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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.

Number 6

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## Editorial

The CCP5 Newsletter, "Information Quarterly", continues to thrive. As is evident from the number of contributors, there is a lot of enthusiasm for an informal circular such as this and it is a pleasure to thank the authors of the various articles appearing in our sixth issue. D.M. Heyes (Royal Holloway) has collaborated with his colleagues, D. Fincham (Queen Mary College) and K. Singer (Royal Holloway), and the result is two interesting articles on integration algorithms in molecular dynamics. N. Quirke (Royal Holloway) has provided an article on Monte Carlo simulation to remind us that Monte Carlo methods still have much to contribute in the simulation of liquids. M. Evans (Aberystwyth) has provided a review of the work of his group in the previous few months. It is pleasing to note that Dr. Evans has made substantial use of the CCP5 Program Library in his work. D.J. Adams (Southampton), in anticipation of the forthcoming CCP5 meeting in Reading, has provided a thought-provoking article on computing facilities. Both Dr. Evans and Dr. Adams have also provided some announcements which are of general interest. Our thanks go to all concerned for their efforts.

As a final point it is worth noting that the newsletter once again demonstrates the width of subject matter that is of interest in CCP5. We should therefore be very pleased to produce any other articles that our readers would like to have circulated to the CCP5 community at large. The editor and deputy editor can testify to the interest abroad in the various issues of the newsletter. Please let your ideas be known.

## General News

1. The seventh CCP5 meeting is due to take place on 16th/17th December 1982 at Reading University. It is entitled, "New Computers/The Simulation of Quantum Mechanical Systems". The invited speakers are Prof. D.M. Ceperley (Livermore), Prof. G. Jacucci (Trento) and Prof. K.R. Wilson (San Diego). Short contributions are welcome, an abstract of which should be sent to Professor R.W. Hockney, Department of Computer Science, Reading University, Whiteknights Park, Reading RG6 2AX, U.K. Information on the meeting is available from Dr. D. Heyes (address on newsletter cover) together with the application forms (to be returned before 22nd November 1982).
2. The eighth CCP5 meeting will occur on 29/30th March 1983 at Hull University. The subject of the meeting is "The Computer Simulation of Molecular Liquids and Liquid Mixtures". Short contributions are again welcome. Abstracts should be sent to Professor J.G. Powles, Physics Laboratory, University of Kent, Canterbury, Kent CT2 7NR, U.K. This meeting follows on from the Royal Society of Chemistry Meeting on "Liquids and Liquid Mixtures".
3. Two more programs have been added to the CCP5 Program Library. D. Heyes has contributed the program MCRPM, which is a Monte Carlo program suitable for dilute, charged, hard spheres (the Restricted Primitive Model). W. Smith has contributed the program MDMULP, which is a molecular dynamics program for polyatomic molecules possessing long-range point multipole interactions. Copies of these programs, or any others, are

available from the program librarian. Dr. W. Smith, SERC Daresbury Laboratory, Daresbury, Warrington WA4 4AD, U.K. Please send a magnetic tape with your request.

A list of the programs available in the CCP5 Program Library is attached.

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<br>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                    |
| MCRPM   | "                                  | MC dilute, charged, hard spheres                 |
| HSTOCH  | W.F. Van Gunsteren<br>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                        |
| MDMULP  | "                                  | MD polyatomic molecules with point multipole     |
| 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  |

## Integration Algorithms in Molecular Dynamics

by

D. Fincham and D.M. Heyes.

The Verlet algorithm<sup>1</sup> in its leapfrog formulation is perhaps the most commonly used method for integrating the translational equations of motion of simple molecules by the Molecular Dynamics, MD, method. In order to obtain more accurate trajectories and possibly enable a larger time step to be used more complicated algorithms must be adopted. It is shown below that, as a result of the many-bodied nature of molecular dynamics, many "first-choice" higher order schemes, which are used to solve differential equations in other fields, are not worthwhile here.

The following algorithms were investigated<sup>2</sup>. A contracted notation in which particle subscripts are omitted and  $\Delta t = m_i = 1$  is employed. Verlet (explicit two-level) or leapfrog.

The Verlet algorithm is an explicit two-level scheme,

$$\tilde{r}^{n+1} = 2\tilde{r}^n - \tilde{r}^{n-1} + \tilde{a}^n, \quad (1)$$

where  $\tilde{a}^n$  is the acceleration ( $= F_i^n/m_i$ ).

Stormer's (explicit three level).

at time step n. Stormer's algorithm is a three level approximation,

$$\tilde{r}^{n+1} = 2\tilde{r}^n - \tilde{r}^{n-1} + \frac{1}{12}(13\tilde{a}^n - 2\tilde{a}^{n-1} + \tilde{a}^{n-2}). \quad (2)$$

A Simple predictor-corrector.

A simple predictor-corrector approach involves an explicit two-level formula to estimate the new positions,  $\rho^{n+1}$ ;

$$\underline{\rho}^{n+1} = 2\underline{r}^n - \underline{r}^{n-1} + \underline{a}^n . \quad (3)$$

Then from  $\underline{\rho}^{n+1}$  the acceleration  $\underline{a}^{n+1}(\underline{\rho}^{n+1})$  is evaluated. A three-level implicit equation ('Numerov's Royal Road') provides the corrector step;

$$\underline{r}^{n+1} = 2\underline{r}^n - \underline{r}^{n-1} + \frac{1}{12} (\underline{a}^{n+1} + 10\underline{a}^n + \underline{a}^{n-1}) . \quad (4)$$

Each of the above three methods was implemented within a Leapfrog framework, i.e.,

$$\underline{v}^{n+1/2} = \underline{v}^{n-1/2} + \underline{A}^n , \quad (5)$$

where  $\underline{A}^n$  is one of the above acceleration terms, and,

$$\underline{r}^{n+1} = \underline{r}^n + \underline{v}^{n+1/2} . \quad (6)$$

The two methods give identical trajectories and values for the velocities (and hence kinetic energies) at the step point. They each require storage of three vectors:  $\underline{r}^n$ ,  $\underline{r}^{n-1}$  and  $\underline{A}^n$  for the first method, called A and  $\underline{v}^{n-1/2}$ ,  $\underline{r}^n$  and  $\underline{A}^n$  for the Leapfrog formulation, called B. However, method B has several advantages over method A.

Method A is more complicated to program because the periodic boundary conditions must be applied to both current and past co-ordinates, whereas in B there is only one set of positions. Method A needs the re-arrangement of values between current and past co-ordinates at the end of each step. This is not necessary in B as the updating of the co-ordinate arrays is performed directly through eqn. (6). Also the velocity setting and scaling is achieved rather

clumsily in A by resetting the past co-ordinates relative to the current co-ordinates rather than by direct modification of the "velocities",  $\tilde{v}^{n+1/2}$ , in eqn. (6) for approach B.

The expressions for the n step velocities,  $\tilde{v}^n$ , in methods A and B are:

$$\tilde{v}^n = \frac{1}{2}(r^{n+1} - r^{n-1}), \quad (7)$$

and

$$\tilde{v}^n = \frac{1}{2}(\tilde{v}^{n+1/2} + \tilde{v}^{n-1/2}). \quad (8)$$

Consequently,  $\tilde{v}^n$  from eqn. (7) may be subject to rounding errors because it is the difference between two nearly equal quantities. In contrast, eqn. (8) does not suffer from this problem.

If it is required to save velocities for autocorrelation function analysis in method A, the step velocities  $\tilde{v}^n$  must be used. They are accurate to  $\Delta t^2$  as well as containing possible rounding errors. Furthermore, extra storage arrays are necessary to hold them for writing. In method B the more accurate mid-step velocities, which are accurate to order  $\Delta t^3$ , are already stored and may be used instead.

Finally, A involves more arithmetic operations than B and that storage requirement for B may be reduced by accumulating the forces directly onto the velocities, if  $\tilde{v}^n$  is not needed. The kinetic energy at step n may then be calculated from the approximation,

$$K^n = \frac{1}{2}(K^{n+1/2} + K^{n-1/2}) + \frac{1}{8}(\phi^{n+1} - 2\phi^n + \phi^{n-1}). \quad (9)$$

where  $\phi^n$  is the potential energy of the system at step n.



### Gear Four-level Formula.

The fourth algorithm to be considered is by Gear who developed a general theory of predictor-corrector solutions for stiff first order differential equations in order to maximise both accuracy and stability. The four-level formula below uses the notation  $\underline{v} = \dot{\underline{r}}$ ,  $\underline{a} = \ddot{\underline{r}}$ , and  $\underline{b} = \dddot{\underline{r}}$ . The predictor expressions are,

$$\underline{r}_{n+1}^p = \underline{r}^n + \underline{v}^n + \frac{1}{2}\underline{a}^n + \frac{1}{6}\underline{b}^n, \quad (10)$$

$$\underline{v}_{n+1}^p = \underline{v}^n + \underline{a}^n + \frac{1}{2}\underline{b}^n, \quad (11)$$

$$\underline{a}_{n+1}^p = \underline{a}^n + \underline{b}^n. \quad (12)$$

The acceleration correction is:

$$\Delta \underline{a} = \underline{a}(\underline{r}_{n+1}^p) - \underline{a}_{n+1}^p, \quad (13)$$

then the corrector move is,

$$\underline{r}^{n+1} = \underline{r}_{n+1}^p + \frac{1}{12}\Delta \underline{a}, \quad (14)$$

$$\underline{v}^{n+1} = \underline{v}_{n+1}^p + \frac{5}{12}\Delta \underline{a}, \quad (15)$$

$$\underline{a}^{n+1} = \underline{a}_{n+1}^p + \Delta \underline{a}, \quad (16)$$

$$\underline{b}^{n+1} = \underline{b}_{n+1}^p + \Delta \underline{a}. \quad (17)$$

It is necessary to have a criterion with which to compare these approaches. The conservation of the average total energy per particle,  $u$ , is used here:

$$u = (\Phi + K)/N. \quad (18)$$

The average of any property A during a simulation is:

$$\bar{A} = (NT)^{-1} \sum_{k=1}^{NT} A_k \quad (19)$$

where NT is the number of time steps and  $A_k$  is the value of A at time step k. The root mean square fluctuation in A is,

$$\Delta_A = \langle \delta A_k^2 \rangle^{\frac{1}{2}}, \quad (20)$$

where

$$\delta A_k = A_k - \langle A \rangle \quad (21)$$

In passing, an estimate of the confidence in  $\langle A \rangle$  is given by the standard error,  $\Delta_A / (NT)^{\frac{1}{2}}$ . The  $\Delta_u$  for a Lennard-Jones liquid near triple point is given in Fig.1 for a range of  $\Delta t$  values using the four integration schemes outlined above and implemented in program MDATOM<sup>3</sup>.

The results in Fig.1 indicate that the simple Leapfrog Verlet algorithm is superior to the more complicated methods discussed above for time steps larger than  $10^{-14}$ s. This is perhaps not surprising as the theory upon which these higher order algorithms is based assumes that each particle moves in a fixed field of force. However, in the fluid state, although certain interactions with close neighbours will possibly be strongly coupled to form a local quasi-conservative system, much of the force on a particle is probably determined by the transport of molecules into its field of influence. It is therefore reasonable to

suppose that the force on a particular molecule is not "predictable" from forces on it at previous time steps. Such algorithms become irrelevant and, as shown, even detrimental to the degree of total energy conservation.

Further improvements in the energy conservation behaviour of the leapfrog Verlet scheme could be envisaged as follows. Now,

$$\tilde{v}^n = \tilde{v}^{n-\frac{1}{2}} + \frac{1}{2} \tilde{a}^n, \quad (22)$$

from eqn. (17). This velocity is accurate to second order only. Possible alternatives are<sup>4</sup>

$$\tilde{v}^n = \tilde{v}^{n-\frac{1}{2}} + \frac{1}{3} \tilde{a}^n + \frac{1}{6} \tilde{a}^{n-1}, \quad (23)$$

and

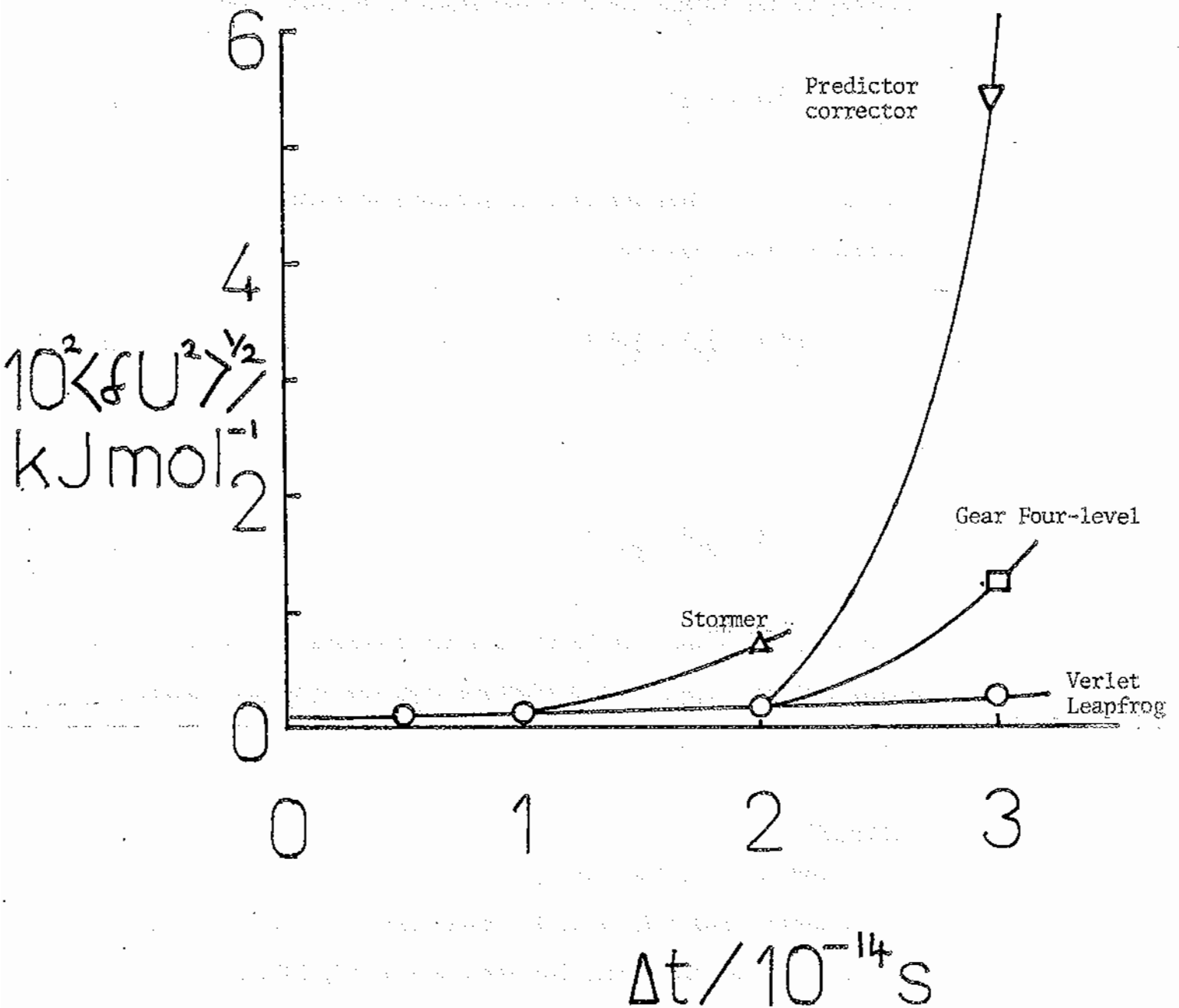
$$\tilde{v}^n = \tilde{v}^{n-\frac{1}{2}} + \frac{3}{8} \tilde{a}^n + \frac{1}{8} \tilde{a}^{n-1}. \quad (24)$$

believed by the authors to be third order accurate. However, neither method gave any significant difference from the straight leapfrog expression of eq. (22).

#### References.

1. L. Verlet, Phys.Rev., 1967, 159, 98.
2. L. Lapidus and J.H. Seinfeld, Numerical Solution of Ordinary Differential Equations. (Academic Press, NY, 1971).
3. D. Fincham, Comp.Phys.Comm., 1980, 21, 247.
4. P. Schofield, Comp.Phys.Comm., 1973, 5, 17.

Fig.1



"The Root-mean-square Fluctuations in the total energy per particle,  $\langle \delta u^2 \rangle^{1/2}$ , for a near triple point Lennard-Jones fluid. The number of particles is 108".

# A Very Accurate Molecular Dynamics Algorithm

by

D.M. Heyes and K. Singer.

## 1. Introduction.

At the December, 1981 CCP5 meeting on "Interfaces" Dr. S. Toxvaerd (University of Copenhagen, Denmark) proposed a new algorithm for integrating the equations of motion in a Molecular Dynamics, MD, program<sup>1</sup>. This algorithm, which involves up to second derivatives of the forces at time  $t$  is claimed to yield more accurate trajectories than that of Verlet, and to give significantly different results, particularly in simulations of interfacial properties.

We have made an independent assessment of this algorithm and indeed find that, with sufficiently small integration time steps, it gives two to three orders of magnitude better energy conservation than the Verlet scheme, with only a threefold increase in computer time. At larger time steps, however, this algorithm is more prone to a drift in total energy than that of Verlet. This limits the time step values to less than  $10^{-14}$ s for a triple point Lennard-Jones system.

We also give convenient algebraic expressions for the evaluation of the required higher derivatives for the shifted force Lennard-Jones potential.

## 2. The New Algorithm.

It has been concluded that, to be successful, any high order algorithm must incorporate the many-body rearrangement of particles in the vicinity of each molecule in order to obtain that particle's trajectory accurately<sup>3</sup>. The position of a particle at time  $t \pm \Delta t$  can be obtained by using a Taylor expansion from its position at time  $t$ ,  $\underline{r}(t)$  and the higher time derivatives of  $\underline{r}(t)$ . The Verlet algorithm is obtained by expanding up to  $\ddot{r}(t)$ . The Toxvaerd algorithm achieves improved accuracy by also incorporating  $\dot{r}(t)$  and  $\ddot{r}(t)$ . These two latter terms (importantly) include the relative motions of neighbouring particles explicitly in the updating scheme.

The necessary equations of motion are rigorously derived below.

We adopt the following contracted notation for conciseness. If the position and velocity of particle  $i$  at time  $t$  are  $\underline{r}_i(t)$  and  $\dot{\underline{r}}_i(t)$ , respectively then these reduce to  $\underline{r}$  and  $\dot{\underline{r}}$ . The vector notation (wavy underline) is dropped unless necessary later. Similarly,  $\underline{r}_+ = \underline{r}_i(t+\Delta t)$  and  $\underline{r}_- = \underline{r}_i(t-\Delta t)$ , where  $\Delta t$  is the time step in the MD simulation.

The force on particle  $i$  is denoted by  $\underline{F}_i(t)$  (later contracted to  $\underline{F}$ ) and is given in terms of a sum over pair potential interactions,  $\phi_{ij}$ , between particles  $i$  and  $j$ .

$$\underline{F}_i(t) = \sum_{j \neq i} \frac{\underline{r}_{ij}}{r_{ij}} \frac{d\phi}{dr_{ij}}(r_{ij}) \quad (1)$$

Now let ,

$$\underline{f} = \underline{F}_i \Delta t^2 / m_i \quad (2)$$

$$\dot{\underline{f}} = \dot{\underline{F}}_i \Delta t^3 / m_i \quad (3)$$

and

$$\ddot{f} = \ddot{F}_i \Delta t^4 / m_i, \quad (4)$$

where  $m_i$  is the mass of particle  $i$ .

The position of particle  $i$  at time  $t+\Delta t$  is obtainable from quantities evaluated at time,  $t$ , using the following Taylor expansion,

$$r_+ = r + \dot{r}\Delta t + \frac{f}{2} + \frac{\dot{f}}{6} + \frac{\ddot{f}}{24} + O(\Delta t^5). \quad (5)$$

Also, if we expand backwards in time,

$$r_- = r - \dot{r}\Delta t + \frac{f}{2} - \frac{\dot{f}}{6} + \frac{\ddot{f}}{24} + O(\Delta t^5). \quad (6)$$

Now, add equations (5) and (6):

$$r_+ = 2r - r_- + f + \dot{f}/12 + O(\Delta t^6). \quad (7)$$

Now, subtract equation (6) from (5):

$$r_+ - r_- = 2\dot{r}\Delta t + \frac{\dot{f}}{3} + O(\Delta t^5), \quad (8)$$

or

$$\dot{r} = \{(r_+ - r_-)/2 - \frac{\dot{f}}{6}\}/\Delta t + O(\Delta t^4). \quad (9)$$

In order to obtain  $\dot{f}$  and  $\ddot{f}$  it is necessary to have  $\dot{r}$  already. This can be obtained approximately using another Taylor expansion as below,

$$\dot{r} = \dot{r}_- + \{f_- + \frac{\dot{f}}{2} + \frac{\ddot{f}}{6}\}/\Delta t + O(\Delta t^4), \quad (10)$$

where  $\dot{f}_-$  and  $\ddot{f}_-$  are the reduced force derivatives at time  $t-\Delta t$ .

Before proceeding with the derivation of expressions for  $\dot{F}$  and  $\ddot{F}$  the following definitions will prove useful:

$$G_{ij} = \frac{1}{r_{ij}} \frac{d}{dr_{ij}} \phi_{ij}(r_{ij}), \quad (11)$$

which is the scalar factor in equation (1).

Also,

$$G_{ij}^A = \frac{1}{r_{ij}} \frac{d}{dr_{ij}} G_{ij}, \quad (12)$$

and,

$$G_{ij}^B = \frac{1}{r_{ij}} \frac{d}{dr_{ij}} G_{ij}^A. \quad (13)$$

Differentiation with respect to time leads to,

$$\dot{G}_{ij} = \frac{dG_{ij}}{dr_{ij}} \frac{dr_{ij}}{dt}. \quad (14)$$

But,

$$\frac{dr_{ij}}{dt} = r_{ij} \cdot \dot{r}_{ij} / r_{ij}. \quad (15)$$

Hence,

$$\dot{G}_{ij} = G_{ij}^A (r_{ij} \cdot \dot{r}_{ij}). \quad (16)$$

From equations (1) and (16) we obtain,



$$\begin{aligned}\dot{\mathbf{F}} &= \frac{d}{dt} \mathbf{F}_i = - \sum_{j \neq i} \frac{d}{dt} [G_{ij}(r_{ij}) \mathbf{r}_{ij}] \\ &= - \sum_{j \neq i} \{G_{ij} \dot{\mathbf{r}}_{ij} + G_{ij}^A (r_{ij} \cdot \dot{\mathbf{r}}_{ij}) \mathbf{r}_{ij}\}.\end{aligned}\quad (17)$$

Similarly,

$$\ddot{\mathbf{F}} = \frac{d^2}{dt^2} \mathbf{F}_i = - \sum_{j \neq i} \frac{d^2}{dt^2} [G_{ij}(r_{ij}) \mathbf{r}_{ij}]. \quad (18)$$

Hence,

$$\ddot{\mathbf{F}} = - \sum_{j \neq i} \frac{d}{dt} \{G_{ij} \dot{\mathbf{r}}_{ij} + G_{ij}^A (r_{ij} \cdot \dot{\mathbf{r}}_{ij}) \mathbf{r}_{ij}\}, \quad (19)$$

Now,

$$\frac{d}{dt} \{G_{ij} \dot{\mathbf{r}}_{ij}\} = G_{ij} \ddot{\mathbf{r}}_{ij} + \dot{G}_{ij} \dot{\mathbf{r}}_{ij}, \quad (20)$$

where,

$$\ddot{\mathbf{r}}_{ij} = \ddot{\mathbf{r}}_i - \ddot{\mathbf{r}}_j = \mathbf{F}_i/m_i - \mathbf{F}_j/m_j \quad (21)$$

and

$$\begin{aligned}\frac{d}{dt} \{G_{ij}^A (r_{ij} \cdot \dot{\mathbf{r}}_{ij}) \mathbf{r}_{ij}\} &= G_{ij}^A [(\dot{\mathbf{r}}_{ij} \cdot \dot{\mathbf{r}}_{ij}) + (r_{ij} \cdot \ddot{\mathbf{r}}_{ij})] \mathbf{r}_{ij} \\ &+ G_{ij}^A (r_{ij} \cdot \dot{\mathbf{r}}_{ij}) \dot{\mathbf{r}}_{ij} + \dot{G}_{ij}^A (r_{ij} \cdot \dot{\mathbf{r}}_{ij}) \mathbf{r}_{ij}.\end{aligned}\quad (22)$$

Further, with the use of equation (13) this becomes,

$$\begin{aligned}
\ddot{\mathbf{F}} = & \sum_{j \neq i} \{G_{ij} (\mathbf{F}_i/m_i - \mathbf{F}_j/m_j) \\
& + G_{ij}^A r_{ij} [\dot{r}_{ij} \cdot \dot{r}_{ij} + r_{ij} \cdot (\mathbf{F}_i/m_i - \mathbf{F}_j/m_j) \\
& + 2G_{ij}^A (r_{ij} \cdot \dot{r}_{ij}) \dot{r}_{ij} + G_{ij}^B (r_{ij} \cdot \dot{r}_{ij})^2 r_{ij}] \}. \quad (23)
\end{aligned}$$

where use of equation (16) has been made.

Note that  $\ddot{\mathbf{f}}$  requires two passages through on MD two-particle double loop at each time step. The first time the  $\mathbf{F}_i$  (also  $\dot{\mathbf{F}}_i$  and part of  $\ddot{\mathbf{F}}$ ) are evaluated. The second time  $\mathbf{F}_i$  and  $\mathbf{F}_j$  which are already obtained for each pair are then used to complete the calculation of  $\ddot{\mathbf{F}}_i$  using equation (23).

Equation (7) can be rewritten in a "Leapfrog" form which is more convenient to program:

$$r_+ = r + \delta r, \quad (24)$$

where

$$\delta r = \delta r_- + f + \ddot{f}/12 + O(\Delta t^6). \quad (25)$$

Now similarly for the velocity equation (9) becomes,

$$\begin{aligned}
\dot{r} &= \{(\delta r + \delta r_-)/2 - \dot{f}/6\}/\Delta t \\
&= \{(2\delta r_- + f + \ddot{f}/12)/2 - \dot{f}/6\}/\Delta t \\
&= \{\delta r_- + f/2 - \dot{f}/6 + \ddot{f}/24\}/\Delta t + O(\Delta t^4). \quad (26)
\end{aligned}$$

Rather than use equation (10) to predict the velocities at the next time step (needed for  $\dot{f}$  and  $\ddot{f}$ ) Toxvaerd uses the slightly less accurate predictor formula,

$$\dot{r} = \{\delta r_{-} + f/3 + f_{-}/6\}/\Delta t \quad (27)$$

This can be obtained from equation (26) by dropping the  $\ddot{f}$  term and substituting  $(f-f_{-})$  for  $\dot{f}$ .

### 3. The Algorithm tested.

In order to eliminate spurious total energy fluctuations caused by particles moving in and out of the interatomic potential truncation sphere, the algorithm was tested using a Lennard-Jones shifted force potential<sup>4,5</sup>. The Verlet and modified Toxvaerd programs are available on the CCP5 program library as HLJ5 and HLJ6, respectively.

The intermolecular potential  $\phi$  and necessary higher derivatives are given below. The Lennard-Jones, LJ, parameters  $\epsilon$  and  $\sigma$ , and particle subscripts have been omitted for conciseness.

Let  $r^{-6}$ ,  $r^{-12}$ ,  $r_c^{-6}$  and  $r_c^{-12}$  be denoted by  $S_6$ ,  $S_{12}$ ,  $SC_6$  and  $SC_{12}$  respectively. Then,

$$\phi = 4\{S_{12} - S_6 + \frac{r}{r_c} (12SC_{12} - 6SC_6) - 13SC_{12} + 7SC_6\}. \quad (28)$$

Also,

$$G = -\frac{4}{r^2} \{12S_{12} - 6S_6 - \frac{r}{r_c} (12SC_{12} - 6SC_6)\}, \quad (29)$$

$$G^A = \frac{4}{r^4} \{168S_{12} - 48S_6 - \frac{r}{r_c} (12SC_{12} - 6SC_6)\}, \quad (30)$$

$$G^B = -\frac{4}{r^6} \{2688S_{12} - 480S_6 - 3\frac{r}{r_c} (12SC_{12} - 6SC_6)\}, \quad (31)$$

where  $r_c$  is the cut-off distance ( $= 2.5\sigma$  here).

The test calculations were made on the popular LJ state:

$\rho^* = N\sigma^3/V = 0.8442$  and  $T^* = kT/\epsilon = 0.722$  which is near the LJ triple point.

The average single particle total energy

$$u = \frac{1}{N} \sum_{i=1}^N \left\{ \frac{1}{2} m_i \dot{r}_i^2 + \frac{1}{2} \sum_{j \neq i}^N \phi_{ij}(r_{ij}) \right\}, \quad (32)$$

where  $N (=256)$  is the number of molecules in the MD cell, was evaluated each time step. The Verlet and modified Toxvaerd algorithms are compared in Table 1.

The Verlet algorithm is a second-order method, and the modified Toxvaerd algorithm is a fourth-order method. The Verlet algorithm is simpler and more stable, but the modified Toxvaerd algorithm is more accurate and efficient for long-time simulations.

| Algorithm         | Order | Stability | Accuracy | Efficiency |
|-------------------|-------|-----------|----------|------------|
| Verlet            | 2     | High      | Low      | High       |
| Modified Toxvaerd | 4     | Low       | High     | Low        |

TABLE 1.

The root mean square fluctuations in the average total energy per particle per time step:  $\langle \delta u^2 \rangle = \langle u^2 \rangle - \langle u \rangle^2$

(a) reduced units averaged over 100 time steps;

(b) real units for argon ( $\epsilon/k_B = 119.8$ ,  $\sigma = 3.405 \text{ \AA}$ )

(a)

| $\Delta t$<br>$/\sigma(m/\epsilon)^{1/2}$ | Verlet<br>Leapfrog<br>$\langle \delta u^2 \rangle^{1/2}/\epsilon$ | Modified<br>Toxvaerd<br>Leapfrog<br>$\langle \delta u^2 \rangle^{1/2}/\epsilon$ |
|---|---|---|
| 0.002                                     | $1.9 \times 10^{-5}$  | $< 3 \times 10^{-8}$  |
| 0.005                                     | $1.0 \times 10^{-4}$  | $1.3 \times 10^{-6}$  |
| 0.010                                     | $4.4 \times 10^{-4}$  | $2.0 \times 10^{-5}$  |
| 0.015                                     | $9.9 \times 10^{-4}$  | $4.6 \times 10^{-4}$  |
| 0.020                                     | $1.8 \times 10^{-3}$  | $4.4 \times 10^{-3}$  |

(b)

| $\Delta t$<br>$/10^{-14} \text{ s}$ | Verlet<br>Leapfrog<br>$\langle \delta u^2 \rangle^{1/2}/k\text{Jmol}^{-1}$ | Modified<br>Toxvaerd<br>Leapfrog<br>$\langle \delta u^2 \rangle^{1/2}/k\text{Jmol}^{-1}$ |
|-------------------------------------|--|--|
| 0.43                                | $1.9 \times 10^{-5}$   | $< 3 \times 10^{-8}$   |
| 1.08                                | $1.0 \times 10^{-4}$   | $1.3 \times 10^{-6}$   |
| 2.16                                | $4.3 \times 10^{-4}$   | $2.0 \times 10^{-5}$   |
| 3.23                                | $9.8 \times 10^{-4}$   | $4.6 \times 10^{-4}$   |
| 4.31                                | $1.8 \times 10^{-3}$   | $4.4 \times 10^{-3}$   |

The relative times per time step are 0.054s and 0.172s for a 256 LJ particle system on the Daresbury CRAY-1 computer, using the Verlet and Toxvaerd algorithms respectively.

One may conclude from Table 1 that the Toxvaerd algorithm exhibits approximately two orders of magnitude better energy conservation than that of Verlet for time steps of order and less than  $1 \times 10^{-14}$  s. It would also appear that larger time steps can be used with this method as this favourable comparison continues for time steps up to  $4 \times 10^{-14}$  s; certainly over the 100 time step test calculations. As higher derivatives of the pair potential are required in the new method than in Verlet (which only goes up to the first derivative) it is perhaps not surprising that it is more prone to exhibiting noticeable total energy instability. The Verlet method is quite stable for all time step values up to  $4 \times 10^{-14}$  s. In contrast only for time steps up to  $0.4 \times 10^{-14}$  s can the Toxvaerd algorithm be claimed to be free of total energy drift. This is quantitatively illustrated in Table 2 and has also been pointed out by Toxvaerd<sup>1</sup>. As the energy fluctuations are much smaller than the drifts for these short runs, the Toxvaerd algorithm appears, misleadingly, to have better energy conservation for larger values of the time step than is in fact the case.

The observed drift may well be associated with the comparatively inaccurate prediction for  $\dot{r}$ , used in equation (10).

TABLE 2.

The mean total energy drift per particle per time step, which is denoted by  $\Psi$ . The runs were for 100 time steps, except those labelled by \* which were for 500 time steps.

(a)

| $\Delta t$<br>$/\sigma(\pi/\epsilon)^{1/2}$ | Verlet<br>Leapfrog<br>$\Psi/\epsilon$ | Modified<br>Toxvaerd<br>Leapfrog<br>$\Psi/\epsilon$ |
|---|---------------------------------------|---|
| 0.002                                       | $\approx 0$                           | $\approx 0$ *                                       |
| 0.005                                       | $\approx 0$                           | $4 \times 10^{-9}$ *                                |
| 0.010                                       | $\approx 0$                           | $-0.5 \times 10^{-6}$                               |
| 0.015                                       | $\approx 0$                           | $-1.65 \times 10^{-5}$                              |
| 0.020                                       | $\approx 0$                           | $-1.54 \times 10^{-4}$                              |



#### 4. Conclusions.

We have confirmed that this new algorithm, proposed by Toxvaerd, is greatly superior to the conventional Verlet Leapfrog algorithm when used with sufficiently small integration time steps.

For the Lennard-Jones system near the triple point a time step of not more than  $0.5 \times 10^{-14}$  s is suggested, to avoid a drift in the total energy.

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Discussions with Dr. S. Toxvaerd are gratefully acknowledged.

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## Metropolis Monte Carlo Computer Simulation (N. Quirke)

Monte Carlo techniques are ways of simulating the behaviour of processes described by probability distributions. The probability distributions are generated by the use of random numbers, hence the term Monte Carlo. In the study of condensed matter we are very often concerned with 'thermodynamic' averaging over the probability distributions given by statistical mechanics. These describe the probability of finding a particular state of a model system given various constraints, such as a constant number of particles or fixed pressure. For this type of application, when we are dealing with classical behaviour, a special variation of the general Monte Carlo method called Metropolis<sup>(1)</sup> Monte Carlo is employed and it is this approach which is the subject of the present article.

For velocity independent interactions, the statistical mechanical averages in phase space factor into a momentum (kinetic) and a co-ordinate (configurational) part. The momentum integrals can be performed analytically leaving only the co-ordinate integrations to be evaluated by Metropolis Monte Carlo simulation. In the following, we first describe the basic simulation algorithm and then give an example of a Metropolis Monte Carlo programme for the case of the solid on solid model of interfaces, finally we discuss some methodological problems associated with Metropolis Monte Carlo.

In describing the way in which the Metropolis algorithm works we shall assume that averages are to be taken for a canonical ensemble of interacting particles in three dimensions but it could just as well be a system of interacting spins, or one of different dimensionality.

If we keep  $N$  the number of particles,  $V$  the volume and  $T$  the temperature fixed, then the average of a function  $f(X^{3N})$  of the particle co-ordinates  $(X^{3N})$  is given by

$$\langle f \rangle = \int dX^{3N} f(X^{3N}) e^{-\beta U(X^{3N})} / \int dX^{3N} e^{-\beta U(X^{3N})} \quad (1)$$

where  $f(X^{3N})$  could be for example the potential energy function  $U(X^{3N})$ .  $\langle f \rangle$  would then correspond to the configurational part of the internal energy of the system. For many problems of interest  $N$  is of the order of  $10^{23}$  and  $U(X^{3N})$  a complicated function of the particle co-ordinates. No analytical solution of equation 1 is therefore possible nor is a numerical solution practical unless the number of particles is reduced dramatically. As for molecular dynamics, this reduction of  $N$  is conventionally achieved by representing a small number of particles (32-10,000) in the computer and imposing periodic boundary conditions.

The limited number of significant figures which can be used in a computer to represent particle co-ordinates requires that equation 1 be rewritten as a sum over all possible states  $\{s\}$ .

$$\langle f \rangle = \frac{\sum_{i=1}^S e^{-\beta U_i} f_i}{\sum_{i=1}^S e^{-\beta U_i}} = \sum_{i=1}^S P_i f_i \quad (2)$$

$$P_i = e^{-\beta U_i} / \sum_{i=1}^S e^{-\beta U_i}$$

However despite the approximations introduced above,  $S$  is usually so large that a direct computation of all states is not possible. In order to make progress a way of selecting those states which are of high probability must be found. One possibility is to sample configurations from the  $s$  available with a probability proportional to  $P_i$  of equation 2, this is called importance sampling.

The central problem which must be overcome in order to do this is that we do not know the normalisation constant  $\sum_{i=1}^S e^{-\beta U_i}$ . In fact if we did, the problem would already be solved since this sum corresponds to the configurational integral of the model system. The Metropolis M.C. method avoids the necessity of knowing the normalisation of  $P_i$  by appealing to

the theory of Markov chains<sup>(2)</sup>, describing processes that can be characterised by a one step transition probability  $P_{\ell, \ell+1}$  of going from a state  $\ell$  to a successor state  $\ell+1$ , where  $P_{\ell, \ell+1}$  does not depend on the states prior to  $\ell$ . By imposing certain constraints on  $P_{\ell, \ell+1}$  it is possible to generate successive states such that in the limit of an infinite number of states in the chain, they are distributed according to a desired probability distribution function. In our case, the chain consists of particle configurations and in the following we describe the simple prescription due to Metropolis for  $P_{\ell, \ell+1}$  which ensures that in

the limit of a very large number of configurations generated using this one step transition probability, they are distributed according to the canonical ensemble distribution function  $P_i$  of equation 2. This will allow the average  $\langle f \rangle$  to be calculated from the unweighted average  $\bar{f}$  of the function over the  $M$  generated configurations.

$$\langle f \rangle = \bar{f} = \frac{1}{M} \sum_{i=1}^M f_i$$

Configurations are generated using the following procedure. Given an initial configuration of the  $N$  particles in a volume  $V$ , for example the lattice structure of the system, a new trial configuration is obtained by a random displacement of one of the particles. The potential

energy of this new configuration ( $U'$ ) is calculated and compared with the potential energy ( $U$ ) of the old, starting configuration. If  $DU = U' - U$  is negative then the trial configuration is accepted and becomes the second configuration in the Markov chain. If it is more positive the factor,

$$B = \exp(-\beta DU)$$

is calculated and compared to a random number RAN between 0 and 1. If  $B > \text{RAN}$  then the trial configuration is accepted as before. If  $B < \text{RAN}$  it is rejected and the old, initial configuration is used again in equation 3. It is therefore possible for successive configurations to be identical. The second configuration in the chain now becomes the old configuration and a new trial configuration is obtained as before by a random displacement of one of the particles. This procedure is repeated until  $m$  configurations are obtained.

Unless the starting configuration is an equilibrium configuration of the system studied, the first part of the simulation is used to bring the system to equilibrium. The equilibrium state is assumed to have been

reached when the desired average ( $\bar{f}$ ) or averages are observed not to drift with increasing number of configurations but to fluctuate about some mean value. The number of equilibrium configurations required for convergence to the ensemble average depends upon the quantity being averaged and the system studied but is usually in the range of  $10^5$  to  $10^7$  configurations.

One very important advantage of Monte Carlo simulation over the molecular dynamics method is its flexibility, in particular we are not limited to the simulation of particles. In order to emphasise this point (and because of its simplicity) we shall look in detail not at a programme for the Metropolis Monte Carlo simulation of a fluid of particles but a cell model of the crystal interface, the solid on solid (SOS) model of the crystal surface in contact with its mother phase<sup>(3)</sup>. In this model three dimensional space is filled by cubes which are labelled solid or fluid. The model is specified by the positions of the cubes and their state. If we assign positions using a Cartesian frame then the  $x$  and  $y$  directions are equivalent but the  $z$  axis stretches from completely solid at  $-\infty$  to completely fluid at  $+\infty$ . The interface is conveniently located initially at  $z = 0$ . Thus far we have done nothing more than define a three dimensional Ising model with special boundary conditions. The new feature of the SOS model is the SOS restriction preventing inclusions of fluid inside the solid. This amounts to insisting that no fluid cell be lower (in the  $z$  direction) than a solid cell. We always have a solid cell sitting on a solid cell. In this case the state of the system can be completely specified by giving the  $x, y$  co-ordinates of a column of cells and the height ( $h$ ) of the highest solid cell in the column. The Hamiltonian can be written,

$$H = \epsilon \sum_{\langle ij \rangle} |h_i - h_j|^p, \quad p = 1, \epsilon > 0$$

The sum is over all columns  $i$  and, for this example, the four nearest neighbour columns  $j$  of  $i$ . The Monte Carlo simulation technique can be used to study this Hamiltonian in two ways. Firstly at equilibrium,

using the standard Monte Carlo procedure outlined above and secondly out of equilibrium, in the 'kinetic' version. In this last case a supersaturation is imposed on the mother phase or fluid cells in order to force the solid to grow. The equilibrium form can be used to study the phase behaviour of surface, especially the so-called 'Roughening Transition' and the 'kinetic' model has proved to be extremely useful in picking out the major mechanisms involved in surface growth under various degrees of supersaturation<sup>(3)</sup>. For the purposes of this article, however, we confine attention to the equilibrium form of the simulation.

The programme set out below generates Metropolis Monte Carlo configurations for a surface of  $NX \times NY$  sites with periodic boundary conditions in the x and y directions.  $H(NX+2, NY+2)$  is an array containing the column height at each site and  $E(NX+2, NY+2)$  is an array containing the energy at each site. The figure below shows the boundary conditions for a  $5 \times 5$  surface, the numbers in each box represent the xy co-ordinates of the column, the numbers in brackets are the periodic replicas at

|   |       |       |       |       |       |       |       |
|---|-------|-------|-------|-------|-------|-------|-------|
| 7 |       | (2,2) | (2,3) | (2,4) | (2,5) | (2,6) |       |
| 6 | (6,6) | 6,2   | 6,3   | 6,4   | 6,5   | 6,6   | (6,2) |
| 5 | (5,6) | 5,2   | 5,3   | 5,4   | 5,5   | 5,6   | (5,2) |
| 4 | (4,6) | 4,2   | 4,3   | 4,4   | 4,5   | 4,6   | (4,2) |
| 3 | (3,6) | 3,2   | 3,3   | 3,4   | 3,5   | 3,6   | (3,2) |
| 2 | (2,6) | 2,2   | 2,3   | 2,4   | 2,5   | 2,6   | (2,2) |
| 1 |       | (6,2) | (6,3) | (6,4) | (6,5) | (6,6) |       |

the boundaries. We have NITS Monte Carlo iterations per site during which we attempt to alter the height of a column up or down by one unit. All energies have been reduced by  $\epsilon$ , the reduced temperature is  $TSTAR = 1/\beta\epsilon$ .

```

DIMENSION H(7,7),E(7,7)
READ (5,x) NX,NY,NITS,TSTAR
SUME = 0.0
SUME2 = 0.0
NYES = 0
c   MONTE CARLO ITERATIONS
DO 100 ISX = 1,NX
DO 100 ISY = 1,NY
c   THERE ARE NITS ITERATIONS PER SITE (NX*NY SITES)
DO 100 IT = 1,NITS
c   CHOOSE A SITE AT RANDOM (RANF(c) = RANDOM NUMBER)
c   X - COORDINATE
I = RANF(0.)*FLOAT(NX)+2.
```

```

C      Y - COORDINATE
      J = RANF(1.)*FLOAT(NY)+2.
C      DECIDE RANDOMLY TO RAISE OR LOWER THE COLUMN ON THIS SITE
C      BY ONE UNIT
      XX = RANF(2.)*0.5
      PROPOSE = SIGN(1.,XX)
C      NEW TRIAL HEIGHT = OLD HEIGHT + PROPOSE
      HT = H(I,J) + PROPOSE
C      FIND HEIGHTS OF NEAREST NEIGHBOUR COLUMNS
      H1 = H(I,J-1)
      H2 = H(I,J+1)
      H3 = H(I-1,J)
      H4 = H(I+1,J)
C      CALCULATE NEW ENERGY OF TRIAL COLUMN AT I,J
      EST = 0.5*(ABS(HT-H1)+ABS(HT-H2)+ABS(HT-H3))
x      + ABS(HT-H4)
C      ENERGY CHANGE, NEW SURFACE - OLD SURFACE
      DELTAE = 2.*(EST - E(I,J))
C
C      METROPOLIS MONTE CARLO TEST OF NEW STATE
C      - 'DISPOSE'

      IF (DELTAE.LE.O.)GO TO 1
      B = EXP(-DELTAE/TSTAR)
      RAN = RANF(3.)
      IF(B.LT.RAN)GO TO 2
C
C      IF DELTAE.LE.O OR B.GE.RAN THEN NEW
C      CONFIGURATION ACCEPTED AND USED IN AVERAGING
C      AS BELOW
1     CONTINUE
      NYES = NYES + 1
      E(I,J) = EST
C      THE NEAREST NEIGHBOURS OF I,J NOW HAVE A
C      NEW INTERACTION ENERGY; UPDATE N-N ENERGIES
      E(I,J-1) = E(I,J-1)+0.5*(-ABS(H(I,J)-H1)+ABS(HT-H1))
      E(I,J+1) = E(I,J+1)+0.5*(-ABS(H(I,J)-H2)+ABS(HT-H2))
      E(I-1,J) = E(I-1,J)+0.5*(-ABS(H(I,J)-H3)+ABS(HT-H3))
      E(I+1,J) = E(I+1,J)+0.5*(-ABS(H(I,J)-H4)+ABS(HT-H4))
C      IF CHANGED SITE WAS ON PERIMETER OF SURFACE,
C      WE MUST TAKE INTO ACCOUNT THE NEW BOUNDARY CONDITIONS
      H(I,J) = HT
      E(I,2) = E(I,2)+0.5*(-ABS(H(I,2)-H(I,1))
x      + ABS(H(I,2) - H(I,NY+1)))
      E(I,NY+1) = E(I,NY+1)+0.5*(-ABS(H(I,NY+1)-
x      H(I,NY+2))+ABS(H(I,NY+1)-H(I,2)))
      E(2,J) = E(2,J)+0.5*(-ABS(H(2,J)-H(1,J))
x      +ABS(H(2,J)-H(NX+1,J)))
      E(NX+1,J) = E(NX+1,J)+0.5*(-ABS(H(NX+1,J)-
x      H(NX+2,J))+ABS(H(NX+1,J)-H(2,J)))
C      UPDATE BOUNDARY HEIGHTS
      H(1,J) = H(NX+1,J)
      H(NX+2,J) = H(2,J)
      H(I,1) = H(I,NY+1)
      H(I,NY+2) = H(I,2)

```

```

c      ET IS CURRENT SURFACE ENERGY
      ET = ET+DELTA E
c      CALCULATE MEAN ENERGY AND MEAN SQUARE ENERGY
      SUME=SUME+ET
      SUME2=SUME2+ET*ET
      GO TO 100
c      IF DELTA E.GT.O OR B.L.T.RAN THEN NEW
c      CONFIGURATION REJECTED AND OLD ONE USED
c      AGAIN IN AVERAGING
2     CONTINUE
      SUME = SUME+ET
      SUME2 = SUME2+ET*ET
100   CONTINUE
c     WRITE MEAN ENERGY AND SITE SPECIFIC HEAT.
      C1=1/FLOAT(NITS)
      C2=1/FLOAT(NX*NY)
      AVE=SUME*C1
      AVE2=SUME2*C1
      SS=(AVE2-AVE*AVE)*C2/(TSTAR*TSTAR)
      WRITE(6,x)AVE,SS
      STOP
      END

```

The basic difference between this cell model simulation and that of a fluid of particles is that instead of generating a new configuration by choosing a site and changing the height of the column, for the fluid one of the particles would be moved a small random amount, thus changing its interaction energy. However the new trial configurations are generated, the fundamental requirement is that no bias is built into their construction. The ratio of the number of accepted configurations to those rejected varies according to the system and the algorithm but is usually in the range from 30-60%.

Since Metropolis et al<sup>(1)</sup> described their Monte Carlo method relatively little has been done to study the properties of the algorithm or to find possible improvements. Some exceptions are Fosdick's reduction of variance<sup>(4)</sup>, the use of difference acceptance recipes<sup>(5)</sup> and "Smart Monte Carlo"<sup>(6)</sup>. In the remainder of this article we point to two methodological topics which we believe deserve further study. For a more complete discussion the reader is referred to reference<sup>(7)</sup>.

The Monte Carlo algorithm described above accepts or rejects a new configuration whose energy  $U'$  is more positive than the previous configuration  $U$  by comparing the Boltzmann factor of the difference  $\beta(U'-U)$  with a random number between 0 and 1. It is clear that for new configurations to have a reasonable chance of being accepted during the run, this internal energy change must be of the order of  $kT$ . For simulations using particles it has generally been assumed that new configurations should be generated by moving only one of the  $N$  particles to a new position. However, in principle by moving all  $N$  particles a small distance to new positions the energy change could be kept to around  $kT$ . As far as the author is aware there is no information as to whether an optimum number of particles exists which when moved together produces the most efficient sampling of configuration space. For 32 particle systems, the experience has been that it is better to move all 32 particles rather than 1, but

that for 108 particles it is better to move only 1 rather than all 108<sup>(7)</sup>.

Averages obtained using the Metropolis Monte Carlo method correspond to the required ensemble average only in the limit of an infinite number of steps. As a result, all averages obtained from these algorithms are subaverages of the infinitely long run. It has been shown recently<sup>(8)</sup> that in the canonical ensemble version of the Metropolis procedure (fixed NVT, see above) these subaverages can still be associated with canonical

ensemble averages but at an effective temperature  $T$  not necessarily equal to that imposed by the Metropolis algorithm through the factor  $B$ . These effective temperatures can be used to correct Monte Carlo averages to those for the desired temperature. This raises some very interesting questions about the nature of the Metropolis procedure and more work is required.

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Part I

The CCP5 algorithms TETRAH and TRI2 have been used to simulate a wide variety of spectral properties for a series of methane derivatives. These results are in press as primary research articles or reviews. The molecules studied so far include  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CHBr}_3$  (rotator and liquid planes), acetone, t-butyl chloride (rotator and liquid),  $\text{CH}_3\text{I}$  and  $\text{CH}_3\text{CN}$ .

The model potential is a Lennard-Jones atom-atom type with point-charges simulating the electrostatic interactions. Tables of correlation times have been drawn up and compared with their experimental equivalents from sources such as NMR relaxation, infra-red, Raman and Rayleigh band-shapes, dielectric relaxation, far infra-red absorption, neutron-scattering and picosecond-scale time resolved spectroscopies. The overall pattern of agreement is good, except for acetonitrile and methyl iodide, in which association and polarisability effects (respectively) are important. The simulation method is a convenient means of producing self-consistently a range of spectroscopic parameters. It is therefore useful as a means of assessing the range and self-consistency of the available experimental data, and of measuring the importance of extraneous effects, such as collision-induction.

The experimental data are far from being self-consistent in an inter-technical sense, and sometimes also in the intra-technical sense. For chloroform, for example, we have reviewed over 150 papers on the spectroscopic properties relevant for a full and thorough testing of our 5x5 algorithm. It is clear that the range of pressure and temperature used by the spectroscopists is insufficient for a satisfactory appreciation of the dependence of parameters such as correlation times on P and T. A serious effort is needed to coordinate the spectroscopic work, and plans are being made to carry this out on a European scale (see EMLG-news).

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## Part II

The CCP5 algorithm TRI2 (originally written by Singer et al) has been modified to deal with non-linear field effects on molecular dynamics in liquids. This work has led to a series of exciting developments by combining the results with the powerful analytical methods developed by Grigolini [ref.8 above, chapters 9 and 10].

i) The Langevin functions have been constructed by computer simulation from the linear response region to saturation.

ii) The nature of molecular dynamical auto-correlation functions under a saturating external field of force has been investigated in detail for the first time by computer simulation.

iii) It has been discovered that a strong enough external field causes a decoupling of the dynamics of an individual molecule from its thermal bath. This effect was predicted analytically by Grigolini in 1976 for vibrational relaxation, and has been observed for the first time by molecular dynamics computer simulation by Evans [ref.5, below]. The decoupling effect is a new physical phenomenon which should be observable by pico-second time-resolved spectroscopy. It is intrinsically non-Markovian in nature.

iv) The break-down of the fluctuation - dissipation theorem brought about by intense external fields) has been monitored by computer simulation for the first time through the construction of rise and fall transients on a picosecond time scale. Grigolini has shown very recently that the properties of the orientational fall transient provide us for the first time, with clear and unambiguous evidence of the intrinsically non-linear nature of the interaction of the tagged molecule with its thermal bath. The new computer simulation method allows us to isolate the non-linear properties of molecule-bath interaction from the memory effect that causes the governing statistics to become non-Markovian. This provides us with a tie-up between the fields of molecular dynamics theory and simulation and areas of non-linear physics in which the research activity is intense. This is a major breakthrough brought about by a combination of analytical theory and computer simulating using the CCP5 algorithm TRI2, modified by Evans. It poses the obvious challenge to experimentalists of direct observation, and is an illustration of the predictive power of the numerical computer simulation method.

v) The nature of molecular rotation/translation coupling has been described in the presence of a saturating field using rotating frame auto-correlation matrices. This opens up a whole new field of "cybernetic spectroscopy". These functions provide an example of how the CCP5 algorithms can be used to describe phenomena not yet observable by the classical methods of experimental observation or analytical theory.

vi) More new "cybernetic" observations are referred to below in the relevant primary-journal articles.

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European Molecular Liquids Group News

NATO has awarded a grant for a summer school at San Miniato in July 1983 based on the three cornered philosophy of EMLG: the coordinated use of theory, numerical simulation and experimental observation. Speakers include Zwanzig, Steele, Kenney-Wallace (from across the Atlantic) and leading European experts in the fields covered by EMLG. We hope that the European Science Foundation will hold its promised Round Table Discussion at this Summer School, with the aim of setting up an ESF "Additional Activity". Refs.(1) to (8) above, show objectively the pressing need for such an injection of support on a European level. Computer simulation is now of fundamental importance in this area, and CCP5 a cornerstone.

## A PROPOSAL FOR CCP5

D. J. ADAMS

This short piece is a hurried attempt to put forward an idea I should like to have discussed at the CCP5 meeting in December. I propose that CCP5 should jointly apply to SERC for money to buy and run its own mini computer. This machine should be capable of serious calculations, should have a substantial disc storage capacity, and must be accessible over SERC net both for interactive terminal access and file transfer. The only suitable machine I know of is the Prime, which also has the advantage that SERC has considerable experience with them.

The idea is that this machine would be available to all groups in this country associated with CCP5. Almost all academic sites have access to SERC net either directly or via PSS and access is bound to improve. A CCP5 committee would have to vet applications of course. The purposes of the machine would include the following, which I list in no particular order:

1) As a mainframe machine dedicated to computer simulation

Of course, there are a number of groups which on their own could saturate any mini with work given the chance, and there is much work which is quite unsuitable for minis. Priority should be given to newcomers to the field, to work of a particularly novel sort, to the development of programmes intended ultimately for larger machines and to work particularly suited to a mini.

2) As a front-end for access to larger machines

All CCP5 members would have accounts and an allocation of disc space on the mini so that they could keep and edit source program files on it. These could then be submitted as jobs to a range of large computers, for which users would need separate authorization. Job submission in this way is already available to the Rutherford-Appleton and Daresbury Laboratories, and is possible, via more roundabout ways, to the ULCC complex including the QMC DAP and to a number of university sites including Cambridge and Newcastle. Access to UMRCC in this way is not possible at present, but could very well be so by the time our mini was installed. In this way CCP5 members would have a unified means of access to a range of big machines, a means of better access than most universities can currently provide.

cont./

3) Graphical and other post-processing

Having run long calculations on big machines selected data could be sent to users' disc files on the mini for subsequent examination and plotting. CCP5 could build up a library of routines for such things as plotting radial distribution functions, calculating memory functions from correlation functions and working out cumulant expansions. I would hope that this would be useful for all members and would provide programming help not just for newcomers, but also be very much 'state-of-the-art'. The transfer of files between machines on SERC net is straightforward between most minis on the network and possible to and from RAL and Daresbury Lab., it is possible in principle over PSS and within some regional networks, though not METRONET. Again, much work is being done to widen the range of this facility.

4) As an Information Centre

The CCP5 mini would be invaluable as an informal means of communication. It would be most useful to know that everybody logged on to the machine was interested in computer simulation. Computer networks are a marvellous means of human communication. I have been surprised to find how much better it is to send and reply to messages using the computer keyboard rather than pen and paper, particularly when messages are sent to users' 'Postfiles' or 'Mailboxes' for examination at their convenience. I think the mini would be very useful indeed for giving and getting help, disseminating good ideas and advancing the state of the art. More formally the mini would be a repository of CCP5 programs, as Daresbury is at the moment, but with easier access for users. It would be simple to set up a data base on published papers in computer simulation to which users could themselves contribute. It might prove feasible to set up a molecular-dynamics data base containing thermodynamic results, structural data (i.e. radial distribution functions) and time-correlation functions. Then A at University X does not have to do his own molecular dynamics to test his sparkling new theory of (say) diffusion or have to write to B and C at Y and Z colleges in the hope they will send him listings of their results (which have to be repunched by A!) or, if he is lucky great wads of punched cards. Instead A may simply extract what he needs from the data base, perhaps plotting the results using CCP5 programs. Points requiring explanation can be raised with Y or Z by quick message to their 'MAIL' files.

cont./

5) As an SERC Host

The mini could be located at Daresbury, but it would kill two birds with one stone to have it as the local machine at a site which does not have ready access to SERC net already. It would then act as a gateway to SERC net for all users at that institution, not just CCP5 people. I believe the University of Kent has no direct access to SERC net. Or the ageing GEC 2050 at Royal Holloway College could be replaced. There must be other candidates.

Any takers?

12th August 1982



## Daresbury to ULCC Removals Service

D. J. ADAMS

The Cray-1S computer, as by now all must know, is to be moved from Daresbury to ULCC in "the second quarter of 1983". It will no longer be an SERC facility, but a regional computing centre facility. The new front-end machine for this, the Amdahl 470/V8 is already installed and running a limited user service. No doubt SERC and ULCC will take steps to aid existing users, where appropriate, to transfer files from the AS7000 at Daresbury to the Amdahl. However, I am prepared to offer an immediate unofficial one-way file transfer service for CCP5 members.

I undertake to create a copy of a Daresbury file on the Amdahl within the following limitations:

- 1) "Customers" must already have a valid jobnumber on the Amdahl.
- 2) The file to be transferred must not be binary or graphics and should consist of records not more than eighty characters long. It must be online, i.e. not archived, and only the transfer of sequential data sets to sequential data sets will be possible.
- 3) The final stage of the transfer is the running of a job on the Amdahl. Because of this, unpredictable results will follow if the file contains /\* in columns 1-2 of a line. Files must be altered in advance if they contain /\*. However, // will be acceptable. The numbering of TSO files will appear either at the beginning or end of each line of the catalogued Amdahl file, according to the data set type of the original file. I recommend that an unnumbered file be created especially for the transfer.
- 4) I cannot be responsible for problems of copyright or file ownership, or responsible for the consequences if an existing Amdahl file is specified for the transfer or the wrong file name given.

"Customers" should write to me specifying:

- i) The full name of the file at Daresbury.
- ii) The full name of the file to be catalogued on the Amdahl. (Please distinguish clearly between zero and the letter O.)
- iii) Their authorized jobnumber on the Amdahl.
- iv) A specified SPACE subparameter if the default of SPACE = (6160,(1,2), RLSE) is likely to be inadequate.
- v) The means by which they would like notice of success or failure. I would prefer not to have to 'phone people. I suggest either a preaddressed post-card or the specification of the terminal to which Amdahl line-printer output should be sent (for example OUT = ULCC/HX for Southampton).

I can be reached by writing to:

Dr. D. J. ADAMS  
Department of Chemistry  
The University  
Southampton SO9 5NH

# MEMORANDUM FOR THE RECORD

Date: 1/15/2024

The purpose of this memorandum is to provide a summary of the meeting held on January 10, 2024, at the [Location]. The meeting was attended by [List of Attendees]. The agenda items discussed were [List of Agenda Items]. The key findings and recommendations are as follows:

1. [Item 1]: [Summary of discussion and action items]

2. [Item 2]: [Summary of discussion and action items]

3. [Item 3]: [Summary of discussion and action items]

4. [Item 4]: [Summary of discussion and action items]

5. [Item 5]: [Summary of discussion and action items]

6. [Item 6]: [Summary of discussion and action items]

7. [Item 7]: [Summary of discussion and action items]

8. [Item 8]: [Summary of discussion and action items]

9. [Item 9]: [Summary of discussion and action items]

10. [Item 10]: [Summary of discussion and action items]

11. [Item 11]: [Summary of discussion and action items]

12. [Item 12]: [Summary of discussion and action items]