

DARESBUY LABORATORY

# INFORMATION QUARTERLY

for

# MD & MC SIMULATIONS

An Informal Newsletter associated with Collaborative Computational Project No. 5 on Molecular Dynamics and Monte Carlo Simulations of Macroscopic systems.

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CONFIDENTIAL

# MEMORANDUM FOR THE DIRECTOR

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Editorial

In the tradition of the past newsletters, we begin the ninth newsletter by thanking the contributors for the articles appearing. Their efforts, we know, are greatly appreciated by the (now world wide) readership of this little bulletin.

Once again we remind our readers that their own contributions would always be welcome. There are surely many useful computational or theoretical ideas that could be printed in these pages, plus, of course, news of events and research. Why not give it a try?

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## General News

1) The next CCP5 meeting on the subject of 'Phase Transitions' is scheduled to take place in Southampton on 19/20th December 1983. The estimated fee for the meeting is £32. The provisional speakers include Professor D. Landau (Georgia) who will speak on 'Size Effects in Phase Transitions', and Professor G.R. Luckhurst (Southampton) who will speak on 'Phase Transitions in the Simulation of Liquid Crystals'.

Anyone wishing to contribute a paper on the subject of phase transitions in solids, liquids and gasses, should write to Dr. Dominic Tildesley or Dr. David Adams at the Chemistry Department, The University, Southampton SO9 5NH, UK.

2) The Cray-1S computer left Daresbury Laboratory in May and is now at the University of London Computer Centre (ULCC) undergoing demonstration tests. User access to it is expected to occur in mid June, though it is not guaranteed that all possible access routes will become available simultaneously. Users should note that data stored on the Cray discs at Daresbury will be re-created at ULCC (with ULCC identifiers) provided they are not over their allowed allocation. Data stored on the Daresbury NAS AS7000 system will have to be transferred by magnetic tape to ULCC. Advice on this is available from the Daresbury User Support Group (Tel. 0925-65000, Ext.351).

3) The University of Manchester Regional Computer Centre (UMRCC) have received the Amdahl 470/V7A computer to replace the existing ICL 1904S and 1906A front-end processors. Acceptance of the new computer is scheduled for August 1983 and user service should start in October. The ICL machines will be phased out over two years. The Amdahl will have a MVS operating system with the ROSCOE editing and job submission system. The computer will front-end the CDC7600 and CYBER 205 computers. The CYBER 205 arrived in April and is currently undergoing acceptance trials.

4) The SERC Rutherford and Appleton Laboratories (RAL) took delivery of the new ICL ATLAS 10 computer in April. The computer is currently undergoing acceptance and software validation trials. Time on the ATLAS 10 is

shared between ICL and RAL until 1st September. A limited production service is scheduled for 1st June.

5) Readers are reminded of the existence of the CCP5 Program Library which is available to any applicant, on the submission of a magnetic tape to the librarian. Listings and documentation are also available. The services are free of charge to academic establishments. A list of the programs available is provided overleaf.

Anyone wishing to donate programs to the CCP5 Program Library should also contact the librarian: Dr. W. Smith, SERC 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.

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  $r > d$ . The properties calculated are the average configuration energy and its R.M.S. deviation, the pair radial distribution function and the melting factor.

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 (Rosky, 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.

A Review of the Eighth CCP5 Meeting held at  
'The Lawns Centre', University of Hull between  
the 29th and 30th March, 1983. The subject of  
the Meeting was: 'The Computer Simulation of  
Molecular Liquids and Liquid Mixtures'

by

D.M. Heyes and W. Smith.

The last CCP5 Meeting was well attended, by approximately sixty people, drawn from a wide range of disciplines. It was heartening to see an increasing interest in computer simulation being expressed by experimentalists, who were present in great numbers. As MD and MC continues to make progress towards simulating more complex liquids, then this trend will surely continue.

Molecular liquids and liquid mixtures can be investigated in many ways, as the number of variables which characterise them increases with the complexity of the system. This was certainly evident from the wide variety of effects and systems discussed at the conference.

The first speaker outlined the problems of obtaining the chemical potential of these systems and reviewed the work already performed on the computer modelling of mixtures.

PROFESSOR K.E. GUBBINS (Cornell University, U.S.A.) presented a talk called 'Computer Simulation and Perturbation Theory Studies of Molecular Liquids'. He began by reviewing the computer simulation methods for calculating the chemical potential of a fluid. The most obvious method available is the Grand Canonical Monte Carlo method, which is unfortunately computationally expensive, but has found some applications in the study of adsorption problems, phase transitions and other phenomena at low density (e.g. towards the critical region).

Of more recent interest is the Test Particle method (or Widom's method). In this method the test particle is an imaginary particle, which is inserted as a probe of the state of the fluid. Technically, this only requires minor modifications of standard MC or MD programs. The particle does not participate in the interaction within the fluid and does not contribute to the ensemble

averages. The location of the test particle in phase space is governed by a probability function ( $f$ ), which is determined by the simulation.

A variation of the method (known as the Inverse Widom method) uses a real particle in place of the imaginary one. The probability function in this case ( $g$ ) is dissimilar to the function  $f$  and does not sample regions of high potential energy as efficiently. As a result of this, the method does not appear to be as useful generally. However, the functions  $f$  and  $g$  are related and thus, in regions of high density, where Widom's method is not applicable, the Inverse Widom's method may be used effectively to determine  $f$ . In these circumstances the two methods may be considered to be complementary. The Inverse Widom method has recently been adapted by Powles et al. (1982) for use in molecular dynamics simulations.

To summarise, the test particle methods are convenient to use in all but high density liquids or for mixtures containing large solute molecules. A method which can be used when the test particle routes are unsatisfactory is discussed below, but which requires quite major changes in a computer program to implement it.

An alternative to the Test Particle method is the Umbrella Sampling method of Torrie and Valleau (1974). In this method the simulator attempts to bias the sampling procedure to obtain better statistics for the region of phase space of most interest. Effectively, the method requires the multiplication of the probability function  $f$  by a suitable weighting function ( $w$ ). The selection of the appropriate weighting function is problematical and a common technique is to calculate  $f$  first by conventional simulation and then use  $1/f$  as the weighting function in a repeat simulation. This has the effect of 'flattening' the distribution functions in the repeat simulation, resulting in more efficient sampling of the extremes. The method has the disadvantage of being more difficult to implement than Widom's method and does not provide meaningful ensemble averages for all the properties of the system that are usually evaluated (e.g. correlation functions) in the same run.

Despite the wealth of data on model mixtures of simple spherical molecules, relatively little work has been performed on non-spherical molecule mixtures. Professor Gubbins then described the results of computer simulations for molecular liquids and liquid mixtures by Wojcik and Gubbins (1982). Comparatively little was reported on such systems previously. The systems studied consisted of hard spheres (HS), and hard dumb-bells (HD), hard dumb-bells with fractional quadrupole charges (HDQ), oblate spherocylinders (SC) and two-centre Lennard-Jones molecules.

The influence of molecular size and shape on the system pressure was found to be small in HS and SC systems but much larger in HD systems. The incorporation of a quadrupole (in HDQ) causes a pressure decrease and the potential energy becomes more negative. There is also an increase in potential energy with increasing bondlength. These effects are further apparent in the site-site correlation functions, where the inclusion of the quadrupole causes a sharper nearest-neighbour peak.

The mixtures studied involved the systems HDQ/HSQ (HSQ = hard spheres plus fractional charge quadrupole) and HDQ/HDQ and included changes in the quadrupole sign. In the case of the HDQ/HSQ mixture, the potential energy was found to be more negative than the corresponding HD/HS system. Also the use of oppositely charged quadrupoles in the HDQ(+)/HDQ(-) system gave the most negative energy. This effect was less pronounced in the HSQ/HSQ system, suggesting a bondlength effect. The site-site correlation functions indicated that a 'T' conformation of molecules was most favoured in HDQ(+)/HDQ(-), but that both parallel and end-on configurations occurred in HDQ(+)/HDQ(-). These observations were substantiated by the calculated angular correlation parameters  $P_2$ .

Professor Gubbins concluded his talk with a short description of the perturbation theory methods used in simulation. In the spherical systems it is the objective to simulate a fluid (the reference fluid) with properties closest to the real fluid of interest. The results may then be improved upon using perturbation theory. For nonspherical systems the perturbation may be regarded as the effect of the molecular shape. The short range repulsive forces form the basic model of the reference fluid, while the longer ranged attractive forces constitute the perturbation. For example, a diatomic molecule may be represented as a hard dumb-bell reference fluid with a soft perturbation. Although such perturbation theories of molecular fluids can now cope well with either strong multipolar forces or with a non-spherical shape, there are serious deficiencies in mixtures of the two types of molecule. Good reference systems for these latter mixtures have yet to be developed.

This theme was continued by DR. N. QUIRKE (University of Maine, U.S.A.), co-authors D. Fincham and D.J. Tildesley, who reported the results of MD simulations of molecular liquid mixtures on the Distributed Array Processor (or D.A.P.). The goal of their calculations was to determine the phase diagrams for molecular liquid mixtures. In order to achieve this the chemical potentials of the fluid and liquid phases were calculated by the particle insertion method, described above. This technique enables the chemical potential to be obtained from the MD run at the desired state (intermediate or reference states are not

needed). The details are that the average of the Boltzmann factor for the insertion of an extra particle into a liquid configuration at different positions is accumulated. A thousand insertions per time step for a  $\sim 10,000$  time step simulation are needed. The DAP performs these insertions independently and consequently is efficient at this. A fixed and moveable grid (which underwent random displacements in position and orientation) were both tried but showed much the same behaviour in breaking down at  $\rho^* \gtrsim 0.45$  ( $\rho^* = 0.63$ ,  $T^* = 2.0$ ).

The modelled system was  $\text{CO}_2/\text{C}_2\text{H}_6$  at low density. The Lorentz-Berthelot rules for equimolar mixtures lead to large negative pressures. To compare with experiment the pressure is needed to a precision of less than one atmosphere, in order to approach the experimental excess mixing pressures. This is a resolution which is difficult to achieve by MD. Nevertheless the structures of the mixtures compared favourably with the theory of Tildesley and Encisco (except for the peak heights which is attributable to the important role of the attractive potential in this mixture). Modifications to the  $\text{CO}_2/\text{C}_2\text{H}_6$  potentials were described and the use of the particle insertion method combined with a virial expansion to locate the density of the vapour along the coexistence line was illustrated. Dr. Impey in the discussion agreed that there are large technical problems here because of the small pressure differences between the two pure components. Pressure fluctuations of order 1 kbar are not unusual by MD.

Other aspects of liquid mixtures which are more accessible by computer simulation were discussed by PROFESSOR F. KOHLER (University of Bochum, Germany), co-author C. Hoheisel. They were interested in testing the assumption of randomness in the structure of Lennard-Jones liquid mixtures. In perturbation theories for liquid mixtures, random mixing is usually assumed. Further refinements, which introduce a certain degree of "non-randomness" have been formulated in terms of the repulsive term for different sized molecules. Significantly the attractive term is assumed not to introduce any extra structural order. This was borne out by MD simulations of mixtures with components of different interaction energy and/or different molecular size. The Lorentz-Berthelot mixing rule was assumed. For mixtures of equally sized molecules the regular solution prescription of non-randomness was found to be a reasonable description. For mixtures of differently sized molecules the effects of size differences (which favour unlike contacts) was much more important than the effects of interaction energy at long range.

DR. C. HOHEISEL (University of Bochum, Germany), co-author M. Schoen, talked about the dynamical aspects of the above systems. The mutual diffusion coefficients in Lennard-Jones (mainly) equimolar mixtures were investigated and compared

with an ideal prediction based on a linear combination of the component self-diffusion coefficients in the pure state. In contrast to work on molten salts, it was discovered that the mutual diffusion coefficient was larger than the ideal prediction. For  $\epsilon_1/\epsilon_2 = 2$  a ~5% enhancement due to cross-correlations was discovered for  $\sigma_1 = \sigma_2$ . This is an artefact of the Berthelot combination rule,  $\epsilon_{12}^{LB} = (\epsilon_1 \cdot \epsilon_2)^{1/2}$ . The minimum in this potential is ~6% shallower than in the ideal system which is described by the average combination rule:  $\epsilon_{12}^{AV} = \frac{1}{2} (\epsilon_1 + \epsilon_2)$ . Consequently as would be expected this fact causes an increase in the mutual-diffusion coefficient. These effects are lessened when the sizes (i.e.,  $\sigma$  values) of the molecules are made different. The liquid structure is a compromise between the demands of the 1:1, 1:2 and 2:2 potentials. As  $\sigma_1/\sigma_2$  increases these two species will spend less time in their most favoured relative separations in the vicinity of the minimum of  $\phi_{12}$ . Therefore its influence on cross-correlations is significantly reduced.

DR. M. CLAESSENS (University of Brussels, Belgium), co-authors M. Ferrario and J.-P. Ryckaert, investigated the short range order in model liquid benzene, using the technique of MD by constraints. He raised doubts about the current opinion that benzene in the liquid state tends to favour a perpendicular arrangement of molecules between their planes and axes. Three potential models were employed, a 6-centre Lennard-Jones model, LJ6; a similar model with a point quadrupole, LJ6Q and the Evans-Watts model (1976, Mol.Phys., 32, 93). The parameters of the first two potentials were empirically adjusted to give simulated pressure and polarization properties which were similar to those of the experimental liquid.

The carbon-carbon pair distribution functions were little different for the three cases and all compared well with experiment. A more discriminative function was the centre of mass pair distribution function. Earlier workers had used the angle between the  $C_6$  axes of benzene as the variable defining relative orientation. This is, however, quite insensitive to the precise conformation and all models gave similar results. On defining alternative orientation parameters, it was found that for the Evans-Watts model a preference for a parallel configuration was apparent, but this was less marked for LJ6 and in fact vanished for LJ6Q. Therefore no model led to an overall excess of perpendicular arrangements when compared with an orientationally disordered system. Further tests of the models in predicting the static structure of benzene crystals showed that the LJ6Q potential did indeed provide the best description of benzene.

DR. S. DE LEEUW (University of Oxford), co-author N. Quirke, calculated the dielectric and thermodynamic properties of two-centre Lennard-Jones molecules, each with an axial point-dipole moment. The dielectric constant decreases with increasing elongation ( $\lambda^*$ ) as predicted by perturbation theory (but which underestimates the magnitude quite significantly). Nevertheless, a simple perturbation theory approximation was shown to obtain qualitative information on the effects of molecular shape. For increasing  $\lambda^*$  the anti-parallel configuration is favoured at close distances. Further out a head-to-tail relative configuration becomes possible again. Evidence for two phase behaviour was presented. Evidence for three-body correlations for  $\lambda^* \leq 0.2$  was not found. However as  $\lambda^*$  increases the 3-body correlation became more positive at short separations, decreasing rapidly as distance increases.

DR. D. ADAMS (University of Southampton) investigated cross-correlations in dipolar fluids. Although it is often assumed that the molecular dipole cross-correlation function,  $\langle \underline{\mu}_1(0) \cdot \underline{\mu}_2(t) \rangle$  decays on the same time scale as the autocorrelation function,  $\langle \underline{\mu}_1(0) \cdot \underline{\mu}_1(t) \rangle$ , MD calculations revealed that this was not the case. Stockmayer fluid simulations using the Ewald summation show that when  $\langle \underline{\mu}_1(0) \cdot \underline{\mu}_2(0) \rangle$  is small and positive then  $\langle \underline{\mu}_1(0) \cdot \underline{\mu}_2(t) \rangle$  decays more slowly than  $\langle \underline{\mu}_1(0) \cdot \underline{\mu}_1(t) \rangle$ . However, if  $\langle \underline{\mu}_1(0) \cdot \underline{\mu}_2(0) \rangle$  is small and negative then  $\langle \underline{\mu}_1(0) \cdot \underline{\mu}_2(t) \rangle$  decays more rapidly than  $\langle \underline{\mu}_1(0) \cdot \underline{\mu}_1(t) \rangle$ . There is a bias towards initial orientations. Different behaviour is observed if the computer simulation used a truncated dipole-dipole interaction. The time and space behaviour of these dipole correlations were discussed in terms of classical electrodynamics, using the generalised Kirkwood g-factor and Debye relaxation theory.

DR. B. JONSSON (Chemical Center, Lund, Sweden) performed MD simulations of quadrupole relaxation of  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{Cl}^-$  ions in dilute aqueous solution. The nmr relaxation mechanism is believed to be due to coupling between the ion nuclear quadrupole moment and the field gradient at the nucleus. The latter is caused by the surrounding water molecules. The potential energy and field gradient functions (assumed pair wise additive) were obtained from ab initio quantum mechanical calculations. The simulations demonstrated that the first hydration shell is primarily responsible for field gradient fluctuations at an ion. Two processes, one fast ( $\sim 1$  ps) and one slow ( $\sim 10$  ps) are responsible. The former is mainly translational in origin (i.e. involving a change between 5 and 6 coordination) and the other is principally rotational. Small cations relax mainly by the former mechanism, whereas  $\text{Cl}^-$  is influenced by both mechanisms more or less equally. The relaxation of a water molecule around a  $\text{Li}^+$  is slower than for  $\text{Cl}^-$ , although the relaxation time for field gradient is just the reverse. The field gradient time correlation function has a very rapid initial decay (inertial in origin). This is then followed by a slower diffusional decay.

The cooperative rearrangement of the first hydration shell is responsible for this. The relaxation rates calculated are within a factor of 2 of those measured by nmr.

PROFESSOR H.J.C. BERENDSEN (University of Groningen, The Netherlands), co-author J.P.M. Postma, dealt primarily with the simulation of water using the 'constraint method' to provide unexpected insights into the bandshapes of vibrational spectra.

In constraint dynamics the motion of rigid molecules is handled by Newton's equations in a cartesian reference frame. The forces on each atom are evaluated in the usual way by molecular dynamics techniques, but an additional force is added (the constraint force) which allows the molecule to retain its original shape in the subsequent motion. The constraint forces are calculated by the method of 'Lagrangian undetermined multipliers' and the imposed constraints are the intramolecular interatomic distances, which remain constant. This resetting, using the SHAKE subroutine, effectively computes internal forces within the molecule. These forces can be considered as perturbations on the intramolecular oscillators and as such are useful to predict intramolecular spectra.

The relationships between the intramolecular spectrum and the perturbing forces and molecular motion are complex. The fundamental stretching frequency of the OH or (OD) bond is affected by the surrounding liquid. These forces have both 'fast' components, which give rise to an homogeneous (Lorentzian) broadening of the spectrum, and 'slow' components which produce heterogeneous (non-Lorentzian) broadening. In addition there is the rotational motion of the molecule which will couple with the vibrational motion. These effects are convoluted in the observed Infra-red and Raman spectra of the liquid. The value of constraint dynamics in simulating such liquids is that it permits the simulator to begin with a simple rigid molecule - representing the gas phase structure - and then to determine the perturbing forces operating on it in the liquid state. The constraint forces are calculated in a cartesian reference frame, but may be resolved into an intramolecular reference frame allowing the effects of hydrogen bonding etc. on the bond stretch and bend frequencies to be considered separately. In fact, this interaction: O-H...O and H...O-H was specifically treated. The criteria for identifying a hydrogen bond were of necessity somewhat arbitrary. They were that an O...H bond distance is less than 0.29 nm. Also additional criteria regarding the relative orientation of two adjacent molecules are necessary to remove "odd" bonds from the scheme.

These criteria identify nine distinct types of water molecule according to the degree of hydrogen bonding experienced. The average internal force in the direction of the OH bonds in the H<sub>2</sub>O molecule is always in an outward direction. This force is much stronger when the H atom participates in hydrogen bonding. Hydrogen bonding to the oxygen only increases this force to a small extent, while that to the other H atom in H<sub>2</sub>O has no influence. The internal force acting on the H-O-H bending does not correlate with hydrogen bonding.

The force on OH fluctuates slowly when compared with the stretching frequencies, producing a heterogeneous shift and broadening of the resonance frequencies. The bending frequency is not perturbed by hydrogen bonding. Average shift and shape of the OH Infra-red or Raman bands of HDO were reproduced from the force distribution, using an anharmonic term twice as large as the gas phase anharmonicity. A comparison between the spectrum from constraint forces and the observed bandshape for OH stretch of H<sub>2</sub>O in D<sub>2</sub>O showed strong correlation. However, the results for OD were not as good. It is possible that the assumption that frequency shift is proportional to the constraint force should be questioned and further more complicated coupling schemes should be introduced to account for these discrepancies.

JOHN QUINN (Birkbeck College) compared a number of water potentials and their consequences for orientation in computed liquid structure. A variety of water models, PE, ST2, MCY, TIPS2, SPC were compared for dimers in certain significant relative orientations, viz., in the hydrogen bonding region, hydrogen-hydrogen close contact regions and lone pair-lone pair contact regions. A common failure of these models is insufficiently repulsive H-H regions in the potential surface. These were improved by including hard cores on the hydrogens for ST2, SPC and TIPS2. MCY was also improved by altering the potential in this region. The complexity of the 6-dimensional surfaces was highlighted by some quite remarkable three dimensional perspectives on slides of the water-water potential. The PE model was improved by adding a dipole-quadrupole term to the current quadrupole-quadrupole model. Better agreement with quantum mechanical potentials was obtained.

PROFESSOR J.G. POWLES (University of Kent), co-author R.F. Fowler, presented a very entertaining and stimulating talk on the MD simulation of small Lennard-Jones and Stockmayer ( $\mu^* = 1$ ) drops of ~150 particles. Cyclic boundary conditions were employed. At the centre of a drop the liquid is subjected to an excess pressure (above that of the vapour) of  $\{2\gamma/R + P(R) - P(\infty)\}$ . This is of order 200 bar. The macroscopic surface tension  $\gamma$  does not change greatly even down to these small systems. A knowledge of the compressibility leads to a prediction of a ~4% density increase in the centre of the drop. This was not

observed and was shown to be because the density fit is governed by the liquid in the surface region where the effective hydrostatic pressure is much lower than at the centre.

DR. M. WHITTLE (U.M.I.S.T.), co-author J.H.R. Clarke, described the relationships between shear viscosity and molecular orientations in simple diatomic fluids, based on Legendre polynomial expansions of the molecular pair correlation functions. By comparing with MD simulation results a reasonable decoupling between centre of mass and orientational contributions to the shear viscosity was achieved at low density. A number of revealing insights into the effects of orientational movements on shear viscosity were given. Using an Alignment Tensor, which is especially useful at low density, it was shown that the alignment of molecules during shear flow decreases the viscosity.

DR. J.H.R. CLARKE (U.M.I.S.T.), co-author D. Brown, continued this theme by discussing the mechanism of non-Newtonian flow in model n-hexane. A 6-centre LJ model of n-hexane using the Ryckaert and Bellemans potential parameters was used. The effect of applying a shear strain rate was to elongate the conformers (trans-configurations being more important) leading to a rapid rise in shear stress. Interestingly the molecular re-orientation resulting from this perturbation was a much slower process (~20 psec) and which hardly contributed to the observed shear stress changes. A lively discussion ensued. Drs. Ryckaert and Kohler speculated on the effects changing the pair potential parameters would have.

The conference concluded with a talk by GISELE MARECHAL (University of Brussels, Belgium), co-author J.-P. Ryckaert, on the Collective transport coefficients of semi-rigid model liquid n-butane near its boiling point by equilibrium molecular dynamics simulations. The shear viscosity and thermal conductivity were evaluated by flux autocorrelation functions (Kubo formulae) on 192 molecules using a new Ryckaert-Bellemans potential representing a semi-rigid chain (Farad.Disc.Chem.Soc., 66, 95 (1978)). The uncertainties were ~35%. The shear viscosity was in reasonable agreement with experiment; but the thermal conductivity was twice as large as experiment. The self-diffusion coefficients were also investigated by both mean squared displacement and velocity autocorrelation function methods. Interestingly, the trans-conformation had a larger value than that of the gauche. The various fluxes were expressed in terms of "centre of mass" and "atomic" components. Each were similar in area but different in shape and zero-time value.

PROFESSOR K. SINGER (Royal Holloway College), co-author C.S. Murthy, attempted to characterise the definition of a liquid by investigating single molecule space and time behaviour in diatomic liquids.  $\text{Cl}_2$  near the boiling point was simulated. Single particle trajectories were plotted and showed a very irregular path. There were some trends apparent however. During regions of rapid movement through space, the molecular axis tended to lie in the direction of principal motion. Similar plots of single particle kinetic energy and potential energy were presented.

At the end of the first day of the meeting Professor Powles initiated a lively exchange between attendees on the relative merits of Monte Carlo, MC, versus Molecular Dynamics, MD, computer simulation techniques. Perhaps surprisingly, there was quite a large body of support for the unique uses of MC. Professor Kohler mentioned certain routes to free energy were unique to MC. Dr. E.B. Smith said that MC could be used as a self-improvement technique for performing integrals. Professor Gubbins mentioned hard-soft potentials as a system which was much easier to employ by MC than MD. Path integrals were other uses. Dr. Impey was sceptical of certain advantages of MC because MD could also be used for them. For example, constant pressure and temperature MD simulations could be performed just as well as by MC.

The authors would like to thank the following for supplying abstracts of their talks: D.J. Adams, H.J.C. Berendsen, M. Claessens, K.E. Gubbins, C. Hoheisel, B. Jönsson, F. Kohler, S.W. de Leeuw, J.G. Powles, J.E. Quinn, N. Quirke and J.-P. Ryckaert. These were used extensively in preparing this report.

A New Method for Performing MD and MC  
on Point Charge Systems. I: The lamina

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by D. M. Heyes.

In the early days of MD of ionic systems the Evjen method was dismissed as a method for performing the Coulomb lattice summations.<sup>1</sup> Quite rightly, because it gave unphysical structures even if the first shell of image cells was included in these sums. This set the pattern for the next ten years. The Ewald method reigned supreme and quite an enormous amount of literature has been written on it and its convergence characteristics for simulation since 1970.<sup>2,3</sup> In this note, the Evjen method<sup>1</sup> is returned to and with a small modification is shown to be a preferable method to that of Ewald for lamina ("surface") MD i. e. when periodicity is only in two dimensions (say, x and y).

Let there be  $N/2$  positive and  $N/2$  negative point charge ions in the MD (or MC) cell. The potential at a point  $\vec{r}$  within the origin MD cell is required,

$$V(\vec{r}) = \sum_i^N q_i \sum_{\vec{n}} \frac{1}{|\vec{r} - \vec{r}_i - \vec{R}_{\vec{n}}|} \quad (1)$$

where  $\vec{n}$  is the index of an image cell ( $\vec{n} = 0$  is the origin or "real" MD cell),  $q_i$  is the point charge on ion  $i$ ,  $\vec{r}_i$  is its position relative to the origin of the cell (i. e., it is an internal coordinate).  $\vec{R}_{\vec{n}}$  is the displacement vector between the real and an image MD cell, characterised by  $\vec{n}$ . Let the MD cell have a square (x, y) cross-section of sidelength  $S$ .

Fig. 1 - The image cells in the (x, y) plane.

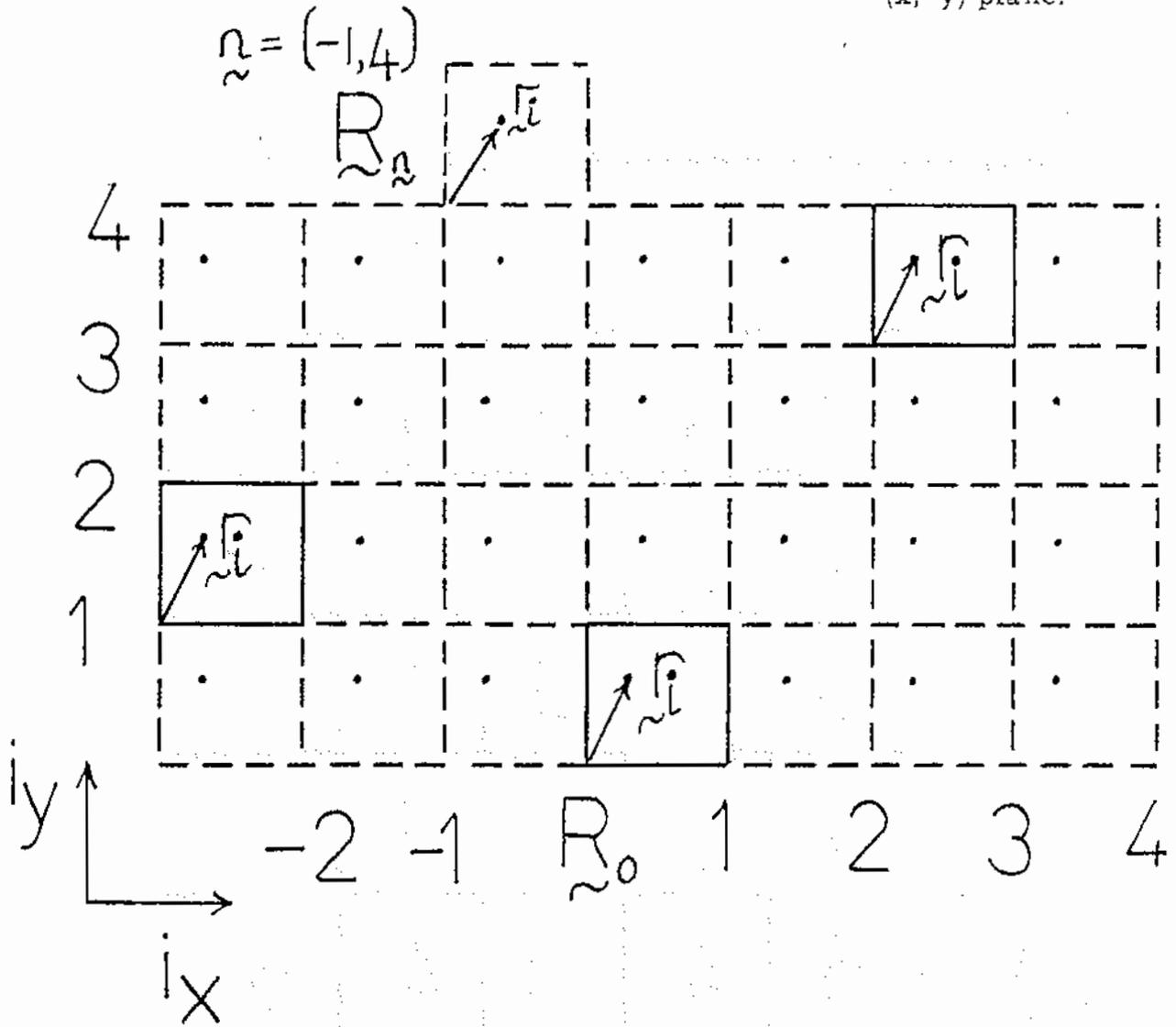
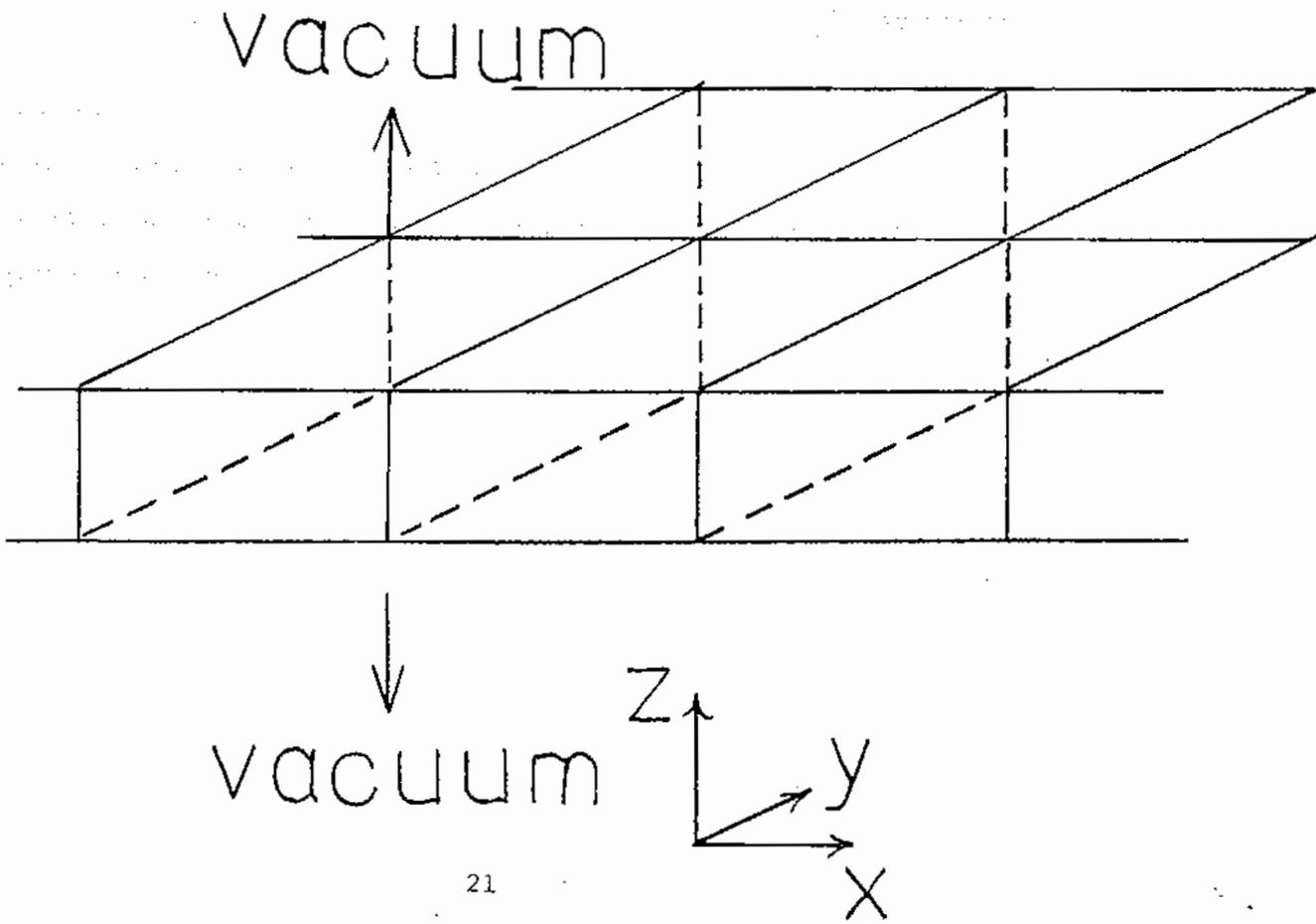
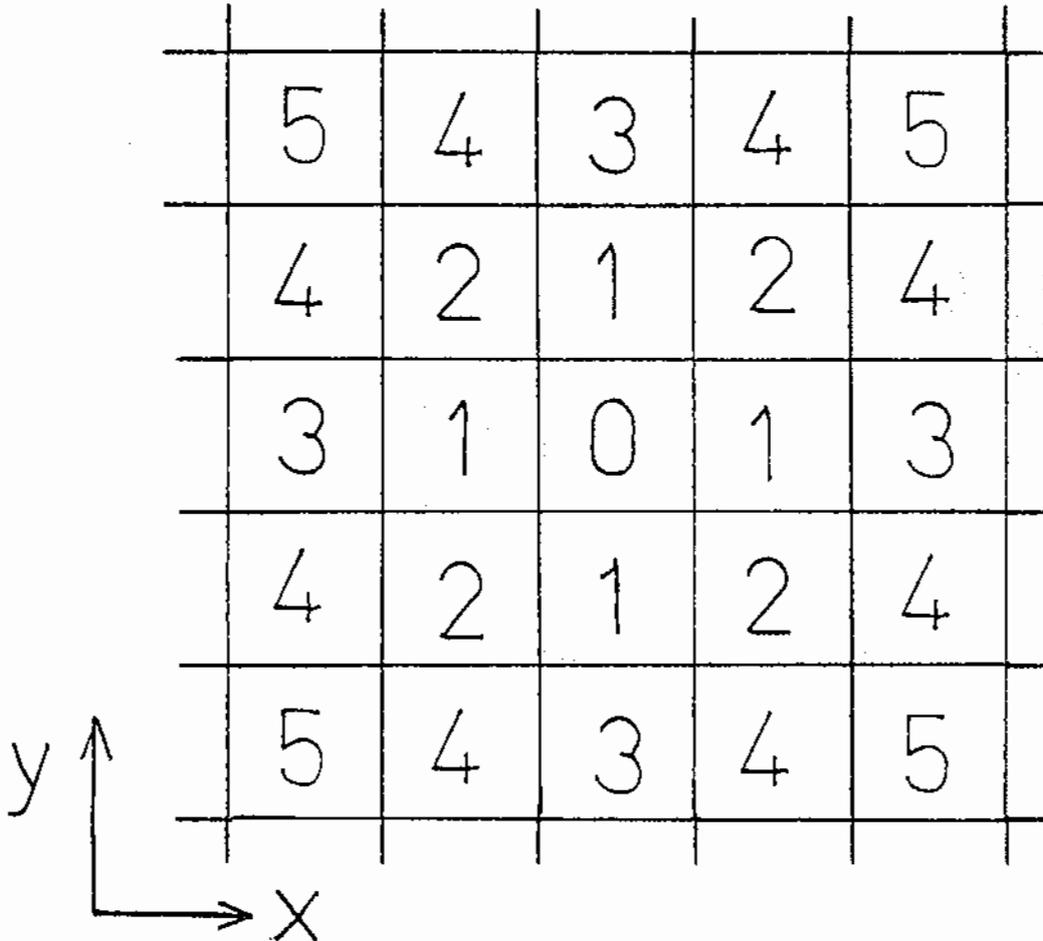


Fig. 2. The lamina



Figs. 1 and 2 should clarify the system studied. The order in which the image cells are included in the sum is illustrated in Fig. 3.

Fig. 3. The image shells.



The image cells are summed in the order of their proximity to the origin cell  $n = 0$ . As  $n$  increases this shell more closely becomes circular. Also the effect of this shell of image cells can be represented by a simple expression involving the dipole moment of the whole cell, as is explained below.

$$\begin{aligned}
 V(\mathcal{F}r_i) &= V(0) - \sum_i^N q_i (\mathcal{F}x_i X_n + \mathcal{F}y_i Y_n + \mathcal{F}z_i Z_n) R_n^{-3} \\
 &- \frac{1}{2} \sum_i^N q_i \left( \frac{\mathcal{F}x_i^2 (1-3X_n^2)}{R_n^2} + \frac{\mathcal{F}y_i^2 (1-3Y_n^2)}{R_n^2} \right. \\
 &\left. + \frac{\mathcal{F}z_i^2 (1-3Z_n^2)}{R_n^2} \right) R_n^{-3} + \dots \dots \dots \quad (2)
 \end{aligned}$$

where  $\{x_i$  is the x-component of,  $\underline{r} - \underline{r}_i = \{x_i$ , etc., and  $X_n$  is the x-component of  $\underline{R}_n$  etc. This expression is a simple Taylor expansion. Let us restrict the sum of equation (2) to those image cells for which  $R_n \gg R_c$ , some critical cut-off radius in the x, y plane. As  $Z_n = 0$  here and the sum in equation (2) can be rewritten as an integral in a two dimensional plane for "large" n then,

$$V(r) \approx - \frac{1}{2S^2} \sum_{i=1}^N q_i \int_{R_c}^{\infty} \frac{R dR}{R^3} \int_0^{2\pi} \left\{ \{x_i^2 (1-3 \cos^2 \theta) + \{y_i^2 (1-3 \sin^2 \theta) + \{z_i^2 \right\} d\theta, \quad (3)$$

where  $X = \cos \theta$  and  $Y = \sin \theta$ . Here a uniform surface density of cell dipoles is implicit in the treatment. Hence

$$V(r) \approx \sum_{i=1}^N (q_i \pi / 2 S^2 R_c) \left\{ \{x_i^2 + \{y_i^2 - 2 \{z_i^2 \right\} \quad (4)$$

Thus it becomes easy to define the effect at long range of the cell dipole moment from an ever increasingly wider and more truly circular annulus of MD cells about the origin. The correction (or "Depolarisation") potential has been discussed elsewhere by the author for static systems.<sup>4</sup> For two dimensional (xy) periodicity, then,

$$V(r) = \lim_{R_c \rightarrow \infty} \sum_{i=1}^N \left[ \sum_n q_i \frac{(r - r_i - R_n)^{-1}}{R_n} + \frac{\pi}{2 S^2 R_c} \left\{ (r_x - r_{xi})^2 + (r_y - r_{yi})^2 - 2 (r_z - r_{zi})^2 \right\} \right] \quad (5)$$

taking  $R_n \ll R_c$

Similarly for the x and z forces,

$$F_x = \lim_{R_c \rightarrow \infty} \sum_{i=1}^N \left[ \sum_{\substack{n \\ \sim}} q_i (r_x - r_{xi} - R_{xn}) (r - r_i - R_n)^{-3} - \frac{\bar{\Lambda}}{S^2} \frac{1}{R_c} (r_x - r_{xi}) \right] \quad (6)$$

and

$$F_z = \lim_{R_c \rightarrow \infty} \sum_{i=1}^N \left[ \sum_{\substack{n \\ \sim}} q_i (r_z - r_{zi} - R_{zn}) (r - r_i - R_n)^{-3} + \frac{2\bar{\Lambda}}{S^2} \frac{1}{R_c} (r_z - r_{zi}) \right] \quad (7)$$

The convergence characteristics of the Evjen, Depolarised Evjen and lamina-Ewald<sup>4</sup> methods are compared in Table 1. The main point to appreciate from this table is the (usually) excellent agreement between the Depolarised Evjen method and the exact potential or force just from only considering the first 3 surrounding image cells (compare the underlined values). The Evjen method is seriously in error and, for these test configurations, can even give the wrong sign for a force. Thus even for this small number of shells the long range (dipolar) correction is still a valid and great improvement on the overall convergence.

On implementation in an MD program, a NaCl (Rigid ion model) N=216 sample at 1200K takes 0.14 sec per time step on the CRAY-1S. The total energy is 674.89 kJ mol<sup>-1</sup> ± 0.02 kJ mol<sup>-1</sup> (r. m. s. deviation) using a Tosi/Funi Born-Mayer-Huggins potential. This is roughly the same speed as MDIONS<sup>5</sup>, an Ewald program. The chief advantage of the Depolarised Evjen method is that it is much easier to code than the Ewald method and one does not lose sight of the principal features of the model employed.

The program used for this new long range correction method is called SURF and is available from the CCP5 library.

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Table 1:

The potential at a point  $\underline{r} = 0$  due to two square planar sublattices:  $q_1 = q$  at  $(x_1, y_1, z_1)$  and  $q_2 = -q$  at  $(x_2, y_2, z_2)$ .  $V(r)$  in units of  $qS^{-1}$ . The x component of the force,  $F_x$ , and  $F_z$  the z component of the force are in units of  $qS^{-2}$ .  $E_w$  - Ewald-like expansion; E - Evjen summation, DE - ~~depolarised~~ Evjen from equations herein.  $R_c = (\tilde{n}^2 + 1)^{\frac{1}{2}} S$  in these expressions and where  $\tilde{n}$  is the integer index of the image cell (shown in Fig 3),  $h = 0.7S$  in  $E_w; (x_1, y_1, z_1)$  and  $(x_2, y_2, z_2)$ :

- (a)  $-(-0.499, 0.15, 0.1)$  and  $-(0.1, 0.32, 0.05)$
- (b)  $-(-0.499, 0.15, 0.1)$  and  $-(0.1, 0.32, 0.4)$
- (c)  $-(0.25, 0.15, 0.0)$  and  $-(0.4, 0.32, 0.0)$
- (d)  $-(0.25, 0.15, 0.1)$  and  $-(0.4, 0.32, 0.4)$ .

Table 1, continued.

$n^2$	V	V	V	$F_x$	$F_x$	$F_x$	$F_z$	$F_z$	$F_z$
	$E_w$	E	DE	$E_w$	E	DE	$E_w$	E	DE
a 0	-0.9588	-1.0653	-0.8390	-4.9334	-5.9086	-4.0268	-0.1755	-0.6142	-0.3001
a 1	-0.6929	-0.8439	-0.6838	-2.5708	-3.8389	-2.5083	0.2491	-0.0342	0.1880
a 2	-0.6662	-0.7986	<u>-0.6680</u>	-2.3557	-3.4651	<u>-2.3786</u>	0.2730	0.0729	<u>0.2542</u>
a 64	<u>-0.6649</u>	-0.6935	-0.6654	<u>-2.3419</u>	-2.5800	-2.3465	<u>0.2738</u>	0.2339	0.2729
b 0	0.6944	-0.0312	0.6899	-3.1013	-4.0444	-2.1626	-4.3103	-2.1440	-4.0290
b 1	1.0909	0.5434	1.0533	-0.7273	-1.9670	-0.6363	-4.2540	-2.8300	-4.1629
b 2	1.1271	0.7060	<u>1.1224</u>	-0.5352	-1.6320	<u>-0.5456</u>	-4.2612	-3.2001	<u>-4.2883</u>
b 64	<u>1.1287</u>	1.0375	1.1270	<u>-0.5214</u>	-0.7593	-0.5259	<u>-4.2610</u>	-4.0231	-4.2569
c 0	1.3195	1.4778	1.1991	7.2602	7.1123	7.5835	0	0	0
c 1	1.1963	1.3984	1.2014	7.3758	7.0438	7.3770	0	0	0
c 2	1.1443	1.3047	<u>1.1438</u>	7.5650	7.2900	<u>7.5616</u>	0	0	0
c 64	<u>1.1434</u>	1.1786	1.1440	<u>7.5693</u>	7.5096	7.5680	0	0	0
d 0	1.8354	1.7058	1.8984	4.6573	7.0809	7.5522	-1.7093	1.9581	-1.8118
d 1	2.1976	1.9970	2.1332	6.3130	6.6581	6.9913	-0.7499	0.7790	-1.8867
d 2	2.1809	2.0451	<u>2.1563</u>	6.9620	6.7457	<u>7.0177</u>	-0.8492	0.2569	<u>-1.9197</u>
d 64	<u>2.1691</u>	2.1447	2.1686	<u>6.9699</u>	6.9108	6.9693	<u>-0.8701</u>	-0.6314	-1.0990

Molecular Dynamics and Graphics: A review of the work at  
IBM UK Scientific Centre

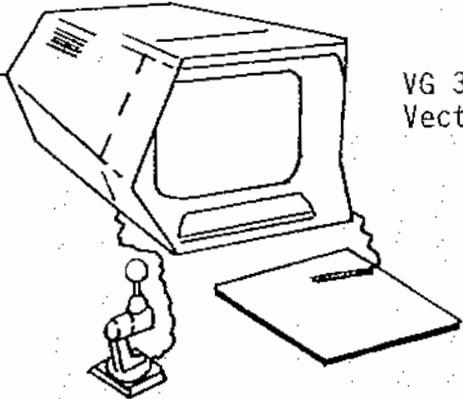
by A J Morffew

The graphics group at the IBM UK Scientific Centre has been doing research into molecular graphics systems for the last four years. We have been interested in many applications of computer graphics for molecular modelling, mainly in collaboration with university research groups. One of these collaborations introduced our group to the problem of molecular dynamics. This collaboration is with Professor Tom Blundell's group, the Crystallography Department of Birkbeck College, London. We have a CASE student with Birkbeck, Ilyas Haneef. Birkbeck collaborated with Wilfrid van Gunsteren, Groningen, on a molecular dynamics simulation of avian pancreatic polypeptide. Haneef then brought a subset of these data to UKSC.

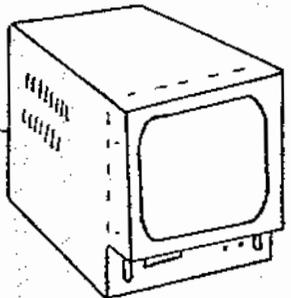
The group at UKSC began investigating ways of displaying these data to emphasise various features. The first step was to set up an interactive animation system [1]. This had been attempted in several other laboratories, for example, R Ladner (Harvard), S Wodak (Brussels), H Bosshard (EMBL), and Ames Research Centre, Moffett Field [2]. The diagram on the next page shows the current UKSC hardware. We are fortunate that our hardware includes a channel attachment of our minicomputer to our mainframe. This allows us to pass data at a very high rate between these machines. When we use animation, we set up the frames on the mainframe and stream them to our Vector General 3300 high level vector graphics device. We can then interact with the display using a tablet and pen or a three-axis joystick [3], in real time without stopping the animation. Using our relational data base [4], we are able to partition the data as we may wish, selecting a subset of the atoms, such as the alpha carbons. These facilities have been found to be very powerful for examining data.

IBM Series/1  
minicomputer

IBM 3031 mainframe  
8 Mb real storage



VG 3300  
Vector graphics system



Ramtek 9460  
Raster graphics system



IBM 3279 Colour display  
station

Another approach we have tried involves finding new ways of plotting trajectories [5]. We have experimented with 4-D transformations, using time as the fourth dimension. Normally trajectories are displayed superimposed on the molecule in its starting conformation. The 4-D transformation allows the researcher to link the end points of the trajectories to the pen position so they can be pulled away from the molecule, to be examined. The whole picture may still be rotated, panned, zoomed, etc. We have also linked three adjacent frames to the pen so that they can be superimposed to highlight variations.

We have spent some time considering ways of finding the collaborative motions in the simulation. One technique we have developed for finding atoms moving together is to animate the distance matrices for successive conformations [6].

We use the term 'distance matrix' for the matrix  $D_{(n,n)}$  where

$$D_{(i,j)} = s(X_{(i)}, X_{(j)})$$

$X$  is the positional vector in orthogonal space and  $s$  is the distance function [7]. The term is also used by some theoretical chemists for a matrix which defines molecule connectivity.

We usually invert and scale the distances so close contacts are the dominant features. A further step that is quite useful is to animate the difference distance matrices, which have been calculated by deducting the elements of a distance matrix from the previous matrix. This gives us a feeling for which atoms are fluctuating most from the mean position and which move together. Should there be any soliton like motion through the molecule, this may also be apparent in the distance and difference distance matrices.

Our most recent work has been finding ways of monitoring the changes in the backbone dihedral angles during the simulation. We have recently implemented the animation of Balasubramanian plots [8]. We

are very pleased with the results, our only problem is in the wrapping round of the vectors as an angle flips between  $180^\circ$  and  $-180^\circ$ . We are presently considering ways of improving this representation.

All of these animated representations are very informative and we have considered several others as well. We are now arranging for some other researchers to use our facilities to help us to evaluate our work and, of course, to help them to investigate the results of their simulations.

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##### UKSC Graphics Group

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Andy Morffew

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David Moss                                        Ian Tickle

##### Groningen collaborator with Birkbeck

Wilfrid van Gunsteren

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## PROGRAM UNITS FOR MOLECULAR DYNAMICS

### I: LENNARD-JONES POTENTIAL

D.M. Heyes

One of the most troublesome aspects of any Molecular Dynamics project is the choice of a system of so-called program units. These link the molecular parameters (such as interaction potential, velocity, mass and position) to the physical characteristics of a particular state (such as MD cell box side length, which is derived from the density and the number of particles, and temperature). In this, the first of two notes, convenient program units for the Lennard-Jones, LJ, system are presented.<sup>1</sup> These have been used by the author for many applications and have proved to be extremely adaptable.

The LJ system is defined by the potential,

$$\phi(r) = 4\epsilon \left\{ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right\}, \quad (1)$$

which is a special case of the general  $n = m$  potential,

$$\phi_{nm}(r) = A e \left\{ \left( \frac{\sigma}{r} \right)^n - \left( \frac{\sigma}{r} \right)^m \right\}, \quad (2)$$

where  $A = \left\{ \frac{1}{(n/m)^{m/n-m}} - \frac{1}{(n/m)^{n/n-m}} \right\}^{-1}$ , (3)

$\epsilon$  is the well depth at the minimum,  $r_{\min}$ ,

$(r_{\min}/\sigma) = (n/m)^{1/n-m}$  and where  $\sigma$  is the interatomic separation at which  $\phi(r) = 0$ .

The LJ and program units are summarised in Table 1. Quantities read-in to a program are in LJ reduced units:

density ( $\rho^*$ ) e.g. 0.8442, temperature ( $T^*$ ) e.g. 0.722, time step ( $\Delta t^* = DT$ ) e.g. 0.005.

It is worth noting that during the mechanics of a LJ program

a minimum of LJ parameters are required. Distance in units of the box-sidelength  $L(=(N/\rho)^{1/3})$  serve to define co-ordinates  $RX(I)$  and co-ordinate increments  $DX(I)$  (which can then be used to evaluate velocity and hence kinetic energy).

TABLE 1

Quantity	LJ unit	Program unit	LJ unit in Program unit
distance	$\sigma$	$(N/\rho)^{1/3} = 1$	$(\rho/N)^{1/3}$
energy	$\epsilon$	1	—
mass	m	1	—
temperature	$\epsilon/k_B$	—	—
pressure	$\epsilon\sigma^{-3}$	—	—
time	$\sigma(m/\epsilon)^{1/2}$	—	—
time step	$\Delta t$	DT	—
velocity	$(\epsilon/m)^{1/2}$	—	—
density	$\rho = \frac{N}{V}\sigma^3$	—	—
number of particles in the MD cell (cubic)	—	N	—
volume of MD cell	—	V	—

Let  $\underline{r}_i$  be the position of molecule  $i$  then the usual algorithm is,<sup>2</sup>

$$\underline{r}_i(t + \Delta t) = \underline{r}_i(t) + \Delta \underline{r}_i(t), \quad (4)$$

where  $\Delta \underline{r}_i(t) = \Delta \underline{r}_i(t - \Delta t) + \Delta t^2 \ddot{\underline{r}}_i(t), \quad (5)$

and  $\dot{\underline{r}}_i(t) = \Delta \underline{r}_i(t - \Delta t) + \frac{1}{2} \ddot{\underline{r}}_i(t) \Delta t. \quad (6)$

Hence in FORTRAN and taking the X components :

$$\text{VELX} = (\text{DX(I)} + 0.5 * \text{FX(I)} * \text{DT} ** 2) * \text{CFV}, \quad (7)$$

$$\text{DX(I)} = \text{DX(I)} + \text{FX(I)}, \quad (8)$$

and

$$\text{RX(I)} = \text{RX(I)} + \text{DX(I)}, \quad (9)$$

in the above order.

Here  $\text{VELX} = \dot{\underline{r}}_i(t), \text{DX(I)} = \Delta \underline{r}_i(t), \text{RX(I)} = \underline{r}_i(t),$

$$\text{FX(I)} = \ddot{\underline{r}}_i(t)$$

where

$$\Delta t = \text{DT} * \sigma(m/\epsilon)^{1/2}, \quad (10)$$

and

$$\text{CFV} = (N/\rho)^{1/3} / \text{DT}. \quad (11)$$

Further details of this scheme can be found in the documentation to CCP5 programs HLJ1, HLJ2, HLJ3 and HLJ4.

### References

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## PROGRAM UNITS FOR MOLECULAR DYNAMICS

### II : BORN-MAYER-HUGGINS POTENTIAL

D.M. Heyes

For an  $n:m$  potential the emphasis in the choice of program units is towards those reduced variables which characterise the potential.<sup>1</sup> This is because many systems can be represented by such a form. It is usually less informative to consider a specific system as one loses the insights provided by highlighting the corresponding states capacity of the potential.

In contrast, an ionic potential is conventionally treated with a particular material in mind. Consequently, the potential and program units are more conveniently expressed in terms of "real" quantities such as Å, seconds etc. As an illustration of this change in technique, a potential which is frequently employed to model alkali halide condensed phases is discussed.

The Born-Mayer-Huggins potential with Tosi-Fumi parameters is considered,<sup>2</sup>

$$\phi_{ij}(r) = q_i q_j r^{-1} + \beta_{ij} b \exp((\sigma_{ij} - r) / \rho) + C_{ij} r^{-6} + D_{ij} r^{-8} \quad (1)$$

The first term is the coulomb interaction between ions  $i$  and  $j$ , with charges  $q_i$  and  $q_j$  separated by a distance  $r$ . The second term in equation (1) is the short range repulsion due to the overlapping charge distributions centred on each ion. The latter two components are the dipole-induced dipole and dipole-induced quadrupole interactions. Maintaining the change in methodology, the salt KCl is considered. The parameters for equation (1) are given in Table 1.

TABLE 1

species combination	$\sigma_{ij}/\text{\AA}$	$\beta_{ij}^b$ /10 <sup>-19</sup> J	$\rho_{ij}^{-1}$ /Å <sup>-1</sup>	$-C_{ij}$ /10 <sup>-79</sup> Jm <sup>6</sup>	$-D_{ij}$ /10 <sup>-99</sup> Jm <sup>8</sup>
++	2.926	0.423	2.97	24.3	24.0
+ -	3.048	0.338	2.97	48.0	73.0
- -	3.170	0.253	2.97	124.5	250.0

It is the aim to print the MD results for distance, time, energy and pressure in the popular units: Å, psec, kJmol<sup>-1</sup> and kbar, respectively. The internal or program units are most conveniently expressed in terms of quantities of order unity; a constraint which governs the choice of program units to be described below.

A. THE POTENTIAL IN PROGRAM UNITS

Now the coulomb interaction in S.I. units is<sup>3</sup>

$$\phi_c(r) = q_i q_j / 4\pi \epsilon_0 r, \quad (2)$$

where

$$|q_i| = 1.6021917 \times 10^{-19} \text{C}$$

$$4\pi \epsilon_0 = 1.11264 \times 10^{-10} \text{C}^2 \text{J}^{-1} \text{m}^{-1},$$

for monovalent alkali halides.

$$\phi_c(r) = \pm 23.071417 \times 10^{-19} \text{J} / (r/\text{\AA}) \quad (3)$$

Therefore the unit of energy (€) internal to the program is 23.071417 x 10<sup>-19</sup> J. As a result equation (1) becomes,

$$\frac{\phi_{ij}(r)}{\epsilon} = \pm \frac{1}{r} + B_{ij} \exp(r/\rho) + C_{ij} r^{-6} + d_{ij} r^{-8} \quad (4)$$

where r is in Å. TABLE 2 gives these new modified parameters.

TABLE 2

species combination	$B_{ij}$	$C_{ij}$	$d_{ij}$
++	108.9885	1.0532513	1.0402481
+-	125.1178	2.0804963	3.1640882
--	134.55001	5.3962874	10.835918

B. CONVERTING THE PROGRAM POTENTIAL ENERGY PER ION TO  $\text{kJ mol}^{-1}$

If the average potential energy per ion is  $\phi^*$  in units of  $\epsilon$ , then scaled to a mole ( $2 \times 6.02252 \times 10^{23}$  ions) this is equivalent to,

$$\begin{aligned} \phi / \text{kJmol}^{-1} &= \phi^* \times 23.071417 \times 10^{-19} \times 2 \times 6.02252 \times 10^{23} \\ &\times 10^{-3} = 2778.9614 \phi^* \end{aligned}$$

Let  $k_E = 2778.9614$  for reference.

C. PROGRAM UNITS OF MASS AND TIME

The program unit of mass is arbitrarily defined to be that of the positive ion or cation,

$$\begin{aligned} m_+ &= 39.102 \times 10^{-3} / 6.02252 \times 10^{23} \text{ kg} \\ &= 6.4926309 \times 10^{-26} \text{ kg, for } K^+ \end{aligned}$$

Consequently the reduced mass of the anion,

$$m_-^* \text{, is } 0.9066799 \text{ , for } Cl^-$$

The program unit of time is  $\sigma(m/\epsilon)^{1/2}$  using notation which was borrowed from the Lennard-Jones system.<sup>1</sup> Here though:

$$\sigma = 10^{-10} \text{ m,}$$

$$m = 6.4926309 \times 10^{-26} \text{ kg}$$

$$\text{and } \epsilon = 23.071417 \times 10^{-19} \text{ J}$$

This produces a reduced unit of time  $t^*$  of  $1.6775412 \times 10^{-14} \text{ s.}$

#### D. THE VERLET ALGORITHM IN PROGRAM UNITS

The Verlet algorithm for following the equations of motion in time increments of  $\Delta t$  is<sup>4</sup>

$$\delta \underline{r}_i(t) = \delta \underline{r}_i(t - \Delta t) + \underline{F}_i(t) \Delta t^2 / m_i \quad (5)$$

$$\underline{r}_i(t + \Delta t) = \underline{r}_i(t) + \delta \underline{r}(t) \quad (6)$$

where  $\underline{r}_i$  is the position of ion  $i$  and  $\underline{F}_i$  is the force on ion  $i$ . The program unit of force is  $\epsilon A^{-1}$ . The program unit of distance is  $\text{\AA}$ . Therefore, in program units (which are starred),

$$\delta \underline{r}^*(t) = \delta \underline{r}^*(t - \Delta t) + A \underline{F}_i^* \Delta t^{*2} / m_i^*$$

where  $A = \frac{(\epsilon / J) (t^*/s)^2}{(\sigma / 10^{-10} \text{ m}) (m_+ / \text{kg})}$

$$= \frac{23.071417 \times 10^{-19} \times (1.6775412 \times 10^{-14})^2 \text{ Js}^2}{10^{-10} \times 6.4926309 \times 10^{-26} \text{ mkg}}$$

$$= 0.99999984 \text{ m} \quad (\text{i.e. } A = 1\text{m})$$

Thus  $A = 1$  and the units are self-consistent when incorporated into an update algorithm.

#### E. THE TEMPERATURE

$$\text{Let } \underline{v}(t) = \delta \underline{r}_i(t - \Delta t) + \frac{1}{2} \underline{F}_i(t) \Delta t^2 / m_i \quad (7)$$

i.e. a "position increment" proportional to the velocity.

Therefore,

$$\frac{1}{2} m v^2(t) \Delta t^{-2} = \frac{3}{2} k_B T \quad (8)$$

where  $k_B$  is Boltzmann's Constant. Consequently,

$$T = k_T m_i^* v_i^2(t) / \Delta t^{*2} \quad (9)$$

where

$$k_T = \frac{m_+ \times 10^{-20} \text{ m}^2}{(3k_B t^{*2})}$$

$$= \frac{6.4926309 \times 10^{-26} \times 10^{-20}}{3 \times (1.6775412 \times 10^{-14})^2 \times 1.38054 \times 10^{-23}}$$

Hence,

$$k_T = 55706.27$$

#### F. KINETIC ENERGY

Similarly,  $k_{KE}$  converts the distance increment squared for a single ion to a kinetic energy in  $\text{kJmol}^{-1}$ , as follows,

$$\text{kinetic energy /kJmol}^{-1} = k_{KE} m_i^* v^2(t) / \Delta t^2 \quad (10)$$

where

$$k_{KE} = \frac{3}{2} k_T \times 2 \times N_A \times k_B \times 10^{-3}$$

( $N_A$  is Avogadro's number)

$$= 55.70627 \times 3 \times 6.02252 \times 10^{23} \times 1.38054 \times 10^{-23}$$

$$k_{KE} = 1389.4807$$

#### G. PRESSURE (kbar)

The pressure is given by

$$P = \frac{1}{V} \left\{ \sum_i m_i v_i^2 + \sum_{i < j} r_{ij} \frac{d\phi}{dr_{ij}} \right\} / 3 \quad (11)$$

$$= \frac{1}{V(\text{\AA}^3)} \left\{ k_{PK} \langle T \rangle + k_{PE} \langle \Psi \rangle (\epsilon) / 3 \right\} \quad (12)$$

where  $k_{PK} = \frac{k_B}{10^{-30}} \times 10^{-8} = 0.138054$ ,

$\langle T \rangle$  is the average temperature and  $\langle \Psi \rangle = \sum_{i < j} r_{ij} \frac{d\phi}{dr_{ij}}$

and  $k_{PE} = 23.071417 \times 10^{-19} \times 10^{30} \times 10^{-8}$   
 $= 23071.417$

Another useful conversion parameter is  $k_{TE}$  which converts temperature in K to kinetic energy in  $\text{kJmol}^{-1}$

$$k_{TE} = \frac{3}{2} \times 1.38054 \times 10^{-23} \times 6.02252 \times 10^{23} \times 2 \times 10^{-3}$$

$$= 0.024942989.$$

To conclude, a system of program units for a Born-Mayer-Huggins alkali halide ionic program has been described. This is one of many choices that have been used. Another form by D. Fincham, and used in CCP5 program MDIONS, uses the box-sidelength as an internal unit of distance.

#### REFERENCES

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2. D.J. Adams and I.R. McDonald, J. Phys. C., 1974, 77, 2761.
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## Neighbour Lists Again

by

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In a recent article, Thompson [1] described the use of neighbour lists in simulations, giving a detailed account of the implementation and the resulting economies. This note deals with a simple variant on the method, and discusses the choice of neighbour list technique, if any, to be used in various circumstances.

The idea was originally introduced in the classic paper of Verlet [2] on the simulation of a dense Lennard-Jones fluid. Using a cut-off radius slightly greater than the truncation radius of the interaction potential [1], a list is made for each molecule of all other molecules which are, or could soon be, within interaction range. The lists are renewed at intervals [1], and during the intervening steps only the listed pairs are considered in calculating the pair interaction energies and forces. With a cut-off radius equal to half the (cubic) box length only about half of the distinct pairs need be listed, and the resulting savings in computer time grows rapidly with  $N$  because the number of pairs is  $N(N-1)/2$ . However, the conventional method requires that an integer index be stored for every active pair, so that the list grows roughly as  $N^2/4$ . This can quickly become burdensome in machines with limited storage, or where costs or priority depend on the amount of storage used. The alternative implementation described here combines the efficiency inherent in the use of neighbour lists with compact storage.

For a given molecule, any other molecule is either within the cut-off range, or it is not, and this situation is ideally suited to a binary representation. The first form described here is particularly suitable for conventional Monte Carlo simulations, where the use of single particle moves requires that one be able to identify all neighbours of the molecule being moved. For molecular dynamics simulations, where all active pair interactions are required at each step, a simple and obvious modification can be used to reduce the required storage by another factor of two, and the coding is even simpler. FORTRAN, still the dominant medium for simulation code, had no bit-handling facilities under the old standard, and rumour has it that the implementation of the new standard is not yet uniform. Many compilers offer non-standard extensions for manipulating bit strings, but the details vary from site to site. For these reasons the code given here is more cumbersome than it need be, but it should be easily adapted to run on any compiler, and those with enlightened compilers can use more direct implementations.

The neighbour lists are held in a two-dimensional array, LIST, of dimension NWORDxN. The column length, NWORD, is the smallest integer number of words capable of holding N bits, given a wordlength of NBITS.

```

NWORD=N/NBITS
IF(MOD(N,NBITS).NE.0) NWORD=NWORD+1

```

LIST must be cleared before the lists are established or revised, and this is easily done by setting each word in LIST to .FALSE.

```

      DO 1 J=1,N
        DO 1 I=1,NWORD
          LIST(I,J)=.FALSE.
1

```

Before creating the lists for the first time, a LOGICAL array MASK

```

MASK(1)    1000...0
MASK(2)    0100...0

```

```

MASK(3)      0010...0
MASK(4)      0001...0
MASK(NBITS) 0000...1

```

must be generated; the easiest way to do it is to treat MASK as an integer array in a subroutine, using

```
MASK(I)=2**(NBITS-I)
```

When a new list is being created the double sum over molecules is done in the usual way, but with a little extra code.

```

      DO 1 I=1,N-1
        IWORD=1+(I-1)/NBITS
        IBIT=MOD(I-1,NBITS)+1
        DO 1 J=I+1,N
          (Calculate the distance, and jump to 1 if out of range)
          JWORD=1+(J-1)/NBITS
          JBIT=MOD(J-1,NBITS)+1
          LIST(IWORD,J)=LIST(IWORD,J).OR.MASK(IBIT)
          LIST(JWORD,I)=LIST(JWORD,I).OR.MASK(JBIT)
1      CONTINUE

```

The logical .OR. operator generates a word which has a 1 in each bit position which was non-zero in either of the operands; it would also set to 1 any position which was 1 in both operands, but that situation cannot arise here. As a result, the NWORDS for molecule I contain a list of N bits with 1's in the locations of those molecules within the cut-off distance. The interaction of I with itself is set as out of range, by default, and it may be necessary to change this when internal degrees of freedom are considered. The lists are easy to use, as shown here.

```

      (choose a molecule, I, to be moved, and move it)
      (begin the calculation of the change in energy)
      JWORD=1
      JBIT=0
      DO 3 J=1,N
        JBIT=JBIT+1
        IF(JBIT.LE.NBITS) GO TO 4
        JWORD=JWORD+1
        JBIT=1
4      IF(.NOT.(LIST(JWORD,I).AND.MASK(JBIT))) GO TO 3

      (Test for the true potential cutoff, etc.)

```

The logical .AND. generates a word containing 1's only in those positions which are non-zero in both of the operands; because the mask has a single non-zero bit, this constitutes a test for the corresponding bit in the list. In this test, if the bit in the list is zero the logical product results in a zero word (.FALSE.), and the .NOT. operator converts it to .TRUE., so that the GO TO is executed. The success of this code depends on the compiler recognizing as "true" a word that has a single non-zero bit somewhere within it; the standard IBM compilers do this, as do most others, but it is worth testing in case a slight modification of the code is needed with a particular compiler. Because the operations are logical, this method runs very quickly, as well as being compact. The integer divide and MOD operations used here for clarity can be replaced by simple counting, and this usually results in slightly faster execution.

The MD form is simpler because the double sum over molecules enumerates the (complete) list of pairs in the same sequence each time, so that no bookkeeping information need be stored. The list is simply a string of  $N*(N-1)/2$  bits, and is written and tested in much the same way as for the MC case.

```

        KWORD=1
        KBIT=0
        DO 10 I=1,N-1
            DO 10 J=I+1,N
                KBIT=KBIT+1
                IF(KBIT.LE.NBITS) GO TO 11
                KWORD=KWORD+1
                KBIT=1
11      CONTINUE

```

(if this pair is not active jump to 10)

```

        LIST(KWORD)=LIST(KWORD).OR.MASK(KBIT)

```

10 CONTINUE  
Again, the logical .OR. operation is used to insert a "1" in the appropriate position in the list to flag an active pair. The use of the list is equally simple.

```
      KWORD=1  
      KBIT=0  
      DO 12 I=1,N-1  
        DO 12 J=I+1,N  
          KBIT=KBIT+1  
          IF(KBIT.LE.NBITS) GO TO 13  
          KWORD=KWORD+1  
          KBIT=1  
13      CONTINUE  
        IF(.NOT(LIST(KWORD).AND.MASK(KBIT))) GO TO 12  
      (this is an active pair)  
12      CONTINUE
```

The logic here exactly parallels that described before.

The storage saved depends on the system size and the range of interaction, as well as on the word length. For 256 molecules, with the cut-off at half the box length, and using 16-bit integers, the MC form uses 16x256 words, and the MD form 8x256, compared with around 128x256 and 64x256, respectively. For larger system sizes the savings are correspondingly greater, and it is with larger systems that the extra effort in coding this version becomes not only worthwhile, but necessary. However, the range of interaction can have a profound influence on the situation. For very large systems having only short ranged interactions the average number of neighbours may be less than  $N/NBITS$ , and the conventional technique then becomes more efficient. If the system size is very large, even comparatively short neighbour lists per particle can prove troublesome, and the logical testing of every pair is inefficient. Then, it may be worth using the cell index method. Each edge of the box is divided into an integer number of pieces of equal length, the pieces being

at least as long as the radius of interaction. Each coordinate is assigned an integer index based on the subsection in which it falls, so that  $3N$  words of storage are required. In testing, only molecules in the same or next-neighbour boxes can be in range. By testing each coordinate in turn, so the vast majority of possible neighbours are rejected at the first test etc., a relatively efficient algorithm with minimal storage requirements is obtained. One final word of warning deals with dilute systems. Even though the expected average number of neighbours may be small, condensation can change that very dramatically. The method described here gives the correct result, whatever the state of the system. In the conventional form the storage required for the lists increases with the number of interacting neighbours, and this can lead to problems in a system which can condense.

For modest sized systems with an interaction range which is a substantial fraction of the box length, the binary form of the neighbour lists is compact and efficient. As the system size increases, so does the advantage of the binary form, as long as the ratio of the range of interaction to box length does not get too small.

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ON THE EFFICIENT EVALUATION OF SQUARE ROOTS IN MOLECULAR  
DYNAMIC SIMULATIONS

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In many molecular dynamic programs it is unavoidable to take the square root inside the inner loop of the forces and torques evaluation subroutine. If, as has proved to be the case too often, see Singer (1), the standard system square root subroutine is inefficient, then this can have a severe detrimental effect on the running speed of the simulation. Singer (1) has proposed an alternative coding in Fortran that for his application afforded a considerable improvement over the standard routine supplied by the operating system of the CDC 7600 at U.L.C.C.

Singer's method was based on using a polynomial approximation to the square root over the range  $.1 \leq x \leq 1$  which, with his choice of units, covers all the likely arguments given a system with hard cores and taking the unit of length as half the box side length. Then about 2 or 3 Newton-Raphson "refining" cycles were done on the initial polynomial approximation. Note there is no need in MD applications to "waste" time in checking the sign of the argument as the letter, being  $|\underline{r}_i - \underline{r}_j|^2$ , is inherently positive definite, and the routine in (1) takes advantage of this.

The point of this letter is to point out that Singer's technique can be further optimised at the expense of departing from Fortran in order to access the binary mantissa and exponent of the argument of the square root subroutine. This has to be done in machine code and will vary from machine to machine. Since the mantissa is a number between .10000 and .11111 (i.e. between .5 and 1 in decimal) and the exponent is an integer we can proceed as follows:-

i) If the exponent is even, divide it by two and then take the square root of the mantissa. This involves the root of a number between .5 and 1 and a very good cubic polynomial approximation can be constructed over this limited range

$$\text{e.g. } \sqrt{x} \approx .2634840898 + 1.106421066x - .5061956629x^2 + .1363437494x^3$$

gives an approximation accurate to better than 4 significant figures. This is followed by just one Newton-Raphson "refining" cycle to yield a result to 9 significant figures (decimal). A further Newton-Raphson cycle would double, approximately, the number of significant figures (for double precision work).

ii) If the exponent, E, is odd we take  $\left\lfloor \frac{E-1}{2} \right\rfloor$  and shift the decimal point of the mantissa one to the right. Then we are faced with having to take the root of a mantissa number in the range  $1 \leq x \leq 2$  and again over this restricted domain the polynomial

$$\sqrt{x} \approx .3709873472 + .7857392625x - .1812429321x^2 + .02460047827x^3$$

gives an approximation valid to better than 4 significant figures. As before a Newton "refining" cycle gives a result to about 9 significant figures.

If properly implemented, the above should be near optimal for MD applications. Note that the routine involves only one IF statement (to check whether the exponent is even or odd). From thereon to the eventual answer to 9 significant figures involves only 3 multiplications and 3 additions (for cubic polynomial evaluation) plus 2 multiplications and one addition for the Newton "refining" cycle.

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CCP5 Literature Survey - Addendum

W. Smith, F. Gibb

The literature survey issued with the last CCP5 newsletter (Information Quarterly No.8) was generally well received. However, as expected, the survey managed to miss a number of relevant papers. The list printed below presents some of the papers that have been missed and which have been drawn to our attention by the authors concerned. Our sincere thanks go to them for their diligence.

We hope to produce a second literature survey later in the year.

Isomerization dynamics in liquids by molecular dynamics.

R.O. Rosenberg, B.J. Berne, D. Chandler.

Chem. Phys. Lett. Vol.75, 162-8, 1980.

A molecular dynamics simulation of the structure of water in the vicinity of a solvated ion.

M. Rao, B.J. Berne.

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A Monte Carlo procedure for the study of solvent effects on quantum molecular degrees of freedom.

M.F. Herman, B.J. Berne.

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Intramolecular rate process: Isomerization dynamics and the transition to chaos.

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On path integral Monte Carlo simulations.

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Isomerization dynamics and the transition to chaos.

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J. Phys. Chem. Vol.86, 2166, 1982.

Computer experiments on heterogeneous systems.

R.V. Mikkilineni, B.J. Berne.

Topics in Current Physics, Vol.29, 99, 1982.

Computer simulation of Coulomb explosions in doubly charged xenon microclusters.

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The hydrophobic effect on chain folding: The trans to gauche isomerization of n-butane in water.

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Reaction dynamics in a non-ergodic system: the Siamese stadium billiard.

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Monte Carlo simulation of solvent effects on vibrational and electronic spectra.

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Monte Carlo simulation of RRKM unimolecular decomposition in molecular beam experiments. II. Application to angular distributions and absolute cross sections for the system: atomic potassium and rubidium chloride.

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Chem. Phys. Vol.60, 405-20, 1981.

Monte Carlo simulation of RRKM unimolecular decomposition in molecular beam experiments I. Basic considerations and calculational procedure.

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Chem. Phys. Vol.60, 393-404, 1981.

Monte Carlo simulation of a lattice model of intramolecular exciplex formation.

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Methane in aqueous solution at 300 K.

B.J. Berne.

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Sampling methods for Monte Carlo simulations of n-butane in dilute solution.

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A Monte Carlo study of structural and thermodynamic properties of water: dependence on the system size and on the boundary conditions.

C. Pangali, M. Rao, B.J. Berne.

Molec. Phys. Vol.40, 661-80, 1980.

On the force bias Monte Carlo simulation of water: methodology, optimization and comparison with molecular dynamics.

M. Rao, C. Pangali, B.J. Berne.

Molec. Phys. Vol.37, 1773-98, 1979.

Impulsive stochastic models of molecular relaxation and isomerization reactions.

B.J. Berne, J.L. Skinner, P.G. Wolynes.

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Nucleation in finite systems: theory and computer simulation.

M. Rao, B.J. Berne.

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Radical correlations in associated liquids.

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