

DARESBURY LABORATORY

# INFORMATION QUARTERLY

## for

# COMPUTER SIMULATION OF CONDENSED PHASES

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

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Editorial.

The recent visit to the U.K. by Professor B.J. Berne proved to be a highly successful venture. Those fortunate enough to attend one of the seminars arranged for Professor Berne's visit will surely have been impressed by his expertise and profound knowledge. It is a pleasure to thank him on behalf of CCP5 for the stimulating and arduous series of seminars he undertook for CCP5 and we hope he found the trip enjoyable. We should thank also those people at Cambridge, Oxford and London for helping to organise the local events and the participants themselves who travelled to the venues and helped make the venture successful. We will be reporting on the visit of Professor Berne in our next issue.

Meanwhile CCP5 continues to be an active project. Three workshops are being organised at present to cater for special areas of interest; these being Graphics, Ceramics and Transport properties. Announcements regarding these events have already been circulated to everyone on the CCP5 mailing list.

Lastly we thank our friends in the computer simulation community who have contributed the articles appearing in this month's issue. We are very pleased with the wide range of material that has been presented to us and we hope that our readers recognise the value of a willing public in producing such a newsletter!

Best wishes to all for 1985!

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### General News.

a) CCP5 is to collaborate with the Statistical Mechanics and Thermodynamics Group of the Royal Society of Chemistry in organising a two day meeting on: 'Dense Fluids: Dynamic and Static Properties' at Bristol in April 1985 (10th. - 11th.). Papers will be welcome in any of the following areas:

The computer simulation of time dependent properties and complementary theory.

The gas-liquid interface and surface induced phenomena, such as wetting; (papers on phase transitions in adsorbed monolayers are inappropriate).

Equilibrium properties of molecularly simple liquids and their mixtures.

The speakers who have agreed to attend so far include G. Stell (University of New York at Stonybrook), W. Steele (University of Pennsylvania), J.-P. Hansen (University of Paris) and R. Evans (University of Bristol).

The conference organisers see a particular role for some papers dealing primarily with experimental results, provided that such work is directly related to theoretical development and/or to simulation studies. Those interested should write to Mr. A. J. B. Cruickshank, School of Chemistry, The University of Bristol, Cantock's Close, Bristol BS8 1TS.

Readers may also be interested to know that CCP5 is also planning a meeting on 'Large Molecules and Stochastic Methods', which will take place in York in September 1985.

b) Future Applications of Atomistic Simulations in Ceramics. A workshop on this subject will be held at I.C.I. Runcorn on 17 th. and 18 th. January 1985. The workshop is being jointly organised by Dr. C.R.A. Catlow (U.L.C.) and Dr. W.C. Macrodt (I.C.I.). The meeting will begin with lunch on 17 th. and end at lunchtime on 18 th. Accommodation will be available for all participants for the night of the 17 th. The number of participants will be strictly limited. Anyone wishing to attend should contact Dr. C.R.A. Catlow, Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0J2, (Tel. 01-387-7050x441).

c) Transport Properties. A workshop on this subject is being organised by Prof. K. Singer and Dr. D.M. Heyes at Royal Holloway College for 10 th to 11 th. January 1985. Once again, the number of participants will be strictly limited. Accommodation has been arranged for participants for the night of the 10 th. Readers should note however that it is nominally already too late to apply for this meeting, though through cancellations etc. late entries may be permitted. Please contact Prof. K. Singer, Department of

Chemistry, Royal Holloway College, Egham, Surrey, (Tel. 0784-35351).

d) Daresbury Laboratory recently took delivery of a FPS 164 attached processor to augment the computing power available there. The FPS 164 is currently connected to the NAS AS5000 (itself a recent addition to Daresbury) and is expected to become available through the NAS AS7000 mainframe in March 1985. Information on the availability of the machine will be circulated to CCP Chairmen and other notables shortly.

e) At the Rutherford and Appleton Laboratory, the split of the Computing Division into the Central Computing Division (under Dr. C. J. Pavelin) and the Informatics Division (under Prof. F. R. A. Hopgood) announced in our last newsletter has taken place. The post of Director of S.E.R.C. Computing, recommended by the recent 'McFarlane Report' on computing in the S.E.R.C., has been awarded to Dr. Brian Davies, the former Head of Computing at Daresbury.

R.A.L. intend to introduce the IBM MVS batch service on their mainframes in early December 1984. The current MVT service will then run overnight and will be discontinued not later than March 1985. The supported compilers will be VS FORTRAN and Extended-H. R.A.L. is to circulate a conversion guide to users on the changes before the intended switch to MVS.

Other changes scheduled for December 1984 include the replacement of the FR80 graphics device by the XEROX Laser Printer and the NCR 5330 microfiche recorder and the final deletion of the ELECTRIC filestore following the switch-off in 1983.

From R.A.L. we learn that Argonne National Laboratory has acquired a Denelcor HEP multiprocessor computer and are looking to encourage research on the machine by considering applications for resources. Anyone interested should contact Bob Maybury, R.A.L. User Support and Marketing Group.

Lastly, R.A.L. are updating their documentation distribution database INFO. To this end they have sent out forms to all addresses on the database to assess its accuracy. Users should respond to this if they do not wish to be deleted from the database!

f) Users of the University of London Computing Centre should note that the new Cray Is FORTRAN compiler CFT 1.13 is available for trial. The new compiler offers improvements in execution speed of up to 10 percent, due to a new instruction scheduler. (For example indirect addressing within loops, of the SCATTER and GATHER type, no longer inhibit vectorisation). Re-entrant code for multi-tasking is also available. Further details are in the December issue of the U.L.C.C. newsletter.

CCP5 members, who are also users of U.L.C.C. may be interested in the Statistical Analysis System (SAS) available there. This is a commercial package of software which has capabilities a simulator may consider exploiting. Two recent additions to the SAS package include SAS/ETS and SAS/GRAPH. These allow the analysis of time series data (multivariate autoregressive and spectral analysis etc.) and some sophisticated plotting. Information is available from program advisory. This package of programs is also available at Daresbury.

Users curious or confused about resources management at U.L.C.C. should consult their December newsletter, in which a detailed account of the 'Allocation and Control of Computer Resources' is presented.

g) The University of Manchester Regional Computing Centre has received the CYBER 176 computer announced in our last issue. The computer is now available to users. It is accessed in practically the same way as the CDC 7600's and runs under the same Scope 2.1 operating system. Originally obtained to offset LCN degradation, the CYBER 176 offers 112K SCM and 186K LCM thus permitting much larger jobs than the CDC 7600's. Taken altogether, the combined computing power available at U.M.R.C.C. is very impressive (i.e. Amdahl 470/V8, 2X CDC 7600, CYBER 176 and CYBER 205).

There are however still some problems to contend with. The CYBER 205 service is not all it should be; the FORTRAN 200 compiler has many known bugs and the machine appears heavily loaded at present. Also the MASSTOR system recently experienced problems and this resulted in long delays in restoring datasets. Time and effort will no doubt cure these frustrations.

h) Readers may be interested to know of a meeting on 'Molecular Replacement' being organised by our sister project CCP4 (Protein Crystallography). The meeting is to be held at Daresbury Laboratory on 15th. - 16th. February 1985. The speakers include D.M. Blow, T.L. Blundell, P. Brick, M. Buehner, E.J. Dodson, P.R. Evans, W.J.G. Hol, R. Huber, D.S. Moss and I.J. Tickle - clearly a lively meeting is likely! Anyone interested should contact Eleanor Dodson (094 59861 Ext. 343) or Pella Machin (0925 65000 Ext. 528) for further details.

i) Anyone wishing to make use of the CCP5 Program Library is invited to do so. Documents and programs are available free of charge to academic centres upon application to Dr. M. Leslie (\*) at Daresbury Laboratory. Listings of programs are available if required but it is recommended that magnetic tapes (to be supplied by the applicant) be used. Users wishing to send magnetic tapes are instructed to write to Dr. Leslie for information before sending the tape. PLEASE DO SEND TAPES WITHOUT CONTACTING DR. LESLIE FIRST. Delays are caused by applicants sending new tapes which have to be initialised at Daresbury (i.e. tape marks have to be written on

them). Also tapes sent in padded bags have to be cleaned before use. Please do not use this form of packing. (A list of programs available follows in the next few pages.)

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

\* (Full address: S.E.R.C. Daresbury Laboratory, Daresbury, Warrington WA4 4AD, U.K.)

List of Programs in the CCP5 Program Library.

MDATOM by S. M. Thompson.

M.D. simulation of atomic fluids. Uses 12/6 Lennard - Jones potential function and fifth order Gear integration algorithm. Calculates system average configuration energy, kinetic energy, virial, mean square force and the associated R.M.S. deviations and also system pressure, temperature, constant volume specific heat, mean square displacement, quantum corrections and radial distribution function.

HMDIAT by S. M. Thompson.

M.D. simulation of diatomic molecule fluids. Uses 12/6 Lennard - Jones site - site potential functions and a fifth order Gear algorithm for centre - of - mass motion. Angular motion is calculated by fourth order Gear algorithm with quaternion orientation parameters. Calculates system average configuration energy, kinetic energy, virial, mean square force, mean square torque and the associated R.M.S. deviations and also system pressure, temperature, constant volume specific heat, mean square displacement and quantum corrections.

MDLIN by S. M. Thompson.

M.D. simulation of linear molecule fluids. Uses 12/6 Lennard - Jones site - site potential functions and a fifth order Gear algorithm for centre - of - mass motion. Angular motion is calculated by fourth order Gear algorithm with quaternion orientation parameters. List of calculated properties is the same as HMDIAT.

MDLINQ by S. M. Thompson.

M.D. simulation of linear molecule fluids. Uses 12/6 Lennard - Jones site - site potential functions plus a point electrostatic quadrupole. Uses a fifth order Gear algorithm for centre - of - mass motion. Angular motion is calculated by fourth order Gear algorithm with quaternion orientation parameters. List of calculated properties is the same as HMDIAT.

MDTETRA by S. M. Thompson.

M.D. simulation of tetrahedral molecule fluids. Uses 12/6 Lennard - Jones site - site potential functions and a fifth order Gear algorithm for centre - of - mass motion. Angular motion is calculated by fourth order Gear algorithm with quaternion orientation parameters. List of calculated properties is the same as HMDIAT.

MDPOLY by S. M. Thompson.

M.D. simulation of polyatomic molecule fluids. Uses 12/6 Lennard - Jones site - site potential functions and a fifth order Gear algorithm for centre - of - mass motion. Angular motion is calculated by fourth order Gear algorithm with quaternion orientation parameters. List of calculated properties is the same as HMDIAT.

ADMIXT by W. Smith.

M.D. simulation of monatomic molecule mixtures. Uses 12/6 Lennard - Jones atom - atom potential functions and a Verlet leapfrog algorithm for centre - of - mass motion. Calculates system average configuration energy, kinetic energy and virial and associated R.M.S. deviations and also pressure, temperature, mean square displacements and radial distribution functions.

MDMIXT by W. Smith.

M.D. simulation of polyatomic molecule mixtures. Uses 12/6 Lennard - Jones site - site potential functions and a Verlet leapfrog algorithm for centre - of - mass motion. Angular motion is calculated by the Fincham leapfrog algorithm using quaternion orientation parameters. Calculates system average configuration energy, kinetic energy and virial and associated R.M.S. deviations and also pressure and temperature.

MDMULP by W. Smith.

M.D. simulation of polyatomic molecule mixtures. Uses 12/6 Lennard - Jones site - site potential functions and point electrostatic multipoles (charge, dipole and quadrupole). Long range electrostatic effects are calculated using the Ewald summation method. Uses a Verlet leapfrog algorithm for centre - of - mass motion. Angular motion is calculated by the Fincham leapfrog algorithm using quaternion orientation parameters. Calculates system average configuration energy, kinetic energy and virial and associated R.M.S. deviations and also pressure and temperature.

MDMPOL by W. Smith & D. Fincham.

M.D. simulation of polyatomic molecule mixtures. Uses 12/6 Lennard - Jones site - site potential functions and fractional charges to represent electrostatic multipoles. Long range electrostatic effects are calculated using the Ewald summation method. Uses a Verlet leapfrog algorithm for centre - of - mass motion. Angular motion is calculated by the Fincham leapfrog algorithm using quaternion orientation parameters. Calculates system average configuration energy, kinetic energy and virial and associated R.M.S. deviations and also pressure and temperature.

DENCOR by W. Smith.

Calculation of density correlation functions. Processes atomic M.D. data to produce the Fourier transform of the particle density, the intermediate scattering functions and the dynamic structure factors.

CURDEN by W. Smith.

Calculation of current density correlation functions. Processes atomic M.D. data to produce the Fourier transform of the current density, the current density correlation functions and their temporal Fourier transforms.

HLJ1 by D. M. Heyes.

M.D. simulation of atomic fluids. Uses 12/6 Lennard - Jones site - site potential function and a Verlet leapfrog algorithm for centre - of - mass motion. Calculates system average configuration energy and kinetic energy and associated R.M.S. deviations and also pressure, temperature, mean square displacements and radial distribution function.

HLJ2 by D. M. Heyes.

M.D. simulation of atomic fluids. Uses 12/6 Lennard - Jones site - site potential function and a Verlet leapfrog algorithm for centre - of - mass motion. Calculates system average configuration energy and kinetic energy and associated R.M.S. deviations and also pressure, temperature, mean square displacements, radial distribution function and velocity autocorrelation function.

HLJ3 by D. M. Heyes.

M.D. simulation of atomic fluids. Uses 12/6 Lennard - Jones site - site potential function and a Verlet leapfrog algorithm for centre - of - mass motion. The link - cell method is employed to enable large simulations. Calculates system average configuration energy and kinetic energy and associated R.M.S. deviations and also pressure, temperature, mean square displacements and radial distribution function.

HLJ4 by D. M. Heyes.

M.D. simulation of atomic fluids. Uses 12/6 Lennard - Jones site - site potential function and a Verlet leapfrog algorithm for centre - of - mass motion. The algorithm allows either the temperature or the pressure to be constrained. Calculates system average configuration energy and kinetic energy and associated R.M.S. deviations and also pressure, temperature, mean square

displacements and radial distribution function.

HLJ5 by D. M. Heyes.

M.D. simulation of atomic fluids. Uses 12/6 Lennard - Jones site - site shifted potential function and a Verlet leapfrog algorithm for centre - of - mass motion. This method removes the discontinuities at the potential cutoff radius. Calculates system average configuration energy and kinetic energy and associated R.M.S. deviations and also pressure, temperature, mean square displacements and radial distribution function.

HLJ6 by D. M. Heyes.

M.D. simulation of atomic fluids. Uses 12/6 Lennard - Jones site - site shifted potential function and the Toxvaerd algorithm for centre - of - mass motion. This algorithm is more accurate than the Verlet algorithm. Calculates system average configuration energy and kinetic energy and associated R.M.S. deviations and also pressure, temperature, mean square displacements and radial distribution function.

MCRPM by D. M. Heyes.

M.C. simulation of electrolytes. Monte Carlo program using restricted primitive model of an electrolyte. The potential is regarded as infinite for  $r < d$  and Coulombic for  $r \geq d$ . The properties calculated are the average configuration energy and its R.M.S. deviation, the pair radial distribution function and the melting factor.

SURF by D. M. Heyes.

M.D. simulation of model alkali halide lamina. Molecular dynamics simulation for ionic laminae using the Tosi-Fumi / Born-Mayer-Huggins potential and the Evjen method for evaluating the lattice sums. The integration algorithm used is the Verlet method. The program calculates the system potential and kinetic energies, the pressure and the final averages and R.M.S. fluctuations. The program also calculates density profiles such as number density, temperature, energy and pressure.

HSTOCH by W. F. van Gunsteren & D. M. Heyes.

S.D. or M.D. simulation of molecules in vacuo or in a rectangular cell with solvent or lattice atoms (i.e. Langevin or Brownian dynamics of large molecules).

MDATOM by D. Fincham.

M.D. simulation of atomic fluids. Uses 12/6 Lennard - Jones potential function and Verlet leapfrog integration algorithm. Calculates system average configuration energy, kinetic energy, virial and the associated R.M.S. deviations and also system pressure, temperature, mean square displacement and radial distribution function.

MDDIAT by D. Fincham.

M.D. simulation of diatomic molecule fluids. Uses 12/6 Lennard - Jones site - site potential functions and the Verlet leapfrog algorithm for centre - of - mass motion. Angular motion is calculated using the constraint algorithm. Calculates system average configuration energy, kinetic energy, virial and the associated R.M.S. deviations and also system pressure, temperature and mean square displacement.

MDDIATQ by D. Fincham.

M.D. simulation of diatomic fluids. Uses 12/6 Lennard - Jones site - site potential functions and a point quadrupole electrostatic term. Employs the Verlet leapfrog algorithm for centre - of - mass motion. Angular motion is calculated using the constraint algorithm. Calculates system average configuration energy, kinetic energy, virial and the associated R.M.S. deviations and also system pressure, temperature and mean square displacement.

MDIONS by D. Fincham & N. Anastasiou.

M.D. simulation of electrolytes. Uses exp/6/8 potential function and the Coulomb electrostatic potential. Long range interactions are calculated using the Ewald summation method. Uses the Verlet leapfrog algorithm for particle motion. Calculates system average configuration energy, kinetic energy, virial and the associated R.M.S. deviations and also system pressure, temperature, radial distribution functions, static structure factors and mean square displacements.

MDMANY by D. Fincham & W. Smith.

M.D. simulation of polyatomic molecules. Uses 12/6 Lennard - Jones site - site potential functions and fractional charges to represent electrostatic multipoles. Long range electrostatic effects are calculated using the Ewald summation method. Uses a Verlet leapfrog algorithm for centre - of - mass motion. Angular motion is calculated by the Fincham leapfrog algorithm using quaternion orientation parameters. Calculates system average configuration energy, kinetic energy and virial and associated R.M.S. deviations and also pressure and temperature. FORTRAN 77 standard program.

CARLOS by B. Jonsson & S. Romano.

M.C. simulation of a polyatomic solute molecule in an aqueous cluster. (i.e. a molecule surrounded by water molecules). The water-water potential is calculated using an analytical fit to an ab initio potential energy surface due to Matsuoka et al. The solute-solvent potential is optional. The program provides an energy and coordinate 'history' of the M.C. simulation. An analysis program CARLAN for processing the data produced by CARLOS is also available.

MCN by N. Corbin.

M.C. simulation of atomic fluids. Standard (Metropolis) Monte Carlo program for atomic fluids.

SCN by N. Corbin.

M.C. simulation of atomic fluids. Standard (Rossky, Friedman and Doll) Monte Carlo program for atomic fluids.

SMF by N. Corbin.

M.C. simulation of atomic fluids. Standard (path integral method) Monte Carlo program for atomic fluids.

REVIEW OF THE CCP5 MEETING ENTITLED 'POTENTIAL MODELS FOR  
COMPUTER SIMULATION' HELD AT THE DEPARTMENT OF CHEMISTRY,  
UNIVERSITY COLLEGE, LONDON 20/21 SEPTEMBER 1984.

M. Leslie and W. Smith.

Potential modelling is a matter dear to the hearts of everyone involved in physical chemistry (or its alter ego, chemical physics). A knowledge of the effective potential acting in any given system provides (theoretically) the basis of a full description of the properties of the material under all conditions of interest. Allied to the techniques of computer simulation, model potentials contribute to the most powerful methodology for linking the properties of individual molecules to behaviour of bulk material. Many methods are available for producing effective potentials and all of them have advantages and failings. The art of good computer simulation lies partly in the ability to choose the correct effective potential for the system and the state point that is being simulated. This is the problem that faces everyone employed in the simulation of materials by computer. The importance of the subject to CCP5 is reflected in the fact that this is the second occasion when it has raised a meeting on potentials. As on the previous occasion, the topic attracted a large and varied interest.

The first speaker of the meeting was Dr. J. Kendrick (I.C.I. Runcorn), who spoke on the subject of 'Ab Initio Calculations of Potentials in Ionic Solids'. This proved to be an interesting tour through the techniques and problems of the calculation of potentials in ionic materials. These potentials are exploited by the powerful lattice simulation programs HADES and PLUTO devised by Harwell.

The potentials must account for diverse phenomena such as charge induced dipoles, short range repulsion, covalency and dispersion or Van der Waals forces. A variety of potentials are available, such as Born - Meyer, Lennard - Jones, Morse or Harmonic potentials. The parameters of the potentials are determined by 'fitting' some physical property of the lattice e.g. lattice, dielectric or elastic constants or the lattice energy. These potentials have been used successfully but have drawbacks, namely; shortage of experimental data for comparison; the difficulty of physical interpretation of the parameters; the flexibility of the function and the short range over which the potential is 'proved'. Some of these difficulties can be overcome by the use of electron gas potentials, but these cannot include covalency and are hard to modify in circumstances where they are known to be inadequate.

Ab Initio methods provide the best alternative to empirical potentials. These methods use the Hartree - Fock Self Consistent

Field (HF-SCF) method to provide the basic molecular orbitals and Many-Body Perturbation Theory (MBPT) or Configuration Interaction (CI) to calculate electron correlation. These methods were developed by quantum chemists and are optimally efficient; exploiting symmetry where possible. Dr. Kendrick illustrated the application of these methods to lattice studies by reference to the two systems; magnesium oxide (MgO) and alpha phase sodium hydroxide (NaOH).

The calculation of the oxygen-oxygen potential in magnesium oxide was complicated by the high symmetry of the parent lattice. A change in separation reduced the symmetry and produced multipole terms into the calculation which were difficult to allow for. For this reason the calculation was modelled by two oxygen anions without a lattice. Each ion was given an effective charge  $Z$ , which was determined from polarisability or ionisation potential calculations. Ten electrons were assigned to each ion. Different orbital basis sets were used; (A) double zeta gaussian orbitals with polarisation orbitals, (B) as A with diffuse orbitals also. The method required the calculation of the energy of the anion pair and then the subtraction of single ion energies and induction and coulombic energies to give the effective pair potential. Allowance had to be made for the so-called basis superposition error by using the ghost orbital technique. Calculation B included a CI calculation. For both basis sets the results were comparable. Neither showed an attractive component to the potential at longer ranges; a feature expected from empirical potentials. Dr. Kendrick concluded that determination of the effective charge  $Z$  was probably too crude as it differed in different determinations ( $Z=8.85e$  and  $Z=9.65e$  from polarisability and ionisation potential determinations respectively) and probably required a proper pseudopotential treatment.

The treatment of alpha phase sodium hydroxide required embedding a NaOH cluster within an 87 point-ion lattice (chosen to give the best Madelung energy). The model required a consistent estimate of the hydroxide anion charge distribution for both regions and some effort went into determining this. The potentials of interest were the Na - OH potential (of which there were two types; linear and nonlinear), the HO - OH potential and the O - H potential. The basis orbitals used were double zeta gaussians with polarisation orbitals for sodium and oxygen, with additional diffuse orbitals for oxygen and finally, double zeta orbitals for hydrogen. The methods used were HF-SCF and Generalised Valence Bond (GVB) and included a CI calculation. (GVB was also used because of the known failure of HF-SCF to calculate the O - H anion correctly at long range). The potentials were calculated as expectation values over hamiltonians excluding lattice and coulombic contributions. The potentials produced were used to determine the alpha phase of the crystal structure using the program PLUTO, with good agreement with experiment if allowance for 'swing arm' oscillation was made. A cross check using the Direct Cluster

Optimisation (DCO) method; a quantum method which allows relaxation to energy minimum, gave similar results. Overall the results showed that the OH anion was a definite chemical entity not much affected by the lattice environment and that the Na - O distance is sensitive to the point charge model chosen.

Dr. Kenrick concluded that ab initio methods were viable in the determination of potentials in ionic materials provided sufficient care was taken in setting up the model system.

Quantum mechanical methods was also the subject of the lecture by Dr. B.H. Wells (Oxford), which was entitled 'Ab Initio Calculations of Intermolecular Forces: The Van der Waals Interaction between Rare gas Atoms'. The strategy used by Dr. Wells and his collaborators (Drs. E.B. Smith and S. Wilson) was the 'Supermolecular' approach in which the potential of interest was obtained by subtraction of the free atom energies from the calculated energy of the whole system (allowing for the basis set superposition error mentioned above). The basis set used was always an 'even tempered' gaussian basis set (i.e. one in which the exponents of the primitive gaussians of the orbital were in a defined mathematical progression). Electron correlation was treated by the Many Body Perturbation Theory method, which did not suffer from the 'size inconsistency' of direct CI methods. In the MBPT method electron correlation is treated as a perturbation of the independent electron model i.e. the zeroth order hamiltonian is the Hartree-Fock. The perturbation series is expressed diagrammatically and the expansion may be summed as either a Taylor series or a Pade approximant.

The results for the helium-helium potential using basis orbitals optimised for 5.6 a.u. showed that the HF-SCF energy was uniformly positive but was compensated by a uniformly negative correlation energy to give a net potential close to that calculated by Aziz. The best results were obtained using a basis including f - type orbitals. The equilateral helium trimer (separation 5.6 a.u.) gave a net energy of -.43 micro-a.u. compared with the Axilrod - Teller prediction of .37 micro-a.u., perhaps demonstrating that effective potentials are not valid in specific instances though satisfactory overall. The Argon-Argon potential was calculated from a 17s/15p basis optimised at 7.5 a.u. separation and then contracted to 12s/10p and d functions added. Results showed that the HF-SCF results were constant for these bases but the successive addition of d - type orbitals greatly improved the correlation energy. Yet higher angular functions improved the result further. Overall a 12s/10p/4d/1f basis set on each atom gave 66 percent of the empirical correlation energy and 49 percent of the total interaction energy. These results show clearly the importance of high angular quantum number functions in the determination of the dispersion energy and that inclusion of these represents a better strategy than using even higher order perturbations in the MBPT.

Dr. A.J. Stone, in a lecture entitled 'Intramolecular Potentials - Insights from Quantum Mechanical Calculations' was concerned with the strategies available for representing the electrical forces between molecules.

The long range electrostatic force can, in principle be evaluated using the standard electron repulsion integral, but for large separations in practice this is cumbersome and unnecessary. Instead the charge distribution may be expanded as the series: charge + dipole + quadrupole + etc., using ab initio methods. The interaction between molecules may be expressed as a sum of the product of multipoles and angular functions. Induction energies (due to distortion of the charge distribution by electrostatic fields) and the dispersion energy (expressed as an integral over products of polarisabilities evaluated at imaginary frequency) may both be calculated using Coupled Hartree Fock Perturbation Theory, which is a very efficient technique; permitting many perturbations and all their components to be calculated simultaneously. The method is the basis of the Cambridge Analytical Derivatives Package; CADPAC.

For medium range forces, the multipole expansion converges only slowly, if at all. (If the charge distributions are represented by realistic 'spheres' or 'volumes', the multipole expansion method will not converge if these 'volumes' overlap between neighbouring molecules). Hence the multipole expansion is not very useful for condensed phases. The problem can be overcome in one of two ways; distributed multipole expansions (DME) and Distributed Multipole Analysis (DMA). In the former several sites are chosen (e.g. atom nuclei positions, bond centres etc.) and multipoles are expanded about each. This strategy works well (the example of the Nitrogen molecule was given) but a large number of site - site interactions may need to be considered. The DMA method is more efficient, it uses the overlap densities between atoms and expands these about the neighbouring atoms (or about other nominated sites if desired). Requiring only the density matrix, the method is computationally efficient (especially with gaussian orbitals). It can provide multipoles to many orders and single site expansions can be obtained. The disadvantages of the method are the inherent ambiguity in the multipole expansion obtained (different resolutions being possible - but all should have a similar net electrostatic field) and the tendency toward overcompleteness of large multicentre basis sets. Both nitrogen and water molecules were used as examples from which it appeared that the fewer the expansion sites, the higher the multipole expansion that was required to obtain best accuracy.

In the calculation of short range forces, no multipole expansion would work; exact integrals were required. Also polarisation and dispersion forces were modified by overlap. The additional terms required were; exchange, repulsion (Pauli exclusion), charge transfer and various dispersion forces. Quantum mechanical methods were available for these phenomena, though not all required the same level of treatment. At zeroth

order were the isolated subsystem energies, at first order were the electrostatic, exchange and repulsion energies and at second order were the single excitation energies (polarisation and charge transfer) and the double excitation energies (intramolecular correlation, dispersion, double charge transfer, extension and charge transfer correlations etc.).

Dr. Stone concluded his lecture with a description of H-bonded Van der Waals molecules, in which the DMA method was particularly successful.

Dr. D.G. Bounds (Oxford) was concerned with economic ways of reproducing potential energy surfaces. His lecture 'Intermolecular Potentials from Energy Gradients' provided a simple scheme for producing such surfaces, with the minimum of calculation. Usually, given a good basis set, it takes many ab initio calculations to describe the multi-dimensional potential energy surface of molecule - molecule interactions. Additionally, the surface must be interpolated or fitted by some function, a process which may give rise to large deviations from the ideal. For molecular dynamics and 'smart' Monte Carlo simulations, where a knowledge of the first derivative is also required, the errors are accordingly greater.

Taking the ionic systems  $K^+/H_2O$ ,  $Li^+/H_2O$  and  $Na^+/H_2O$  as examples Dr. Bounds outlined a method he had found to be both economic and sufficiently accurate. Firstly, the water molecule was represented by a site model (a three site model was chosen initially). Next an empirical function was chosen to represent the ion - site interactions, (the T-Rittner function:  $E(R)=A\exp(-bR)-C/R^4-D/R^6+q/R$  for ion - oxygen and  $E(R)=A\exp(-bR)+q/R$  for ion - hydrogen). Then a suitable basis set for describing the system molecular orbitals was chosen. Finally the potential parameters were determined by fitting the first derivative of the potential functions to the ab initio values of the first derivative at selected site - ion separations calculated using the quantum chemistry program HONDO. The separations were chosen to sample the range of the potential and were just sufficient in number to permit good determinations of the parameters. They were derived from ion - water configurations where the ion was held perpendicular to the plane of the water molecule. This reduced polarisation effects, which would otherwise contribute to the calculation.

The three - site water model results were compared with the extensive results of Kistenmacher, Popkie and Clementi and showed very good agreement. Repeating the procedure with the more sophisticated results of Dacre for  $Na^+/H_2O$ , which used a more elaborate basis set, provided an effective potential accurate to 5 percent at the potential minimum. A slightly more elaborate four - site model for water produced an error of only 0.3 percent at the potential minimum and was comparable with the three - site model overall. The method was thus shown to be entirely suitable to producing cheap, effective potentials in these systems.

Dr. P. van Duijnen (Groningen) discussed potentials for systems containing large molecules with of the order of 1000 atoms. Since interest is focused on chemical problems a quantum mechanical treatment is necessary. Therefore the system is divided into two parts, "Q", the chemically interesting part which is treated quantum mechanically and "C", the classical part. Interactions between "Q" and "C" are treated semi-classically. This gives a Hamiltonian

$$H = H_0 - 1/2 \sum_i Q_i F_{ip} B_{pq} F_{qj} Q_j + \sum_e Z_e \psi_{ei} Q_i - 1/2 \sum_e Z_e F_{ep} B_{pq} F_{qi} Q_i \\ + \sum_e Z_e Q_e Z_d - 1/2 \sum_e Z_e F_{ep} B_{pd} Z_d$$

B is a response matrix. Long range interactions may be described by interacting polarisabilities giving rise to a dispersion like contribution. An upper limit to this energy may be obtained. The charges are determined using a distributed multipole model up to dipole, as discussed by B. T. Thole and P. Th. van Duijnen *Theor. Chim. Acta.* (1983) 209. The determination of the response or relay matrix B is also discussed in the literature. (B. T. Thole *Chem. Phys.* (1981) 341). Care is needed to avoid excessive polarisation in the system. To avoid this the dipole-dipole interaction is modified. The calculation of B is currently one of the key limiting factors to the size of problem which may be attempted, since B is the inverse of a large matrix.

Dr. van Duijnen then went on to discuss applications of this method. A study of the water dimer has been reported. (B. T. Thole. *Chem. Phys.* (1982) 71, 211. The active site of an enzyme Actinidin is currently being studied. Finally the formamide dimer and trimer were compared with supermolecule SCF calculations.

Dr. J. O. Baum gave a talk entitled "Problems in the use of the supermolecular approach at the SCF and CI levels to describe accurate water - organic molecule interactions". Current models of the water organic molecule interaction use one point charge and one 12/6 potential per atom. This model needs to be improved because 1) Induction effects have been ignored 2) The electrostatic model is crude and takes no account of lone pair effects and pi bonds 3) The 12/6 parameters need to be fitted to data and are therefore not independent of the charge model. Ideally the potential should be accurate to less than kT corresponding to 2.5 kJ mole<sup>-1</sup> at 300K. A simple model fitted to data gives an RMS deviation of 3 kJ mole<sup>-1</sup>, whereas ideally better than 0.5 kJ mole<sup>-1</sup> is sought. The model may be improved by using a multisite multipole expansion for the electrostatic part and fitting induction terms from experimental data. The 12/6 potential requires accurate intermolecular data to fit, and quantum mechanics can provide a wider sampling of the surface. Therefore a supermolecule approach has been used. The SCF and CI basis set superposition errors (BSSE), and the size-inconsistency of truncated CI calculations were estimated,

using the counterpoise method for the former and that of Davidson for the latter. The size of the BSSE gives an indication of the shortcomings of the basis set, so ideally the molecular basis set needs to be increased until the BSSE is less than the desired accuracy. A special feature of the water organic molecule system is that the dispersion energy is of the same order as the electrostatic energy. Also the basis set will be limited by the size of the system. Preliminary results were presented on the water dimer, where 35 basis functions were used per molecule. The Davidson correction is mostly an order of magnitude smaller than the BSSE. It would appear from these and other results that this method cannot yield sufficiently accurate potentials at present.

Dr. M. Rigby (London) spoke on the subject of 'Intermolecular Potentials for Simple Molecules: Corrections For Non - Additivity'. The importance of three - body corrections for obtaining good thermodynamics results from theoretical calculations has been demonstrated by Barker. Dr. Rigby has examined the importance of non - additive dispersion forces, such as the Axilrod, Teller and Muto (ATM) triple - dipole potential, in simple molecules systems. The magnitude and sign of the ATM potential depends on the relative displacement of the triangle of atoms considered, but it usually amounts to a positive correction in the configuration energy of an ensemble (6 percent of the lattice energy in solid argon, and about the same order in the liquid). There is also a substantial correction to the pressure arising from this contribution.

The ATM potential is not valid for nonspherical molecules but Stogryn has shown that the triple - dipole interaction can be written in terms of polarisabilities. The potential is then determined by the orientation of the molecules as well as their relative displacement.

Dr. Rigby has shown that in two solid phases of nitrogen (the low temperature alpha phase and the high temperature and pressure gamma phase) the orientation effects appear largely to cancel, though there remains a significant contribution from the relative displacements. In the liquid, the inclusion of triple - body effects makes the molecular dynamics calculation very slow, but following the example of Barker, who determined three body effects in a simulation as a perturbation of the system with only pair forces operating, Dr. Rigby has applied the method to liquid chlorine. Once again the orientational effects were seen largely to cancel though a significant overall effect remained. Thus it was concluded that such three - body effects should be considered in simulations of molecular liquids.

Dr. Rigby concluded by pointing out that triple - dipole interactions are not the only three - body effects present. At short ranges exchange forces are important and the triple - dipole expression also requires modification. These factors and others need to be considered and determined in the future.

Dr. Leslie (Daresbury) talked about a three body potential model for the static simulation of defects in ionic crystals. Since the details of this talk have been presented in previous issues of this newsletter, nothing further will be given here.

The talk of Dr. Scoles (University of Waterloo, Canada) was in two parts. The first dealt with intermolecular forces obtained via hybrid Hartree Fock SCF and damped dispersion energy calculations. The second part discussed potentials derived from surface scattering. The energy is partitioned thus

$$V(R) = \Delta E(\text{SCF}) + \Delta E(\text{CORR})$$

where  $\Delta E(\text{SCF})$  is the SCF energy calculated at the Hartree Fock limit and  $\Delta E(\text{CORR})$  is the interaction energy arising from electron correlation. The correlation terms can be calculated semi-empirically very well at long range, but can still be used at short range provided the effects of charge overlap are corrected for by damping the interaction. A doubly corrected dispersion series is used

$$\Delta E(\text{CORR}) = -[\sum C_n(\theta) R^{*-n} g_n(\rho R)] f(\rho R)$$

$$\text{with } n = 6, 8, 10, 12, 14, \dots$$

$g_n$  and  $f$  are universal functions which are scaled by the scaling parameter  $\rho$ .  $g_n$  corrects the various terms in the sum for charge overlap effects and  $f$  corrects the entire sum for exchange overlap and higher order effects. The functions  $g_n(R)$  and  $f(R)$  which are used are (Douketis et al. J. Chem. Phys. 76 (1982) 3057)

$$g_n(R) = [1 - \exp(-2.1R/n - 0.109R^{**2}/(n^{**1/2}))]^{**n}$$

$$f(R) = 1 - R^{**1.68} \exp(-0.78R)$$

When we consider interactions between molecules and atoms we will need to have 1) a good SCF calculation 2) the  $\theta$  dependence of the  $C_n$  coefficients 3) The  $\theta$  dependence of the scaling parameter  $\rho$ . This is somewhat of a problem at present. Results for the hydrogen argon system were presented and good agreement with experiment were obtained. However for higher non-sphericity the method fails badly, the cause being the attractive term. Therefore the dispersion needs to be decentralised. The potential for the argon HF system was discussed, again good agreement with experiment was obtained.

Turning briefly to the topic of surface crystallography, Dr. Scoles discussed the basic phenomena, which are well understood. However there is no system for which the whole potential is known, because most data cannot be treated exactly and the interaction involves many parameters leading to non-trivial problems in fitting to the data. A suitable system for study is H or He scattering from Xe adsorbed on graphite. A calculation based on summing over the H Xe gas phase

interactions, with a correction for the graphite, gave good agreement with experiment. This shows that the H Xe interaction is additive and that many body effects are not important.

Dr. J.H.R. Clarke (U.M.I.S.T.) in his lecture; 'Computer Simulation of Ionic Liquids without Coulomb Interactions' was concerned to show how ionic liquids can be modelled cheaply and effectively using short ranged potentials. In a general treatment of ionic liquids, the pair potential is usually represented as a sum of coulombic, repulsive, dispersive and polarisation terms. The coulomb interactions are both attractive and repulsive in the same system and are effective over a long distance, hence they require complicated treatments such as the Ewald sum, which is computationally difficult and expensive.

Dr. Clarke argued that in simulations where the structure, internal energy and perhaps the diffusion coefficients are required, a full recourse to the Ewald method is not necessary. In ionic liquids there are grounds for believing that the coulomb effects are shielded and are not effective over the ranges supposed. In this case short ranged potentials, suitably parameterised may prove effective in calculating the desired properties. The factors contributing to the construction of the effective potential have been found to be; (i) the balance of the repulsive and attractive forces, (ii) the effective particle sizes, (iii) the potential well depth for the attractive forces, (iv) the force constant of the potential (as given by the second derivative of the potential, (v) the choice of the potential truncation (an abrupt cut - off has been found to distort the structure) and (vi) the simplicity of the potential form. The type of potentials used by Dr. Clarke and his collaborators hitherto have been of the N - M type (c.f. Lennard - Jones; N=12, M=6) with either a modified 'tail' to smooth the cut - off or adjusted by the so called 'shifted - force' technique.

Dr. Clarke presented results for potassium chloride modelled with an 8 - 4 and an 8 - 3 potential. The partial radial distribution functions showed the 'charge oscillation' characteristic of ionic liquid structure out to several particle diameters. The combined RDFs showed that the charge ordering was exactly complementary, leading to overall charge neutrality. In this regard the results compared well with simulations using the Ewald sum. However, the RDF peak heights were much exaggerated, though this could be compensated for by adjustment of the well depths. The internal energy for the ionic system was calculated via perturbation theory (the Lambda Expansion method), which converged rapidly and required only the first term. The internal energy was found to be acceptably close to the known value, as were the diffusion coefficients of the ions. Thus the use of short ranged effective potentials was shown to be a promising strategy for future work.

Dr. M. Zoppi (Florence) then described a method of obtaining "experimental" pair potentials from the density behaviour of the neutron structure factor. A function  $F_2(k)$  is

defined as the zero density limit of  $(S(k, \rho) - 1)/\rho$  and the function is determined from the experimental data. The Fourier transform of  $F_2(k)$  will give  $g_0(r)$ . However  $F_2(k)$  is incomplete at low and high  $k$ . The zero  $k$  limit may be determined from compressibility data, and at low  $k$   $F_2(k)$  is assumed to be parabolic in  $k$  squared. The high  $k$  region poses problems however. The Fourier transform of the truncated form has oscillations from which the  $\sigma$  and  $\epsilon$  of a 6/12 Lennard-Jones potential may be estimated. These parameters may then be used to calculate the high  $k$  tail of  $F_2$ . This is repeated iteratively until the desired convergence is obtained. Results were presented for krypton, which agree well with the empirical potential of Barker et al.

Dr. W. Busing (Oak Ridge) then described effective potentials for the simulation of molecular crystals. He discussed his techniques using a series of examples, which attempt to answer the question of whether unexpected molecular geometries in crystals are due to packing forces between the molecules. The first example was 1,3,5 triphenylbenzene, which has three different torsion angles for the three phenyl groups (-39.2, +35.9, -35.8). The crystal has space group  $Pna_2$ , with four molecules per unit cell. The structure is simulated using rigid benzene rings. The non-bonded potential has coulomb, Van der Waals and Born-Meyer repulsion terms. The coulomb potential has charges of +0.153e on H and -0.153e on C. The non-bonded potential is applied to both inter and intra molecular interactions except for intermolecular nearest neighbour and next nearest neighbour interactions. The torsion angle potential used was

$$V(\phi) = E(\phi)/4(1 - \cos^2 \phi)$$

It should be noted that there are four different torsion angles about each bond. The non-bonded potential was held fixed and  $E(\phi)$  was fitted to reproduce the structure as well as possible. The best value of  $E(\phi)$  was 8.68 kcal mole<sup>-1</sup> which gives torsional angles of -38.1, 36.5 and -35.2. The predicted cell constants were in reasonable agreement with experiment, and the net translation and rotation of the molecule from its observed position was very small. This shows clearly that the differences in the torsional angles may readily be explained using simple effective potentials.

Dr. Busing then went on to discuss 1,8 diphenylnaphthalene and 1,4,5,8 tetraphenylnaphthalene, which, despite their chemical similarity, have completely different structures in the solid state. The differences involve torsional angles within the naphthalene ring. The model in this case involves a far larger number of degrees of freedom as the naphthalene ring is broken up into individual atoms, although the phenyl rings are still treated as rigid bodies. The effective potential used has torsional inter-ring and intra-ring terms, a bond angle bending term a bond stretching term and an out of plane term

$$V(d_{op}) = 1/2k_{op}d_{op}^{**2}$$

where  $d_{op}$  is the distance of an atom out of the plane of the three nearest neighbours. Following the same procedure outlined above, it was possible to predict the structure of both crystals very well. When the potential was applied to the isolated molecules, the geometries adopted by the naphthalene rings became very similar, showing that crystal packing forces cause the differences in the solid state.

Dr. S. Price (University of Cambridge) gave a talk entitled "Intermolecular forces - new clues from molecular crystal structures". Traditional models of molecular crystals have used isotropic atom atom potentials. However the valence electrons are not spherically distributed, and electrostatic terms are important even for non-polar molecules. Therefore anisotropic atom atom or site site potentials must be used. A complete set of expansion functions for the orientational dependence may be obtained. For the electrostatic part a distributed multipole analysis of the SCF wavefunctions is made. If isotropic potentials are applied to the crystal structure of chlorine, an incorrect structure is predicted. In the plane of the observed structure, either intermolecular bonding or anisotropic repulsion must be taking place. A DMA is used at each chlorine site to simulate the electrostatic part of the potential. The anisotropic part is fitted to the observed structure, and results in a potential which 'looks like' lone pairs.

Dr. Price then went on to describe some modelling of 6 membered ring nitrogen containing heterocyclic aromatic compounds. There are 6 interaction sites per molecule. Anisotropic C(H)-C(H), C(H)-N and N-N potentials are used. In other words the hydrogen is modelled by an anisotropic potential. The potential contains electrostatic, dispersive and repulsive parts. The electrostatic part comes from a DMA of the SCF wavefunctions. The dispersion term has an isotropic site site form. The repulsive part was found by fitting to the structures of benzene, pyrazine(1,4 diazine) and pyrimidine (1,3 diazine). Terms in the anisotropic potential were found which stabilise C-H...N as compared with C-H...H-C and N-N. This may be interpreted as a lone pair packing effect, or as hydrogen bonding or it could simply be an electrostatic effect. Dr. Price then went on to describe the application of these potentials to the structures of pyridine and 1,3,5- triazine.

Dr. Maitland then gave a talk on Potential energy functions from inversion of thermophysical properties. A number of procedures have been devised in recent years whereby potential functions may be obtained directly from thermophysical properties by inversion of data over a range of temperatures. These have been justified largely on the basis of numerical simulations and successfully applied to a wide range of spherical systems. Dr. Maitland described how the generality of these methods could be extended in two directions. Firstly, the iterative inversion techniques involved are shown to follow

naturally from the relevant statistical mechanical expressions for both second virial coefficients and transport coefficients. This establishes a rigorous theoretical basis for the methods and indicates how they may be extended to other properties or to more complex systems. Secondly, the application of the methods to non-spherical molecules is shown to define an effective spherical potential which is a particular locus average of the full anisotropic potential surface. For simple model monotonic anisotropic potential functions, the inversions may be carried out analytically. The results may be used to give insight into the nature of effective potentials generated in this manner for systems interacting with realistic non-spherical potential energy surfaces.

Dr. E.B. Smith (Oxford) began his lecture, 'The Determination of Effective Potentials from Inversion Methods', by outlining some of the difficulties associated with effective potentials deduced from thermophysical data. For example, they sometimes do not give an adequate account of other thermophysical properties or even of the same property over a broad range of temperatures. A method which appears to overcome some of these limitations is the Inversion Method devised by Dr. Smith and his colleagues.

The Inversion Method allows the deduction of the effective potential in a system without requiring the assumption of the analytical form of the potential. A temperature dependent characteristic length 'a' is defined in terms of a thermophysical variable, such as the second virial coefficient or the viscosity (e.g. for the second virial coefficient  $B(T)$  this is:  $a = ((B + T(dB/dT)) / (2\pi N/3))^{1/3}$ ). The intermolecular potential at this separation is then given by:  $U(a) = G(T^*) \cdot kT$ , where  $T^* = kT/\epsilon$  and  $\epsilon$  is the potential well depth and  $G(T^*)$  is the so-called Inversion Function, which is insensitive to the detailed shape of the potential energy function  $U(r)$ . This permits an estimate of  $G(T^*)$  using an approximate potential.  $G(T^*)$  is then used to construct a more accurate potential. The procedure may be repeated (three iterations only are sufficient) to produce a converged and accurate potential  $U(r)$ . The procedure requires an estimate of the well depth  $\epsilon$  and so trial values are used to find the value which minimises the deviation between calculated and observed values of the thermophysical variable (the position of minimum deviation is quite sharply defined).

Applying this method to non-isotropic molecules; such as diatomic molecules, where the method is not expected to work, shows surprisingly, that the effective potential obtained is identical, whether it is obtained from the second virial, viscosity or self diffusion data. The potential obtained is, in fact, similar to the median potential defined by Lebowitz and Percus, which is obtained as a spherical average of an explicit angularly dependent (anisotropic) potential. The new potential has been used as an effective spherical potential in a Monte Carlo simulation of liquid nitrogen, where it gave the internal

energy to about 1.4 percent accuracy and the pressure to within 100 atm.. The method thus appears to provide a very useful way of proceeding from gas phase data to potentials that are effective in the liquid phase also. Though as Dr. Smith pointed out, some modification of the outlined method is required in systems of polar molecules.

The final speaker of the meeting was Professor C. Hoheisel (Bochum), whose lecture; 'Four Effective Potentials for the Simulation of N<sub>2</sub>' assessed different models for the potential acting in liquid nitrogen. A number of options are available. The nitrogen molecule has a short bondlength, which suggests that spherical potentials may be useful. The molecule also possesses a quadrupole moment and Professor Hoheisel sought to evaluate the importance of this and also of triple - dipole three - body effects. Four model potentials were compared: (i) a single Lennard - Jones centre (LJ1C), (ii) two Lennard - Jones centres (LJ2C), (iii) two Lennard - Jones centres with a quadrupole (LJ2CQ) and (iv) a single Lennard - Jones centre with triple - dipole (LJ1CT). Since it is known that the calculated pressure is very sensitive to the model potential used, the potentials were compared in the high and the low pressure regions. The triple - dipole expression used was the Axilrod - Teller expression.

In general, all the simulations gave reasonable values for the pressure, though the LJ2CQ model gave a pressure that was too low in the high pressure region. Only the LJ1C model gave a pressure that was lower than the experimental value, though not over the entire region studied. In general the deviations from experimental values seemed to depend upon the density. Prof. Hoheisel also suggested that the deviations could be reduced by a more careful optimisation of the well depth parameters and the strength of the triple - dipole interaction. The LJ1CT model showed that the triple - dipole contribution to the internal energy is positive, despite the known fact that the energy for some three - particle arrangements may be negative. (This result agrees with the report by Dr. Rigby above).

There appears to a degree of flexibility in the choice of a suitable potential for N<sub>2</sub> on the strength of Prof. Hoheisel's results. However he pointed out that the simplest model (LJ1C) required only 1.6 s. per 100 timesteps, while the complicated LJ1CT model, which calculates three - body interactions, required 258 s.. This is clearly a factor likely to influence the experimenter's choice of potential !

LETTER FROM AUSTRALIA: "SIMULATIONS DOWN-UNDER!"

D.M. Heyes

I am at present in Australia working with Drs. Denis J. Evans and Gary P. Morriss (Research School of Chemistry, Australian National University, GPO Box 4, Canberra, ACT 2601, Australia). This has provided me with an excellent opportunity to discover, at close quarters, the work being performed here in the broad area of the theory and computer simulations of fluids and solids. (It is a healthy sign of the times that one often cannot neatly categorise scientists as theorists or simulators. The two areas of research are so complementary that investigators are frequently deeply engaged in both.) It occurred to me that readers of the CCP5 Newsletter might like to learn about the topics of research interesting the workers here. Consequently an account of these activities will be given below.

Before I present a summary of current research interests here may I bring to your attention, Dr. C.K. Ong (Department of Physics, National University of Singapore, Lower Kent Ridge Road, Singapore 0511, Singapore) whom I had the pleasure of meeting while on my way to Australia. He leads a group with many interests in condensed matter physics. He has contributed to our understanding of vacancy-type defects in  $\alpha$ -iron and  $\alpha$ -zirconium<sup>1-2</sup>, using static lattice techniques. His strong links with AERE Harwell have resulted in collaborations investigating, for example, the electronic structure and luminescence of CsI:Na<sup>3</sup>. His present interests are in the effects of intense laser light on crystalline silicon surfaces which produce "flash" melting of the surface layers<sup>4</sup>. He is keen to understand this phenomenon and I am sure would welcome correspondence with anyone interested in exchanging ideas on this subject.

Canberra is a centre of excellence for liquid state theorists. The work of my hosts, Denis Evans and Gary Morriss will need no introduction to the molecular dynamics community. Their pioneering work in simulating and characterising non-equilibrium fluid states (especially, but by no means

exclusively, under shear) is well known<sup>5,6</sup>. Their work on shear thinning and new methods for obtaining transport coefficients such as self-diffusion and thermal conductivity is given in an excellent review published recently<sup>6</sup>. They are at present diversifying into methods for evaluating dielectric constants of dipolar fluids using MD. This work is being performed in close association with Dr. Denis Isbister (Department of Chemistry, Royal Military College, University of New South Wales, Duntroon, ACT 2600, Australia; which is only a few kilometres from the A.N.U). Also at the RMC are other simulators. These include Professor Richard J. Bearman and Dr. Donn L. Jolly who work on evaluating by MD the self- and collective diffusion coefficients of Lennard-Jones fluids<sup>7-9</sup>. Their work involves a detailed analysis of statistical errors. Drs. Ben C. Freasier and Norman D. Hamer are also in the same department and have a very broad range of interests. They have performed MD/MC calculations on collisional energy transfer between a highly excited bromine molecule and a non-reactive host fluid<sup>10,11</sup>. Other topics of interest are modelling collision induced light absorption<sup>12</sup> and equations of state of fused hard spheres<sup>13</sup>. Ben Freasier has also collaborated with Professor Sture Nordholm (Department of Theoretical Chemistry, University of Sydney, NSW 2006, Australia) on a generalised Van der Waals model for solvation forces between solute particles in a colloidal suspension<sup>14</sup>. This area is also actively researched by Drs. W. Van Meegen and I. Snook (Department of Applied Physics, Royal Melbourne Institute of Technology, Melbourne). They have, almost alone, pioneered the application of MC and MD to colloidal suspensions<sup>15-23</sup>. In the latter method MD becomes Brownian Dynamics, BD, which eliminates the necessity of explicitly including solvent molecules in the model. They are also interested in another area which is somewhat related to this, the physical adsorption of gases at high pressure<sup>24,25</sup>. They have investigated the adsorption of modified Lennard-Jones molecules on plane rigid solid surfaces using grand canonical MC.

Also at Melbourne is Dr. E.R. Smith (Department of Mathematics, University of Melbourne, Parkville, Victoria 3052, Australia) who is well-known for his work on producing formulae for determining the electrostatic potential in arbitrarily shaped lattices<sup>26</sup>. He is at present collaborating with Dr. P.A. Wielopolski (permanent address: Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland) in using

molecular dynamics to study the dielectric behaviour and orientational correlations of liquid ethylene oxide and related molecules<sup>27</sup>. They are also concerned with the sometimes startling surface effects in the response of polarizable lattices to external fields<sup>28</sup>.

In the field of rheology, Australia can boast the presence of Professor David V. Boger and Dr. Rod J. Binnington (Department of Chemical Engineering, University of Melbourne, Parkville, Victoria 3052, Australia) who have made innumerable contributions to our understanding of "large molecule" (e.g. polymer melts and solutions) flow behaviour. They have many experimental projects in progress which include flow in constricting channels, extensional effects in rubber extrusion and temperature/viscosity effects of crude oil. The large molecular problem is being tackled from a modelling viewpoint by Drs. Nicholas Anastasiou and Clive A. Croxton (Department of Mathematics, Statistics and Computer Science, University of Newcastle, NSW 2308, Australia). They are investigating structural conformations of polymers and proteins using a variety of techniques. Models of polymer chains consisting of flexibly joined hard sphere segments have been formulated using cluster-diagrammatic theory. They write:

"Of particular importance in the study of protein molecules is the folding pathway. This work is directed towards observing the initial stages of folding from the extended state to the secondary structure. Proteins are atoms of repeating units. The units are peptide groups, made up of monomers called amino acids. Here, using a simplified model each residue is replaced by one interaction centre. The crystallographic positions of the  $\alpha$  and  $\beta$  carbon atoms are used to define the direction along which the interaction centre is placed. Each interaction centre is represented by the side chain of its residue. These side chains interact by a non-bonded term and a pairwise approximation of the solvent contribution to the free energy of association. There is also a hydrogen bonded term between residue  $i$  and  $i+4$  which determines the formation of the  $\alpha$  helix.

We use the Monte Carlo computer simulation technique to simulate all nine helices of myoglobin from their initial extended structure to the secondary helical structure."

Dr. Croxton has many intrests, which include descriptions of inter-facial structure of liquid crystals and water using statistical mechanical approaches and the Landau-de Gennes expression for the free energy density.

Drs. A.J. Easteal and L.A. Woolf (Research School of Physical Sciences, Australian National University, GPO Box 4, Canberra ACT 2601, Australia) have made significant progress in applying the rough hard sphere model and MD on smooth hard spheres to "real" molecular fluids<sup>31-33</sup>. Molecular dynamics calculations of mixtures of hard spheres at liquid densities are similarly successful for systems in which the effects of molecular interactions are not strong<sup>34</sup>.

Bob Watts (Research School of Physical Sciences, Australian National University, GPO Box 4, Canberra, ACT 2601, Australia) has been involved in MD computer simulation for many years. He has many diverse interests and a large group of collaborators. These include J.R. Reimers and D.F. Coker working on simulations, and R.E. Miller, P.F. Vohorali, Gad Fischer, C.V. Boughton, M.J. Norman, G. Briant, K. Jones and D. Clarke who work on the molecular beam research. Dr. Watts has kindly supplied me with a summary of his research interests, which is reproduced with one also generously supplied by Professor Nordholm below.

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## SIMULATION IN CANBERRA

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Computer simulation methods have been applied to three problems during the past one or two years. First, a semiclassical method has been developed for calculating the infrared spectrum of liquid water and ionic solutions. Next, this method has been adapted to the study of infrared predissociation spectra in van der Waals clusters. Finally, an extensive study of random walk methods in quantum statistical mechanics is underway.

The infrared simulations of water and ionic solutions are based on a reasonably accurate pair potential for the water dimer. It consists of two parts, an intramolecular interaction based on three Morse oscillator potentials together with quadratic coupling between the stretching modes, and a semi-empirical intermolecular potential. Details of both parts of this surface have been published during the past couple of years. Briefly, the intramolecular part is fitted to 56 vibrational energy levels of the water monomer and its isotopes, using local mode theory. The intermolecular part is based on a rigid molecule surface fitted to the second virial coefficient of steam and the lattice energies and lattice parameters of three phases of ice. It is then assumed that the full flexible molecule pair interaction can be constructed as a superposition of these two surfaces. The full surface is then used in a classical Monte Carlo program to generate a sequence of configurations of the liquid, or ice, in the usual way. An important assumption is then introduced, essentially a vibrational Franck-Condon approximation. It is assumed that the infrared spectrum of the dense phase can be constructed from the superimposed spectra of a subset of the Monte Carlo configurations. The vibrational analysis needed to identify the infrared active modes, and their frequencies, is based on a local mode analysis. Extensive studies of this semiclassical approach have established that it gives an excellent description of the infrared spectrum in the stretching and bending region. Furthermore, the simulations have suggested that the second neighbour maximum in the O-O radial distribution

function is due to intramolecular relaxation rather than to strongly directional electrostatic interactions.

The method has also been adapted to the study of the infrared spectrum of van der Waals clusters. This interest arose out of experimental results from a supersonic molecular beam apparatus that we have recently constructed. We have used the semiclassical simulations to assign bands observed in both nitrous oxide and water clusters. This analysis has required us to examine properties such as the dipole transition moments of the molecules and the influence of dipole moment functions on spectral shifts when molecules enter the condensed phase.

The third topic of interest, quantum simulation, is based on the random walk method of Anderson. We have applied this method to several problems, with the aim of establishing a general approach for molecular problems. A particularly successful application was to the structure and ground state energy of small clusters of water molecules. The molecular beam experiments produce strongly cooled clusters and consequently quantum effects can be extremely important. The method was used to generate infrared spectra, giving very good agreement with experiment. Other applications of the method have been to the ground state of solid hydrogen, to liquid helium, and most recently to electronic problems. In the last named studies we have concentrated on methods for avoiding the necessity to know the positions of nodes and on methods for including exchange directly. Early results appear to be very encouraging.

RESEARCH INTERESTS OF S. NORDHOLM

(Department of Theoretical Chemistry, University of Sydney, Sydney,  
NSW 2006, Australia)

I. Equilibrium statistical mechanics:

Development of the Generalised Van der Waals theory of fluids and solids (a free energy density functional theory based on continuum cell theory and fluctuation analysis).

Applications to adsorption, surface tension and thermodynamic properties of simple fluids, polar fluids and electrolytes (with students and Dr. Freasier at Duntroon).

II. Non-equilibrium statistical mechanics:

a) Theory of unimolecular reactions with special attention to collisional energy transfer and internal vibrational relaxation and degree of ergodicity. Both statistical theory and MC/MD simulation methods are used and thorough investigations of diatomic rate processes have been carried out (with Drs. Freasier and Jolly at Duntroon).

b) Brownian motion theory:

Both exact projection operator techniques and phenomenological arguments.

III. Quantum theory of decay:

a) Development of the absorbing boundary method of decay (with G. Bacshay).

b) Development of the GIPM/D (ground-state inversion potential + diffraction) theory of photoionization cross sections:

- a "chemical" theory combining atoms-in-molecule concept with diffraction approximation of molecular effects (with N.S. Hush and students).

IV. Statistical theory of electronic structure:

a) Development of improved Thomas-Fermi functionals for atoms and molecules.

b) Development of a statistical electron correlation analysis at the Hartree-Fock level (with students).

THE METHOD OF CONSTRAINTS FOR MOLECULAR  
SYSTEMS: FIXED PRESSURE-FIXED TEMPERATURE  
MOLECULAR DYNAMICS

M. Ferrario and J-P. Ryckaert

1. GENERAL CONTEXT

Molecular Dynamics (MD) simulations of liquids and solids at equilibrium can now be performed at fixed Pressure and/or at fixed Temperature instead of imposing the traditional constant Volume and Energy conditions <sup>1-5)</sup>. In the "extended variable" methods of Andersen <sup>2)</sup> and Nosé <sup>4b)</sup>, time averages do correspond to well defined ensemble averages, such as isobaric -isoenthalpic or canonical ones.

Here we describe how these techniques can be effectively extended to polyatomic molecules with intramolecular geometrical constraints. Using atomic coordinates, these holonomic constraints <sup>6)</sup> can always be written as  $\sigma(\{\underline{r}_{i\alpha}\}) = 0$  where  $\{\underline{r}_{i\alpha}\}$  is a restricted set of atomic coordinates of the molecule  $\alpha$ ,  $\sigma$  being an invariant function for a translation or a rotation of the molecule as a whole. In the literature two kinds of constraints have been considered explicitly: The bond constraint

$$(\underline{r}_{i\alpha} - \underline{r}_{j\alpha})^2 - d_{ij}^2 = 0 \quad (1)$$

in which two atoms are held at fixed distance  $d_{ij}$ , and the linear constraint

$$\sum_{i=1}^{n_\alpha} C_{ki} \underline{r}_{i\alpha} - \underline{r}_{k\alpha} = 0 \quad (2)$$

where the cartesian coordinates of atom  $K$  are expressed as a linear combination of the cartesian coordinates of a rigid set of  $n_b$  basic atoms connected by  $\frac{1}{2} n_b (n_b - 1)$  rigid bonds. The constraint (2) are necessary or at least useful when a rigid set of atoms is linear and contains more than 2 atoms ( $n_b = 2$ ), is planar with more than 3 atoms ( $n_b = 3$ ) or is 3 dimensional with more than 4 atoms ( $n_b = 4$ )<sup>6b)</sup>.

These two kinds of constraints are certainly not the only possibilities: it appeared recently<sup>7)</sup> that to freeze some specific high frequency vibration modes in a full atomic model of normal alkanes, other forms of geometrical constraints have to be introduced.

In references 1, 2, 4), the fixed pressure, fixed temperature "extended variables" methods in M.D. have been discussed whilst in references 3, 5), their adaptation to molecules with constraints has been considered mainly from a theoretical point of view. Here we shall focus on the form and the integration schemes of the cartesian equations of motion of individual atoms for molecules with arbitrary constraints and in various external conditions<sup>5)</sup>. We will give the methods to evaluate the constraint forces but we will not discuss in detail here the techniques particular to specific constraints. The reader is referred to original papers<sup>6)</sup> for that purpose.

## 2. EQUATIONS OF MOTION RELATIVE TO NVE, NVT, NPH AND NPT ENSEMBLES

In the M.D. simulations where the pressure is externally fixed, the volume  $V$  of the sample is allowed to change in order to equilibrate internal and external pressures<sup>2)</sup>. In Nosé's method<sup>4b)</sup>, the coupling with a heat bath at a given temperature is realized through a scaling of velocities by an extra variable  $S$  obeying to a well defined equation of motion.

In the derivation of such methods for molecules with constraints at fixed pressure and/or temperature <sup>5)</sup> the space scaling governing the time evolution of the volume of the sample is applied to the center of mass of molecules whilst the velocity scaling affects all degrees of freedom.

The molecular system itself is described by the hamiltonian

$$H_1 = \sum_{\alpha=1}^N \sum_{i=1}^n \frac{p_{i\alpha}^2}{2m_i} + U(\{\underline{r}\}) \quad (3)$$

to which a specific set of, say  $l$  constraints (1) or (2) per molecule, has to be added.  $U(\{\underline{r}\})$  is the potential energy term containing intermolecular and possibly intramolecular contributions. Defining an "extended" mechanical system in some scaled variables with  $V$  and/or  $S$  as extra-variables, one derives their equations of motion. Applying a judicious non canonical transformation to these variables, a new dynamics of the set  $\{\underline{r}_{i\alpha}, \underline{p}_{i\alpha}, V, S\}$  is generated. The essential point is that the new mechanical system and the variable transformation are such that the configurations  $\{\underline{r}_{i\alpha}, \underline{p}_{i\alpha}\}$  of the system of interest obtained in such trajectories appear with a frequency proportional to the density of probability of well defined ensembles relative to the mechanical system specified by  $H_1$  (3)<sup>2,5)</sup>. The  $\{\underline{p}_{i\alpha}\}$  are no longer conjugate momenta of the  $\{\underline{r}_{i\alpha}\}$  in any "extended variable" method; we have the property

$$\underline{p}_{i\alpha} = m_i \left( \dot{\underline{r}}_{i\alpha} - \underline{R}_\alpha \dot{V}/3V \right) \quad (4)$$

where  $\underline{R}_\alpha$  is the center of mass coordinate. Note that the second term in the r.h.s. of (4) is absent when the volume remains fixed as in the canonical ensemble case.

There is still a (non hamiltonian) conserved quantity in the new dynamics,

$$H_2 = H_1(\{\underline{r}_{i\alpha}, \underline{p}_{i\alpha}\}) + \frac{1}{2} \frac{W_Q}{S^2} \dot{V}^2 + P_{ext} V + \frac{1}{2} \frac{W_S}{S^2} \dot{S}^2 + g k_B T_{ext} \ln S \quad (5)$$

where  $W_Q$  and  $W_S$  are inertial parameters driving the fluctuations in pressure and temperature respectively.  $g = N(3n - l)$  is the number of degrees of freedom ( $l$  constraints per molecule).  $k_B$  is the Boltzmann constant and  $T_{ext}$  and  $P_{ext}$  are parameters fixing the heat bath temperature and the external pressure.

The final equations of motion, written as second order differential equation of the cartesian atomic coordinates, are of the following general form

$$m_i \ddot{r}_{i\alpha} = \underline{F}_{i\alpha} + \underline{G}_{i\alpha} + \underline{A}_T^{(i\alpha)} + \underline{A}_P^{(i\alpha)} \quad (5)$$

$$W_Q \ddot{V} = S^2 \left\{ (3V)^{-1} \sum_{\alpha=1}^N \left( \frac{P_{i\alpha}^2}{M} + \underline{F}_{i\alpha} \cdot \underline{R}_{i\alpha} \right) - P_{ext} \right\} + B_T \quad (7)$$

$$W_S \ddot{S} = W_S \frac{\dot{S}^2}{S} + S \left\{ \sum_{\alpha=1}^N \sum_{i=1}^n \frac{p_{i\alpha}^2}{m_i} - g k_B T_{ext} \right\} \quad (8)$$

where

$$A_T^{(\alpha)} = \dot{S}/S \quad \underline{r}_{i\alpha} \quad (9)$$

$$B_T = W\alpha \quad \dot{S}/S \quad \dot{V} \quad (10)$$

$$A_P^{(\alpha)} = m_i \left( \ddot{V} - \frac{2}{3} \dot{V}^2 V^{-1} \right) \underline{R}_{i\alpha} / 3V \quad (11)$$

$M = \sum_{i=1}^n m_i$ ,  $\underline{F}_{i\alpha} = \sum_{j=1}^m \underline{F}_{ji\alpha}$  and  $\underline{P}_{i\alpha} = \sum_{j=1}^m \underline{p}_{ji\alpha}$  are molecular quantities.  $\underline{F}_{i\alpha}$  is the force on atom  $i$  of molecule  $\alpha$  deriving from the potential energy term.  $\underline{G}_{i\alpha}$  is the total force of constraint on the same atom and can be written as

$$\underline{G}_{i\alpha} = - \sum_{k=1}^l \lambda_k^\alpha \left( \frac{\partial \sigma_k^\alpha}{\partial \underline{r}_{i\alpha}} \right) \quad (12)$$

$\{\sigma_k^\alpha\}_{k=1, \dots, l}$  are the  $l$  constraints of molecule  $\alpha$  and  $\{\lambda_k^\alpha\}$  are lagrange multipliers to be fixed by requiring that the constraints are satisfied at all times.

The M. D. equations relative to specific ensembles are obtained in a unified way from (6-8).

NVE: use (6) with  $A_T^{(\alpha)} = A_P^{(\alpha)} = 0$  and  $\underline{p}_{i\alpha} = m_i \dot{\underline{r}}_{i\alpha}$   
 NVT: use (6) and (8) with  $A_P^{(\alpha)} = 0$  and  $\underline{p}_{i\alpha} = m_i \dot{\underline{r}}_{i\alpha}$   
 NPH: use (4), (6) and (7) with  $S=1$  and  $A_T^{(\alpha)}, B_T = 0$   
 NPT: use (4), (6-8)

Time averages of any property  $G(\underline{r}_{i\alpha}, \underline{p}_{i\alpha})$  correspond to related ensemble averages  $\langle G \rangle$ . Note however that these ensembles,

including the NVE, differ somewhat from their traditional definition<sup>2, 4b,8)</sup> by additional restrictions on the total linear momenta. Moreover, independently from the last remark, the correspondance between time and ensemble averages is exact only up to terms  $O(N^{-\epsilon})$  for intensive properties in the NPH case.

### 3. INTEGRATION OF THE EQUATIONS OF MOTION

#### i) The general case

The integration of eq 6 in presence of constraint forces is made in two successive steps. Let us rewrite (6) as

$$\ddot{\underline{r}}_{i\alpha} = \ddot{\underline{r}}'_{i\alpha} + \underline{G}_{i\alpha}/m_i \quad (6')$$

Considering the system as unconstrained in a first step, the use of Verlet algorithm gives

$$\underline{r}'_{i\alpha}(t+\Delta t) = 2 \underline{r}'_{i\alpha}(t) - \underline{r}'_{i\alpha}(t-\Delta t) + \Delta t^2 \ddot{\underline{r}}'_{i\alpha}(t) \quad (13)$$

Then the final coordinates  $\underline{r}_{i\alpha}(t+\Delta t)$  are obtained by adding the constraint contribution, i.e.

$$\underline{r}_{i\alpha}(t+\Delta t) = \underline{r}'_{i\alpha}(t+\Delta t) + \frac{\Delta t^2}{m_i} \underline{G}_{i\alpha} \quad (13')$$

The set of  $\{\lambda\}$  in  $\underline{G}_{i\alpha}$  (12) can be effectively evaluated (within the accuracy of the algorithm) by solving the set of  $l$  equations with  $l$  unknowns (per molecule) obtained in requiring

that the atomic coordinates (13') at  $t + \Delta t$  do satisfy the constraints; in compact notations we write

$$\left\{ \sigma_k^* ( \{ \underline{r}_{\alpha} (t + \Delta t) \} ) \right\}_{k=1, \dots, l} = 0 \quad (14)$$

The central part of the method of constraints is to solve eq (14): the input is the set of  $\{ \underline{r}' (t + \Delta t) \}$  defined in (13) and the set of  $\{ \underline{r} (t) \}$  appearing in the constraint forces. The output is a set of  $\{ \lambda \}$  from which the  $\underline{C}_{\alpha}$  (12) and then the set  $\{ \underline{r}_{\alpha} (t + \Delta t) \}$  (13) can be evaluated. Let us denote this part of the calculation as

$$\underline{r} (t + \Delta t) = \text{CONSTRAINT} ( \underline{r}' (t + \Delta t), \underline{r} (t) ) \quad (15)$$

This step consists mainly in solving a set of  $l$  (non linear) algebraic equations with  $l$  unknowns. They are always obtained in an iterative way by variants of the Newton method. The so called "matrix method" and "SHAKE" algorithm <sup>6a)</sup> are two different but equivalent procedures to realize the step 15 for molecules with bond constraints only.

ii) The special case of rigid molecules with linear constraints

Linear constraints relate the cartesian coordinates of a "secondary" atom to the coordinates of  $n_b$  basic atoms. In <sup>6b)</sup>, it was shown that the Lagrange multipliers  $\{ \underline{\mu} \}$  associated to the linear constraints can be explicitly solved. The dynamics of a molecule can then be expressed in terms of the cartesian equations of motion of the basic atoms only; their general expression (in NVE conditions) are <sup>6b)</sup>,

$$m_i \ddot{\underline{r}}_{i\alpha} = \underline{f}_{i\alpha} + \underline{g}_{i\alpha} \quad (16)$$

where

$\underline{F}_{i\alpha}$  is a linear combination of atomic forces,  $\underline{g}_{i\alpha}$  is the residual constraint force, function of the Lagrange multipliers  $\{\eta\}$  associated to the bond constraints connecting the  $n_b$  basic atoms. For the present purpose, let us mention that in the context of fixed pressure - fixed temperature ensembles, equations 6, 7, 8 are easily modified to the special case of rigid molecules with linear constraints. Equation 6 for a given molecule become a set of  $3 n_b$  equations of the same type in which  $\underline{F}_{i\alpha} + \underline{G}_{i\alpha}$  is replaced by  $\underline{J}_{i\alpha} + \underline{g}_{i\alpha}$  like in the NVE case (16). This is a consequence of the fact that the Lagrange multipliers  $\{\mu\}$  are not modified by the presence of additional coupling terms  $\underline{A}_T^{(i\alpha)}$  and  $\underline{A}_P^{(i\alpha)}$  in (6). The integration of these equations of motion is similar to the general case in which (6') and (13') become respectively

$$\ddot{\underline{x}}_{i\alpha} = \ddot{\underline{x}}'_{i\alpha} + \frac{\underline{g}_{i\alpha}}{m_i} \quad (17)$$

$$\underline{x}_{i\alpha}(t+\Delta t) = \underline{x}'_{i\alpha}(t+\Delta t) + \frac{\Delta t^2}{m_i} \underline{g}_{i\alpha} \quad (18)$$

The set of  $\frac{1}{2} n_b (n_b - 1)$  Lagrange multipliers  $\{\eta\}$  in  $\underline{g}_{i\alpha}$  is explicitly evaluated by requiring as usual that the  $\{\underline{x}_{i\alpha}(t+\Delta t)\}$  in (18) do satisfy the bond constraints. The positions of the basic and secondary atoms are then successively evaluated using (18) and the linear constraints (2) themselves.

#### 4. COMPUTATIONAL ASPECTS

i) The NVE ensemble: this is the simplest case as the acceleration  $\ddot{\underline{x}}_{i\alpha}$  is velocity independent for its unconstraint part

$\ddot{\underline{r}}_{i\alpha}$  in (6'). Using (13) and the constraint procedure (15) gives the coordinates at the next step.

ii) The NPH\_ensemble :  $\ddot{\underline{r}}_{i\alpha}$  and  $\ddot{\underline{V}}$  are now velocity dependent so that the usual Verlet algorithm for velocities, which for arbitrary variable  $x$  is

$$\dot{x}(t) = \frac{x(t+\Delta t) - x(t-\Delta t)}{2\Delta t} \quad (19)$$

cannot be applied immediately. Therefore we used an iterative procedure on the velocity determination starting with the trial value

$$\dot{x}^{(0)}(t) = \left( 3x(t) - 4x(t-\Delta t) + x(t-2\Delta t) \right) / 2\Delta t \quad (20)$$

which implies the storage of an additional configuration in comparison with the standard Verlet algorithm. In the NPH ensemble case, this iterative procedure is decoupled from the calculations of the forces. The coupling term  $\underline{A}_p^{(\alpha)}$  in (6) is identical for all atoms of a molecule and doesn't interfere therefore with the evaluation of constraint forces. We adopted the following scheme

- 1) Evaluation of  $\underline{r}'_{i\alpha}(t+\Delta t)$  with  $\underline{A}_p^{(\alpha)} = 0$  using (13)
- 2) Evaluation of  $\underline{r}_{i\alpha}(t+\Delta t)$  using constraint procedure (15)
- 3) Estimation of  $\ddot{\underline{V}}^{(0)}$  and  $\{\dot{\underline{r}}^{(0)}(t)\}$  with (20)
- 4) Evaluation of  $\ddot{\underline{V}}$  and  $\underline{A}_p^{(\alpha)}$  with current value of velocities
- 5) Estimation of  $\underline{V}(t+\Delta t)$  and  $\underline{r}_{i\alpha}(t+\Delta t)$  including  $\underline{A}_p^{(\alpha)}$  (Verlet)
- 6) Evaluate new velocities  $\{\underline{V}(t), \underline{r}_{i\alpha}(t)\}$  using (19)
- 7) Go back to 4 until convergence is reached.

The iterative procedure, which can be performed explicitly on the center of mass positions and velocities, converges typically in 2 or 3 steps and doesn't add any sensible computer time.

iii) The NVT and NPT ensembles: The coupling term  $A_T^{(i\lambda)}$  in (6) depends on atomic velocities and does interfere with constraint forces in general. Therefore, the iterative procedure on atomic velocities implies that constraint forces have to be evaluated at each step of the iteration. The scheme given for the NPH case must therefore be slightly modified

- 1) Estimate  $\{r_{i\lambda}'(t+\Delta t)\}$  with  $A_P^{(i\lambda)} = 0$  and  $A_T^{(i\lambda)} = 0$  in (13) and save it as  $\{r_{i\lambda}''(t+\Delta t)\}$
- 2) Estimate  $\dot{V}^{(0)}(t)$ ,  $\dot{S}^{(0)}(t)$  and  $\{\dot{r}_{i\lambda}^{(0)}(t)\}$  using (20)
- 3) Evaluate  $\dot{V}(t)$ ,  $\dot{S}(t)$ ,  $A_P^{(i\lambda)}$ ,  $A_T^{(i\lambda)}$  and  $B_T$  using current values of velocities
- 4) Evaluate  $V(t+\Delta t)$ ,  $S(t+\Delta t)$  using Verlet algorithm and add to  $\{r_{i\lambda}''(t+\Delta t)\}$  the contributions of  $A_P^{(i\lambda)}$  and  $A_T^{(i\lambda)}$  to get  $\{r_{i\lambda}'(t+\Delta t)\}$
- 5) Evaluate new atomic positions  $\{r_{i\lambda}(t+\Delta t)\}$  using constraint procedure (15)
- 6) Evaluate new velocities estimates (19)
- 7) Go back to 3 until convergence is reached.

The evaluation of constraint forces more than once during a M.D. time step is not a very satisfactory situation. However, in practise, this part of the calculations is very often a rather small part (5- 15%) of the total computing time. As the first guess of velocities (20) is already a very good approximation, it is sometimes even not necessary to iterate when a high precision is not required.

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The dependence of the velocity autocorrelation function on  
the intermolecular potential and on the memory function \*

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A new molecular dynamics algorithm (J.Comput.Phys. 47, 444 (1982)) enables us to calculate the coefficients in the Mori-expansion of the velocity autocorrelation function  $\phi(t)$  accurately. These coefficients are used to analyse the influence of the attractive forces and to find memory functions for  $\phi$ . The computations are performed for systems of Lennard-Jones particles with - (LJ) and without (WCA) attractive forces. The results (Fig. 1) show that the attractive forces contribute to  $\phi$  with a gaussian-like term and with the maximum at a time which corresponds to about five mean collision times. The effect on  $\phi$  of increasing the density can be separated into a short-time effect, caused by a short-time memory, and an effect of the same form and location as the effect from the attractive forces (Fig. 2). The short-time memory can be described by a simple gaussian and with a relaxation time in good agreement with the mean collision time obtained from perturbation theories (Table I).

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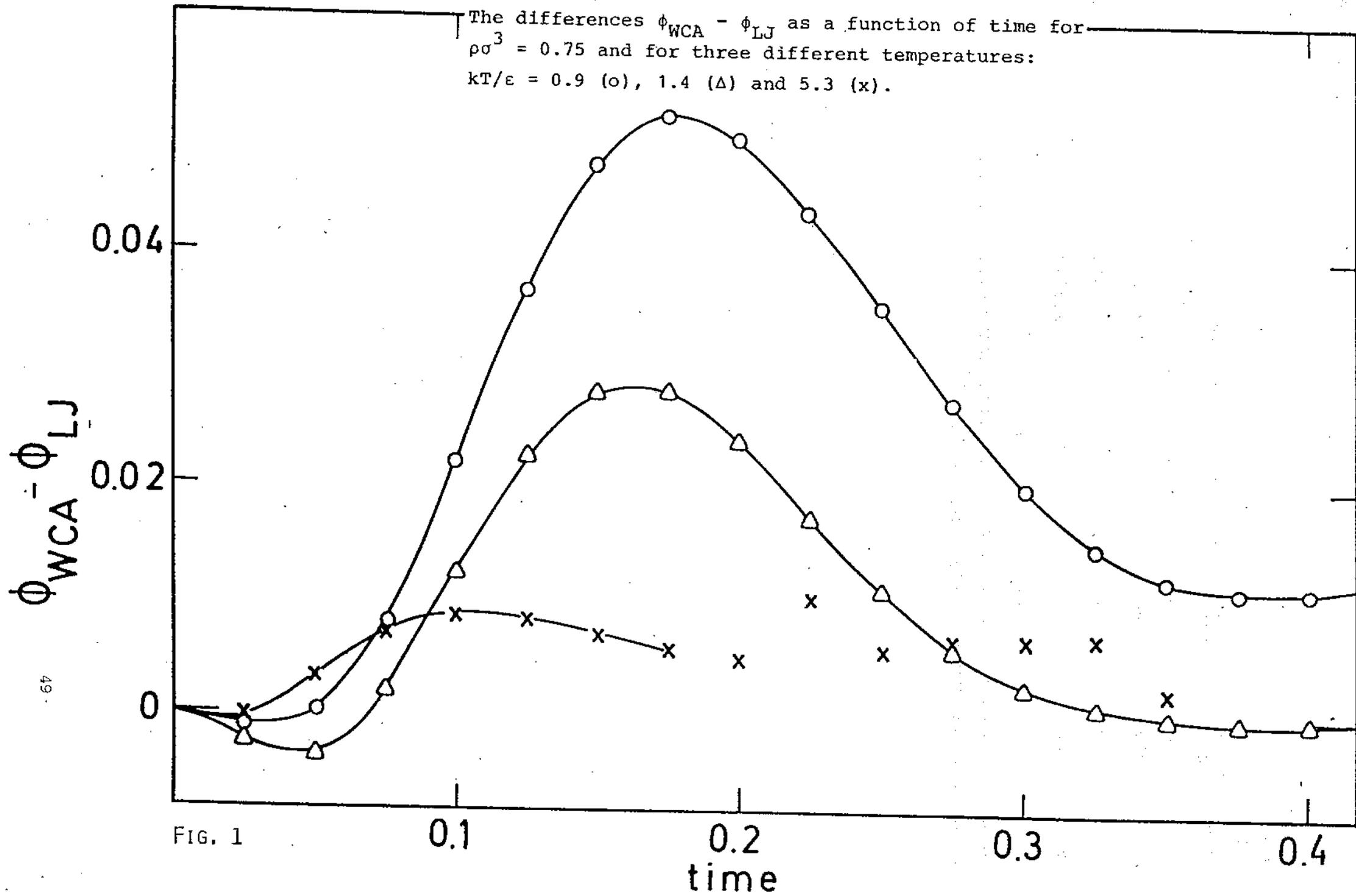


TABLE I. Collision times and relaxation times

Density	Temperature	Collision time $\tau$	Relaxation time $\tau_1$	
			WCA	LJ
0.75	0.900	0.0488	0.0517	0.0551
0.75	1.400	0.0442	0.0431	0.0453
0.75	5.300	0.0333	0.0240	0.0240
0.80	0.900	0.0405	0.0513	

The numbers are for  $\rho\sigma^3$ ,  $kT/\epsilon$  and  $\tau(\epsilon/m)^{1/2}\sigma^{-1}$

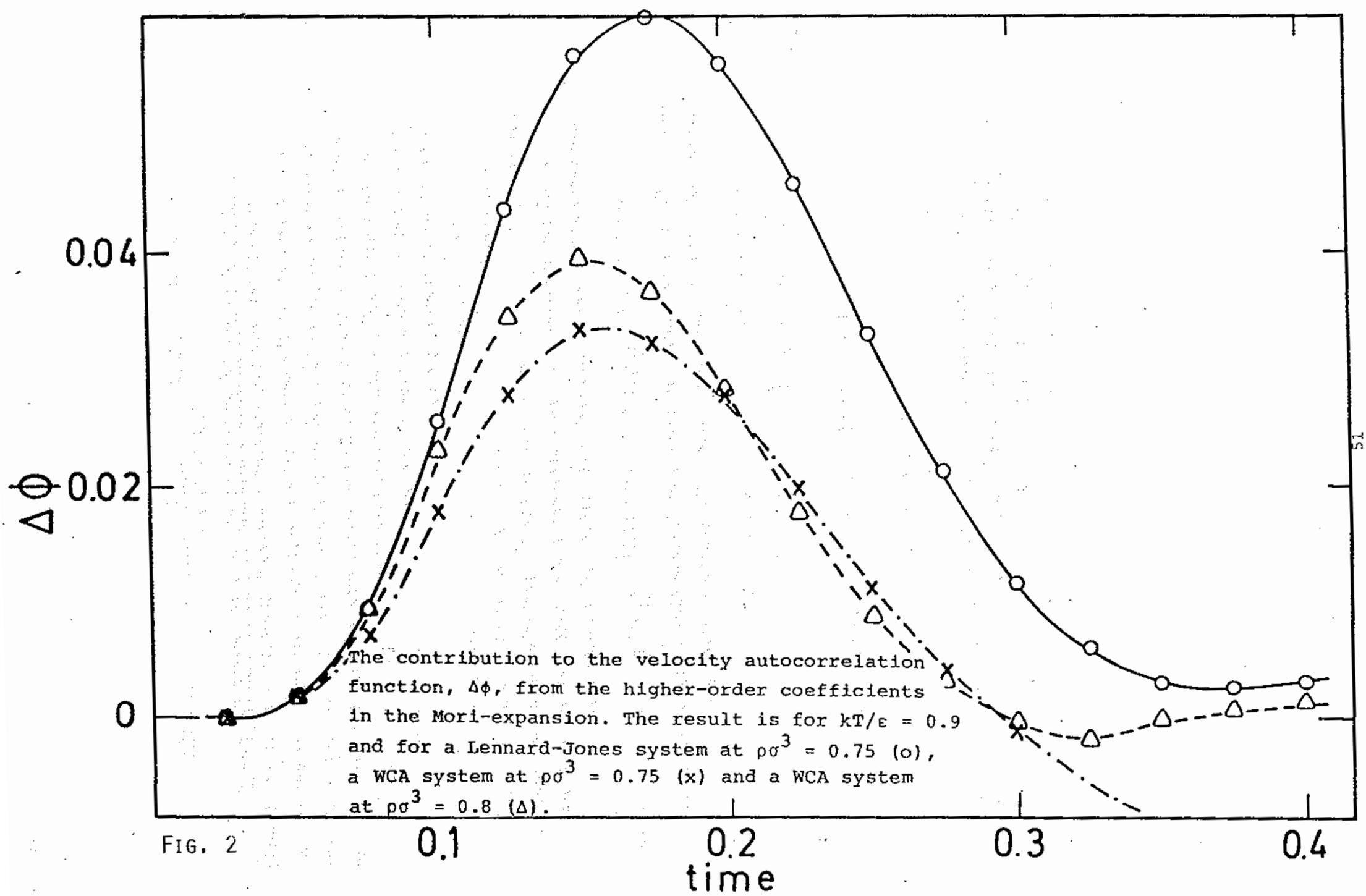


FIG. 2

## A NOTE ON NOSÉ'S CONSTANT TEMPERATURE MOLECULAR DYNAMICS ALGORITHM

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Nosé [1] has recently proposed a pseudo-Lagrangian in which the kinetic energy is a constant of the motion. Without wishing to get into a discussion as to the relative merits of this and other similar tricks, I would like to discuss a technical aspect of Nosé's work. In his paper, Nosé remarks that the algorithm must be implemented using a non-constant time step. In this note, I wish to describe a simple generalization of the usual leapfrog algorithm which could be used to integrate Nosé's equations of motion.

In the usual notation, let  $\underline{r}_i(t)$  denote the position of the  $i^{\text{th}}$  particle at time  $t$ . Let  $\epsilon$  denote the time step and let  $\phi(r)$  denote the inter-particle potential. Let  $m_i$  be the mass of the  $i^{\text{th}}$  particle. Nosé introduces a velocity scaling function  $s(t)$  and a constant  $Q$  and shows that the following pseudo-Lagrangian gives a canonical distribution of trajectories:

$$L(t) = 1/2 s(t)^2 \sum_{i=1}^N m_i \dot{\underline{r}}_i(t)^2 + 1/2 Q \dot{s}(t)^2 - \sum_{i < j} \phi(|\underline{r}_i - \underline{r}_j|) - f k_B T \ln[s]$$

where  $f = 3N + 1$  is the number of degrees of freedom plus 1,  $k_B$  is Boltzmann's constant and  $T$  the absolute temperature. The dynamical equations are

$$m_i d/dt [s(t)^2 \dot{\underline{r}}_i(t)] = \underline{F}_i, \quad i = 1, 2, \dots, N$$

$$Q d^2 s(t)/dt^2 = s(t) \sum_{i=1}^N m_i \dot{\underline{r}}_i(t)^2 - f k_B T / s(t),$$

where  $\underline{F}_i$  is the actual force on particle  $i$ . We discretize these differential equations using

$$\dot{z}(t) = [z(t + \epsilon) - 2z(t) + z(t - \epsilon)]/\epsilon^2$$

$$z(t) = [z(t + \epsilon) - z(t - \epsilon)]/(2\epsilon)$$

where  $z(t)$  stands for any dynamical variable. The difference equations have to be solved successively, given the initial conditions

$$\dot{\underline{r}}_i(0) = \underline{v}_i, \quad i = 1, 2, \dots, N$$

$$s(0) = 1, \quad \dot{s}(0) = 0,$$

the last condition being somewhat arbitrary. Assuming that the algorithm has been started, we first find the new positions  $\underline{r}_i(t+\epsilon)$  in terms of the as yet unknown quantity  $s(t+\epsilon)$ , obtaining

$$\underline{r}_i(t+\epsilon) - \underline{r}_i(t-\epsilon) = \frac{\underline{f}_i \epsilon^2 + 2s(t)^2 [\underline{r}_i(t) - \underline{r}_i(t-\epsilon)]}{s(t)[s(t+\epsilon) + 2s(t) - s(t-\epsilon)]}$$

where  $\underline{f}_i(t) = \underline{F}_i(t)/m_i$ .

This may then be inserted into the discrete form of the equation for  $s(t)$  to obtain an algebraic equation

$$s(t+\epsilon) - 2s(t) + s(t-\epsilon) = \frac{s(t) \left\{ \sum_{i=1}^N \|\epsilon^2 \underline{f}_i(t) + 2s(t)^2 [\underline{r}_i(t) - \underline{r}_i(t-\epsilon)]\|^2 \right\}}{4[s(t+\epsilon) + 2s(t) - s(t-\epsilon)]^2} - k_B T \epsilon^2 / s(t)$$

for the unknown quantity  $s(t+\epsilon)$ , which is conveniently solved by iteration. We note that  $s(t+\epsilon)$  does not appear in the summation, which need only be performed once.

**Reference:**

1. S. Nosé, *Molec. Phys.* 52, 225-268, (1984).

Effective Potentials for Ionic Oxides

Recent studies<sup>(1-3)</sup> have shown that it is possible to derive empirical potentials for alkali halides that can be successfully used in defect simulation studies. Schottky and vacancy migration energies calculated using these potentials are in good agreement with experiment<sup>(4)</sup>. These potentials are based upon a shell model description<sup>(5)</sup> and parameters are derived by fitting calculated crystal properties ( $\epsilon_0$ ,  $\epsilon_\infty$ ,  $C_{11}$  etc) to experimental data. An interesting feature of these potentials is the transferability of parameters representing short-range interactions between ions and polarisation effects.

We have adopted a similar approach to derive empirical potential parameters for oxides and considered modifications necessary before such potentials can be used in mixed oxide systems. Shell model potentials are used, but unlike the case for the alkali halides, within which polarisability and short-range interaction parameters can be transferred, modifications must be introduced when transferring potential parameters between different oxides. In particular anion polarisability varies with structure and the nature of the host cation since the oxide ion's second electron is bound only by the Madelung potential. Potential parameters must also be modified to reflect changes in cation coordination.

These potentials have been used to calculate perfect lattice, defect and surface properties of a range of binary and ternary

oxides. The successful application of this method of potential derivation to a range of oxides should enable the number of oxides for which effective potentials are available to be extended.

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A COMPUTER MODELLING AND EXAFS STUDY OF RbBiF4

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RbBiF4 is an exceptionally good ionic conductor. It adopts the fluorite structure (with an apparently random distribution of Rb and Bi ions), but the conductivity is considerably higher than that of comparable simple fluorite structured halides e.g. BaF2.

A recent EXAFS study (see SRS bulletin No.5, p39) revealed two intriguing structural features of this system. First there was found to be a remarkably large difference between the Rb-F and Bi-F bond lengths: the former is increased by approximately 0.3A and the latter reduced by the same amount relative to the mean M-F bond length in the structure. In view of the surprising magnitude of this effect, support from other techniques was needed. Secondly, it was found that the Rb-F bond length decreases with temperature. We interpreted this result in terms of the preferential formation of vacancies at higher temperatures in the vicinity of the lower charged Rb ions; outward relaxation of the Rb around the vacancies would lead to a decrease in the mean Rb-F bond length.

In the light of these results we have recently examined this mixed fluoride by lattice modelling techniques. Calculations were performed on a large unit cell. After energy minimisation it was found that the Rb-F and Bi-F bond lengths differed by 0.6A - a result in excellent agreement with the EXAFS study. In addition, the magnitudes of the relaxation of Rb ions around F vacancies accords well with the magnitudes of the shift in the Rb-F bond length with temperature.

Further work is in hand; but the present results provide a good illustration of the value of the concerted use of EXAFS and computer modelling techniques.

CCP5 CIRCULAR: STOCHASTIC DYNAMICS AND MACROMOLECULES,  
UNIVERSITY OF YORK, SEPTEMBER 1985.

This is the title of the second CCP5 Meeting of 1985, which will be held at the University of York. The dates are September 11th. (evening arrival) to September 13th. Make a note in your diary now! A registration form will appear in the next CCP5 Newsletter.

If you think you might like to contribute a talk or a poster, it would be a help if you could send a short note indicating your interest to one of the organisers presented below. As always with our meetings the proceedings will be fairly informal and accounts of work in progress, or discussion of methodology or computational techniques will be welcome.

The title of the meeting will be interpreted broadly. There are likely to be sessions on polymers, colloids and biological macromolecules, not necessarily limited to stochastic methods. Theoretical developments in stochastic methods would also be relevant.

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