

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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## Editorial

Once again we begin the newsletter by thanking all those people who have kindly contributed to its production. Special thanks go to Dr. M. Whittle (UMIST) for agreeing to write the review article on the sixth CCP5 meeting at short notice. He is also thanked for contributing a second article to this issue. Dr. David Heyes (Royal Holloway) has once again provided an article or two and thoroughly deserves praise for his enthusiasm. Dr. G.S. Pawley (Edinburgh) has provided an answer to some points raised at his talk at Royal Holloway and Dr. M.P. Allen (Oxford) has donated a worthy article on Quaternion Parameter Algorithms. Both are sincerely thanked for their efforts. It is very pleasing to note that most of the articles appearing in this issue were unsolicited. It is to be hoped that such willing help will always be available.

Lastly it is appropriate here to praise the work of the Daresbury reprographics group who reproduce and circulate the newsletter. It is through their flexibility and skill that such newsletters as this are possible at all.

## General News

- 1) The following announcement comes from Dr. David Heyes, CCP5 Secretary

It is now possible for postgraduate students in the UK to claim for travel expenses to attend the CCP5 meetings. Requests will be considered on their merits and the availability of funds. Applications should be sent to one of the members of the CCP5 Executive Committee.

Professor J.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) Yet more programs have been donated to the CCP5 program library by David Heyes, N. Corbin and W. Smith. A list of the programs available is attached. Readers requiring copies should forward a magnetic tape to Dr. W. Smith, SERC Daresbury Laboratory, Daresbury, Warrington WA4 4AD. Copies will be provided free of charge.

- 3) Louise Copeland (UMIST) has asked for the following announcement to be made:

### MD SIMULATION OF A LJ MIXTURE

I have written a program to simulate a liquid mixture using a LJ(12,6) potential. This will soon be available on the CRAY-1 as part of the CCP5 program library.

The program calculates configurational properties, (i.e. temperature, pressure and potential energy), as well as mean square displacement, distribution and fluctuation functions for a mixture of two or more components. Any ideas for future development would be most welcome. Program details will be available shortly.

- 4) The next CCP5 meeting will be at Reading 16th/17th December 1982. The title of the meeting is: 'New Computers/The Simulation of Quantum Mechanical Systems'. Interested readers should contact Professor R. Hockney, Computational Science Department, University of Reading, Whiteknights Park, Reading RG6 2AX.

CCP5 Program Library: Program Catalogue

Program	Author	Purpose
MDATOM	S. Thompson	MD on monatomic liquids
HMDIAT	"	MD on homonuclear diatomics
MDLIN	"	MD on linear molecules
MDLINQ	"	As MDLIN but with point quadrupole
MDTETRA	"	MD on tetrahedral molecules
MDPOLY	"	MD on polyatomic molecules.
MDATOM	D. Fincham	MD on monatomic liquids
MDDIAT	"	MD on homonuclear diatomics
MDDIATQ	"	As MDDIAT but with point quadrupole
MDIONS	D. Fincham and N. Anastasiou	MD on ionic liquids
HLJ1	D. Heyes	MD on monatomic liquids
HLJ2	"	As HLJ1, with velocity autocorrelation
HLJ3	"	As HLJ1, with link cells
HLJ4	"	As HLJ1, with constant P or T
HSTOCH	W.F. Van Gunsteren and D. Heyes	Stochastic dynamics program
EWALD1	W. Smith	Subroutines to calculate potential, forces
EWALD2	"	or torques in multipole system.
MDMIXT	"	MD for molecular mixtures
MCN	N. Corbin	MC (Metropolis) simulation of monatomic liquids
SCN	"	MC (Rossky, Friedman, Doll) of monatomic liquids
SMF	"	MC (Path integral method) for monatomic liquids

## A REVIEW OF THE SIXTH CCP5 MEETING

The Computer Simulation of Transport Processes held at Royal Holloway College, Egham between 29th- 30th March 1982.

M. Whittle

The opening session of the meeting was devoted to the measurement of transport coefficients by non-Equilibrium Molecular Dynamics (NEMD). Professor Hoover (Livermore, USA) as the first invited speaker, presented a review of these techniques and described some recent applications. In equilibrium systems, statistical mechanics can be used to derive an equation of state from a knowledge of the pair potential. In NEMD the essential problem is how to modify the equations of motion while retaining this connection between the microscopic and macroscopic points of view. This problem has been solved for several types of system which the author classified as homogeneous, where the normal periodic boundaries are retained though perhaps modified, and heterogeneous systems which may involve moving boundary layers or the inclusion of an external field. A modified equation of motion which effects an isothermal simulation was then presented and the resulting trajectory plots for a simple three particle system compared with those at constant energy. The isothermal plots were considerably more complex. A further modification of the Hamiltonian using the Doll's tensor  $g_{ij}$  allows isothermal adiabatic simulations and this was used to simulate plastic flow at shear rates between  $10^9 - 10^{12} \text{ s}^{-1}$ . Extrapolation of the results to lower shear rates  $10^8 \text{ s}^{-1}$  agreed well with experimental data in that region. As a further example of the use of modified equations of motion, Hoover described recent work on the behavior of the heat flux vector in a rotating system which was stimulated by a conflict of theoretical views. A novel 2-D disk simulation was invoked using a wedge shaped region with periodic boundaries at each wall and a heat source at the centre. The equations of motion were modified by a transformation to rotating coordinates. The results agreed with the microscopic prediction that Fourier's law is violated in a rotating system, while the application of the material frame indifference principle to this problem is suspect. In the discussion that followed Professor Singer asked if there was any distinction between the definitions of temperature used by Andersen and Hoover. Hoover replied that they were both the same in the large system limit.

The next paper was presented by Professor Singer (Royal Holloway College) who discussed methods of measuring the shear viscosity in liquid diatomic systems with particular reference to fluorine. He had used both the well known Green-Kubo method and the newer perturbation NEMD technique pioneered by Ciccotti and Jaccuci. In the latter method (and in steady state NEMD) it is normal to shear the system, however Singer showed that it is also possible to elongate the MD box along an axis while reducing its dimensions perpendicular to that axis. This method rather simplifies the boundary conditions. A step function perturbation of either type of strain produces a stress response that should rise to a plateau value proportional to the viscosity. In molecular systems however a plateau is reached only slowly due to coupling of the orientational variables to the stress relaxation as found by Kivelson and Allen. Integration of the total stress correlation function using 500 particles and 76 000 steps agreed quite well with the perturbation results although both sets were noisy in the plateau region. However, a larger calculation using 864 particles and 50 000 steps surprisingly indicated a lower viscosity for this system. Professor Singer pointed out that quite large discrepancies between methods are found even for monatomic liquids.

Dr Ciccotti (Centre d'Etudes Nucléaires de Saclay, France) gave the second invited lecture and discussed the applications of NEMD perturbation methods to the study of transport processes and dynamics. The phenomenological linear transport coefficients are usually related to fluctuations in dynamical properties via the Kubo formulae and there is no net transport of the property under consideration. However, by imposing an external field on the system which couples to the dynamic variable of interest the transport coefficients may be measured directly. For very small fields the perturbation or 'subtraction' technique is useful to observe the tiny responses in the presence of statistical noise. It was shown that for conserved variables the equilibrium and NEMD perturbation approach give identical results according to linear response theory and that the derivation can be generalised to express transport coefficients as a power series for larger imposed fields. Ciccotti then discussed the advantages and disadvantages of the methods. Although equilibrium techniques can in principle measure all transport properties in a single simulation while NEMD methods are limited to the properties coupled to the external field, the latter have the advantage that they do not depend upon linear response theory and can therefore be used to investigate

the range of validity of this approximation. In addition they can be used to study classes of dynamic properties inaccessible by equilibrium methods, e.g. rare fluctuations. However, it is sometimes difficult to tailor the correct perturbation and the onset of noise at long times can be troublesome. An expression for the variance of the noise was derived which depends upon the magnitude of the response and he concluded that the perturbation should be microscopically large but macroscopically small.

The following paper given by Dr W.A.B. Evans (Canterbury), described an application of the perturbation method to compute the dynamic structure factor  $S(\underline{q}, \omega)$ . He used a  $\delta$  function perturbation in time, proportional to  $\cos(\underline{q} \cdot \underline{r})$  with  $\underline{q}$  the wave vector and  $\underline{r}$  the particle position. However, since the responses of different wavevectors are independent, it is possible to 'kick' the system with several values of  $\underline{q}$  at once. The resulting responses  $g(\underline{q}, t)$  can then be combined via their transforms  $D(\underline{q}, \omega)$ , to give the structure factor. The method was tried on a Lennard-Jones system close to the triple point and gave a result which compared favourably with that obtained previously by Levesque using conventional techniques. Evans commented that this was a reliable method for small  $\underline{q}$  values which are subject to large errors when the usual transform of  $g(\underline{r})$  is employed. He also suggested that it may be possible to obtain partial structure factors in mixtures by inventing a field that couples to only one type of particle.

Dr Gillan (Harwell), considered the use of the perturbation method to measure thermal conductivities. Previous results have all been obtained at non-zero wavevector because the form of the perturbation used becomes a constant at zero frequency. By investigating the perturbed equations of motion and subtracting a portion which has no effect on the heat current a modified perturbation was obtained which is effective at zero wavevector. The results compare well with the usual correlation method. Professor Powles asked generally how meaningful it is to talk about zero wavevector results in periodic systems. The conference could not supply a direct answer but Hoover thought that the dependence of viscosity on system size was less pronounced for homogeneous shear experiments than for Green-Kubo methods. Ciocotti commented that system size differences in the perturbation technique often appear to be established before the acoustic traversal time.

Professor Powles then moved a brief discussion on hardware in anticipation of the next CCP5 meeting. Dr Moser made the case for a hierarchy of computers but thought that the Cray was not necessarily an obvious choice partly because users are reluctant to modify existing programs. He challenged anyone to produce work on the Cray that could not be accomplished on smaller machines. A great deal of good work has been done by workers with unlimited time on smaller computers of their own. Those with experience of the DAP made a strong case for these machines which are well suited to MD work, the only drawback being that they require a completely new style of programming. Purpose built MD computers were deemed to be too inflexible in a rapidly developing field.

Dr J.H.R. Clarke (Manchester, UMIST) started the second day of the meeting with a talk on structural relaxation and glass formation in liquids. Structural relaxation can be described in terms of the total density collective correlation function and assigned a relaxation time  $\tau_s$ . Experimentally, this is related to and may be estimated from the dielectric, volume and shear relaxation times. In model liquids  $\tau_s$  determines the timescale of equilibration and is also related to the probability of nucleation at high densities. It is therefore of relevance in glass transition phenomena. Important factors that may affect  $\tau_s$  include the system size, intermolecular potential and molecular shape, and in a simulation a convenient monitor of structural relaxation is provided by the configurational energy and pressure. When preparing a glass by quenching, the relaxation of these properties is somewhat slower than the thermal equilibration rate and is size dependent for small systems. Such observations are important since the glass transition temperature may be artificially depressed if a system is not completely relaxed at the time of quench. Although the radial distribution function does not change sharply at the glass transition temperature, more dramatic changes had been observed in a related 'radial fluctuation function' defined as  $\langle n(r)^2 \rangle - \langle n(r) \rangle^2$ . It was suggested that this function may be more informative about the glass transition than  $g(r)$ . Professor Powles suggested that this function was related to the zero wavevector structure factor and Dr Jacucci commented that some very long runs on Lennard-Jones Argon had recently raised the simulated glass transition temperature closer to the experimental value.

Our third invited speaker, Professor W.A. Steele (Pennsylvania, USA) spoke next about orientational correlation functions of experimental interest. He concentrated first on the self correlation functions  $P_L(\cos \theta)$  with  $L=1-4$ . The memory functions derived from these data  $K_L(t)$ , provide a stringent test of model memory functions particularly for higher values of  $L$ . The author cited recent work on liquid  $\text{Br}_2$  and showed simulated memory functions that were irreconcilable with small step diffusion although both the Nee-Zwanzig and Torque models were quite successful. However, on increasing the angular dependence of the potential using a quadrupole moment, the memory functions acquired a dip which could not be reproduced by the Torque model. He moved on to discuss translation - rotation coupling and its effect on coordinate displacements which is of particular relevance to quasi-elastic neutron scattering results. He recognised two kinds of coupling: one which produces a local anisotropy relative to the molecular orientations at zero time, and a second coupling between molecular orientation and the centre of mass motion. It was shown that in the absence of coupling of the second kind one can generate the atomic distribution function by convoluting the orientational and centre of mass distribution functions. Comparison of this approximation with the simulated atomic distribution function then serves to isolate T-R coupling of the second kind. In the system studied both types of coupling were insignificant. It was suggested that T-R coupling only becomes important when the decay of the velocity correlation function is short compared to that of the angular correlation time. In this case molecules maintain their orientations while the translational functions decay.

R.M. Lynden-Bell used a different approach to the analysis of rotational correlation functions and expressed them as a cumulant expansion in terms of the angular velocity correlation function (AVCF). Simulations were carried out at three temperatures for which the AVCF showed markedly different behaviour. The first term of the expansion was a second order cumulant integral and produced good agreement with the initial slope of the orientational correlation functions which were measured up to order 4 and coincident at short times. At longer times functions of different order display different slopes on a logarithmic plot and this behaviour could be described by the inclusion of higher order cumulants. The direct link thus forged between reorientational motion and the AVCF means that the correct behaviour of the latter is essential in any useful model

of molecular rotation. Various models were tested on this basis. Although J diffusion and the Langevin models can reproduce the departures of higher order correlation functions from simple Debye behaviour the AVCF for these models is inadequate at high density where the simulated function has a negative portion. Truncated Mori expansions cannot be directly related to the cumulant method but provide a different approach. They require many terms to describe a cage effect involving the reversal of angular velocity. The cumulant expansion treats the AVCF as an observable quantity.

Dr M. Zopi (Florence, Italy) used MD on Argon with a Barker multi-dimensional potential to find the best fit of a three parameter polarizability model by calculating the interaction induced Rayleigh spectrum and comparing spectral moments with experimental data. The three parameters corresponded to a long range DID contribution, an effective intermediate range term and a short range electron overlap term. Two sets of parameters were found to give reasonable agreement with the first two moments in the gas phase but in the liquid phase there was only poor comparison. The author suggested that this may be due to the importance of three body terms neglected in the simulation.

Dr D.J. Tildesley (Southampton) returned to the theme of reorientational motions and presented simulation results for CS<sub>2</sub> at three temperatures. Single particle correlation times are in good agreement with Raman and NMR data for this system. Memory functions showed a pronounced negative dip at low temperature and it was found that a Mori three variable theory was an insufficient description. The time correlation function of the collective orientation fluctuations forms a major contribution to the depolarised Rayleigh spectrum and the ratio of the collective time to the single particle relaxation time is therefore of importance when comparing Raman and Rayleigh data. It was found to be around unity at high temperature but somewhat reduced in the cooler simulations. Translational diffusion was observed to be anisotropic and the ratio of coefficients  $D_{\parallel} / D_{\perp}$  increased down the orthobaric curve from 1.6 to 2.2.

Dr P. Madden (Cambridge) described the application of the maximum entropy method, unashamedly stolen from data reconstruction methods in astrophysics (Nature 272 p686 S.F. Cull and G.J. Daniell), to the analysis of noisy data in which low intensity features may be hidden or confused by spurious Bessel functions left over from a Fourier analysis. The data

is fitted in Fourier transform space by curves  $j(\omega)$  which are acceptable in the sense that the chi-squared parameter is sufficiently small. Using these as 'states' to define an 'entropy' in a manner reminiscent of statistical thermodynamics, one curve is chosen which maximises the 'entropy'. From an alternative viewpoint, spectral features correspond to a quantity of information and the  $j(\omega)$  obtained in this way has an information content warranted by the data and no more. The method was applied to a Rayleigh spectrum of water and showed that the data was insufficient to support claims for a second Brillouin peak.

Owing to the unfortunate absence of Dr Frenkel through illness, Dr Madden presented an extra paper describing work by R. Impey and I. McDonald on the isotope effect on librational motions in water. These can be studied by Neutron scattering IR and Raman spectroscopy. Deuterating shifts the bands to lower frequency. Using the MCY potential, hydrogen bonding effects can be reproduced in simulations and it was shown that by scaling the D<sub>2</sub>O orientation correlation functions with the square root of the moment of inertia they become coincident with those of water.

Dr R. Impey (Cambridge) described MD of ionic solutions using the MCY and Clementi potentials. Ion-H<sub>2</sub>O radial distribution functions were presented which clearly demonstrated structural enhancement around the lithium ion. The data suggested a 'tilt angle' (between the ion-oxygen separation vector and the dipole vector of water) of about zero. Results for K<sup>+</sup> showed a less pronounced structural effect in agreement with evidence from a wide variety of experimental sources. The presence of 'solventbergs' is known to have a dramatic effect on diffusion coefficients and these were estimated from the mean squared displacement and the velocity correlation function. Although statistics are poor with only a single ion, both methods agreed on values of  $0.3 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$  for Li<sup>+</sup> and  $0.2 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$  for K<sup>+</sup>. The VCF was computed by normal methods and by the perturbation technique. The latter however, was subject to strong oscillations at about the acoustic traversal time which subsequently destroy the credibility of the signal. The form of the VCF's suggested that Li<sup>+</sup> was trapped in a long lived solvent cage while K<sup>+</sup> was not. Residence times of solvent molecules within the cage or hydration shell can be estimated by introducing a correlation function dependent on whether or not a water molecule is a member of the shell. This gave crude estimates of  $\tau_R \approx 3.2 \text{ ps}$

for  $K^+$  and  $\tau_R > 18$ ps for  $Li^+$  with 5-8 ps being the experimental value for pure water. The reorientational correlation function for water in the vicinity of the ions was also computed and showed a pronounced librational glich for  $Li^+$  which was not present for  $K^+$ . Dr Clarke asked how the ratios of diffusion coefficients compared with experimental values and Dr Impey replied that  $D_{K^+}/D_{H_2O}$  was about right while  $D_{Li^+}/D_{H_2O}$  was rather too small indicating that the solventberg induced by the ion was too large in the simulation.

Dr Vallauri (Florence, Italy) discussed the momentum transfer of a test particle in collision with neighbouring shells of atoms. Using a velocity cross correlation function he compared results for a Lennard-Jones system and one using a 'softer' potential, the maximum value being used as a measure of momentum transfer. The results apparently suggested that more momentum is passed to the bulk liquid for a soft potential than for a normal Lennard-Jones system.

Dr Stepto (Manchester, UMIST) described recent work by C.J.C. Edwards relating the diffusion coefficient of macromolecules to the chain structure. The simulation involved a chain model with no assumptions regarding the segment distribution and the solvent was a continuum of chosen viscosity. Configurations were chosen by metropolis sampling techniques. The results demonstrated significant deviations from the standard Kirkwood-Rieseman theory.

Dr Pawley (Edinburgh) presented latest results obtained on the DAP in a study of the plastic crystal phase transition in  $SF_6$ . Each element of the 4096 array is assigned a molecule and calculations are then performed parallel. Arranged in the orientationally disordered plastic crystal phase at 80 K the system was cooled to 25 K when cooperative behaviour resulted in the formation of domains of orientational order which could clearly be seen on diagrams taken through the crystal planes.

Dr M. Neumann (Wien, Austria) described simulations of the depolarised Rayleigh wing spectrum for systems of almost spherical molecules. Four and six centre Lennard-Jones potentials were chosen which give good agreement

with a range of experimental data for  $\text{CCl}_4$ ,  $\text{CF}_4$  and  $\text{SF}_6$ . The depolarised spectra of these systems are slightly different in form from each other and from Argon which is now 'well understood'. Various polarisability models were tried and good agreement with the experimental spectrum was found for  $\text{CCl}_4$  and  $\text{CF}_4$  except at low frequency where these materials exhibit a lorentzian character. The atom-atom DID model produced the best fit. Better agreement at low frequencies was found for the  $\text{SF}_6$  simulations but non of the models could reproduce the double exponential form of this spectrum.

D. Heyes

In the continuing effort to promote "grassroots" participation in CCP5, an informal discussion on computing facilities was held during the March, 1982 CCP5 meeting at Royal Holloway College. This took place at the end of the first session.

Professor J.G. Powles (University of Kent) chaired a lively debate on what computing facilities the computer simulators want in the near future. Professor Powles had a leaning towards the widespread availability of small computers, which each group could devote entirely to its own work, rather than share time on a large remotely sited machine.

Dr. D. Fincham (D.A.P. Support Group, Q.M.C.) said that we are now entering a new era of computer technology in which it will be necessary for each worker to choose between one of many differently designed computers. Each problem will be best suited for one particular computer "architecture". We are now entering an age of task designed computers.

Professor C. Moser (C.E.C.A.M., Paris) and Professor R.W. Hockney (Reading) made the point that the large mainframe machines such as the ICL D.A.P., CRAY-1 and CYBER 205, and the smaller (mini-) computers such as the V.A.C.S. 780 were not incompatible and were, indeed, complementary.

Professor Moser said that the CRAY-1 was a powerful scalar computer with flexible vector processing capabilities using a variable vector length. The CYBER 205, however, handles longer vectors and needs considerable reprogramming of a CDC 7600 code, for example, to take advantage of this. Also the CRAY-1 was a more tested machine. He said that Monte Carlo programs cannot be vectorised and for this one would use a distributed processor, although Ising model problems are suitable for the CRAY-1. Dr. G.S. Pawley (Edinburgh University) added that an I.C.L. machine equivalent to twenty CRAY-1's was being planned.

At the other end of the market one could buy about 8 Ahmdahl 780's for the price of one CRAY-1 and Professor Hockney said that an I.C.L. Perk mini-computer would only cost £20,000. Professor Hockney said that the S.E.R.C. established these large remotely accessible computer bases to provide small users, who cannot even afford mini-computers, with access to powerful computing facilities. Consequently, he supported such centres. Professor Moser added, in support, that there are certain problems such as those involving Fluid Mechanics which can only be performed on a large mainframe machine.

Dr. P. Madden (University of Cambridge) considered that we should encourage small computers on philosophical grounds for student use, as this is probably going to be the future trend in computing.

This debate will, no doubt, continue at the next CCP5 meeting to be held at Reading University on the 16/17th December, 1982. The title of the conference is:

"New Computers/The Simulation of Quantum Mechanical Systems".

Non Equivalence of the Step and Delta Function in  
Perturbation Experiments.

M. Whittle

At the last CCP5 meeting we raised the question of equivalence between step and delta function perturbation experiments and provoked some incredulity among members of the audience. We would like to qualify our statements by presenting some data and the germ of an explanation for our results.

The response of an observable  $O(\underline{k})$  at wavevector  $\underline{k}$ , can be related<sup>(1)</sup> to an equilibrium correlation function  $\langle \rangle_0$  by,

$$\langle O(\underline{k}) \rangle_t = \frac{V}{k_B T} \int_{-\infty}^t dt' \langle O(\underline{k}, t) J(-\underline{k}, t') \rangle_0 i \underline{k} \phi(\underline{k}, t') \quad (1)$$

where the perturbation  $\phi(\underline{k}, t)$  couples to a dynamic variable with corresponding current  $J$ . The response of the current itself to a delta function perturbation is then just the correlation function ,

$$\langle J(\underline{k}) \rangle_t = \frac{V}{k_B T} \langle J(\underline{k}, t) J(-\underline{k}, 0) \rangle_0 \quad (2)$$

while a step function gives the integral,

$$\langle J(\underline{k}) \rangle_t = \frac{V}{k_B T} \int_0^t \langle J(\underline{k}, t) J(-\underline{k}, 0) \rangle_0 dt \quad (3)$$

Integration of the response to a delta function perturbation should therefore be identical to the observed response in a step function experiment.

In figures 1 and 2 we make this comparison at two densities in liquid  $Cl_2$  for the  $xz$  component of the stress tensor in response to shear rate perturbations of the same symmetry. These results were obtained by direct subtraction of trajectories rather than by linearising and expanding the equations of motion. Evidently the responses are not identical in that the delta function clearly results in a better signal to noise ratio at long times. This is very desirable, particularly in this instance where the maximum value reached by the response at long times corresponds to the viscosity of the system.

The development of equation (1) rests upon the ergodic theorem in that the angular brackets imply a statistical response obtained by averaging over many pairs of trajectories or 'segments'. Thus although we may expect the responses in figs 1 and 2 to converge after a large number of segments have been taken, for the few runs feasible in practice expressions 1-3 are not strictly valid and the detailed response, i.e. the noise, need not be equivalent.

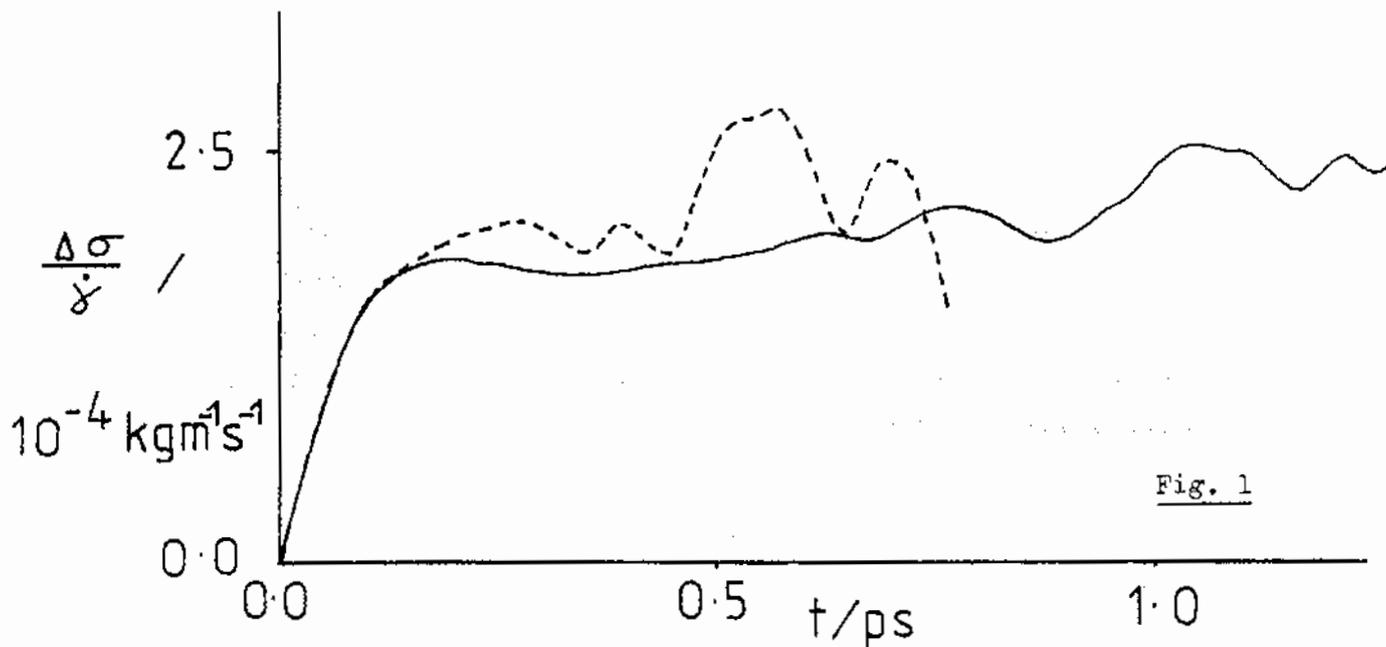


Fig.1 Shear stress response to a step function perturbation in strain rate  $\dot{\gamma}$  (-----), and the integrated response to a delta function perturbation (———). For diatomic Lennard Jones chlorine, bond length 0.65,  $T^* = 1.5$   $\rho^* = 0.49$ . Averaged over 7 and 6 segments respectively.

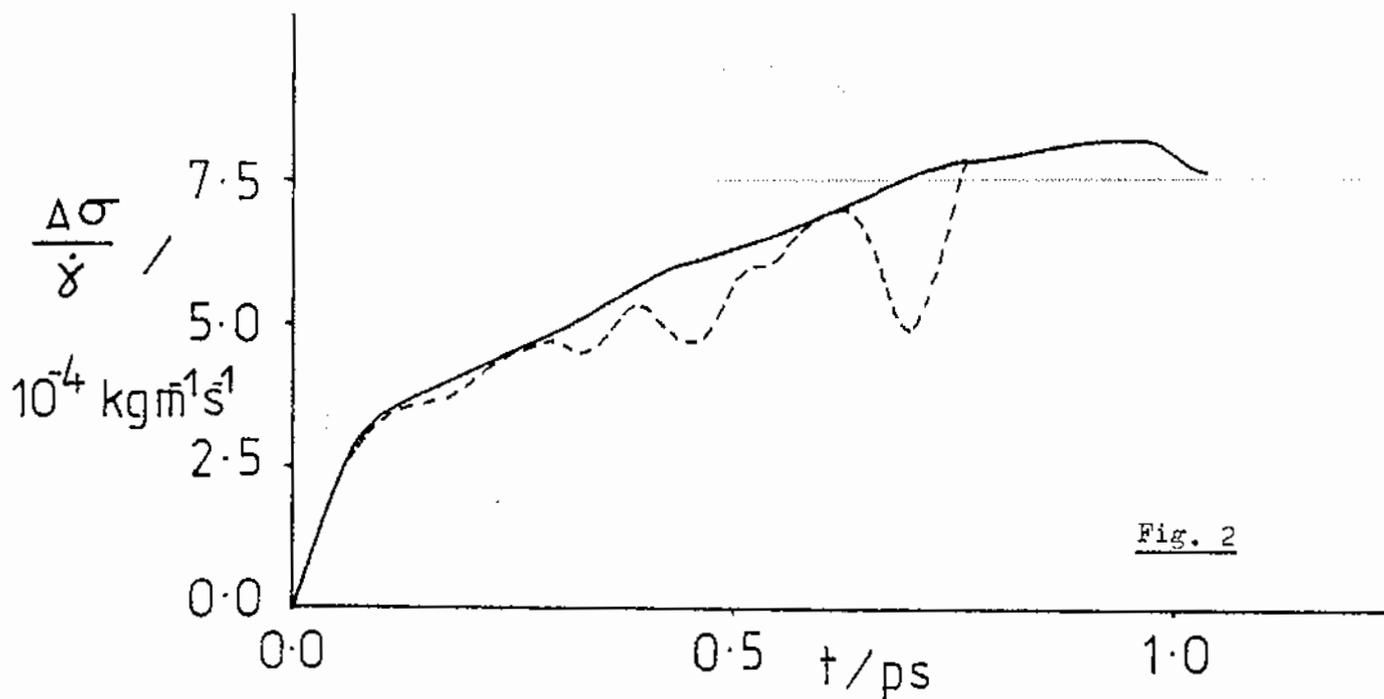
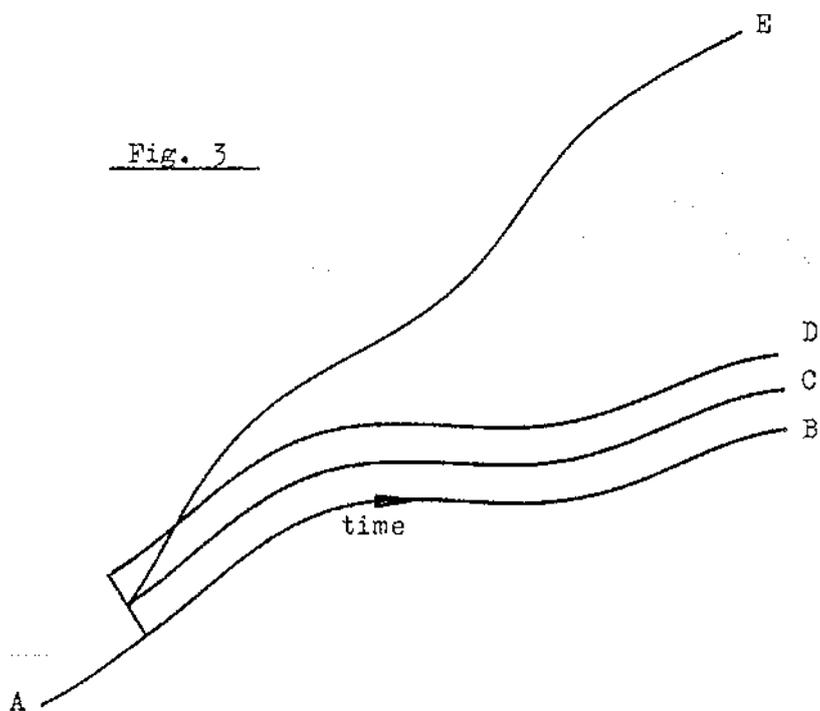


Fig.2 As Fig.1,  $T^* = 0.75$ ,  $\rho^* = 0.59$ . Averaged over 8 segments.

If we represent the trajectory in phase space as a line (Fig 3, AB) then a delta function results in an almost parallel path AC. In the linear response regime, a delta function of twice the magnitude will produce another trajectory AD, again parallel but twice the 'distance' from AB. A step function is equivalent to a series of delta functions and therefore produce a series of configurations AE, which move progressively further from the original set so that at long times considerably more noise appears in the derived responses for small systems.



The noiseless result of linear response theory (Eqs 2 and 3) is obtained only in the limit of large systems or by averaging over very many segments.

Reference

- (1) G. Ciccotti, G. Jacucci, I.R.McDonald, J. Stat. Phys. 21, 1 (1979).

At the recent CCP5 meeting at Royal Holloway College I presented some M. D. results of the plastic crystalline phase of  $SF_6$  which gave a temperature, as calculated from linear velocities, systematically different from that as calculated from angular velocities. The suggestion that this is evidence that the elementary excitations in the system involve a coupling between the translational and rotational motion was not well received, but as there was no clear argument as to why this would not be so I wish to raise the matter in these pages so that people can ponder the matter at length. Equipartition takes place between the elementary excitations of the system, and if there is translational-rotational coupling therein then the use of (say) linear velocities alone to find the temperature is not valid. The system can be expressed in terms of any set of generalised coordinates, and the temperature obtained from the squares of these generalised velocities is independent of the coordinate system as long as the total number of generalised velocities is included. However one cannot take an arbitrary subset and hope to get the right temperature, and the set of linear velocities is such an arbitrary subset.

## QUATERNION PARAMETER ALGORITHMS

M. P. Allen

### Introduction

There has been a steady growth of interest in recent years in the use of quaternion parameters to represent rigid body orientations in classical mechanics. Of most relevance here, of course, are the molecular dynamics algorithms based on quaternion parameters [1], which are represented in the CCP5 program library [2], but the wider interest is clearly shown by the discussion, in some detail, of quaternions in the second edition of Goldstein's text 'Classical Mechanics' [3]. In this article, I wish to summarize the orientational equations of motion, as concisely as possible, in quaternion form, and to draw attention to a way of integrating them which, I believe, has not been studied extensively. This approach may be most useful when the interaction potentials are simply expressed in terms of the quaternions themselves (multipole-multipole interactions are an example). Some of the discussion will be restricted to the case of spherical top molecules, for simplicity, but it should be clear how to extend the treatment to the general case. Much of this material will be familiar to many readers, and I make no great claims of originality as regards this general approach.

### Quaternion parameter notation

I will use lower case symbols to represent scalars and vectors, and upper case for quaternions:

$$Q = (q_0, q_1, q_2, q_3) = (q_0, \vec{q}) \quad (1)$$

I follow Goldstein in numbering the four scalar components of the quaternion from

zero. As indicated here, the triple  $(q_1, q_2, q_3)$  may often be regarded as a vector  $\vec{q}$  in 3D space. Quaternion "multiplication" is defined:

$$P*Q = (p_0q_0 - \vec{p}\cdot\vec{q}, p_0\vec{q} + q_0\vec{p} - \vec{p}\times\vec{q}) \quad (2)$$

This operation is not commutative, so  $Q*P \neq P*Q$ , but it is associative, so we can unambiguously write  $P*Q*R = P*(Q*R) = (P*Q)*R$ . This last property is in contrast to the vector cross product  $\vec{p}\times\vec{q}$  which appears in equation (2). Addition of two quaternions, and multiplication of a quaternion by a scalar, are both simple component-by-component operations. The conjugate of  $Q$  is written  $\tilde{Q}$ :

$$\tilde{Q} = (q_0, -\vec{q}) \quad (3)$$

so that

$$\tilde{Q}*Q = Q*\tilde{Q} = (|Q|^2, \vec{0}) \quad (4)$$

Here,  $\vec{0}$  is the null vector, and the norm  $|Q|^2$  is defined

$$|Q|^2 = q_0^2 + q_1^2 + q_2^2 + q_3^2 \quad (5)$$

For a quaternion  $Q$  with unit norm,  $\tilde{Q}$  is the same as  $Q^{-1}$ , the inverse of  $Q$ , since the resultant  $\tilde{Q}*Q = (1, \vec{0})$  acts as an identity element.

Goldstein discusses the way in which a quaternion  $Q$  with unit norm may represent the orientation of a rigid body, and clarifies the relationship between the components of  $Q$  and the Euler angles  $(\phi\theta\psi)$  in various conventions. The rotation matrix  $\bar{A}$ , defined by

$$\vec{r}^b = \bar{A} \vec{r}^s \quad (6)$$

where  $\vec{r}^b$  and  $\vec{r}^s$  are the components of a vector in body-fixed and space-fixed coordinate systems, respectively, can invariably be written in the symmetrical form:

$$\bar{A} = \begin{bmatrix} q_0^2 + q_1^2 - q_2^2 - q_3^2 & 2(q_1 q_2 + q_0 q_3) & 2(q_1 q_3 - q_0 q_2) \\ 2(q_1 q_2 - q_0 q_3) & q_0^2 - q_1^2 + q_2^2 - q_3^2 & 2(q_2 q_3 + q_0 q_1) \\ 2(q_1 q_3 + q_0 q_2) & 2(q_2 q_3 - q_0 q_1) & q_0^2 - q_1^2 - q_2^2 + q_3^2 \end{bmatrix} \quad (7)$$

To achieve this, one should choose a definition of Q which is consistent with the Euler angle convention employed (this has not always been the case in the past). For example, in the 'y-convention' [4], the definitions

$$\begin{aligned} q_0 &= \cos \frac{1}{2}(\psi + \phi) \cos \frac{1}{2}\theta \\ q_1 &= \sin \frac{1}{2}(\psi - \phi) \sin \frac{1}{2}\theta \\ q_2 &= \cos \frac{1}{2}(\psi - \phi) \sin \frac{1}{2}\theta \\ q_3 &= \sin \frac{1}{2}(\psi + \phi) \cos \frac{1}{2}\theta \end{aligned} \quad (8)$$

yield equation (7). With such a choice, as is well-known, the rotation from body-fixed to space-fixed coordinates can be expressed as a quaternion operation. Defining quaternions  $R^b = (0, \vec{r}^b)$ ,  $R^s = (0, \vec{r}^s)$ , equations (6), (7) are equivalent to

$$R^b = \bar{Q} * R^s * Q \quad (9)$$

### Equations of motion

The orientational equations of motion, in quaternion form, may be derived by straightforward but tedious trigonometry applied to the time derivative  $\dot{Q}$ , or by considering the time-evolution of  $\bar{A}$ . The result is usually expressed in terms of a 4x4 matrix acting on the four components of an angular velocity quaternion  $\Omega^b = (0, \vec{\omega}^b)$  (body-fixed) or  $\Omega^s = (0, \vec{\omega}^s)$  (space-fixed), but is most compactly written:

$$\dot{Q} = \frac{1}{2} Q * \Omega^b = \frac{1}{2} \Omega^s * Q \quad (10)$$

For a spherical top, the time derivative of the angular velocity is given by

$$\dot{\Omega}^b = N^b \qquad \dot{\Omega}^s = N^s \qquad (11)$$

where  $N^b = (0, \vec{n}^b)$ ,  $N^s = (0, \vec{n}^s)$ , and  $\vec{n}^b$  and  $\vec{n}^s$  are the body-fixed and space-fixed components, respectively, of the applied torque, divided by the moment of inertia.

Consider how these equations are integrated. Typically, (e.g. in the CCP5 program library) equations (10) and (11) are treated using a pair of (say) 4<sup>th</sup> order predictor-corrector procedures, coupled together:

- (a) PREDICT the new values of  $Q, \dot{Q}, \dots Q^{(4)}$  from current values of  $Q, \dot{Q}$  etc.;
- (b) PREDICT the new values of  $\Omega^b, \dot{\Omega}^b, \dots \Omega^{b(4)}$  from current values of  $\Omega^b$  etc.;
- (c) EVALUATE  $N^b$  from the predicted  $Q$ ;
- (d) CORRECT the values of  $\Omega^b, \dot{\Omega}^b$  etc., using  $N^b$  (equation (11));
- (e) EVALUATE  $\frac{1}{2}Q*\Omega^b$  from the corrected  $\Omega^b$  and the predicted  $Q$ ;
- (f) CORRECT the values of  $Q, \dot{Q}$  etc., using  $\frac{1}{2}Q*\Omega^b$  (equation (10)).

This sequence is generally followed by a renormalization of  $Q$  to counteract the cumulative effects of algorithm error (hopefully small!). The predictor steps will generally be simple Taylor series, while the corrector will be the Gear formula [5] appropriate for a first order differential equation, (10) or (11).

This approach has been shown to work well. Dealing with body-fixed angular velocities and torques is necessary if the approach is to handle, in a natural way, non-spherical molecules. The angular velocities are available for the computation of kinetic energy. Other beneficial features will be mentioned later. However, one obvious feature, in view of equation (10), is that a lot of redundant information is being stored in the form of  $Q, \Omega^b$ , and the first 4 time derivatives of both. Remember that one main idea behind the quaternion approach was to obtain equations of motion which are not singular (as the Euler equations are) without going so far as to store (for example) all 9 components of the rotation matrix, plus derivatives.

My interest here is with the alternative method, namely the elimination of the angular velocities from equations (10) and (11) to yield a single, second-order, equation of motion. For a spherical top, the result is the same whether one starts from the body-fixed or space-fixed forms of (10), (11), and is

$$\ddot{Q} = \dot{Q} * \dot{Q} * Q + \frac{1}{2} N \quad (12)$$

The second derivative  $\ddot{Q}$  contains a "kinetic" part, but the more interesting term is  $N$  which can be expressed in terms of body-fixed or space-fixed torques:

$$N = 2Q * N^b = 2N^s * Q \quad (13)$$

The chain rule for differentiation shows that  $N$  is actually a quaternion "force" or "torque", and can be expressed

$$N = -(\partial V / \partial q_0, \partial V / \partial q_1, \partial V / \partial q_2, \partial V / \partial q_3) \quad (14)$$

where  $V$  is the potential energy and the derivatives  $\partial / \partial q_i$  may be taken holding the other 3 quaternions constant (see below). The situation for non-spherical molecules is only slightly more complex, in that at some stage the torque must be expressed in body-fixed coordinates so as to divide out the principal moments of inertia.

The suggestion, then, is that equation (12) may be integrated directly, using equation (13) or (14) for  $N$ . Any algorithm suitable for general second-order differential equations could be employed, as long as it does not demand the absence of time derivatives of  $Q$  on the right; the Gear methods would be appropriate for instance. The scheme would be:

- (a) PREDICT the new values of  $Q, \dot{Q}, \dots$  from their current values;
- (b) EVALUATE the right hand side of equation (12) as a function  $F(Q, \dot{Q})$ ;
- (c) CORRECT the values of  $Q, \dot{Q}, \dots$  using  $F(Q, \dot{Q})$  (equation (12)).

Only the quaternions  $Q$  and their time derivatives need be stored; probably 5 derivatives would be needed to achieve an accuracy comparable with the pair of 4<sup>th</sup> order algorithms mentioned above. There would be no need to store angular velocities, Euler angles, direction cosines or rotation matrices; the angular velocities could be obtained from equation (10) and the kinetic energy would be given by  $\frac{1}{2}I\omega^s{}^2 = \frac{1}{2}I\omega^b{}^2 = 2I|\dot{Q}|^2$ .

Now for the caveats. The astute reader will already have noticed that the torque  $N$  is not completely defined by equation (14), since  $V$  is actually a function of 3 independent angular parameters, not 4. In fact, because  $Q$  has unit norm, we could add any function of the form  $\frac{1}{2}f(q_0, q_1, q_2, q_3) \times (q_0^2 + q_1^2 + q_2^2 + q_3^2 - 1)$  to  $V$ , without changing its value, but thereby replacing  $N$  in equation (14) by  $N+fQ$ . The extra term simply affects the time evolution of the norm of  $Q$ .

Remembering that  $|Q|^2 = 1$ , we have

$$\partial/\partial t (|Q|^2) = 2(\dot{Q}^*Q)_0 = 2(q_0\dot{q}_0 + q_1\dot{q}_1 + q_2\dot{q}_2 + q_3\dot{q}_3) = (\Omega^b)_0 = (\Omega^s)_0 = 0 \quad (15a)$$

$$\partial^2/\partial t^2 (|Q|^2) = \frac{1}{2}(\dot{Q}^*N)_0 = \frac{1}{2}(q_0n_0 + q_1n_1 + q_2n_2 + q_3n_3) = (N^b)_0 = (N^s)_0 = 0 \quad (15b)$$

where  $(\dots)_0$  means "zero<sup>th</sup> component of". Both of these quantities should be zero. Since the CCP5 implementation makes use of body-fixed angular velocity and torque components, equations (15a), (15b) are guaranteed, that is the norm remains constant to at least second order. Equation (15b) will also be obeyed in the integration of equation (12) if we obtain  $N$  from  $N^s$  or  $N^b$ , via equation (13). The problem arises if we use equation (14) for  $N$ , when the differentiation should really be carried out subject to the condition (15b). In practice it is simpler (and equivalent) to take unconstrained derivatives, as suggested above, and then correct  $N$ . This can be done by transforming  $N$  to  $N^b$  (equation (13)), setting  $n_0^b = 0$ , dividing  $n_1^b, n_2^b, n_3^b$  by the principal moments of inertia in the non-spherical case (since this is a convenient point to do it) and then transform-  
ing back to  $N$ . Alternatively, in the case of the spherical top, we could simply

compute the projection  $f = q_0 n_0 + q_1 n_1 + q_2 n_2 + q_3 n_3$  and then replace  $N$  by  $N - fQ$ .

A similar procedure would be used to ensure that equation (15a) is satisfied: compute  $f' = q_0 \dot{q}_0 + q_1 \dot{q}_1 + q_2 \dot{q}_2 + q_3 \dot{q}_3$  and replace  $\dot{Q}$  by  $\dot{Q} - f'Q$ . I believe that these procedures are no less important, for the integration of equation (12), than the simple rescaling of  $Q$  to guarantee unit norm. The reader may like to consider whether similar corrections should be applied to the third and higher derivatives of  $Q$ .

I have conducted preliminary runs for single-particle and for many-particle systems of rotors pinned to lattice sites, comparing the direct integration of equation (12) (by 5<sup>th</sup> order Gear algorithm for 2<sup>nd</sup> order differential equations) with the integration of equations (10) and (11) (by a pair of 4<sup>th</sup> order Gear algorithms for 1<sup>st</sup> order differential equations). In each case, point multipole potentials (expressed as simple polynomials of the quaternion parameters) were used, and  $N$  obtained via equation (14). The direct method looks promising in this particular application, but only becomes competitive (as far as energy conservation is concerned) when the corrections suggested above are incorporated at each time step; otherwise the "zero<sup>th</sup> components" of torque and angular velocity in the body-fixed frame soon build up. Merely correcting the torque is itself insufficient: the time derivative  $\dot{Q}$  must be made "orthogonal" to  $Q$ , to prevent the accumulation of error during the run.

### Conclusion

It is possible to integrate the orientational equations of motion, in quaternion form, directly, i.e. as second order differential equations. This approach would be useful when the potential energy can be easily expressed in terms of the quaternions themselves, and it saves a little on storage compared

with the usual treatment, as a pair of first order differential equations. The way in which the direct approach deals with non-spherical molecules, and the corrections which must be applied to ensure that time derivatives of the norm  $|Q|^2$  are zero, are less elegant than the corresponding features of the normal method, but are not particularly time-consuming. Any comments?

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# A RADIATION DAMAGE ALGORITHM

by

D.M. Heyes

During the simulation of radiation damage, RD, events by Molecular Dynamics, MD, isolated high energy collisions take place at the same time as lower energy lattice relaxations. An algorithm which can efficiently accomodate the demands of both of these processes is described below<sup>1</sup>.

In equilibrium state MD a central difference, CD, formula to increment the particle positions,  $\underline{r}(t)$  could be used<sup>2</sup>. This starts from Newton's second law and employs a finite difference scheme to obtain the velocities,  $\dot{\underline{r}}(t+\Delta t/2)$ , at half-time step intervals:

C.D.

$$\underline{r}(t+\Delta t) = \underline{r}(t) + \dot{\underline{r}}(t-\Delta t/2)\Delta t + \underline{F}(t)\Delta t^2/m, \quad (1)$$

$$\dot{\underline{r}}(t+\Delta t/2) = [\underline{r}(t+\Delta t) - \underline{r}(t)] \Delta t^{-1}. \quad (2)$$

$\underline{F}(t)$  and  $m$  are the force on and the mass of a particle, respectively. The CD algorithm has the disadvantage that positions and velocities are not simultaneously defined and thus an instantaneous total energy is not evaluable. The Verlet approach<sup>3</sup>:

Verlet.

$$\underline{r}(t+\Delta t) = 2\underline{r}(t) - \underline{r}(t-\Delta t) + \underline{F}(t)\Delta t^2/m, \quad (3)$$

$$\dot{\underline{r}}(t) = (\underline{r}(t+\Delta t) - \underline{r}(t-\Delta t))/2\Delta t, \quad (4)$$

does not suffer from this drawback.

Both CD and Verlet depend for their success on the forces being small enough not to change the velocities significantly over a few time steps. This is not a valid assumption usually in RD simulations.

An excellent, easily performed, algorithm which can be used for RD which is called the Average Force, A.F., method is described below<sup>4,5</sup>. Essentially it is a single cycle predictor-corrector scheme.

A.F.

(a) Predict tentative new positions of all particles:

$$\underline{r}'(t+\Delta t) = \underline{r}(t) + \dot{\underline{r}}(t)\Delta t + \underline{F}(t)\Delta t^2/2m, \quad (5)$$

(b) Correct new positions by evaluating the forces,  $\underline{F}'$ , derived from the  $\underline{r}'(t+\Delta t)$ :

$$\underline{\bar{F}} = (\underline{F}' + \underline{F}(t))/2, \quad (6)$$

Then,

$$\underline{r}(t+\Delta t) = \underline{r}(t) + \dot{\underline{r}}(t)\Delta t + \underline{\bar{F}}\Delta t^2/2m, \quad (7)$$

$$\dot{\underline{r}}(t+\Delta t) = \dot{\underline{r}}(t) + \underline{\bar{F}}\Delta t/m. \quad (8)$$

In order to economically sample time and space during RD calculations the time step duration,  $\Delta t$ , is varied with a maximum particle displacement criterion. Before incrementing the positions the time step,  $\Delta t$ , is evaluated so that the largest distance moved by any particle,  $\Delta r$ , whether by the action of force,

$$\Delta t_f = \sqrt{d} (2m/F(t)), \quad (9)$$

or by velocity,

$$\Delta t_v = d(m/2T)^{\frac{1}{2}}, \quad (10)$$

(T is the temperature)

does not exceed  $d = d^*r_0/2$ . Here  $r_0$  is the nearest neighbour distance which is equal to 3.14 and 3.615 in KCl and Cu at room temperature.

It is important to accurately compute individual trajectories for RD. To test the properties of the above algorithms a 2000 eV  $K^+$  acting through its short range interaction potential only was directed towards a like stationary particle; both with head-on and off-centre trajectories, as shown in fig. 1.

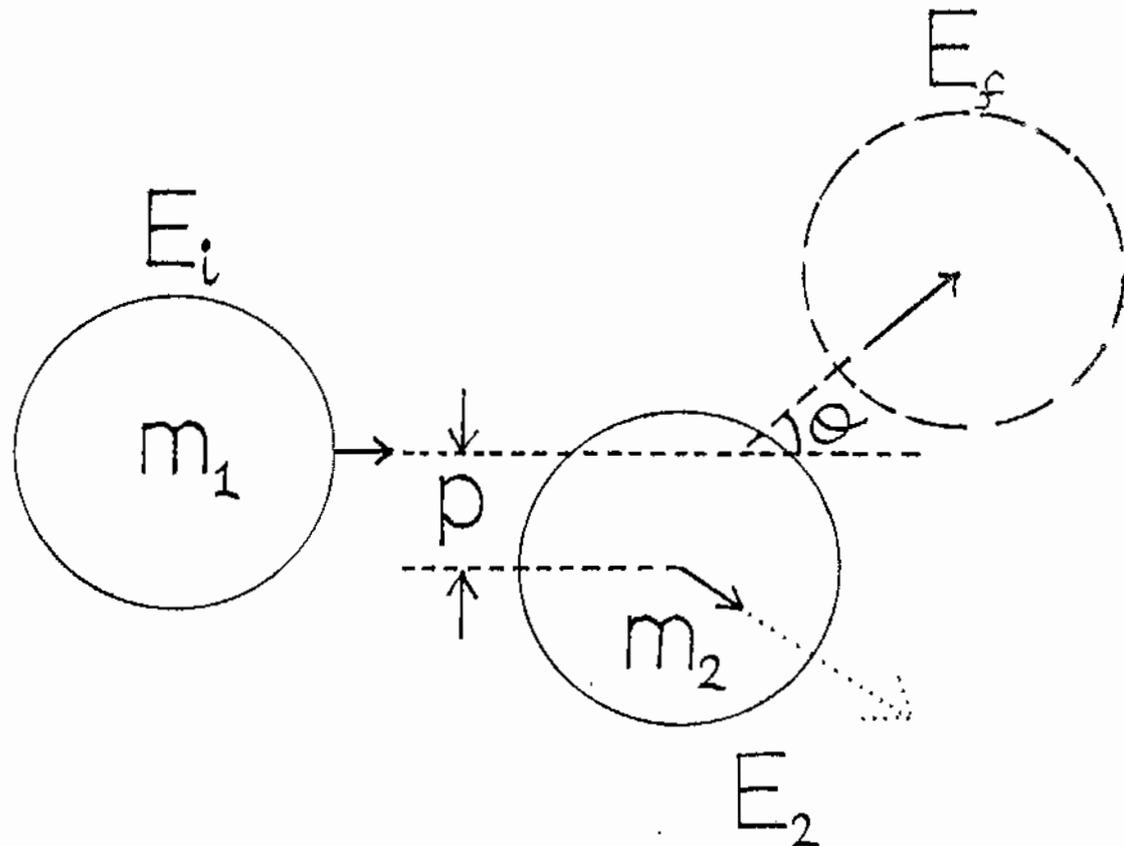


Fig. 1.

A sketch of the two particles colliding.

Here:

$$E_i = 2\text{keV}$$

$p$  is the impact parameter.

If  $p \neq 0$ , then<sup>6-8</sup>

$$\frac{E_f}{E_i} = \left\{ \frac{\cos\theta + (r^2 - \sin^2\theta)^{\frac{1}{2}}}{(r+1)} \right\}^2 \quad (11)$$

where

$$r = m_2/m_1 \quad (12)$$

Note, if  $r = 1$  then,

$$\frac{E_f}{E_i} = \cos^2\theta. \quad (13)$$

Hence,

$$\theta = \cos^{-1} (E_f/E_i)^{\frac{1}{2}} \quad (14)$$

Also if  $p = 0$

$$\frac{E_f}{E_i} = 1 - 4 m_1 m_2 / (m_1 + m_2)^2 \quad (15)$$

$$\text{and if } r = 1, E_f/E_i = 0 \quad (16)$$

In passing, it is of technical interest perhaps to note that the CD approach does not permit simultaneous knowledge of the kinetic and potential energies. Thus when impacting particles are close to

their point of nearest approach, total energy will appear to be more poorly conserved than in fact may be the case.

In Table 1 the energy conservation and trajectory accuracy (through  $\theta$ ) are compared for the above algorithms and a number of potentials of interaction, . The UNRCC CDC 7600 was used for these test runs. It is demonstrated that the AF method gives better than 1% energy and angle of reflection accuracy, whereas the CD approach can have energy decrements of 20% of the initial kinetic energy (= 2000 eV). Increasing  $d^*$  from 0.05 to 0.09 causes the energy loss to rise from 0.63 to 3%, with a head-on composite potential (C) event. The energy decrement for the softer MH collision using  $d^* = 0.09$  is only 0.2%.

Application of linear interpolation between tabulated force values can improve the force accuracy by up to 2.5% for both C and MH potentials. As most of the movement in all time increments is velocity initiated it is perhaps not surprising that 7 and 10 have energy losses differing by 0.1% at most.

Algorithm	$\phi$	$d^*$	Linear Interpolation	$p/\text{\AA}$	$E_f$ eV	$E_2$ eV	Final Energy $E_f + E_2$	$\theta$ from eqn. (13)	$\theta$ actually observed
1. CD	MH	0.05	Yes	0.5	1698.1	299.27	1997.4	22.7570	22.7570
2. AF*	MH	0.05	Yes	0.5	1726.7	294.27	2021.1	21.6878	23.4777
3. AF	MH	0.05	Yes	0.5	1702.7	297.43	2000.2	22.6765	22.6833
4. CD	MH	0.05	Yes	0.0	0.33104	1948.9	1949.2	-	-
5. AF*	MH	0.05	Yes	0.0	22.586	1781.2	1803.8	-	-
6. AF	MH	0.05	Yes	0.0	0.00002	1999.6	1999.6	-	-
7. AF	C	0.05	Yes	0.0	0.02516	1985.8	1985.9	-	-
8. CD'	C	0.05	Yes	0.0	21.044	1610.7	1631.8	-	-
9. AF**	C	0.05	Yes	0.0	0.0082	1991.9	1991.9	-	-
10. AF	C	0.05	No	0.0	0.01976	1987.4	1987.5	-	-
11. AF	C	0.09	No	0.0	0.54054	1934.8	1935.3	-	-
12. AF	MH	0.09	No	0.0	0.00201	1996.0	1996.0	-	-
13. AF	GII	0.09	No	0.0	0.12493	1968.5	1968.6	-	-
14. AF	C	0.05	No	0.5	1716.4	284.67	2001.0	22.12	22.16

TABLE 1.

Caption.

Binary collision results.  $E_i = 2000$  eV. (Potentials/eV).

(a) MH - Mayer-Huggins gas phase [ref. 9]:  $\phi(r) = 5405.829 \exp(-3.8462r)$  where  $r$  is the interparticle separation in  $\text{\AA}$ .

(b) C - composite [ref. 1] which is steeper than (a).

$$\phi(r) = A + Br + Cr^2 + Dr^3 \quad (r \leq 0.794\text{\AA})$$

$$A = 12976.8 \text{ eV}, B = -49859.2 \text{ eV } \text{\AA}^{-1},$$

$$C = 66182.2 \text{ eV } \text{\AA}^{-2} \text{ and } D = -29769.9 \text{ eV } \text{\AA}^{-3}$$

$$\phi(r) = 1.9337 \exp(-r^{*6}/6) r^{*-4}$$

$$-0.2776 r^{*-4} \quad (r > 0.794\text{\AA}) \quad \text{where } r^* = r/2.6666$$

(c) GII - Gibson II for Copper.

$$\phi(r) = 22563.068 \exp(-5.096r)$$

The option of linearly interpolating the potentials and forces between tabulated points separated by  $0.003 \text{\AA}$  - was available.

CD - Central Difference

AF\* - Average Force - only applying operation of eqn. (5) to particle 1

AF - Average Force (complete)

CD' - CD approach using a one cycle predictor - corrector amendment.

AF\*\* - a constant time step throughout the computation,

$$\Delta t = 0.795 \times 10^{-16} \text{ s}, \text{ otherwise AF.}$$

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An Introduction to the Discrete Fourier Transform  
W. Smith

The purpose of this note is to introduce the novice to the discrete Fourier transform (DFT) and as such it is not intended to be comprehensive or even rigorous. It is hoped however, that sufficient insight is provided to enable newcomers to the DFT to understand and avoid some of the problems associated with its use. For a more comprehensive account, readers are referred to reference 1, which provides an excellent introduction to the DFT in general. This note may be regarded, in some part, as being a selective precis of the book. The note begins with a brief description of the general Fourier transform, followed by its adaptation to the discrete case. Lastly the application of the DFT to spectral analysis and the evaluation of correlation functions is briefly discussed.

The Fourier Transform

The Fourier transform  $H$  of a function  $h$  is given by:

$$H(f) = \int_{-\infty}^{+\infty} h(t) \exp(-i 2\pi ft) dt \quad (1)$$

Where, by convention,  $h$  is assumed to be a function of time ( $t$ ) and  $H$  a function of frequency ( $f$ ). It should be noted that either or both of  $h$  and  $H$  may be complex. The inverse Fourier transform is given by:

$$h(t) = \int_{-\infty}^{+\infty} H(f) \exp(i 2\pi ft) df \quad (2)$$

An important question at this stage concerns the actual existence of the Fourier integrals. In general it may be assumed that any function representable by a finite length curve in any chosen interval (i.e. bounded variation) will possess a Fourier transform. There are useful functions which do not comply with this criterion but nevertheless possess Fourier transforms, (such as the impulse and sampling functions mentioned below) but these are best treated here as special cases.

Perhaps the most familiar functions which comply with the above criterion are the trigonometric functions which Fourier transform (symbolised by  $\Leftrightarrow$ ) as follows:

$$\begin{aligned} \cos(2\pi f_0 t) &\Leftrightarrow \frac{1}{2} (\delta(f + f_0) + \delta(f - f_0)) \\ \sin(2\pi f_0 t) &\Leftrightarrow \frac{i}{2} (\delta(f + f_0) - \delta(f - f_0)) \end{aligned} \quad (3)$$

Where the function  $\delta(f - f_0)$  is the so-called impulse function, which is defined by:

$$\begin{aligned} \delta(x - x_0) &= 0 \quad \text{if } x \neq x_0 \\ \int_{-\infty}^{+\infty} \delta(x - x_0) dx &= 1 \end{aligned} \quad (4)$$

Which incidentally, has the very useful property that for any given function  $f(x)$ :

$$\int_{-\infty}^{+\infty} f(x) \delta(x - x_0) dx = f(x_0) \quad (5)$$

Thus the simple trigonometric functions Fourier transform from continuous functions in the time domain to pairs of sharp peaks in the frequency domain. (This is in fact simpler to establish by using the property (5) in the inverse Fourier transform (2)). In view of the traditional role of the Fourier transform in harmonic analysis this result is of course, expected!

Further examples of Fourier transforms of relevance here are the sampling function:-

$$s(t) = \sum_{n=-\infty}^{+\infty} \delta(t - nt_0) \Leftrightarrow S(f) = \frac{1}{t_0} \sum_{n=-\infty}^{+\infty} \delta(f - \frac{n}{t_0}) \quad (6)$$

and the (rectangular) window function:

$$w(t) = \begin{cases} 1 & |t| < T_0 \\ \frac{1}{2} & |t| = T_0 \\ 0 & |t| > T_0 \end{cases} \Leftrightarrow W(f) = 2T_0 \frac{\sin(2\pi T_0 f)}{2\pi T_0 f} \quad (7)$$

Both of these functions are needed in the adaptation of the Fourier integral to the discrete Fourier transform to be discussed later. The Fourier transforms of other mathematical functions can be found in general texts<sup>2</sup>.

The Fourier transform has a number of useful properties which greatly assist the manipulation of the transform. These properties, which include linearity, symmetry, scaling effects and modulation and phase shifting are discussed in reference 1.

### The Discrete Fourier Transform

To convert the Fourier transform from its integral representation (1) to a discrete representation amenable to digital processing, substantial modifications of the original time function are necessary. These modifications result in subtle changes in the properties of the transform that affect the accuracy and the interpretability of the result. It is instructive to examine these modifications in turn to learn of their effects and where possible, the remedies of these effects. The principal modifications referred to here are sampling and windowing in the time domain and sampling in the frequency domain.

#### (i) Sampling in the Time Domain

The continuous function of time  $h(t)$  may be converted to a discrete representation by multiplying it by the sampling function  $s(t)$  given in equation (6). The sampling function consists of an infinite train of re-

gularly spaced 'sharp peaks' of unit area but of infinitesimal width. The peaks are separated by the time interval  $t_0$ . The result of this multiplication is to produce a set of data points, equally spaced in the time domain at intervals of  $t_0$  and with a value related to the function  $h(t)$  at the corresponding abscissa. The effect of this sampling function on the Fourier transform however, is rather more complicated than a simple multiplication of the corresponding Fourier transformed functions  $S(f)$  and  $H(f)$ . The result is in fact, a convolution integral, which may be summarised thus:

$$\begin{array}{ccc}
 & \xrightarrow{\text{time}} & \sum_{n=-\infty}^{n=+\infty} h(nt_0) \\
 h(t) s(t) & \text{domain} & \\
 & \xrightarrow{\text{frequency}} & \int_{-\infty}^{+\infty} S(f') H(f-f') df' \\
 & \text{domain} &
 \end{array} \tag{8}$$

The fact that the result in the frequency domain is a convolution integral, is of sufficient importance to warrant at least a demonstration of its truth. First it is necessary to define a function  $u(t) = h(t) s(t)$ . From the Fourier transforms of these functions (equation (1))  $u(t)$  may be written directly as:-

$$u(t) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} S(f) H(\sigma) \exp(i2\pi(f + \sigma)t) d\sigma df$$

Using the substitution  $f' = f + \sigma$  and re-arranging gives:

$$u(t) = \int_{-\infty}^{+\infty} \left\{ \int_{-\infty}^{+\infty} S(f) H(f' - f) df \right\} \exp(i2\pi f' t) df'$$

By comparison with equation (2) it can be seen at once that the term written in curled brackets above is the Fourier transform of  $u(t)$ , i.e. equations (8) are valid.

The Fourier transform  $S(f)$  as shown in equation (6) is a series of impulse functions separated by the frequency interval  $1/t_0$ . The convolution of this function with the Fourier transform  $H(f)$  results in a continuous function of frequency consisting of periodic superpositions of the function  $H(f)$  centred on the locations of the impulse functions (i.e. repeats of the basic function  $H(f)$  set at intervals of  $1/t_0$  apart):

$$U(f) = \int_{-\infty}^{+\infty} S(f') H(f - f') df' = \frac{1}{t_0} \sum_{n=-\infty}^{+\infty} H\left(f - \frac{n}{t_0}\right) \tag{9}$$

This periodic replication of the function  $H(f)$  is interesting for a number of reasons. Firstly it is clearly an artefact of the discretization of the original function  $h(t)$  as it does not arise in the Fourier transform of the continuous function. Secondly, it is clearly possible

for neighbouring replications of  $H(f)$  to overlap in some circumstances. When they do they constitute an error in the Fourier transform which is known as aliasing.

If however the original function  $h(t)$  is band-limited (i.e. does not possess frequency components higher than a critical frequency  $f_c$  say) then it is possible to prevent the overlapping error by choosing a sampling interval of  $1/(2f_c)$ . In this case, which is known as Nyquist sampling, aliasing does not arise. In the general case, all that can be done is to choose  $t_0$  sufficiently small to reduce aliasing by widening the gaps between the impulse functions  $S(f)$  in the frequency domain.

(ii) Windowing in the Time Domain

The infinite set of data points produced by sampling of the function  $h(t)$  needs to be reduced to a finite set to allow digital processing. The simplest way to achieve this is to multiply the sampled function by the rectangular window function given in (7). This results in a truncated set of data points (and also a truncated time function!). The effect of this operation in the frequency domain is to convolve the Fourier transform of the sampled function given in (9) with the Fourier transform of the window function given in (7) (i.e.  $U(f)$  is convolved with  $W(f)$ ). Since the function  $W(f)$  consists of a sharp central peak with smaller oscillations on either side, the convolution introduces ripples into the periodic function  $U(f)$ . These ripples are the source of an error in the DFT known as leakage. This matter however is best left to the next section where it can be dealt with more fully. Suffice it to say at this stage that if the side oscillations of the Fourier transformed window function could be reduced (as by increasing the width of the window for instance) the problem of leakage may be reduced.

(iii) Sampling in the Frequency Domain

The effect of sampling and windowing on the function  $h(t)$  in the time domain is to produce a finite set of discrete data points. In the frequency domain however, this produced a periodic, continuous function (albeit with ripples). To allow a completely discrete formulation of the Fourier transform, it is also necessary to sample the frequency domain.

To achieve this, the truncated and sampled function in the time domain is convolved with a sampling function similar to that given in (6) which has peaks spaced at intervals of  $T_0$  (the width of the window function). The effect in the frequency domain is to sample the periodic function  $H(f)$  at intervals of  $1/T_0$  in frequency. However, as might be expected, this operation of sampling the frequency domain results in a periodic replication of the function in the time domain as it is described in the interval  $[-T_0/2, T_0/2]$ . Thus as far as the discrete Fourier transform is concerned the functions  $h(t)$  and  $H(f)$  are both periodic functions in their respective domains, the former with a period  $T_0$ , and the latter with the period  $1/t_0$ .

It should be noted that the choice of sampling interval in the frequency domain (i.e.  $1/T_0$ ) is such that the same number of data points are considered in each domain. Also, the possibility of aliasing in the time domain resulting from sampling at this interval in the frequency domain is avoided provided that the window function is purposely chosen to possess extremities that do not coincide with the first and last data points of

the time domain function.

The result of applying all these operations is to produce the discrete version of the Fourier integral:

$$\hat{H}(n/(Nt_0)) = \sum_{k=0}^{N-1} \hat{h}(kt_0) \exp(-i2\pi nk/N) \quad (10)$$

$n=0, \dots, N-1$

The converse of which may be similarly produced.

$$\hat{h}(kt_0) = \frac{1}{N} \sum_{n=0}^{N-1} \hat{H}(n/(Nt_0)) \exp(i2\pi nk/N) \quad (11)$$

$k=0, \dots, N-1$

where  $\hat{H}$  and  $\hat{h}$  represent the sampled functions  $H(f)$  and  $h(t)$  respectively. The number of data points in each domain is  $N$ . (Note that to enable the formulae to be useable on a computer, the summation indices have been taken to run from 0 to  $N-1$  instead of from  $-N/2$  to  $N/2$  as might be expected from the discussion so far. This in fact results in a phase shift of the Fourier transform, but this is of no practical significance).

The problem of leakage mentioned in the previous section arises from the windowing of the time domain function but it manifests itself in the artificial periodicity that the DFT imposes on the functions  $h(t)$  and  $H(f)$ . If for instance the natural periodicity of the function  $h(t)$  is  $T_0'$  and the chosen window function imposes a periodicity of  $T_0$  (where  $T_0 \neq T_0'$ ) then it will be observed that the DFT resolves the frequency dependence of  $H(t)$  into a major and several minor frequency components instead of the single frequency component expected. Hence the use of the term 'leakage'. The origin of these minor components are the side oscillations possessed by the Fourier transformed window function  $W(f)$ , which via the process of convolution introduce spurious peaks into the Fourier transform  $H(f)$ . If however the period  $T_0'$  equals  $T_0$  then it transpires that the peaks of the frequency sampling function coincide exactly with the zero points between the side oscillations of  $W(f)$  and hence, in this special case, the DFT does not give rise to spurious peaks<sup>1</sup>.

For a general function, where the periodicity is unknown leakage is clearly a problem, as spurious peaks may easily arise in the frequency dependence of the function. A much favoured cure for this problem is the use of window functions which have suppressed or non-existent side oscillations in the frequency domain. While this strategy certainly reduces leakage it should be noted that not all window functions are equally good and all of them have drawbacks in their use. Fortunately Harris<sup>3</sup> has carried out a thorough examination of many window functions. His review of them is highly recommended.

#### Application to Spectral Analysis

The object of the exercise here is a straightforward application of the DFT to a sampled function with a view to resolving its frequency components. This is a requirement frequently encountered in molecular dyna-

mics calculations, where the data are invariably produced in a convenient discretized form. The problems arising in this application have been outlined already. They are aliasing and leakage.

Aliasing may be reduced if the sampling rate is kept small, which means that the time step in the molecular dynamics calculation must be reasonable. Fortunately, of necessity, the time step will be sufficiently small to allow adequate modelling of the dynamics and so an adequate sampling rate should naturally be available. It may be worth noting however that if the phenomenon of interest is band limited, then selecting a sampling rate near to the Nyquist sampling rate of  $1/(2f_c)$  should lead to more efficient data processing provided that this sampling interval is equivalent to several time steps.

Leakage is a particular problem if spurious peaks arise to confuse the interpretation of the results. In this case, the use of a suitable window function is essential. Harris<sup>3</sup> recommends a number of window functions for such applications. Perhaps the best of these (allowing good resolution of neighbouring frequency peaks) are the Blackman-Harris windows, which have the form

$$w(k) = \sum_{j=0}^3 a_j \cos(2\pi jk/N) \quad (12)$$

Where the coefficients  $a_0$  to  $a_3$  are constants tabulated by Harris<sup>3</sup>. In the time domain these functions suppress discontinuities at the extremities of the truncated time function (or equivalently have suppressed side oscillations in the Fourier transformed window function) thus removing spurious peaks from the frequency spectrum.

#### Application to Correlation Functions

In molecular dynamics work it is frequently necessary to evaluate integrals of the form:

$$c(t) = \lim_{T \rightarrow \infty} \left( \frac{1}{T} \right) \int_0^T u(\tau) h(\tau + t) d\tau \quad (13)$$

Where  $u$  and  $h$  are both functions of time. (They may in fact be the same function, in which case  $c(t)$  is known as an autocorrelation function). Such functions are used to reveal a cause-and-effect relationship between the functions  $u$  and  $h$ ; by which a change in the value of one function manifests a change in the other at some time interval later.

In molecular dynamics the integral (13) is approximated by the discrete form (14).

$$c(kt_0) = \frac{1}{(N-k)} \sum_{n=0}^{N-k-1} u(nt_0) h((n+k)t_0) \quad (14)$$

$k=0, 1, \dots, N-1$

It has been shown however<sup>4</sup> that this direct method is not always the

most efficient way to proceed and that by employing the DFT considerable improvements in speed can be achieved. This method hinges on the fact that the Fourier transform of integrals of the type (13) produces a simple product of Fourier transformed functions in the frequency domain (i.e. the integral is replaced by the product  $H(f) U^*(f)$ ; the Fourier transforms of  $h$  and  $u$  respectively - the asterisk indicates the complex conjugate). Clearly, provided the Fourier transform can be carried out efficiently, the evaluation of the correlation function in the frequency domain is easy. Thus a proposed scheme for evaluating correlation functions might be:

- (i) Fourier transform  $u(t)$  and  $h(t)$ , obtain  $U^*(f)$ ,  $H(f)$ .
  - (ii) Multiply  $U^*(f) H(f)$ , obtain  $C(f)$ .
  - (iii) Inverse Fourier transform  $C(f)$ , obtain  $c(t)$
- (15)

Though this scheme may appear cumbersome it has to be noted that each of these steps can be accomplished very efficiently. Computer applications of the DFT are generally known as 'Fast Fourier Transforms' and with good reason. They are extremely efficient and as Futrelle and McGinty have pointed out<sup>4</sup> this indirect route is very much faster than the direct method once the number of data points exceeds about thirty. (The direct method requires  $\approx N^2$  operations while the DFT method requires  $\approx 3 N \log_2 N$  floating point operations).

Using the DFT, the discrete correlation function (14) may be written as:

$$\hat{c}(kt_0) = \frac{1}{(N-k)(2N)} \sum_{n=0}^{2N-1} \hat{U}^*(n/(2Nt_0)) \hat{H}(n/(2Nt_0)) \exp(2\pi nk/(2N)) \quad (16)$$

$k=0, 1, \dots, N-1$

It will be noticed that the summation indices range over  $2N$  values and not  $N$  as expected. This is because it is necessary to double the length of the  $u(kt_0)$  and  $h(kt_0)$  vectors in the time domain (by appending  $N$  zeros to each) to prevent spurious correlations arising. This scheme is in accordance with that given by Kestemont and Van Craen<sup>5</sup>.

Sources of DFT routines are listed in reference no.6.

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