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DARESBURY 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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Contents

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CCP5.

CCP5 is an organisation created by the U.K. Government sponsored Science and Engineering Research Council (S.E.R.C.).

Its purpose is to fund conferences and promote co-operative research in the field of Computer Simulation using Molecular Dynamics and Monte Carlo techniques.

We feel that you may be interested in our quarterly newsletter containing CCP5 announcements and articles on computational techniques. You will also be sent notices of forthcoming CCP5 Conferences which we hope you and your colleagues will attend.

For your information there are other CCP's on the following subjects:

CCP1	Correlated Wavefunctions.
CCP2	Continuum States.
CCP3	Surface Science.
CCP4	Protein Crystallography.
CCP6	Heavy Particle Dynamics.

Dr. D.M. Heyes,
CCP5 Secretary.

Editorial

It is always a pleasure to thank the contributors to each CCP5 quarterly newsletter. We are fortunate to have such willing assistance from the CCP5 community. Special thanks should go to David Heyes (Royal Holloway) and David Fincham (Queen Mary) who consistently contribute articles of high quality with the informality that the newsletter requires. We are also specially pleased to reproduce the articles by A.R. Tindell, D.J. Tildesley and J. Walton (Southampton) and D. Brown (UMIST). Their articles on computational matters are the stuff of CCP5 and we invite our readers to follow their example! Thank you to all concerned.

General News

1. David Heyes (CCP5 Secretary) has asked for the following announcement to be made.

CCP5 will now refund travel expenses necessary to perform collaborative research. Applications will be considered on their merits and should be made to members of the CCP5 Executive Committee consisting of:

Prof. P.G. Powles,
(CCP5 Chairman),
Physics Laboratory,
University of Kent,
Canterbury,
Kent CT2 7NR.

Dr. J.H.R. Clarke,
Chemistry Department,
U.M.I.S.T.,
Sackville Street,
Manchester M60 1QD.

Dr. J.L. Finney,
Crystallography Department,
Birkbeck College,
Malet Street,
London WC1E 7HX.

2. The CCP5 Program Library continues to grow. We have further contributions from D. Heyes and W. Smith. A catalogue is given below. Readers intrested in obtaining copies of any of these programs should contact Dr. W. Smith at Daresbury Laboratory.

Program	Author	Purpose
MDATOM	S. Thompson	MD on monatomic liquids
HMDIAT	S. Thompson	MD on homonuclear diatomics
MDLIN	S. Thompson	MD on linear molecules
MDLINQ	S. Thompson	As MDLIN but with point quadrupole
MDTETRA	S. Thompson	MD on tetrahedral molecules
MDPOLY	S. Thompson	MD on polyatomic molecules
MDATOM	D. Fincham	MD on monatomic liquids
MDDIAT	D. Fincham	MD on homonuclear diatomics
MDDIATQ	D. Fincham	As MDDIAT but with quadrupole

Program	Author	Purpose
MDIONS	D.F. & N. Anastasiou	MD on ionic liquids
HLJ1	D. Heyes	MD on monatomic liquids
HLJ2	D. Heyes	As HLJ1, with velocity autocorrelation
HLJ3	D. Heyes	As HLJ1, with link cells
HLJ4	D. Heyes	As HLJ1, plus constant pressure and/or temperature
EWALD1	W. Smith	Subroutines to calculate potential, forces and torques in multipole system.
EWALD2	W. Smith	

These programs are available, free of charge. Readers wishing to contribute programs to the library should contact Dr. W. Smith at Daresbury.

3. The next CCP5 Meeting will take place in Reading on 16th and 17th December 1982. The subject will be 'New Computers/the Simulation of Quantum Mechanical Systems'. Interested readers should contact Professor R. Hockney of the Computer Science Department, Reading University, Whiteknights Park, Reading RG6 2AX.

A Review of the Fifth CCP5 Meeting held at the Physical Chemistry Laboratory, Oxford between the 17th and 18th December, 1981. The subject of the meeting was "The Computer Simulation of Interfaces"

by D.M. Heyes.

The first talk of the conference was given by DR. S. TOXVAERD (University of Copenhagen, Denmark). He reviewed his present interests in surface phenomena. The author warned of the care that must be taken in the choice of the algorithm for integrating the equations of motion when simulating non-uniform systems by Molecular Dynamics or MD. The adequacy of time reversal and energy conservation are misleading criteria. The Verlet algorithm is particularly suspect when using these tests. Satisfactory behaviour in these respects does not necessarily guarantee that the particles are following the correct paths through phase space. A large time step can result in colliding particles going too deep into a collision. He concluded that it is preferable to incorporate higher time derivatives in a Verlet-like scheme than to use a predictor-corrector algorithm (such as a 5th order Nordsieck-Gear algorithm) for these stiff differential equations. Dr. Toxvaerd then turned to Constant Pressure Molecular Dynamics. There are a number of methods for achieving this. The schemes of Andersen, Gilmore and Weeks, and Abraham were mentioned. The Abraham method was criticised. It incorporates a Monte Carlo, MC, selection of a change in volume of the MD cell size. An acceptance of a volume change is determined by calculating the work performed on the system. He claimed that a term is missing in Abraham's treatment. A volume change in the MD cell involves scaling the particle separations and also any inhomogeneities. The surface area of these regions changes and so a work term involving the surface tension is required. The Abraham method as proposed tends to favour volume increases. This would induce premature melting at state points near phase boundaries. In the discussion Dr. Frenkel was not in agreement with Dr. Toxvaerd's modification of the Abraham method. He said that a subtle distinction between internal and external forces should be made. Although the actual pressure in an interphase may differ from the imposed pressure the technique could still be valid.

Three talks on the physical adsorption of gases on solid surfaces followed. DR. W. VAN MEGEN (Melbourne Institute of Technology, Australia) reported the results of Grand Canonical Monte Carlo calculations modelling the absorption of ethene on basal planes of graphite at high pressure in the critical region, i.e. $T^* \approx 1.12$ and $\rho^* \approx 0.35$. A 10:4:3 surface-gas interaction potential was used to represent the effect of a structureless solid wall. The fluid was introduced between two hard walls separated by approximately forty molecular diameters or σ. On varying the gas density, the surface excess density was found to peak at near $\rho^* \approx 0.35$ or $P^* \approx 40$ bar which is in good agreement with experiment. An adsorbed bilayer was evident even at the low density of $\rho^* = 0.041$. A trilayer forms at $\rho^* = 0.19$. He showed that in the adsorption isotherms cusps can be obtained using simple model potentials. The discussion following this talk focussed on the effect on the critical temperature, T^*_c, by truncating the LJ potential at 2.5σ. Professor Rowlinson said that T^*_c should be equal to 1.35 for the untruncated potential. Professor Powles added that at this cut-off, $T^*_c = 1.15$. Dr. Saville said that it was even lower, approximately 0.9, when a different form of modified LJ potential was used in his molecular dynamics studies. There the force goes to smoothly zero at the truncation radius. This is equivalent to making the pair potential shallower over the whole distance range. This causes a much greater change on T_c^* as a result. Dr. Tildesley commented that as the barrier to surface lateral translation is 30-40 K the effects of ridges and valleys on the graphite surface are hardly likely to be noticed at these operating temperatures (~ 100 K).

DR. J.S. WHITEHOUSE (Imperial College) spoke of 3-body effects in Krypton-graphite adsorption. The paper was also authored by D. Nicholson and N.G. Parsonage. In a well presented talk the results of a computer simulation study of 722 model molecules above an idealised graphite surface were shown. Calculations with and without a 3-body potential (well depth ~ 15 K) added to the usual 2-body terms were performed. Two forms of adsorbed registry are possible. The close packed form is characterised by uncorrelated gas structure with the underlying solid. In the epitaxial phase the gas molecules reside mostly in the centre of the carbon hexagons. The introduction of 3-body forces destabilised both forms of packing. This was demonstrated by impressive surface density plots and a decrease in second peak structure for the lateral pair distribution function. In the discussion Dr. Frenkel recalled that a previous two (x,y) dimensional MD study incorporating a substrate with an (x,y) potential showed a tendency to form an epitaxial phase under similar conditions. He also pointed to the possibility of "domain" phases which are intermediate between close packed and epitaxial limits.

DR. D.J. TILDESLEY (University of Southampton) discussed the Molecular Dynamics of Methane on Graphite. This paper was co-authored with E. Severin of Oxford University. Each model methane molecule interacted with 110 carbon atoms on the surface. The well depth of interaction was equivalent to approximately 1000 K. The internal energy, and specific heat were followed as a function of coverage. The structure and motion parallel to the surfaces were monitored. At the operating temperature of ~ 100 K some methanes passed into the vapour. This permitted enhanced re-orientational motion of the surface molecules. A fascinating collective movement of molecules was observed in the adsorbed monolayer. Epitaxial structure was not stable as the temperature was increased. Dr. Clarke suggested that an orientational cross-correlation function could be useful in clarifying the origin of this collective motion. Dr. Allen suggested that phase transitions should be identifiable by large fluctuations in the configurational potential energy.

The first of two papers on the modelling of polymer molecules against solid surfaces was given by DR. R.F.T. STEPTO of U.M.I.S.T. His paper on the effect of potential parameters on the configurational structure of adsorbed polymer molecules was co-authored by D. Rigby and Aguchi. The model polymer chain segments were confined to points on a ghost tetrahedral lattice. Local interaction parameters appropriate to polymethylene chains of up to 160 units were chosen. A typical adsorption energy was $-0.5\ k_BT$. An adsorbed chain had portions up to 10 segments long in direct contact with the surface, called a train, separated by loops and two tails at each end which generally point away from the surface. The mean thickness of the adsorbed layer was found to be determined by the tails. DR. M. LAL (Unilever) and co-author A.T. Clark investigated the configurational structure of chains confined between surfaces. The MC technique is capable of enclosing all the possible configurations between completely extended and coiled, using excluded volume criteria. Long chains can be in contact with two surfaces at once. A train is attached to one surface and the remainder on either side is in contact with the other surface. The two connecting strands spanning the two surfaces can come close to forming a "bridge". As the wall-chain attractions increase both surfaces are pulled together. Interestingly, the mean train length is independent of this variation, for entropy reasons. Only the number of trains increases as a result. The probability of bridge formation goes through a maximum during this variation.

The chain repels the walls for weak adsorption parameters. The walls attracted for strong adsorption parameters. Professor Powles encapsulated these two effects in terms of a simple explanation using a coiled and stretched elastic band.

The remaining talks were concerned with interphases composed of spherical molecules. PROFESSOR L.V. WOODCOCK (University of Amsterdam, The Netherlands) expressed his interest in the liquid-solid phase transition of simple molecules. He demonstrated that two hard sphere phases can be produced in the same MD cell, with an intervening interphase. The two co-existing phases rapidly attain thermal and mechanical equilibrium. However, from simple rate of evaporation considerations he showed that chemical equilibrium is much slower to achieve. This was demonstrated over a long run of 2 million collisions during a (111) crystal-fluid boundary calculation using 2000 particles. Small changes in volume during the equilibration indicated the slow relaxation time. In order to determine the position of the solid-liquid tie line on a (P^*,ρ^*) phase diagram he employed a modification of Hoover and Ree's single occupancy method. There are still some discrepancies with Hoover and Ree's values but the calculations have not yet been completed. In the discussion, Dr. Saville commented that for particles interacting with soft interactions the local temperature is a good indicator of chemical equilibrium.

The next speaker, DR. BUSHNELL-WYE and co-author Dr. J.L. Finney (Birkbeck College) continued the above theme by performing MD calculations on the structure of equilibrium and melting Lennard-Jones crystal-melt interfaces. The number of particles, 860, included two movable crystal planes. He showed localised regions of great movement in the solid phase which presented a curved interface with the liquid phase. There appeared to be an interpenetration of solid-liquid profiles. Failure of a hard sphere model was demonstrated.

DR. S.M. THOMPSON and co-author Professor K.E. Gubbins (Cornell University, U.S.A.) considered a Lennard-Jones drop. The calculations were performed on a PDP11/70 computer. A cluster roughly ten molecular diameters across was created by fitting the largest possible inscribed sphere in a cubic MD cell fitted with a LJ liquid and containing 864 particles. Trapped in the sphere were 454 particles. The periodic boundary conditions were maintained but the box size was expanded. Within a short period approximately 10% of the molecules evaporated into the vapour phase and the cluster cooled to $T^* = 0.641$ as a result. Dr. Thompson introduced the audience to the fascinating problems associated with obtaining structural and thermodynamic radial profiles from the centre to the outer region of the cluster. The radial component of the pressure tensor decays monotonically through the drop. The tangential component of the pressure showed poorer statistics. In the discussion, Dr. Saville suggested that the LJ triple point could be lowered by the 2.5σ truncation used. Problems associated with conservation of angular momentum were raised by Professor Powles and Mr. Walton. Dr. Parsonage suggested that the central region of the droplet could have solidified although in the outer region it could still be in a liquid state.

DR. G. JACUCCI (University of Trento, Italy) presented results of Monte Carlo calculations of the free energy of clusters in the Ising Model. His fellow authors were G. Martin and A. Perini of the Centre d'Etudes Nucleaires Gif sur Yvette, France. A capillary theory cast entirely in terms of bulk properties was used to predict the free energy and nucleation rate. In addition, the overlapping distribution method was used to obtain the free energies by Monte Carlo simulation. The number of moves per particle was 250,000. Excellent agreement between the two approaches was obtained.

DR. D. FRENKEL (University of Utrecht, The Netherlands) enthusiastically presented a review of the theories of melting in two dimensions. There is still uncertainty as to the order of this phase transition. According to the Kosterlitz-Thouless, KT, theory the solid melts in a second order manner via a so-called hexatic fluid phase which is characterised by translational disorder but orientational order of the molecular centre of masses. The solid is itself interesting in that it possesses no long range translational order. It is necessary to characterise each phase in terms of an order parameter. The KT model involves a continuum with dislocations called disclinations. X-ray scattering from a layer of liquid crystal has given some evidence for a hexatropic to isotropic transition near the melting temperature. However, even with computer generated orientational correlation functions it is still a possibility that melting is first order. A LJ sample is slow to relax near its melting temperature even with several million MC moves. There is also an undetermined N-dependence.

MR. N. ANASTASIOU (Royal Holloway College) gave the first of a series of talks on ionic interfaces. He was interested in the (100) alkali halide - liquid water interface. A Molecular Dynamics simulation of 432 alkali halide ions (36 per layer) and 216 water molecules were performed. A 4 psec simulation of the water molecules against a rigid crystal (to represent an insoluble salt) showed that the molecules attach strongly to surface sodium ions. The oxygens point towards the sodium ions and the hydrogens attempt to attach themselves to the surface chloride ions, with a resulting 1° decrease in the HOH angle. Also, evidence was presented for long range correlations of water dipoles away from the surface into the bulk liquid. An almost complete absence of water self-diffusion was observed in the surface layer. This contrasts markedly with the results of Dr. Bushnell-Wye for the LJ solid-liquid interphase, in which surface diffusion was found to be not too different from the bulk liquid. The sodium ions rapidly go into solution when the ions are allowed to move. Significant surface destruction was evident within 0.5 ps. The water molecules enter the vacancies created. The rate of dissolution decreases considerably after 2.5 ps. Significantly at these later stages, a Cl^- is the only ion to have entered far into the bulk water (because of its poorer degree of solvation?). The presentation received a warm response from the audience. However, there was some misunderstanding over the use of periodic boundary conditions perpendicular to the surfaces.

DR. R.G. LINFORD (Leicester Polytechnic) and his co-authors M.P. Williams, R.M.J. Cotterill and P.R. Couchman are interested in solid electrolytes in a compacted powder form at 500 MPa. In order to determine the role of interfaces in their behaviour a MD simulation of the combination of two LJ clusters was performed. The results were unfortunately preliminary and only partial coalescence had occurred within the 1000 time steps performed.

DR. J.P. VALLEAU (University of Toronto, Canada) reviewed electrical double layer phenomena in ionic solutions. This is a difficult region to investigate experimentally by diffraction techniques as the interphase is thin and the ionic concentration so low. This is unfortunate as they are important in nature - stabilising colloids and membranes. Computer simulations of this system usually employ the charged hard sphere model (R.P.M.). The Guoy-Chapman (GC) solution of this system and the exact Grand canonical ensmble MC calculations agree well for low valence electrolytes (better for the charge density profile than the interfacial potential though). At 1 M concentration for a 1:1 electrolyte bilayering near the electrode becomes evident. The agreement with the GC theory is not good for multivalent electrolytes. This was attributed to the poor treatment of the long range charge fluctuations in the both models. Interestingly a 3:3 solution approaches the Helmholtz-Perrin parallel plate capacitor limit. The inclusion of image charges, a local dielectric constant and differential capacity were discussed. Dr. Weeks made a comment about the shortage of interphasial water molecules in the concentrated solutions. The ions would not have enough water molecules to solvate them. Dr. Heyes queried the need for long range electrostatic corrections for these dilute solutions. Dr. Valleau assured the audience that the contribution to the potential from beyond the nearest images could be many times k_BT.

The meeting was concluded by DR. D.M. HEYES (Royal Holloway College) who reported the results of a MD study of molten salt films trapped between two infinite smooth hard walls. These calculations were performed in co-operation with J.H.R. Clarke. In some simulations an equal and opposite continuous charge density was added to each wall. The application of an electric field across the cell produced significant charge multilayering in agreement with accepted theories. Interestingly, the average density profile perpendicular to the surface hardly differed between calculations with and without an applied external electric field. Thermodynamic profiles, surface tension and multilayer capacitance were discussed. Dr. Parsonage asked about the method of treating the long range coulomb forces. Dr. Heyes replied that an Ewald-like expression was used appropriate to periodicity in two dimensions only. Dr. Sluckin said there were theoretical reasons for predicting that average charge densities are unaffected by external electric fields, if the two species share the same soft force characteristics.

Questions and Answers about Molecular Dynamics on the DAP

by

David Fincham
DAP Support Unit, Queen Mary College

1. What is the DAP?

The Distributed Array Processor is a new type of computing device produced by ICL. It consists of 4096 processors arranged as a 64x64 array, each processor being capable of performing single bit arithmetic operations. The processors operate simultaneously, executing the same instruction on their own data. To provide more flexibility each processor has an activity register, under program control, which means that in effect it is either 'on' or 'off' for any particular instruction. The store associated with each processor consists of 4096 bits, making 2 Mbytes in total. (An 8 Mbyte version is also available). The whole device forms a specialised store module of a 2900 series ICL computer, so that the processing power is distributed into the store, avoiding problems of communication between main store and separate processing units which can degrade the performance of more conventional computers.

2. How is the DAP programmed?

The DAP is programmed in DAP Fortran, which is a version of Fortran with extensions for expressing parallel operations on matrices and vectors. For example, two matrices can be added with a single statement, rather than a double DO loop as in traditional Fortran. There are various methods of performing indexing operations, a particularly valuable one being the use of a logical expression in place of subscripts as a method of controlling the activity of the processors. These features result in a very simple, elegant and flexible language: most users describe it as 'fun'. Similar array-processing extensions will appear in the next ANSI Fortran standard.

3. What problems are suitable for the DAP?

To be suitable for the DAP a problem must satify two conditions. First, it must have a high degree of parallelism, so that many logically independent operations can be performed simultaneously. This sounds rather restrictive, but in fact parallelism is intrinsic to many problems, though the programmer may not be aware of it because he has previously been limited to algorithms expressed in strictly sequential languages. Second, for efficient utilisation of the DAP the problem must be mapped in some way onto a 64x64 array (which can also be regarded as a vector of 4096 elements). Thus the programmer must be aware of and able to exploit the architecture of the computer. It has always been true that users working with number-crunching problems at the limit of available computer power have had to do this to some extent.

4. Is the DAP suitable for MD calculations?

Yes. Each step of an MD simulation consists of two essential parts, the force evaluation and the integration of the equations of motion. The starting point of the step is a set of coordinates, three Cartesian components for each of the N particles, forming three 'vectors' of length N. In a simple MD program these are used to form the set of pair separations which can be regarded as an antisymmetric NxN matrix. From these are calculated the matrix of pair forces, and this evaluation is entirely parallel in nature, that is, it can be performed simultaneously for each pair. The pair forces are summed to give a vector of total forces, one for each of the N particles. The equations of motion of the particles can then be integrated, which again may be done in parallel. To use the DAP most efficiently the value of N should be a multiple of 64, 256 being a commonly used number for liquid simulations. If larger systems are to be studied some kind of list technique to avoid considering all pairs in the system, is advantageous as on other computers [1]. The neighbourhood list technique has been implemented on the DAP by Steve McQueen of ICL. He uses a logical mask rather than an actual list of indices; on the DAP logicals are single bit quantities so the storage problems which have made the technique unpopular on the 7600 do not arise. The in-range interactions then need to be 'packed' onto the DAP in 64x64 blocks. (A process akin to the GATHER operation on the Cray [2]). Other techniques are being investigated and I hope to report on these in a future article.

5. <u>How does the DAP compare with the Cray?</u>

Since some of the readers of this Newsletter are familiar with the Cray it is worth comparing the two machines. The Cray works by pipelining, that is overlapping, arithmetic operations in one floating point processor, rather than performing them simultaneously in many processors. However, to be overlapped the operations must be logically independent and so in principle capable of parallel processing, and thus algorithms for the two machines tend to be similar. On the Cray the performance is fairly independent of the vector length, whereas in the DAP blocks of data of size 4096 give maximum efficiency. In other respects the DAP is more flexible and easier to program. The indexing techniques can be used to handle conditionals, whereas these are difficult on the Cray, the only possibility being the choice of one out of two numerical values depending on the sign of a third. On the Cray also the common operation of summing the elements of a vector does not 'vectorise', while the bit-serial arithmetic on the DAP makes it a very rapid operation. (The bit serial arithmetic has other surprising effects, for example SQRT is faster than multiply!). Overall for floating point arithmetic the performance of the DAP lies between that of the CDC 7600 and the Cray. It should be remembered that the Cray-1 is a separate multi-million pound computer, whereas the DAP is an order of magnitude cheaper. In fact, since it provides additional storage on the ICL computer to which it is attached at little greater cost than straight storage alone it can be regarded as almost free by comparison with the Cray.

6. <u>Can I use the DAP?</u>

The first production DAP has been installed at Queen Mary College and is regarded by the Computer Board as a national facility for parallel processing. Communications with the 2980 computer which acts as 'host' to the DAP is possible via PSS, Metronet or SERC net. Anyone interested is using the DAP for MD calculations is invited to contact me in the first instance, though the use of substantial amounts of time requires a formal application to the SERC. The DAP Support Unit exists to give advice, assistance and eduction for users, and also to provide software. I plan to make available a fairly general purpose MD program for handling rigid polyatomic molecules with interactions of the site-site form; and perhaps to extend this to include constant pressure dynamics, point quadrupoles and fractional charges with Ewald sum.

References

[1] D.M. Heyes, CCP5 Newsletter No.2.

[2] D. Fincham and B.J. Ralston, Comp. Phys. Commun. 23 (1981) 127-134.

How accurate should we make our MD calculations?

by

David Fincham
DAP Support Unit, Queen Mary College.

Can anyone answer this question? In a molecular dynamics simulation errors in the trajectories of the particles arise because of the of the use of a non-infinitesimal time step and through rounding. We monitor the errors by checking the conservation of total energy, and I use a rule of thumb which states that the fluctuations in total energy should not be more than a few percent of the fluctuations in kinetic energy. But I don't know where it comes from or how many percent are allowable. This is an important question, because if we can double our timestep we can sample phase space twice as efficiently and halve our computer time. Simple algorithms like the leapfrog give rise to errors that increase fairly steadily as the time-step is increased, whereas higher order algorithms can be more accurate at small time steps but become unstable when the time-step is increased. Which should we use? We need to know how the errors in the trajectories feed through into the properties we measure in the simulated system, and this presumably depends on what property we are studying. Does anyone know of a systematic investigation, either theoretical or practical, into this question? And if it hasn't been done, is this not the sort of thing that CCP5 should be doing?

POINT MULTIPOLES IN THE EWALD SUMMATION

W. Smith

Preamble

The purpose of this paper is to outline one possible treatment of point multipoles in an Ewald Summation. A point multipole in this application is considered to consist of a superimposed point charge, point dipole and point quadrupole; as might be obtained from an arbitrary charge distribution resolved into these components. The physical quantities described are the potential, force and torque experienced by a point multipole in an infinite system of repeating unit cells containing irregularly spaced multipoles.

The Multipole Operators

Taylor's expansion for a scalar function of several variables (i.e. $F(x_1, x_2, x_3, \ldots)$ or $F(\underline{r})$) may be written as:

$$F(\underline{r} + \delta\underline{r}) = F(\underline{r}) + \delta\underline{r}.\underline{\nabla}F(\underline{r}) + \underline{\underline{U}}:[\underline{\nabla\nabla}]F(\underline{r}) + \ldots \text{ etc.} \qquad (1)$$

Where the matrix $\underline{\underline{U}}$ is defined by $U_{ij} = 1/2x_i x_j$ etc.

and the matrix $[\underline{\nabla\nabla}]$ is defined by $[\nabla\nabla]_{ij} = \dfrac{\partial^2}{\partial x_i \, \partial x_j}$ etc.

The operation indicated as : is the dyadic scalar product of the matrices (i.e. $\underline{\underline{A}}:\underline{\underline{B}} = A_{11}B_{11} + A_{12}B_{12} + \ldots$ etc.). (The terms of the series (1) can be regarded as a series consisting of consecutive contractions of tensors of rank 0,1,2, ... etc. to give a scalar result.)

The electrostatic potential at a point $\underline{r}$ due to a multipole at the origin and consisting of n point charges at the points $\{\underline{r}_k\}$ is given by (2). (Where the vectors $\underline{r}_k$ specify the positions of the charges q_k with respect to the adopted origin of the multipole. For our purposes the adopted origin may be taken as the centre of the charge distribution. The position of the multipole in space is thus regarded as the position of its adopted centre.)

$$V(\underline{r}) = \frac{1}{4\pi\varepsilon_0} \sum_{k=1}^{n} \frac{q_k}{|\underline{r}-\underline{r}_k|} \qquad (2)$$

If we assume that the spatial size of the multipole is minute in relation to r (i.e. $r \gg r_k$) we may use Taylor's expansion of 1/r with (2) to obtain the following expression for $V(\underline{r})$ (in which we ignore contributions above quadrupole).

$$V(r) = \frac{1}{4\pi\varepsilon_0} \left\{c_a - \underline{d}_a . \underline{\nabla} + \underline{\underline{Q}}_a : [\nabla\nabla]\right\} \frac{1}{r} \qquad (3)$$

Where: $c_a = \sum_{k=1}^{n} q_k$ is the multipole net charge

$\underline{d}_a = \sum_{k=1}^{n} q_k \underline{r}_k$ is the multipole net dipole

$\underline{\underline{Q}}_a = \sum_{k=1}^{n} q_k \underline{\underline{U}}_k$ is the multipole net quadrupole

If we define the terms in the brackets of (3) to be an operator $\hat{M}_a$ we may rewrite (3) as:

$$V(r) = \hat{M}_a (4\pi\varepsilon_0 r)^{-1} \qquad (4)$$

From which we see that the potential due to a point multipole is obtained by applying the operator $\hat{M}_a$ to the expression describing the potential due to a unit positive charge.

By a similar reasoning we may deduce that the potential ϕ_b of a second point multipole due to the potential field $V(\underline{r})$ of the first, is given by:

$$\phi_b = \hat{M}_b V(r) \quad (\text{or } \hat{M}_b \hat{M}_a (4\pi\varepsilon_o r)^{-1}) \tag{5}$$

Where $\hat{M}_b = c_b + \underline{d}_b \cdot \underline{\nabla} + \underline{\underline{Q}}_b : [\underline{\nabla\nabla}]$ (6)

The force acting on the second multipole will be given by applying the operator $-\underline{\nabla}_b$ to the expression (5) in the usual manner. Thus

$$\underline{F}_b = -\underline{\nabla}_b \hat{M}_b \hat{M}_a (4\pi\varepsilon_0 r)^{-1} \tag{7}$$

The torque acting on the second multipole in the potential field of the first may be written as:

$$\underline{T}_b = -\sum_{k=1}^{n} q_k \underline{r}_k \times \underline{\nabla} V(\underline{r} + \underline{r}_k) \tag{8}$$

From which we may deduce that

$$\underline{T}_b = -\left\{\underline{d}_b \times \underline{\nabla} + 2\underline{\underline{Q}}_b * [\underline{\nabla\nabla}]\right\} V(\underline{r}) \tag{9}$$

and so obtain the torque operator $\hat{L}_b$ as:

$$\hat{L}_b = -\left\{\underline{d}_b \times \underline{\nabla} + \underline{\underline{Q}}_b * [\nabla\nabla]\right\} \tag{10}$$

(The operation implied by * is a vector product of the matrices on either side; according to the recipe:

If $\underline{V} = \underline{\underline{A}} * \underline{\underline{B}}$ then for matrices of dimension 3

$$V_i = \sum_{j}^{m} (A_{i+1,j} B_{i+2,j} - A_{i+2,j} B_{i+1,j}) \tag{11}$$

Where the indices follow a cyclic progression (i.e. if $i=2$ then $i+1 \equiv 3$, $i+2 \equiv 1$. If $i=3$ then $i+1 \equiv 1$, $i+2 \equiv 2$ etc.))

The Ewald Summation

The potential at a point $\underline{r}$ (not at a lattice site) in an infinite periodic lattice of unit point charges is given by the Ewald Summation[1,2] as:-

$$V_E(\underline{r}) = \frac{1}{V_0\varepsilon_0}\sum_{k\neq 0}^{\infty}\sum_{j}^{n} A_k \exp(-i\underline{k}.(\underline{r}_j - \underline{r})) + \frac{1}{4\pi\varepsilon_0}\sum_{j}^{\infty} B_0(|\underline{r}_j - \underline{r}|) \qquad (12)$$

where A_k = $\exp(-k^2/4\alpha^2)/k^2$

$B_0(u)$ = $\mathrm{erfc}(\alpha u)/u$

n = number of point charges in unit cell

α = Ewald's convergence parameter

V_0 = volume of unit cell

$\underline{k}$ = reciprocal lattice vector (e.g. $\underline{k} = \frac{2\pi}{L}(n_a, n_b, n_c)$ for a cubic system

k = index of $\underline{k}$ vector

According to the principles outlined in the previous section we may adapt equation (12) to suit a lattice of point multipoles by applying the set of operators $\hat{M}_j$ defined by:

$$\hat{M}_j = c_j - \underline{d}_j.\underline{\nabla} + \underline{\underline{Q}}_j:[\underline{\nabla\nabla}] \qquad (13)$$

Following this prescription we obtain the expression

$$V(r) = \frac{1}{V_0\varepsilon_0}\sum_{k\neq 0}^{\infty}\sum_{j}^{n}(c_j - i\underline{d}_j.\underline{k} - \underline{\underline{Q}}_j:[\underline{kk}])A_k \exp(-i\underline{k}.(\underline{r}_j - \underline{r}))$$

$$+ \frac{1}{4\pi\varepsilon_0}\sum_{j}^{\infty}(c_j B_0(|\underline{r}_j - \underline{r}|) - (\underline{d}_j.(\underline{r}_j - \underline{r}) + \underline{\underline{Q}}_j:\underline{\underline{I}})B_1(|\underline{r}_j - \underline{r}|)$$

$$+ \underline{\underline{Q}}_j:[(\underline{r}_j - \underline{r})(\underline{r}_j - r)]B_2(|\underline{r}_j - \underline{r}|)) \qquad (14)$$

Where $:[\underline{kk}]$ is a matrix formed from the products $k_i k_j$ etc. $[(\underline{r}_j - \underline{r})(\underline{r}_j - \underline{r})]$ is a matrix formed from the products $(x_j - x)(y_j - y)$ etc.

$B_1(|\underline{r}_j - \underline{r}|) \ldots B_\ell(|\underline{r}_j - \underline{r}|)$ are a series of functions derived from $B_0(|\underline{r}_j - \underline{r}|)$ according to the recursion relation:

$$B_\ell(u) = \frac{1}{u^2}\left\{(2\ell - 1)B_{\ell-1}(u) + \frac{(2\alpha^2)^\ell}{\alpha\sqrt{\pi}}\exp(-\alpha^2u^2)\right\} \qquad (15)$$

Further important properties of the functions $B_\ell(|\underline{r}_j - \underline{r}|)$ are given in the appendix.

Equation (14) describes the potential field due to a lattice of point multipoles. The potential energy of a 'guest' multipole at position $\underline{r}$ is given by applying the operator $\hat{M}_g$ to equation (14) where:

$$M_g = c_g + \underline{d}_g\cdot\underline{\nabla} + \underline{\underline{Q}}_g:[\underline{\nabla\nabla}] \qquad (16)$$

The result of this operation being:

$$\phi_g = \frac{1}{V_0\varepsilon_0}\sum_{k\neq0}^{\infty}\sum_{j}^{n} A_k F_{kjg}\exp(-i\underset{\sim}{k}\cdot(\underline{r}_j - \underline{r})) + \frac{1}{4\pi\varepsilon_0}\sum_{\ell=0}^{4}\sum_{j}^{\infty} B_\ell(|\underline{r}_j - \underline{r}|)G_{\ell jg} \qquad (17)$$

Where the functions A_k and B_ℓ have already been described. The functions F_{kjg} and $G_{\ell jg}$ are as follows:

$$F_{kjg} = (c_g + i\underline{d}_g\cdot\underline{k} - \underline{\underline{Q}}_g:[\underset{\sim}{kk}])(c_j - i\underline{d}_j\cdot\underline{k} - \underline{\underline{Q}}_j:[\underline{kk}]) \qquad (18)$$

$$
\left.
\begin{aligned}
G_{ojg} &= c_g c_j \\
G_{1jg} &= \underline{d}_g \cdot (\underline{r}_j - \underline{r}) c_j - \underline{d}_j \cdot (\underline{r}_j - \underline{r}) c_g - \underline{\underline{Q}}_g : \underline{\underline{I}} c_j - \underline{\underline{Q}}_j : \underline{\underline{I}} c_g + \underline{d}_g \cdot \underline{d}_j \\
G_{2jg} &= \underline{\underline{Q}}_g : [(\underline{r}_j - \underline{r})(\underline{r}_j - \underline{r})] c_j + \underline{\underline{Q}}_j : [(\underline{r}_j - \underline{r})(\underline{r}_j - \underline{r})] c_g \\
&\quad - \underline{d}_g \cdot (\underline{r}_j - \underline{r}) \underline{d}_j \cdot (\underline{r}_j - \underline{r}) + 2\underline{\underline{Q}}_g : [\underline{d}_j (\underline{r}_j - \underline{r})] \\
&\quad - 2\underline{\underline{Q}}_j : [\underline{d}_g (\underline{r}_j - \underline{r})] + \underline{d}_j \cdot (\underline{r}_j - \underline{r}) \underline{\underline{Q}}_g : \underline{\underline{I}} - \underline{d}_g \cdot (\underline{r}_j - \underline{r}) \underline{\underline{Q}}_j : \underline{\underline{I}} \\
&\quad + 2\underline{\underline{Q}}_g : \underline{\underline{Q}}_j + \underline{\underline{Q}}_g : \underline{\underline{I}} \underline{\underline{Q}}_j : \underline{\underline{I}} \\
G_{3jg} &= \underline{d}_g \cdot (\underline{r}_j - \underline{r}) \underline{\underline{Q}}_j : [(\underline{r}_j - \underline{r})(\underline{r}_j - \underline{r})] - \underline{d}_j \cdot (\underline{r}_j - \underline{r}) \underline{\underline{Q}}_g : [(\underline{r}_j - \underline{r})(\underline{r}_j - \underline{r})] \\
&\quad - 4\underline{\underline{Q}}_g : [(\underline{r}_j - \underline{r})(\underline{\underline{Q}}_j \cdot (\underline{r}_j - \underline{r}))] \\
&\quad - \underline{\underline{Q}}_g : \underline{\underline{I}} \underline{\underline{Q}}_j : [(\underline{r}_j - \underline{r})(\underline{r}_j - \underline{r})] - \underline{\underline{Q}}_j : \underline{\underline{I}} \underline{\underline{Q}}_g : [(\underline{r}_j - \underline{r})(\underline{r}_j - \underline{r})] \\
G_{4jg} &= \underline{\underline{Q}}_g : [(\underline{r}_j - \underline{r})(\underline{r}_j - \underline{r})] \underline{\underline{Q}}_j : [(\underline{r}_j - \underline{r})(\underline{r}_j - \underline{r})]
\end{aligned}
\right\} (19)
$$

In the usual situation we wish to evaluate the potential, not of a guest multipole, but of one of the multipoles at a lattice site. We can adapt the formulae (17) to (19) to this circumstance in the following way.

(i) We must extract from the equation (17) all those terms involving both the guest multipole (index 'g') and the multipole at the lattice site of interest (index 'i'). These terms will call for special treatment later.

(ii) In the other terms we simply set the index 'g' to index 'i' and replace $\underline{r}$ by $\underline{r}_i$. Thus as far as these terms are concerned, the guest multipole and the 'ith' multipole are one and the same.

If we now examine the terms separated out from (17) according to (i) above, it is clear that if we are to regard the guest multipole as being the 'ith' multipole, then these terms represent a 'self-interaction' energy, which physically is zero, but mathematically is indeterminate. We may choose simply to exclude these terms from our summation (i.e. set them to zero) but computationally it is more convenient to proceed otherwise.

If we consider the second group of terms on the right of equation (17) and obtain those terms in which both indices 'i' and 'g' appear we will have

$$\frac{1}{4\pi\varepsilon_0}\sum_{\ell=0}^{4} B_\ell(|\underline{r}_i - \underline{r}|)G_{\ell ig} \tag{20}$$

It is clear from the definition of the functions $B_\ell(u)$ in equations (12) and (15) that this term becomes indeterminate when we equate $\underline{r}$ and $\underline{r}_i$. If however we expand these functions as polynomials in the argument u (see Appendix) we obtain in place of (20):

$$\frac{1}{4\pi\varepsilon_0}\sum_{\ell=0}^{4}\left\{\frac{(2\ell)!\ G_{\ell ig}}{\ell!2^\ell\ u^{2\ell+1}} - \frac{(2\alpha^2)^{\ell+1}\ G_{\ell ig}}{(2\ell+1)\alpha\pi^{1/2}} + G_{\ell ig}O_\ell(u)\right\} \tag{21}$$

Where $O_\ell(u)$ represents a sum of terms in u and higher powers of u.

If we now examine the first term of the expansion (21) we are able to equate this term with the conventional (or non-Ewald) description of the potential energy function of two multipoles separated by a distance u. As u tends to zero (i.e. as $\underline{r}_i$ and $\underline{r}$ merge) it is this term that becomes indeterminate. Because of its identity with the conventional potential expression we may simply remove this term altogether (knowing it to be physically zero). We also see that the terms $O_\ell(u)$ necessarily become zero as u tends to zero. Thus the only surviving term is:

$$-\frac{1}{4\pi\varepsilon_0}\sum_{\ell=0}^{4}\frac{(2\alpha^2)^{\ell+1}\,G_{\ell ii}}{(2\ell+1)\,\alpha\pi^{1/2}} \tag{22}$$

Two further comments are in order. Firstly it can be seen from the identities (19) that within the $G_{\ell ii}$ functions themselves many of the terms are zero because of their dependence on $(\underline{r}_i - \underline{r})$, which is zero in this circumstance. Secondly, because of the identification of the first term of the expansion (21) with the conventional potential energy expression, we can be sure that the term (22) represents a complete correction of equation (17) to the case where the guest multipole is at a lattice site. (Note that this also means that we may simply use the index substitution 'g' → 'i' in the Fourier component of (17) without further complication.) Thus we may write:

$$\begin{aligned}\phi_i &= \frac{1}{V_0\varepsilon_0}\sum_{k\neq 0}^{\infty}\sum_{j}^{n} A_k F_{kji}\exp(-i\underline{k}.(\underline{r}_j - \underline{r}_i))\\ &\quad + \frac{1}{4\pi V_0\varepsilon_0}\sum_{\ell\neq 0}^{4}\sum_{j\neq i}^{\infty} B_\ell(|\underline{r}_j - \underline{r}_i|)G_{\ell ji} + C\end{aligned} \tag{23}$$

Where the constant C may be derived from (22) and is:

$$C = \frac{-2\alpha}{4\pi^{3/2}\varepsilon_0}\left\{c_i^{\;2} + 2\alpha^2\left\{\frac{1}{3}\,(2\underline{\underline{Q}}_i:\underline{\underline{I}}c_i + d_i^{\;2}) + \frac{2\alpha^2}{5}\,(2\underline{\underline{Q}}_i:\underline{\underline{Q}}_i + (\underline{\underline{Q}}_i:\underline{\underline{I}})^2)\right\}\right\} \tag{24}$$

It is worth noting at this point that if all the dipoles and quadrupoles are set to zero, this expression will reduce to standard Ewald form for a lattice of point changes[1, 2]. Also if the charges and quadrupoles are set to zero, the result is the Kornfeld expression for a lattice of point dipoles as described by Adams and McDonald[3]. The proof of these statements is left as an exercise for the intrepid reader.

The force acting on the 'i^{th}' multipole in a lattice of multipoles is obtained by applying the operator $-\underline{\nabla}_i$ to equation (23). The result is:

$$
\begin{aligned}
\underline{F}_i = & \frac{-1}{V_0\epsilon_0}\sum_{k\neq 0}^{\infty}\sum_{j}^{n} i\underline{k}A_k F_{kji}\exp(-i\underline{k}.(\underline{r}_j - \underline{r}_i)) \\
& - \frac{1}{4\pi\epsilon_0}\sum_{\ell=0}^{4}\sum_{j\neq i}^{\infty} G_{\ell ji}B_{\ell+1}(|\underline{r}_j - \underline{r}_i|)(\underline{r}_j - \underline{r}_i) + B_{\ell}(|\underline{r}_j - \underline{r}_i|)\underline{\nabla}_i G_{\ell ji}
\end{aligned}
\tag{25}
$$

Where the functions A_k, F_{kji}, $G_{\ell ji}$ and B_{ℓ} have been encountered already. The vector functions $\underline{\nabla}_i G_{\ell ji}$ however, are as follows:

$$
\left.
\begin{aligned}
\underline{\nabla}_i G_{0ji} &= 0 \\
\underline{\nabla}_i G_{1ji} &= c_i\underline{d}_j - c_j\underline{d}_i \\
\underline{\nabla}_i G_{2ji} &= -\ 2c_i\underline{\underline{Q}}_j.(\underline{r}_j - \underline{r}_i) - 2c_j\underline{\underline{Q}}_i.(\underline{r}_j - \underline{r}_i) \\
&\quad + \underline{d}_i.(\underline{r}_j - \underline{r}_i)\underline{d}_j + \underline{d}_j.(\underline{r}_j - \underline{r}_i)\underline{d}_i \\
&\quad + 2\underline{\underline{Q}}_j.\underline{d}_i + \underline{\underline{Q}}_j\underline{\underline{I}}\underline{d}_i - 2\underline{\underline{Q}}_i.\underline{d}_j - \underline{\underline{Q}}_i:\underline{\underline{I}}\underline{d}_j \\
\underline{\nabla}_i G_{3ji} &= \underline{\underline{Q}}_i:[(\underline{r}_j - r_i)(\underline{r}_j - \underline{r}_i)]\underline{d}_j + 2\underline{d}_j.(\underline{r}_j - \underline{r}_i)\underline{\underline{Q}}_i.(\underline{r}_j - \underline{r}_i) \\
&\quad - \underline{\underline{Q}}_j:[(\underline{r}_j - \underline{r}_i)(\underline{r}_j - \underline{r}_i)]\underline{d}_i - 2\underline{d}_i.(\underline{r}_j - \underline{r}_i)\underline{\underline{Q}}_j.(r_j - \underline{r}_i) \\
&\quad + 4(\underline{\underline{Q}}_i.\underline{\underline{Q}}_j + \underline{\underline{Q}}_j.\underline{\underline{Q}}_i).(\underline{r}_j - \underline{r}_i) + 2\underline{\underline{Q}}_i.\underline{\underline{I}}\underline{\underline{Q}}_j.(\underline{r}_j - \underline{r}_i) \\
&\quad + 2\underline{\underline{Q}}_j:\underline{\underline{I}}\underline{\underline{Q}}_i.(\underline{r}_j - \underline{r}_i) \\
\underline{\nabla}_i G_{4ji} &= -\ 2\underline{\underline{Q}}_i:[(\underline{r}_j - \underline{r}_i)(\underline{r}_j - \underline{r}_i)]\underline{\underline{Q}}_j.(\underline{r}_j - \underline{r}_i) \\
&\quad - 2\underline{\underline{Q}}_j:[(\underline{r}_j - \underline{r}_i)(\underline{r}_j - \underline{r}_i)]\underline{\underline{Q}}_i.(\underline{r}_j - \underline{r}_i)
\end{aligned}
\right\}
\tag{26}
$$

To determine the torque acting on a point multipole at a lattice site, we must apply an operator $\hat{L}_i$ analogous to that presented in (10) to the potential field equation given in (14) and proceed in a similar manner to that which produced the result (23). In this case however the result is:

$$\underline{T}_i = \frac{1}{V_0 \varepsilon_0} \sum_{k \neq 0}^{\infty} \sum_{j}^{n} A_k \underline{F}_{kji} \exp(-i\underline{k}.(\underline{r}_j - \underline{r}_i))$$

$$+ \frac{1}{4\pi\varepsilon_0} \sum_{\ell=1}^{4} \sum_{j \neq i}^{\infty} B_\ell(|\underline{r}_j - \underline{r}_i|)\underline{G}_{\ell ji} \tag{27}$$

Where A_k and B_ℓ are the same functions as in the previous formulae. $\underline{F}_{kji}$ and $\underline{G}_{\ell ji}$ however are now vector functions of the following forms:

$$\underline{F}_{kji} = (-i\underline{d}_i \text{ X } \underline{k} + 2\underline{\underline{Q}}_i{*}[\underline{kk}])(c_j - i\underline{d}_j.\underline{k} - \underline{\underline{Q}}_j:[\underline{kk}]) \tag{28}$$

$$\left.\begin{aligned}
\underline{G}_{1ji} &= -\underline{d}_i \text{ X } (\underline{r}_j - \underline{r}_i)c_j - \underline{d}_i \text{ X } \underline{d}_j \\
\underline{G}_{2ji} &= -2\underline{\underline{Q}}_i{*}[(\underline{r}_j - \underline{r}_i)(\underline{r}_j - \underline{r}_i)]c_j + \underline{d}_i \text{ X } (\underline{r}_j - \underline{r}_i)\underline{d}_j.(\underline{r}_j - \underline{r}_i) \\
&\quad - 2\underline{\underline{Q}}_i{*}[\underline{d}_j(\underline{r}_j - \underline{r}_i)] - 2\underline{\underline{Q}}_i{*}[(\underline{r}_j - \underline{r}_i)\underline{d}_j] \\
&\quad + 2\underline{d}_i \text{ X } \underline{\underline{Q}}_j.(\underline{r}_j - \underline{r}_i) + \underline{d}_i \text{ X } (\underline{r}_j - \underline{r}_i)\underline{\underline{Q}}_j:\underline{\underline{I}} - 4\underline{\underline{Q}}_i{*}\underline{\underline{Q}}_j \\
\underline{G}_{3ji} &= -\underline{d}_i \text{ X } (\underline{r}_j - \underline{r}_i)\underline{\underline{Q}}_j:[(\underline{r}_j - \underline{r}_i)(\underline{r}_j - \underline{r}_i)] + 2\underline{d}_j.(\underline{r}_j - \underline{r}_i)\underline{\underline{Q}}_i{*} \\
&\qquad [(\underline{r}_j - \underline{r}_i)(\underline{r}_j - \underline{r}_i)] \\
&\quad + 4\underline{\underline{Q}}_i{*}([(\underline{r}_j - \underline{r}_i)(\underline{\underline{Q}}_j.(\underline{r}_j - \underline{r}_i))] + [(\underline{\underline{Q}}_j.(\underline{r}_j - \underline{r}_i))(\underline{r}_j - \underline{r}_i)]) \\
&\quad + 2\underline{\underline{Q}}_i{*}[(\underline{r}_j - \underline{r}_i)(\underline{r}_j - \underline{r}_i)]\underline{\underline{Q}}_j:\underline{\underline{I}} \\
\underline{G}_{4ji} &= -2\underline{\underline{Q}}_i{*}[(\underline{r}_j - r_i)(r_j - \underline{r}_i)]\underline{\underline{Q}}_j:[(\underline{r}_j - \underline{r}_i)(\underline{r}_j - \underline{r}_i)]
\end{aligned}\right\} \tag{29}$$

It may be safely assumed from the complicated nature of these formulae, that these equations are difficult to program in an efficient manner.

However, it should be pointed out that the Fourier components of the formulae presented above are particularly elegant and straightforward and are little more difficult to program than would be the case in a system containing point charges only. Also, despite the cumbersome nature of the terms derived from the original complementary error function (i.e. the terms involving the B_ℓ functions) they are no more difficult to program than would be the case if the direct summation method were employed, provided that the B_ℓ functions are generated via the recursion relation (15). A primitive version of a program using these formulae is available from the author at Daresbury Laboratory.

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References

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2 J.C. Slater, Quantum Theory of Molecules & Solids III. p.215 (McGraw Hill 1967)

3 D.J. Adams, I.R. McDonald, Molec. Phys. (1976) 32, 931.

Appendix: The B_ℓ Functions

We begin with the function $B_0(u)$:

$$B_0(u) = \frac{1}{u}\,\mathrm{erfc}(\alpha u) \qquad (a)$$

$$\text{Where: } \mathrm{erfc}(\alpha u) = \frac{2}{\pi^{1/2}} \int_{\alpha u}^{\infty} \exp(-s^2)ds \qquad (b)$$

We may also define the recursion relation:

$$B\ (u) = \frac{1}{u^2}\left\{(2\ell - 1)B_{\ell-1}(u) + \frac{(2\alpha^2)^\ell}{\alpha\pi^{1/2}}\exp(-\alpha^2u^2)\right\} \quad (\ell > 0) \qquad (c)$$

If we define $u = |\underline{r}_j - \underline{r}| = \{((x_j)_1 - x_1)^2 + ((x_j)_2 - x_2)^2 + ((x_j)_3 - x_3)^2\}^{1/2}$, then it is easily shown that:

$$\frac{\partial}{\partial x_r} B_\ell(u) = ((x_j)_r - x_r)B_{\ell+1}(u) \qquad (r = 1,2,3)$$

$$\frac{\partial^2}{\partial x_r \partial x_s} B_\ell(u) = ((x_j)_r - x_r)((x_j)_s - x_s)B_{\ell+2}(u) - \delta_{rs}B_{\ell+1}(u) \qquad (r,s = 1,2,3)$$

$$(d)$$

From which we obtain:

$$\underline{\nabla}B_\ell(u) = (\underline{r}_j - \underline{r})B_{\ell+1}(u)$$

$$[\underline{\nabla\nabla}]B_\ell(u) = [(\underline{r}_j - \underline{r})(\underline{r}_j - \underline{r})]B_{\ell+2}(u) - \underline{\underline{I}}\,B_{\ell+1}(u) \qquad (e)$$

These relationships are used throughout the derivations (14) to (29) of the previous sections.

To obtain the expansion (21) of the expression (20) we use the following series expansions:

$$\frac{1}{u}\,\mathrm{erfc}(\alpha u) = \frac{1}{u} - \frac{2\alpha}{\pi^{1/2}} \quad 1\left\{- \frac{(\alpha u)^2}{3} + \frac{(\alpha u)^4}{10} - \frac{(\alpha u)^6}{42} + \frac{(\alpha u)^8}{216} - \dots\right\}$$

$$\exp(-\,\alpha^2 u^2) = 1 - (\alpha u)^2 + \frac{(\alpha u)^4}{2} - \frac{(\alpha u)^6}{6} + \frac{(\alpha u)^8}{24} - \dots \qquad \text{(f)}$$

Combining the expansions (f) in the recursion relation (c) and collecting terms of like powers in u allows the following expansions of $B_\ell(u)$ to be produced.

$$B_0(u) = \frac{1}{u} - \frac{2\alpha}{\pi^{1/2}} + 0(u)$$

$$B_1(u) = \frac{1}{u^3} - \frac{4\alpha^3}{3\pi^{1/2}} + 0(u)$$

$$B_2(u) = \frac{3}{u^5} - \frac{8\alpha^5}{5\pi^{1/2}} + 0(u)$$

$$B_3(u) = \frac{15}{u^7} - \frac{16\alpha^7}{7\pi^{1/2}} + 0(u)$$

$$B_4(u) = \frac{105}{u^9} - \frac{32\alpha^9}{9\pi^{1/2}} + 0(u)$$

etc. Or in general:

$$B_\ell(u) = \frac{(2\ell)!}{\ell!\,2^\ell u^{2\ell+1}} - \frac{(2\alpha^2)^{\ell+1}}{(2\ell+1)\,\alpha\pi^{1/2}} + 0(u)$$

where 0(u) are collected terms of powers of u (i.e. u^n with $n \geqslant 1$).

Apparent Energy Conservation

A.R. Tindell, D.J. Tildesley and J. Walton

One of the constant concerns of a molecular dynamic is his energy conservation. New programs rarely conserve energy and in nine out of ten cases this will be a programming error which calls for prolonged staring. There is an unhappy moment when all the apparent bugs have been removed and the internal energy still fluctuates. One possibility is that the differential equations are too stiff and the choice of algorithm is inappropriate. If this is the case energy conservation normally improves as the timestep is reduced. A more likely cause is that all the relevant contributions to the total energy have not been included. We recently came across an interesting example of the latter problem.

We were developing a program to simulate Lennard-Jonesium in the gas-liquid interface. To begin the project we wrote a simple program to simulate 256 LJ atoms in the bulk liquid. As is our wont we used a fifth-order predictor-corrector method and an interaction cut-off of 2.5σ. We were particularly concerned about energy conservation since we planned long runs in the interface. The program seemed to run well but the energy fluctuation, 1 part in 1200, was too large for comfort. For this system Verlet claims an energy conservation of 1 part in 10^7 (Verlet, 1967) and although we had never seen the energy this steady we were anxious to try and reproduce the result. We obtained little improvement by reducing the timestep and increasing the cut-off to 3σ and we wondered if the leapfrog algorithm was intrinsically more accurate than the Gear method. The problem was eventually traced to the definition of the potential. The force on a particle i from its neighbour j is defined by

$$f(r) = 48\varepsilon\left[\left(\frac{\sigma^{12}}{r_{ij}^{13}}\right) - 0.5\left(\frac{\sigma^{6}}{r_{ij}^{7}}\right)\right] \quad r_{ij} < r_c$$

$$f(r) = 0 \qquad\qquad r_{ij} > r_c\,. \tag{1}$$

There is a small discontinuity at the cut-off, if $r_c = 2.5\sigma$ this is $0.039\ \varepsilon\sigma^{-1}$, which is less than 2% of the well-depth in the force. The potential at r_{ij} is minus the force integrated from infinity to r_{ij},

$$U(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] - 4\varepsilon\left[\left(\frac{\sigma}{r_c}\right)^{12} - \left(\frac{\sigma}{r_c}\right)^{6}\right] \quad r_{ij} < r_c\,. \tag{2}$$

This is the simulation potential; the normal U_{LJ} plus a small constant correction. This means that any time-step the internal energy is given by

$$E = \frac{3}{2} N_c\, kT + \sum_{\substack{i<j \\ r_{ij}<r_c}} U_{LJ}\,(r_{ij}) - \frac{N_c(N_c - 1)}{2}\, U_{LJ}\,(r_c) \tag{3}$$

where N_c is the number of atoms in the cut-off sphere. It is this quantity which is conserved and since N_c fluctuates, failure to include the third term in (3) distorts the real energy conservation. The improvement obtained by including the third term as a correction is shown in table 1. These remarks apply equally to simulations of molecular liquids with discontinuous cut-offs in the force. Even when r_c is taken as half the box-length N_c can still fluctuate. The problem will not occur if we use the minimum image method and include all interactions in the basic cube since the last term in (3) is then a constant, but this will nearly double the number of interactions which have to be considered explicitly and this is prohibitively expensive.

Cut-off	Corrected	Conservation	T^*	U^*	P^*
2.5σ	No	1 part in 1200	1.05	-4.52	-0.05
2.5σ	Yes	1 part in 300000			
3.0σ	No	1 part in 1700	1.02	-4.53	-0.11
3.0σ	Yes	1 part in 500000			

TABLE 1: A simulation of Lennard-Jonesium, ($\rho^* = 0.650$), timestep, (0.863×10^{-14}s). The figures for energy conservation represent the total spread in energies based on timesteps 2500 - 2600 after equilibration. The thermodynamic properties after 3000 timesteps include the long range corrections. All simulationsare started from the same point in phase space and equilibrated for 1300 timesteps. (note that micro- fiche copies of the results are available on request).

These problems can be avoided by using a shifted force potential (Streett *et al.*1978) defined by

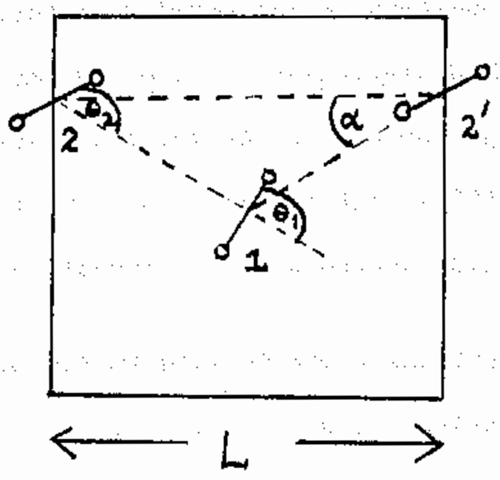
$$U(r_{ij}) = U_{LJ}(r_{ij}) - U'_{LJ}(r_c)r_{ij} + U'_{LJ}(r_c)r_c - U_{LJ}(r_c) \quad r_{ij}<r_c$$

$$U(r_{ij}) = 0 \qquad\qquad r_{ij}>r_c\ , \qquad (4)$$

This kind of potential has a force that goes to zero at r_c, (although it does have a regulation cusp at this point). For those who have simulated with the first term in (2) the energy conservation is probably better than it looks.

Those who believe that snipping at 2.5σ can have very little effect on properties of interest will remember that the critical temperature of Lennard-Jonesium has been estimated at $T_c^* = 1.32 - 1.36$, (Barker and Henderson, 1976). At the last CCP5 meeting on interfaces a number of estimates were given for the critical temperature of truncated Lennard-Jonesium; none of these were over $T_c^* = 1.2$ and for a potential which had been cut and shifted at 2.5σ there was an estimate of $T_c^* = 0.99$, (Saville, 1982). It has also been known for some time that the densities of the coexisting liquid and gas depend on the truncation of the potential (Lee *et al.* 1974)

If we include all the contributions to the internal energy then, in the case of an atomic fluid, we might expect time-step to time-step conservation of energy of better than 1 part in 10^5, (for the Gear method). In the case of a molecular fluid there is an additional problem. Imagine simulating a quadrupolar fluid with a minimum image convention. During a time-step molecule 2 crosses the boundary and 2' enters through the opposite face.



If the relative orientations of molecules 1 and 2 are Θ_1, Θ_2 then the relative orientations of 1 and 2' are $\Theta_1 - 2\alpha$ and $\Theta_2 - 2\alpha$. Now $U_{QQ}(\Theta_1\Theta_2)$ does not equal $U_{QQ}(\Theta_1 - 2\alpha, \Theta_2 - 2\alpha)$ unless $\alpha = 0$, or $\Theta_1 + \Theta_2 = n\pi + 2\alpha$;

(n = 0, or 1), and there will be a small jump in energy of order $Q^2(0.5L)^{-5}$ during the crossing. For a model of liquid nitrogen, (256 molecules, 33.85 cm^3 $mole^{-1}$) we estimate that this energy jump will be of order 1 part in 10^6 of the total energy, (allowing ten particles to cross a boundary at each time-step). Energy would the be conserved at the level of 1 part in 10^5 which is the general experience with this kind of system. In the case of fluids of dipolar molecules the energy jump is of order $\mu^2(0.5L)^{-3}$. For small systems the fluctuations caused by the boundary crossing may well be visible at the level of 1 part in 10^5., (Adams *et al.* 1979; Impey, 1982). In the case of a dipolar molecule, with no symmetry plane perpendicular to the molecular axis, the jump in energy may be more pronounced since the interaction falls off as r^{-3}; energy is still conserved at $\alpha = 0$, but many of the other relative orientations which conserve for quadrupoles do not for dipoles. These small fluctuations in the total energy will mean that properties such as the specific heat, which is measured by monitoring fluctuations in the kinetic energy, are difficult to calculate accurately. For a simulation of water it may be necessary to abandon the minimum image convention for the Ewald sum not just for collective correlation functions but to maintain a sufficiently high standard of energy conservation throughout the simulation (Impey, 1982).

In the case where the multipoles are modelled by partial charges, rather than idealized point moments, we have to consider what happens when a molecule lies across a boundary. In this case one of the charges will be outside the box. If we consider the minimum image of this charge, the central molecule will think itself surrounded by charged ions at approximately half the box length. This problem can be avoided by always using a centre of mass cut-off for models with partial charges.

Finally, although we used the same time-step as Verlet, (1967), in our simulation of atoms we never found the energy constant to 1 part in 10^7 so it is possible that leap-frog algorithms are slightly more stable than predictor-corrector techniques for the simulations of liquids.

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Constant Pressure Molecular Dynamics for Polyatomics

D. Brown

The equations relating absolute to scaled coordinates from reference [1] are:-

$$V = s^3 \tag{1}$$

$$\underline{\rho}_i = \underline{R}_i / V^{1/3} \tag{2}$$

$$\begin{aligned}\dot{\underline{R}}_i &= \underline{p}_i/m_i + (\underline{R}_i/3)\,\frac{d}{dt}\,(\ln V)\\ &= \underline{p}_i/m_i + \underline{R}_i\,\dot{V}/(3V)\end{aligned} \tag{3}$$

$$\underline{p}_i/m_i = \dot{\underline{\rho}}_i\,V^{1/3} \tag{4}$$

where: V = value of MD cell

s = side length of MD cell

$\underline{R}_i$ = position of ith molecule centre-of-mass

$\underline{\rho}_i$ = scaled position if ith molecule centre-of-mass

$\underline{p}_i$ = momentum of ith molecule

m_i = mass of ith molecule

and the equations of motion are:-

$$\ddot{\underline{\rho}}_i = V^{-1/3}\,\underline{F}_i/m_i - 2\,\dot{\underline{\rho}}_i\,\dot{V}_i/(3V) \tag{5}$$

$$\ddot{V} = M^{-1}(P_{cal} - P_{req}) \tag{6}$$

where: M is the 'mass' of the piston

P_{cal} is the calculated pressure

P_{req} is the required pressure

After calculating the pressure at the present time step in the usual way it is possible to integrate (6) using Verlet's algorithm, which gives:-

$$V\,(t+\Delta t) = 2V(t)-V(t-\Delta t)+(P_{cal}-P_{req})\,\Delta t^2/M \tag{7}$$

$$\dot{V}(t) = (V(t+\Delta t)-V(t-\Delta t))/(2\Delta t) \tag{8}$$

where Δt is the time step.

Using equation (1) gives:-

$$s(t+\Delta t) = (V(t+\Delta t))^{1/3}$$

Integrating (5) using Verlet's algorithm gives:-

$$\begin{aligned}\underline{\rho}_i(t+\Delta t) &= 2\,\underline{\rho}_i(t)-\underline{\rho}_i(t-\Delta t)\\ &\quad + \left[\tilde{V}^{1/3}\,\underline{F}_i/m_i - 2\,\underline{\dot{\rho}}_i\,\dot{V}/(3V)\right]\Delta t^2\end{aligned} \tag{9}$$

If we define $\underline{\dot{\rho}}_i = (\underline{\rho}_i(t)-\underline{\rho}_i(t-\Delta t))/\Delta t$ and substitute this into (9) we get:

$$\begin{aligned}\underline{\rho}_i(t+\Delta t) &= \underline{\rho}_i(t) + \underline{\dot{\rho}}_i(t)\,\Delta t\\ &\quad + \left[V^{-1/3}\,\underline{F}_i/m_i - 2\,\underline{\dot{\rho}}_i\,\dot{V}/(3V)\right]\Delta t^2\end{aligned} \tag{10}$$

Now substituting equations (1), (2) and (4) in (10) gives:-

$$\begin{aligned}\underline{R}_i(t+\Delta t)/s(t+\Delta t) &= \underline{R}_i(t)/s(t) + \underline{p}_i(t)\,\Delta t/(m_i\,s(t))\\ &\quad + \left[\underline{F}_i(t)/(m_i\,s(t)) - 2\,\underline{p}_i(t)\,\dot{V}(t)/(3m_i\,s(t)\,V(t))\right]\Delta t^2\end{aligned}$$

which gives us an algorithm for updating the centre of mass as:-

$$\begin{aligned}\underline{R}_i(t+\Delta t) &= \frac{s(t+\Delta t)}{s(t)}\Big[\underline{R}_i(t)+\underline{p}_i(t)\,\Delta t/m_i\\ &\quad + \left[\underline{F}_i(t)/m_i-2\underline{p}_i(t)\dot{V}(t)/(3m_iV(t))\right]\Delta t^2\Big]\end{aligned} \tag{11}$$

and the momenta are updated in the usual way:-

$$\underline{p}_i(t+\Delta t)/m_i = \underline{p}_i(t)/m_i + \underline{F}_i(t)\,\Delta t/m_i \tag{12}$$

Using equation (11) for the centre-of-mass motion allows the use of an absolute coordinate system with only minor changes to the nearest image transformation in the calculation of forces and the update routine.

If we are using a system such that s(0) = 2 box units and $-1 \leqslant \underline{R}_i^{\alpha} \leqslant 1$. Then if HS = 0.5 * s(t) and RHS = 1.0/HS, the nearest image transformation is performed by:

```
XD = X(I)-X(J)

XD = XD - 2 *INT(XD*RHS)*HS
```

and the update for atoms or centre-of-mass leaving the box is:-

```
U = HS * INT(RHS*X(I))

X(I) = X(I) - U - U
```

If the corrections are calculated for the potential energy and the virial, then these will also have to be scaled at each time step by:-

```
VIRLRC (t+Δt) = VIRLRC(t)*V(t)/V(t+Δt)
```

and the same for the potential energy.

The advantages of retaining an absolute coordinate system, are that no changes are required in the rotational algorithm and the calculation of properties such as temperature, pressure, radial distribution function and correlation function remain the same as in a constant volume program.

References

[1] J.M. Haile, H.W. Graben, J. Chem. Phys. (1980) 73. 2412.