being an inability to get two parameter theory to agree well with simulation results obtained for a chain with attractive potentials on a diamond lattice. The latter problem might be helped by simulations of longer chains or else by having some theoretical idea as to the form of corrections to two parameter theory. For example studies based on the full Hamiltonian in eq. (1), retaining the cut-off  $a$  might prove enlightening. For a diamond lattice and without immediate reversals, it takes six steps or more for a chain to return to its starting point, and if  $a \sim 6$ , then a chain might have to be very long before neglecting  $a$  becomes a good approximation.

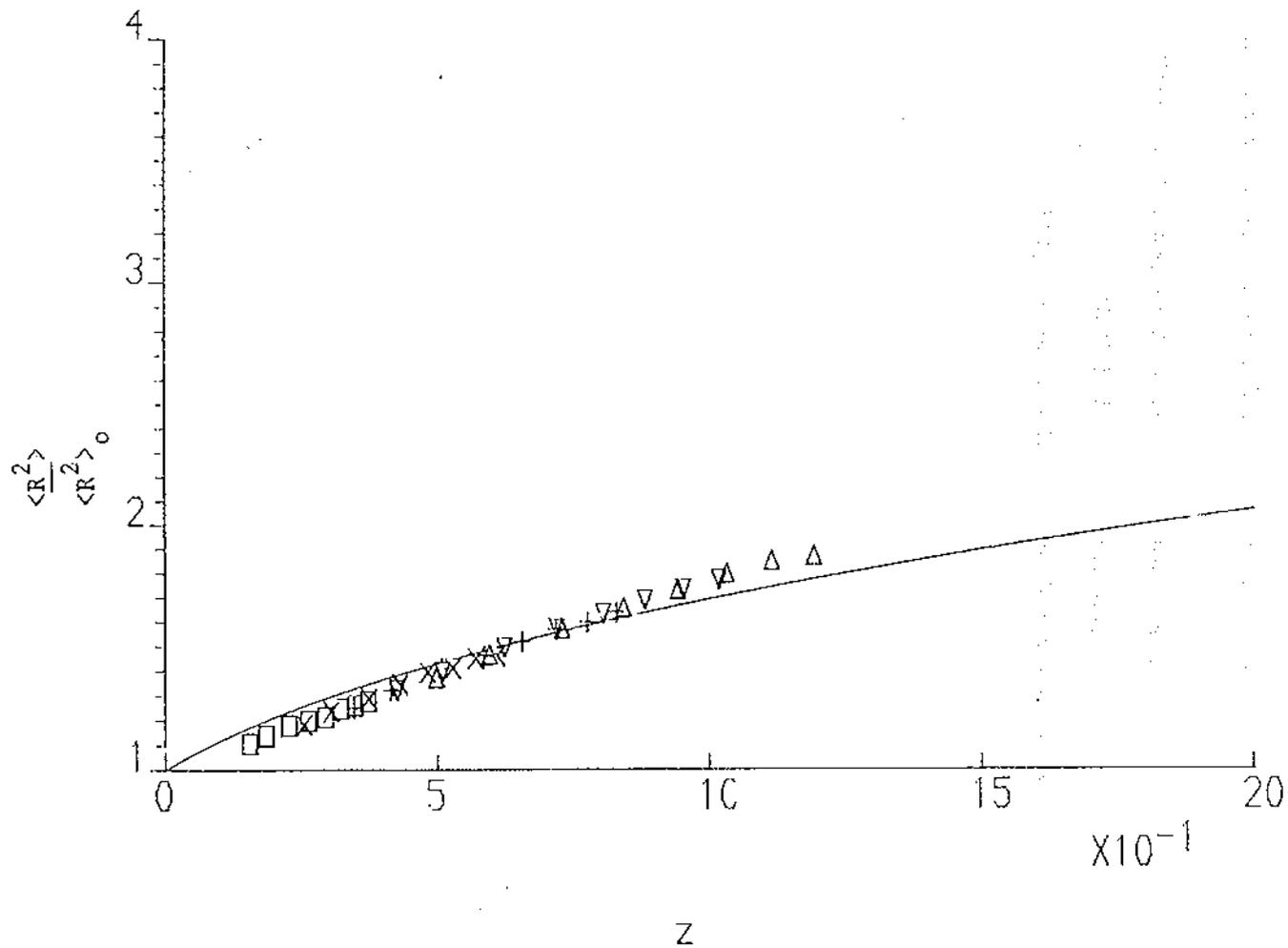
## Acknowledgements

I would like to thank the audience at the polymer workshop for their comments. In particular I would like to thank Professor Marvin Bishop for his good advice and never-ending supply of references and Dr Stepto, whose paper [9] contains much discussion on some of the points I have raised.

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Plot of  $\langle R^2 \rangle / \langle R^2 \rangle_0$  vs.  $z$ , the points from computer simulation of a chain on a diamond lattice and the solid curve from eq. (4). The key is :  $\square$ ,  $\epsilon = -0.4$ ;  $\times$ ,  $\epsilon = -0.3$ ;  $+$ ,  $\epsilon = -0.2$ ;  $\nabla$ ,  $\epsilon = -0.1$ ; and  $\Delta$ ,  $\epsilon = 0.0$ .  $N$  ranges between 42 and 210, and the method for calculating  $z$  is outlined in the text.



## LATTICE DYNAMICS OF ZIRCONIA: FREE ENERGY CALCULATIONS

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### Introduction

The central role that zirconia based ceramics occupies in the range of non-metallic engineering materials is largely due to their remarkable property of transformation toughening. In essence, crack propagation is arrested through a phase transformation in which the symmetry of zirconia grains in the matrix changes from tetragonal to monoclinic. In addition to these two polymorphs there is a high temperature cubic form which has the fluorite structure. When lower valent dopants such as Y or Ca are added in sufficient quantities the cubic form is an excellent fast ion conductor, as demonstrated by Nernst almost 100 years ago.

In the pure  $ZrO_2$  system, only the monoclinic form is stable at room temperature, the two higher temperature forms being unquenchable. The cubic  $\rightarrow$  tetragonal transformation temperature is  $2370^\circ\text{C}$  whilst the mechanically important tetragonal  $\rightarrow$  monoclinic transition occurs at  $1170^\circ\text{C}$ . Both of these temperatures can be lowered by the addition of dopant ions such as the rare earths and Mg or Ca. In this way, the cubic structure can be found down to temperatures of around  $1140^\circ\text{C}$ , or even lower, since the eutectic decomposition reaction is somewhat sluggish.

A number of potential models for zirconia have been developed and some studies of the defect structure and phase relations have been reported. The recent development of a free energy minimisation code has prompted us to investigate the structural phase transitions in zirconia, computationally. This is of special interest for the cubic  $\rightarrow$  tetragonal transition which is hard to investigate experimentally because of the high temperatures involved. In the doped systems, it is known that this transition is of a displacive, non-martensitic type, whereas it has been established that the tetragonal  $\rightarrow$  monoclinic transformation is martensitic in nature.

## Theoretical Background

The PARAPOCS code equilibrates crystal structures to a given temperature (and pressure) by minimising the (Helmholtz) free energy. A range of thermodynamic properties such as entropy, specific heat and Gibbs energy are also calculated.

The method used is based on lattice dynamics and a major limitation turns out to be the use of the quasi-harmonic approximation, which assumes that the vibrational motions in the solid consists of independent quantised harmonic oscillators whose frequencies may vary with cell volume.

The prediction of crystal structures and other temperature dependent crystal properties first requires the calculation of internal stress caused by the vibration of the constituent atoms. As stress is equal to the derivative of free-energy with respect to volume, and the free-energy at a given volume can be evaluated directly from the phonon frequencies, the first step is to determine the frequencies. For a shell model potential, the equations of motion to be solved are:

$$m \frac{d^2 u}{dt^2} = \frac{dV}{du}$$

in which  $u$  is the displacement of the core and  $m$  its corresponding mass. In the case of the massless shells we have the condition:

$$\frac{dV}{dw} = 0$$

where  $w$  is the shell displacement, corresponding to zero net forces on the shells. The potential energy is expanded to second order with respect to ion displacements i.e. the harmonic approximation:

$$V'(r) - V(r) = 1/2(W_{uu} \cdot u \cdot u + W_{uw} \cdot u \cdot w + W_{wu} \cdot w \cdot u + W_{ww} \cdot w \cdot w)$$

assuming the unit cell is at equilibrium and  $W_{uu}$  represents the second derivative matrix between cores,  $W_{uw}$  between core and shell and  $W_{ww}$  between shells.

Finally, before solving for the derivatives with respect to core and shell displacements, the periodic nature of the solid must be

considered, by including the dependence of atomic displacements on the wave vector  $\underline{g}$  i.e.

$$\underline{u} = \underline{u} \exp(i(\underline{g} \cdot \underline{r} - \omega t))$$

and

$$\underline{w} = \underline{w} \exp(i(\underline{g} \cdot \underline{r} - \omega t))$$

where  $\underline{r}$  is the atom position and  $\omega$  the vibrational frequency. The second derivative, or force constant, matrix is similarly affected, for example the force constant matrix for the interactions involving only shells is given by:

$$\underline{S} = \underline{W} \exp(i\underline{g} \cdot (\underline{r}_a - \underline{r}_b))$$

which is summed over all ions  $r_b$ . Similar expressions are obtained for the core-shell (T) and the core-core (R) matrices. Hence we can now solve the equations of motion to get:

$$\omega^2 \underline{m} \cdot \underline{u} = \underline{R} \cdot \underline{u} + \underline{T} \cdot \underline{w}$$

and

$$0 = \underline{T} \cdot \underline{u} + \underline{S} \cdot \underline{w}$$

where  $\underline{m}$  is the diagonal matrix of core masses. Removing the shell displacements  $\underline{w}$  gives

$$\omega^2 \underline{m} \cdot \underline{u} = (\underline{R} - \underline{T} \cdot \underline{S}^{-1} \cdot \underline{T}) \cdot \underline{u}$$

Finally, by defining the dynamical matrix  $\underline{D}$  as:

$$\underline{D} = \underline{m}^{-1/2} \cdot (\underline{R} - \underline{T} \cdot \underline{S}^{-1} \cdot \underline{T}) \cdot \underline{m}^{-1/2}$$

and

$$\underline{u} = \underline{m}^{-1/2} \cdot \underline{n}$$

we get

$$\omega^2 \underline{n} = \underline{D} \cdot \underline{n}$$

which is now an eigen-vector problem and hence the frequencies can be calculated by diagonalising the dynamical matrix. However, the phonon frequencies are dependent on the wave vector, so to determine the phonon density of states, we need to calculate the frequencies over all possible wave vectors.

The need to calculate the frequencies for all wave vectors is overcome in part by determining only those frequencies on a three-dimensional mesh of points within the Brillouin zone, using an appropriate weighting factor. The weighting will depend on the number of times a point appears in the Brillouin zone, thus the zone centre,  $q=(0,0,0)$ , which appears only once, will have a weighting factor of one, whilst  $q=(0.5,0.5,0.5)$  for an orthorhombic crystal, will have a weighting factor of eight. Fortunately the thermodynamic properties converge rapidly with the size of the mesh, for temperatures above 50K. For the range of materials that have been considered so far, there is little difference in the magnitude of the thermodynamic properties for meshes containing more than eight distinct points. The failure at very low temperatures is because acoustic phonons with wave vectors close to the zone centre are the only thermally excited modes, and thus a fine mesh is needed in this region to determine correctly the phonon frequencies and so the thermodynamic properties. This difficulty may be overcome by the use of so-called "uneven sampling" techniques which give an appropriate weighting to wave vectors near the zone centre. Once the phonon frequencies have been determined for points within the irreducible Brillouin zone, we can calculate the thermodynamic functions  $E$ ,  $S$ ,  $F$  and  $C_v$ , i.e. the vibrational energy, entropy, free energy and heat capacity, respectively, using the appropriate weighting factors. They are determined from the following expressions, for a set of harmonic oscillators:

$$E = kT \sum_i^M \left( \frac{x}{2} + \frac{x}{e^x - 1} \right)$$

$$S = k \sum_i^M \left( -\ln(1 - e^{-x}) + \frac{x}{e^x - 1} \right)$$

$$F = kT \sum_i^M \left( \frac{x}{2} + \ln(1 - e^{-x}) \right)$$

$$C_v = k \sum_i^M \left( \frac{x^2 e^x}{e^x - 1} \right)$$

where each is summed over the total number of phonon frequencies,  $M$ , and where  $x = \hbar\omega_i/kT$ . The zero point energy  $\sum \hbar\omega_i/2$  is also included in the vibrational energy and free-energy. In addition, the phonon density of states can be calculated.

This then gives the thermodynamic functions for the strain free crystal structure. However, we also need to include thermal expansion (which, of course, is zero within the harmonic approximation) in order to determine the crystal structure at a given temperature. The quasi-harmonic approximation is then used to calculate the volume dependence of the thermodynamic and structural properties. For example the kinetic pressure is simply the derivative of vibrational free energy with respect to volume. Thus for a cubic material:

$$P_k = dF/dV$$

and is determined by calculating the free-energy at a given volume and then recalculating  $F$  after making a small adjustment  $dV$  to the cell volume.

Once the kinetic pressure is evaluated, the constant pressure energy minimisation technique can be employed for predicting the thermally equilibrated structure, except that the total pressure is now defined as the sum of the kinetic, mechanical and hydrostatic pressure. The problem becomes slightly more complicated for non-cubic materials as the volume will not expand isotropically. For these systems we have to consider six different strain components. However, the same approach is utilised but with a small strain applied in each of the different directions and hence the kinetic pressure becomes the difference in free-energy for each component:

$$P_{kj} = \frac{1}{V} \frac{dF}{de_j}$$

and from the kinetic pressure and the elastic constants we are in a position to determine the resulting strain with which to perform a constant pressure energy minimisation. During the minimisation, each atom

position is adjusted so that it remains at a potential energy minimum, by performing a constant volume energy minimisation, each time the cell volume is modified. This is to reduce the possibility that an atom will be moved to a position where the harmonic approximation will breakdown, such as at a potential energy maximum, leading to imaginary frequencies. Thus by minimising to constant pressure and including the vibrational component of the free-energy, the crystal structure at a given temperature can be predicted.

We use a further approximation in the simulation, by assuming that the vibrational component to the elastic constants is small and hence can be neglected. Recent work by Harding has indeed shown this approximation to be reasonable. The technique outlined above, which is the basis of the computer code PARAPOCS, is used to calculate the thermal expansion coefficient; one approach is to evaluate the crystal structure at two finite temperatures, and simply determine the change in volume, i.e.

$$\beta = - \frac{1}{V} \frac{dV}{dT}$$

which is analogous to the experimental technique of dilatometry in which a small change in volume on heating is measured. An alternative approach is to use standard thermodynamic functions requiring the thermal Gruneisen parameter,  $\gamma$ , the isothermal compressibility,  $K_T$  or the adiabatic compressibility,  $K_S$ , along with the heat capacities:

$$\beta = \frac{\gamma C_V}{K_T V} = \frac{\gamma C_P}{K_S V}$$

The thermal Gruneisen parameter can be determined from the change in frequencies with volume directly, by first calculating the mode Gruneisen parameters for each frequency:

$$\gamma_i = \frac{-d \ln \omega_i}{d \ln V}$$

The bulk, or thermal, Gruneisen parameter is evaluated by taking the average of the heat capacity weighted mode Gruneisen parameters:

$$\gamma = \frac{1}{C_v} \cdot \sum_i C_i \gamma_i$$

where  $C_i$  is the heat capacity for mode  $i$ . Similar expressions can be determined for non-cubic materials; Barron gives an excellent account for determining the properties for non-cubic crystals: i.e. the expansion coefficients in the  $j$ th direction are:

$$\alpha_j = \frac{d(\ln(l_j))}{dT}$$

and

$$\alpha_j = (s_{j1} \cdot \gamma_1 + s_{j2} \cdot \gamma_2 + s_{j3} \cdot \gamma_3) \cdot C_p/V$$

where  $l_j$  is the cell dimension in the  $j$ th direction and  $s_{j,k}$  is the elastic compliance tensor (the inverse of the elastic constant).

The biggest drawback as far as the present work is concerned is the neglect of anharmonic terms. These are expected to be not insignificant at high temperatures, especially at the cubic  $\rightarrow$  tetragonal transition (2370°C), near the melting point of ZrO<sub>2</sub> at 2600°C (approximately).

## Results

Our objective was to calculate the free energy of each polymorph as a function of temperature and thus obtain the transformation temperatures. Our first setback was the observation that at low temperatures both the tetragonal and cubic structures were found to have imaginary modes. This proved to be somewhat of a problem for equilibration at higher temperatures, (for example, within the known temperature range of their stability), because PARAPOCS cannot routinely handle imaginary modes, since these can have no physical contribution to the free energy. Thus equilibration at temperatures around the two phase transitions proved not possible and we had to consider other ways of investigating these transitions.

Our next step was to examine the displacements indicated by the eigenvectors of the imaginary modes. For the cubic fluorite structure, there were three modes corresponding to each of the cartesian axes. First, we displaced the oxygen ions along the directions of one set of eigenvectors (but by a magnitude somewhat less than that of the eigenvectors) and then performed a static lattice energy minimisation on this distorted structure. The final relaxed structure turned out to be exactly that of the equilibrated tetragonal symmetry structure. Thus, we have determined the mechanism of transformation from cubic to tetragonal symmetry. This occurs because of an instability in the cubic fluorite structure associated with the mode calculated to have an imaginary frequency.

Following on from this, we displaced the (oxygen) ions in the tetragonal structure, in the directions implied by the eigenvectors of imaginary eigen-frequencies and performed a similar static lattice relaxation to the one just described. The final relaxed structure turned out to be exactly that obtained by equilibrating the crystallographic monoclinic structure. Thus the two transformations would appear to have similar origins.

This apparently conflicts with the established wisdom, with regard to the tetragonal  $\rightarrow$  monoclinic transformation. However, the tetragonal structure can only be stabilised at temperatures below 1170°C through the incorporation of dopants. One might speculate that this would alter the lattice dynamics of the phase transition. We would argue that it is the lattice instability that underlies the martensitic nature of the  $t \rightarrow m$  transformation. The monoclinic structure has a very low tolerance for dopant additions: its solid solution compositional range is extremely narrow (around 1%). The lattice instability means the transition will occur very rapidly, thus giving the dopants no time to exsolve. We believe, based on our current results, that the martensitic nature is part governed by kinetics. We would not expect the 100% pure  $ZrO_2$  material to show a martensitic  $t \rightarrow m$  transformation.

#### Effects of Dopant Additions

Obviously, a way to investigate the role that foreign cations play in stabilising the high temperature structures is to build a supercell and just substitute some other cation, say calcium, for some of the zirconium ions.

The supercell approach is necessary here because PARAPOCS is a perfect lattice code. (Alternatively, codes that calculate local vibrational modes around defects might also be used).

We initially set up a doubled cell and replaced one of the Zr by Ca (and introduced an oxygen vacancy for charge balance). This had the interesting effect of removing the imaginary modes that were originally present, but, because of the lowering of symmetry, other imaginary frequencies were introduced.

Our next thought was to consider the effect on the normal mode frequencies if one treated all the cations as an average of (Zr + Ca), thus retaining the cubic symmetry. Replacing 1 Zr in 8 by Ca reduces the charge on the cations from a nominal 4+ to a nominal 3.75+. The charge on the oxygen ions were similarly scaled, as were the masses of the ions. With this concentration of dopants, the structure was equilibrated at a temperature of 600K (more about temperature later on). The imaginary frequencies that had been present earlier now disappeared. This strongly suggests that it is the effective charge on the dopant that is responsible for stabilising the cubic phase, rather than just the ion size. Earlier, we had argued that, in the case of Ca, the size of the ion forces the oxygen lattice to be cubic in the vicinity of the dopant, and that when sufficient dopants were added to ensure that the local cubic symmetries associated with each dopant overlapped, one would have a stabilized cubic structure. This argument was based on calculations of the defect structure of Ca doped zirconia (Phil. Mag. in press), but does not easily explain why Mg also stabilises the cubic phase, because the ionic radii of  $Mg^{2+}$  and  $Zr^{4+}$  are very similar. However, both Ca and Mg have the same effective charge and we would thus expect them to have a similar effect in stabilising the cubic structure. Work on this is in progress at Alfred.

Next, we reduced the amount of "dopant" to a nominal 6.25% by increasing the ion charges (and the masses). At the same temperature, the imaginary frequencies were still present, indicating that this was not a sufficient concentration to stabilise the cubic structure. However, this concentration was enough to stabilise the tetragonal structure. These results are consistent with the experimental phase diagram for temperatures around 1750°C, approximately. (We did not have time to explore further these effects; this would obviously be a worthwhile exercise, though).

## Temperatures Effects

The differences between the temperature used in these calculations, 600K, and the approximate experimental equivalent, 2000K, needs further discussion. The calculations did not converge at higher temperatures. We believe that this is because the elastic properties predicted from the potential model are too stiff ( $C_{11}$  is too large). Free energy calculations are a rather severe test of interatomic potentials and the difference of 50% (61 GPa calculated v. 42 GPa measured) for  $C_{11}$  means that the balance between static and kinetic pressures will be attained at lower calculated temperatures than would be measured. It might also be noted that an error of only 0.02eV translates into a temperature difference of about 200K. Thus we should not expect too much in this regard from our potential model. It would be an interesting exercise to see how much improvements to the interatomic potential would be reflected in the temperatures emerging from the calculations.

A final point concerns the actual limitation of the theory behind the calculations. The phonon modes were calculated in the quasi-harmonic approximation which is almost certainly not applicable at temperatures much above the Debye temperature.

Our results, indeed, suggest that this will be a limitation to successful high temperature simulations, especially in the vicinity of the cubic  $\rightarrow$  tetragonal phase transition at 2370°C.

Our results here indicate that anharmonic effects lead to the stability of the cubic phase in pure  $ZrO_2$  which may exhibit a considerable degree of static disorder around the oxygen sites in addition to the thermal motion to be expected. Further work, both theoretical and experimental (e.g. in-situ diffraction studies), are suggested for this problem.

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# Molecular dynamics method

Publication and citation patterns of a research specialty of  
computer simulations

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## Summary

Publication and citation indicators are used to analyse quantitatively the scientific communication in the research specialty "Molecular dynamics (MD) method". The study is based on a bibliography of about 1000 papers published during the four-year period 1982-1985 and the citations of 1982-1987 to these papers. By means of a coherent set of scientometric indicators we characterize both the time series of such indicators (especially the citation impact) and several bibliometric distributions (authors' performance, journal productivity). Moreover, we interpret the influence of fundamental MD papers by means of their citation histories.

## 1. Introduction

In this journal it is not necessary extensively to explain the role of simulation methods in condensed matter studies. On the supposition that a time interval of some picoseconds is enough to learn the main structural and dynamical properties of many particle systems, one models the trajectories of the constituents - atoms and atom groups of matter under consideration - on the computer. Beginning with the source papers of Alder and Wainwright [ 1 ], Rahman [ 2 ], Rahman and Stillinger [ 3 ] has now the molecular dynamics method a well established position within physics, chemistry, and molecular biology. The jump from theoretical research to practical applications is now done [ 4 ].

Only the application of the MD method allows the study of specific aspects of atomic motions - in structureless liquids and complicated proteins. The development of the MD method is tightly connected with the increasing potential of computing techniques. Two main tendencies can be observed:

(i) The high degree of parallelism in supercomputers needs the development of a new type of software and

(ii) the available chips for low prices makes it possible to construct special purpose computers.

Up to now it is not clear what real value the special purpose computers will have in the future on simulation methods.

During the last 10 - 15 years quantitative methods of research evaluation have occupied an important position in research management and science policy. Among other approaches, the quantitative and statistical analyses of scientific literature play an important role to assess the output, i. e. the results of basic research. In 1969 the term "scientometrics" (naukometrija) was created including all kinds of quantitative analyses of the generation, propagation, and utilization of scientific information [ 5 ].

According to the original definition "scientometrics" refers to "those quantitative methods which are dealing with the analysis of science viewed as an information process". Restricting to such fundamental formal units of scientific communication as publications and citations of scientific papers, we suppose explicitly that research results are primarily published in journals and that we can use the citation frequencies of corresponding papers as a measure for the attention paid by scientific communities (or also as a measure of impact, utility, importance or quality). In spite of different publication and citation habits in different fields of science, we can start from the assumption that the mentioned suppositions are generally fulfilled in physics and other fields.

Extensive quantitative studies of the structure and dynamics of science require the possibility of online searches in databases containing bibliographic information on published scientific literature, the availability of appropriate software for statistical analyses and the application of a system of sciento-

metric indicators which allow a reflection of structural and evolutionary aspects of science as well.

By counting the total of articles per year on a particular subject and recognizing the changes in the following years, one can already get a good impression of the varying interest within the research community. By examining papers that become highly cited shortly after publication, one can often realize the so-called "hot spots" in science - areas of research that are actually of special interest to scientists. These highly cited papers are sooner or later cores in research front specialties. Particularly the technique of co-citation analysis has proven to be a powerful tool in studying the specialty structure of science [ 6,7 ].

It is a well-known fact that publication and citation patterns tend to be quite different in the various fields of science and within one field they differ from one research front to another. Therefore, it seems to be a practicable way to eliminate cross-field biases as far as possible to introduce relative indicators of publication performance and citation impact. In the present study we analyse the evolution of the application of MD simulations in science by means of a system of simple publication and citation counts on the one hand and relative indicators on the other hand. Such indicators were also used in other analyses [ 8-10 ]. In order to calculate scientometric indicators, we combined data from two bibliographic databases (INSPEC and Science Citation Index) in this way exploiting the advantages of several types of scientific information.

## 2. Data sources

It should be noted that only in 1982 the term "Molecular dynamics method" became a preferred term in the INSPEC Thesaurus, i. e., 25 years after Alder and Wainwright's first MD paper. The annual number of papers indexed by this term is represented in Fig. 1.

Our scientometric study is based on a comprehensive bibliography of MD papers for the four-year period 1982-1985 (publication years) compiled by computer-assisted searches in INSPEC and complemented by data from Physics Abstracts and the printed version of the Science Citation Index (SCI) of the Institute for

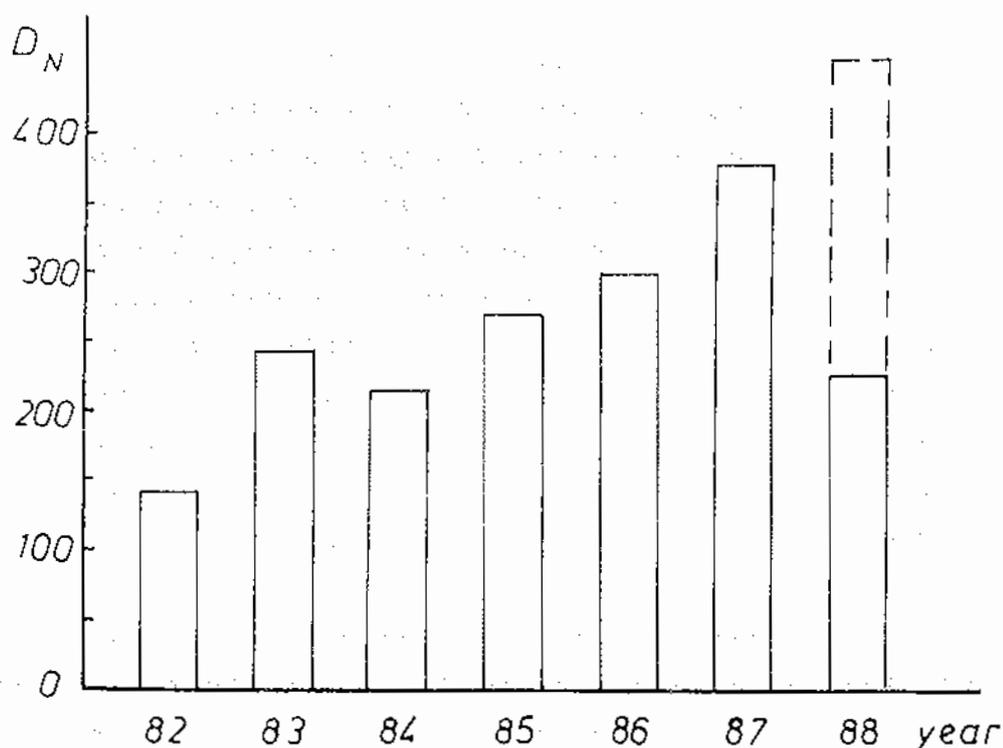


Fig. 1: Annual number of MD papers in INSPEC indexed by the term "Molecular dynamics method" (The frequency of the year 1988 was extrapolated from the first six months.)

Scientific Information (ISI, Philadelphia, PA, USA). We emphasize that the bibliography is not complete, because - as a random test showed - not every relevant paper was indexed in fact by the key word "Molecular dynamics method" or a related term. Under these circumstances, our sample size includes 1008 publications for the given period.

The citation data have been collected by manual search from the 1982-1987 Citation Index volumes of the SCI as well as the 1984-1986 SCI Journal Citation Reports (JCR). Thus, the following data have been used as a source of scientometric indicators:

1. the bibliographic data of 1982-1985 publications,
2. the 1982-1987 citations (altogether nearly 4200 citation frequencies) received by the subset of journal articles also indexed in the SCI, and
3. the journal impact factors according to the JCR.

### 3. Results of the analyses

#### 3.1. Publication activities

Among the 1008 papers published within the period 1982-1985 there are 976 journal articles mainly as letters, notes, original papers, and review articles in SCI source journals (Tab. 1). Non-journal items (contributions in monographs etc.) constitute only a small fraction of publications.

The authors are affiliated with research institutions in 27 countries (Tab. 2); on an average 2.3 authors contributed to one paper. If scientists from several countries published one paper,

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Tab. 1: Publication activities during the period 1982 - 1985

year	number of publications	number of journal articles	among them in SCI journals
1982	189	182	181
1983	276	267	261
1984	253	238	235
1985	290	289	281
sum	1008	976	958

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this was assigned to that country appearing in the corporate address of the first author.

The publication performance reflects the supremacy of some few countries in application of MD simulations; already scientists from five countries published more than 70 per cent of papers.

Many empirical investigations have shown that theoretical as well as methodological papers are often widely spread in classification schemes of bibliographic databases. This is also valid for papers on MD on the account of their various applications. By means of the classification of MD papers in INSPEC (especially in Section A: Physics) one can get a state-of-the-art survey on MD applications. To complete our data, we classified also papers searched in the SCI database according to the INSPEC classification scheme; Tab. 3 lists the summarized results.

Although corresponding findings from the past are not available, two conclusions can be drawn: Firstly, the increasing

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 Tab. 2: Number and proportion of publications by countries  
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rank	country	number of publications	proportion of the world's total (%)
1	USA	362	35.91
2	United Kingdom	150	14.88
3	F.R.Germany	77	7.64
4	USSR	73	7.24
5	Japan	61	6.05
6	Canada	47	4.66
7	France	47	4.66
8	Australia	37	3.67
9	Netherlands	33	3.27
10	Italy	30	2.98
11	Spain	14	1.39
12	Denmark	11	1.09
13	Israel	11	1.09
14	India	9	0.89
15	Sweden	7	0.69
16	Austria	7	0.69
17-27	others	31	3.08

=====  
 importance of MD methods to simulate complex systems (e.g. in biophysics) is obvious, and secondly, MD computations dominate further on in theoretical studies of structure of condensed matter.

### 3.2. Bibliometric distributions

Various phenomena in scientific communication and library science can be described by regularities that one can formulate mathematically. Both deterministic and stochastic models are appropriate to reflect such phenomena.

Within the framework of stochastic methods bibliometric distributions hold an outstanding position. E.g. one can model the distribution of scientific papers in periodicals, the distri-

bution of individual scientific productivity (e.g. the frequency distribution of authors with 1, 2, 3 ... papers in a given

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 Tab. 3: Applications of MD simulations  
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subject field	percentage of publications(%)
-----	
condensed matter physics	
- structure of liquids and solids	40.8
- mechanical and acoustic properties	2.0
- lattice dynamics	
- equations of state, phase equilibria, and phase transitions	9.3
- thermal properties	1.1
- transport properties (nonelectronic)	6.6
- surfaces and interfaces	5.9
- optical properties and spectroscopy	2.9
kinetic and transport theory of fluids	2.7
physical chemistry	3.8
biophysics	7.9
computer algorithms	2.0
other applications	12.5
=====	

period) and the distribution of citation frequencies of publications.

Already simple hyperbolic Zipf-type distributions

$$P(X=i) = \text{const.} / i^\beta$$

$$i = 1, 2, 3, \dots$$

$\beta$  - positive real number

are suitable to describe peculiarities of different social phenomena as the scaling invariance in hierarchically ordered structures (e.g. scientific communities) [ 11,12 ].

### 3.2.1. Lotka's distribution of scientific productivity

A. J. Lotka was ostensibly the first to attempt a measure for the inequality of scientists' productivity. In an article published in 1926, he counted the number of articles by authors

The first part of the document discusses the importance of maintaining accurate records of all transactions. It emphasizes that every entry should be supported by a valid receipt or invoice. This not only helps in tracking expenses but also ensures compliance with tax regulations.

In the second section, the author provides a detailed breakdown of the company's revenue for the quarter. It includes a comparison between actual performance and the budgeted figures. The analysis shows that while sales volume was slightly below expectations, the average price per unit was higher than planned, which helped offset some of the revenue shortfall.

The third section focuses on the company's operational costs. It identifies areas where expenses have increased, such as raw material prices and utility costs. The author suggests that implementing more efficient production processes and negotiating better terms with suppliers could help reduce these costs in the future.

Finally, the document concludes with a summary of the overall financial health of the company. It notes that despite some challenges, the company remains profitable and well-positioned to meet its long-term goals. The author encourages the management team to continue monitoring key financial indicators and to make data-driven decisions to ensure sustained growth.

[13]. In particular, he plotted the frequencies of persons having 1, 2, 3, ... contributions, against these numbers 1, 2, 3, ... of contributions, both on a logarithmic scale; he found that the points were closely scattered across an essentially straight line having a slope value of approximately two. This procedure we will also apply.

Since our bibliography contains many papers with multiple authorship (altogether 78 per cent), the authors' publication performance was evaluated by two measures: whereas the "normal count" procedure allocates full credit to all contributors of a publication (unweighted number of articles), the "adjusted count"

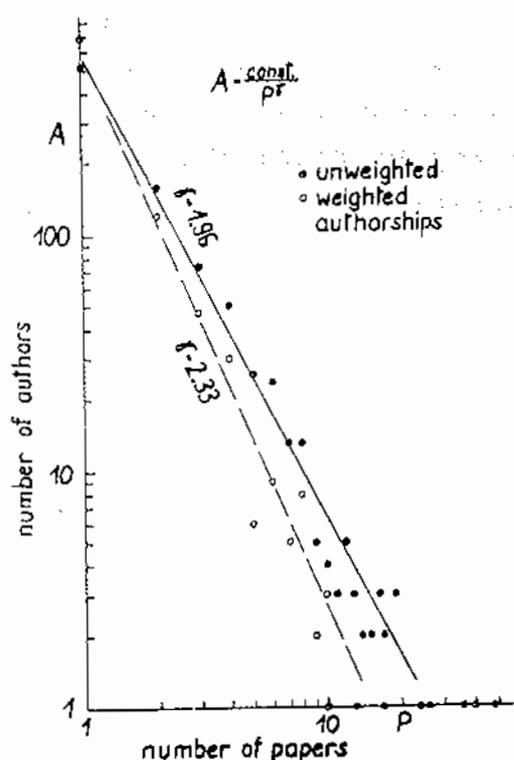


Fig. 2: Distribution of individual performance (Lotka's law)

procedure takes into account the partial contribution of scientists, i.e., for a paper written by  $n$  authors, each author is credited  $1/n$  authorships [14]. We did not exclude such points from the observed data distribution representing both, most prolific authors and low-productive scientists (for our example, among 924 authors, 521 published only one paper).

Nevertheless, the frequency distributions of authors' performance fit Lotka's model ( $A$  - number of authors,  $P$  - number of publications) for unweighted as well as for weighted author-

ships (Fig. 2). In order to calculate the slope  $\beta$  of the regression line, we used the linear least-square method in this study.

### 3.2.2. Scattering of journal articles

If the sources in a bibliography are ranked in decreasing order of productivity, a semilogarithmic plot of the cumulative total of papers vs. the journal rank (Bradford representation) yields in many cases a characteristic stretched S-shape curve (e.g. [ 15-17 ]).

Fig. 3 shows the Bradford's plot of the data taken from Tab. 4. It contains a sample of 978 MD papers scattered among 156 journals. The diagram represents a special class of Bradford-type curves mentioned above, i.e., the resulting graph is concavely increasing and at some point the curve turns to a straight line. According to Bradford this first segment of the curve - the nucleus zone - is corresponding to the most productive journals of the chosen subject field. At some second point the curve drops off, the so-called "Groos droop" appears [ 18 ]. In our example,

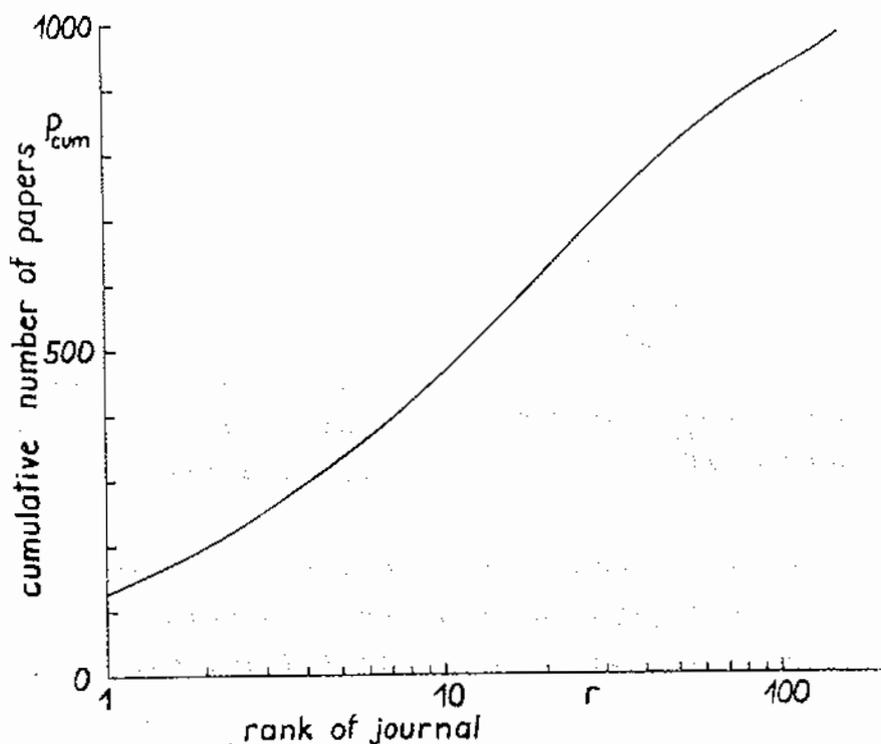


Fig. 3: Distribution of relevant papers on the given subject vs. the rank of the journal in the order of decreasing productivity (Bradford representation)

the nucleus zone contains 9 journals publishing 45.3 % of MD papers. Two thirds of journal articles were published in 24 periodicals as particularly listed in Tab. 4. In comparison with that, in 90 journals only one or two papers were published .

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 Tab. 4: Bradford distribution - share of major journals  
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rank	journal	number of papers	cumulative number of papers
1	J. Chem. Phys.	124	124
2	Mol. Phys.	86	210
3	Chem. Phys. Lett.	45	255
4	Phys. Rev. B	44	299
5	Phys. Rev. A	37	336
6	Phys. Rev. Lett.	32	368
7	Surface Sci.	28	396
8	J. Phys. C	25	421
9	Abstr. Papers ACS	22	443
10	J. Phys. Chem.	21	464
11	Phys. Lett. A	18	482
12	Chem. Phys.	17	499
13	J. Mol. Liquids	17	516
14	Physica A	17	533
15	J. Non-Cryst. Solids	16	549
16	J. Phys. Soc. Japan	15	564
17	Biophys. J.	15	579
18	J. Chem. Soc. Faraday Trans. II	13	592
19	J. Physique	11	603
20	Z. Naturforsch. A	11	614
21	Physica B + C	11	625
22	Comput. Phys. Commun.	10	635
23	Fiz. Tverd. Tela	10	645
24	Sol. State Commun.	10	655
25-156	others	323	978

=====

### 3.3. Citation indicators

The use of citation analysis as a research methodology in the quantitative science of science is based on the assumption that bibliographic citations give an acceptable picture of the actual influence of publications on the advance of scientific knowledge, but not necessarily for their "quality" or "importance". In order to eliminate field differences concerning citation habits, we use a set of citation indicators which has been introduced some years ago for comparative evaluations of scientific activities of research units [ 8-10 ]. To calculate such indicators, the two-year publication outputs (1982-1983, 1983-1984, 1984-1985) were analysed by counting the 1984, 1985, and 1986 citations, respectively, to these publications. This conforms to the procedure applied in the annual JCR in calculating the journal impact factors <sup>1)</sup>. The journal impact factor is this journal. For any set of publications in different journals, the expected number of citations is consequently defined as the weighted number of impact factors, where the number of publications in a specified journal is the weighting factor.

For a two-year publication output, the observed number of citations is the actually received total sum of citations in the immediately following year.

The relative citation rate  $c_{rel}$  is the ratio of the observed to the expected number of citations. Values  $> 1$  ( $< 1$ ) indicate that papers of a given set are more (less) frequently cited than the average of the journals in which they were published. Particularly by means of this indicator we can overcome difficulties concerning field differences in citation habits. The values for  $c_{rel}$  in Tab. 5 demonstrate that MD papers, generally spoken, are integrated into the "normal" communication pattern of science that can be characterized by  $c_{rel} = 1$ . It could be shown that  $c_{rel}$  is much more than 1 [ 19-21 ] for new research specialties in physics which are of topical interest.

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<sup>1)</sup>The impact factor of a journal calculated yearly by ISI is a measure of the average number of citations in a certain year (say 1985), to articles published in that journal in the past two years (1984 and 1983).

The definition of the journal impact factor by Garfield is consistent, because on an average a scientific paper reaches its maximum citation frequency 1-2 years after publication [ 22 ]. On

Tab. 5: Citation indicators

year	observed number number of citations	expected number of citations <sup>x)</sup>	relative citation rate
1984	1044	1021	1.02
1985	1421	1258	1.13
1986	1154	1175	0.98

x) rounded values

the other hand, the citation histories of many pioneering scientific publications contrast sharply with those of an average research paper.

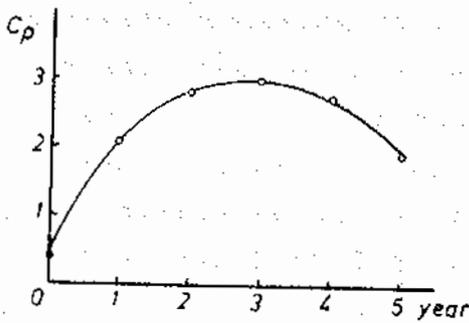


Fig. 4: Mean value of citations per paper in the year of publication and during the following years

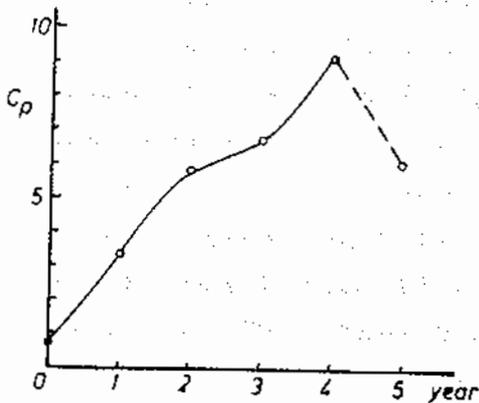


Fig. 5: Application of MD simulations in biophysics: specific aging of the literature

Taking into account all the 958 MD papers published in SCI source journals and calculating the mean citation rate per publication  $c_p$  in the year of publication and the following five years (Fig. 4), we obtain a time series of the ageing (or obsolescence) of literature. One can notice that  $c_p$  shows a rapid rise in the first two years with a not distinct citation peak in the third year after publication; in the fifth year a decrease of  $c_p$  can be observed.

This picture is more differentiated if we analyse the specific obsolescence of literature on special MD applications. Fig. 5 shows the annual citation frequencies of the subset of papers on MD computations in biophysics. (The final value of  $c_p$  is not statistically significant.) The resulting curve illustrates both the "above-the-average" citation of these articles and the unusual ageing of literature.

#### 4. Historical notes and citation histories of fundamental MD publications

After the first publication of Alder and Wainwright [ 1 ] similar works started also in other countries. Even at the beginning of the sixties there have been active groups working in the field of simulation methods in the Soviet Union, e.g. in Leningrad, Moscow and Kiev. Different circumstances prevented the acceptance of the work of these groups. Now, we only can see that methodically important publications could not act to the necessary extent. One example: Already in 1972 Balabayev, Grivzov and Snol published a very effective algorithm for molecular dynamics simulations for systems with constraints [ 23 ], and in 1975 they presented results for the simulation of chain molecules [ 24 ]. Only some years later the papers of Ryckaert et al. [ 25 ] and von Gunsteren and Berendsen [ 26 ] were published as the methodical basis of the well-known SHAKE-algorithm. The influence of the latter publications on the acceptance of the MD method, especially in macromolecular science, can be seen in Figs. 6 e), f).

In his cumulative advantage concept Price suggested that "a paper which has been cited many times is more likely to be cited again than one which has been little cited" [ 27 ], i.e. that highly cited papers age more slowly with elapsed time than less cited papers. Especially key publications have a much longer

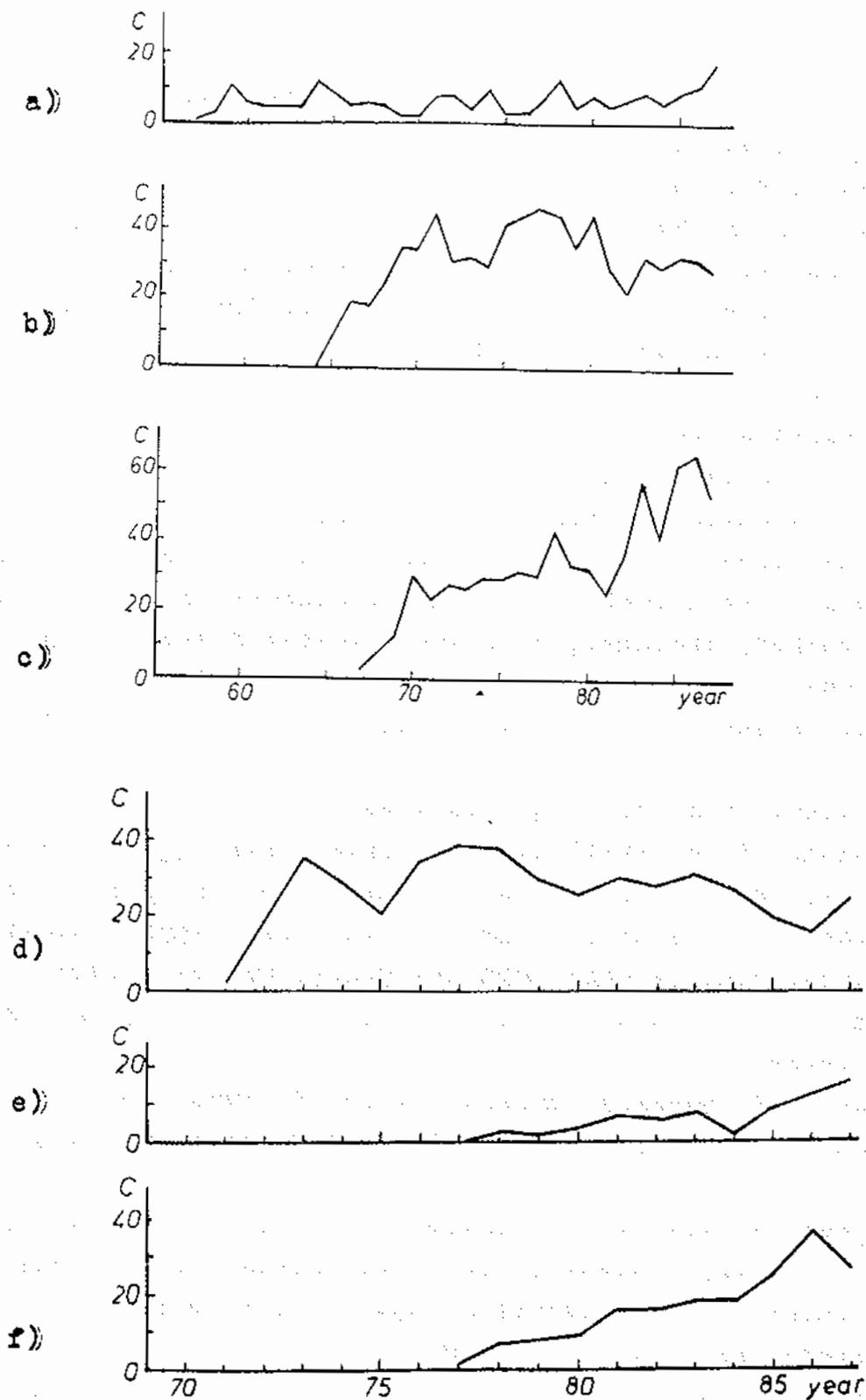


Fig. 6: Citation histories of some fundamental MD papers  
 (a) Alder and Wainwright [1], (b) Rahman [2], (c) Verlet [28], (d) Rahman and Stillinger [3], (e) van Gunsteren and Berendsen [26], (f) Ryckaert et al. [25]

citation life than normal scientific papers, and sometimes they are characterized by unusual longevity. This applies also to some papers mentioned above; their citation histories are illustrated in Fig. 6.

In all cases the continuous influence of these fundamental contributions to MD simulations is remarkable. The most cited papers are those by A. Rahman [ 2 ], cited 728 times, and by L. Verlet [ 28 ] which achieved 696 citations.

## 5. Conclusions

The presented results of scientometrical observations in the field of molecular dynamics method show the specific power of statistical studies and the use of bibliometric distributions to characterize front fields in science. In a sufficient manner could be shown structural and dynamical aspects in the evolution of the MD method, including some non-expected developments.

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# Fortran Computing speed of SUN 3 systems with f68881 floating point processors

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Via use-net we received a useful message concerning a way to improve the speed of FORTRAN code on SUN 3 systems with the floating point processor f68881 which was written by Wayne Little of the University of Missouri-Rolla. Since a lot of users seem to have problems getting the manufacturer-specified speed out of their SUN 3 systems, we think it is useful to forward this information to others, although the idea is not ours.

At least some of the speed problems occur in large (scientific) FORTRAN codes involving complex\*16 arithmetics. Two small test codes showed that all of the speed gain through the use of the f68881 processor in complex arithmetic vanishes if the code uses explicit complex\*16 declarations instead of double real\*8 arrays. The problem was tracked down to inefficiency of stack-data transmission and the proposed solution to this problem is extremely simple and effective:

The data traffic can be reduced by the use of an (assembly level) in-line expansion library. This library contains assembler routines that can be incorporated in the FORTRAN code by in-line substitution. The reason for the large data traffic and the idea to use in-line expansion in order to avoid it, can be found in the SUN Floating-Point Programmer's Guide (volume 10, appendix G).

The *only* necessary adaptation one has to make is in the compiler options (possibly in the "make" file). The option of f77 to be added is the library 'libm.il' which can be found (for SunOs) under '/usr/lib/f68881/libm.il'.

The compiler can be invoked for example like:

```
f77 -c -u -O -o name name.f /usr/lib/f68881/libm.il
```

Or the "make" file could look like this:

```
OBJECTS = name.o  
FFLAGS = -c -u -O /usr/lib/f68881/libm.il  
name : $(OBJECTS)  
-- > f77 $(FFLAGS) $(OBJECTS) -o name
```

The results of this little change vary from speed gains of a factor 2 for code without complex arithmetic (probably due to more efficient optimisation) up to gains of a factor 4.8 for codes with mainly complex\*16 arithmetic. On average we found that our SUN 3/60 with f68881 is a factor 64 slower than the IBM 3090 of SARA in Amsterdam for

code without complex\*16. If we compare this with the list of times needed for a molecular dynamics program published in volume 31 of this quarterly written by D. Brown et al., where the speed ratio between both systems is 111.4; we are inclined to think that their test has been performed without the use of the in-line expansion library. With the in-line library we expect that the SUN 3/60 will take something like 1350 seconds and will be considerably faster (as expected) than the COMPAQ 386-20 rated with 1821 seconds.

We hope that other users may benefit from the suggestions of Wayne Little and that readers will not have the impression that we are trying to get a bonus from SUN MICROSYSTEMS INC.

## Additional Supercomputing Related Papers

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In addition to the Fincham Bibliography (Info. Quart., No. 31, Oct. 1989), some of these papers also contain original information on vector and parallel processing issues involving molecular dynamics simulation methodology.

1. O. Teleman and B. Jonsson, Vectorizing a General Purpose Molecular Dynamics Simulation Program, J. Comput. Chem., 7, 58-66 (1986). (This paper makes some interesting points about vectorization of chain molecules simulation.)
2. A. Wallquist, B. J. Berne, and C. Pangali, Using Supercomputers - Two Examples from Chemical Physics, Computer, May 1987, 9-20. (This paper discusses problems involved in the vectorization of fluids modeled using site-site potentials.)
3. H. L. Nguyen, H. Khanmohammadbaigi, and E. Clementi, A Parallel Molecular Dynamics Strategy, J. Comput. Chem., 6, 634-646 (1985). (Amongst other things, this paper discusses parallel processing when three-body potentials are involved.)
4. F. F. Abraham, Computational Statistical Mechanics: Methodology, applications, and supercomputing, Adv. Phys., 35, 1-123 (1986). (This is a review paper and offers a slightly different perspective of supercomputing than those discussed in the papers referred by the above bibliography of Fincham. I have also expanded this discussion in a paper published in the Proceeding of the 3rd International Conference on Supercomputing, Boston, MA, May 15-20, 1988.) A related paper by Abraham and coworkers is J. Phys. Chem., 91, 4881-4890 (1987) dedicated to Anees Rahman.

Ordinarily, I would not try to add more entries to an annotated bibliography. However, I do hope that an interested reader would find these papers to be complementary to the papers in the bibliography of Fincham.

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