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# Multiple time-step methods in molecular dynamics

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A new method for molecular dynamics computer simulations, called the multiple time-step (MTS) method, is described, in which two or more time steps of different lengths are used to integrate the equations of motion in systems governed by continuous potential functions. With this method computing speeds have been increased by factors of three to eight over conventional molecular dynamics methods in simulations of monatomic and polyatomic fluids, with only marginal increases in computer storage.

## 1. INTRODUCTION

In computer simulations of fluids by the molecular dynamics (MD) method, the Newtonian equations of motion of $N$ molecules (where, typically, $10^2 \leqslant N \leqslant 10^3$) are solved numerically, progressing in small increments of time, $\Delta t$, called the time step. Detailed descriptions of molecular dynamics for systems of spherical [1–3] and non-spherical [3–8] molecules have been published, and the reader is assumed to be familiar with the conventional framework of these methods.

For systems of molecules governed by moderately long-ranged potentials, such as the Lennard-Jones (LJ) potential, as much as 95 per cent of the computing time is spent in examining the complete set of $N(N-1)/2$ pair interactions, and summing the forces and torques over some well-defined subset, which we shall call the cardinal set. The cardinal set is usually defined as all pairs of molecules separated by distances less than a cut-off distance $r_c$, beyond which interactions are neglected. The inessential set is the complete set less the cardinal set. The lists of particles comprising the cardinal and inessential sets change with time.

In simulations of LJ systems $r_c$ is usually taken to be $2{\cdot}5\sigma$, and the size of the cardinal set at liquid-like densities is $\sim 40N$. Thus, for systems containing 200 or more particles, the task of identifying and rejecting pairs in the inessential set can consume a large part of the computing time; however, several book-keeping methods have been devised [2, 9, 10], which reduce this time to virtual insignificance. The essential task of calculating the intermolecular forces for all pairs in the cardinal set, at every time step, remains as the principal time-consuming task, and dramatic increases in computing speed can be achieved only by reducing the time devoted to this task.

We report here a new method, the multiple time-step (MTS) method, which reduces by an order of magnitude the average number of pair interactions explicitly calculated in each time step, resulting in increases in computing speed by factors of three to ten, with only marginal increases in computer storage. The method is particularly appropriate when using a time step of $5 \times 10^{-15}$ s or less, and has been applied with equal success to systems of spherically symmetric LJ molecules and systems of diatomic and tetrahedral molecules governed by atom–atom potentials.

## 2. The multiple time-step method

### 2.1. *General*

In the interest of clarity we describe here the application of the MTS method to a system of molecules governed by the spherically symmetric LJ potential function :

$$\phi(r_{ij}) = 4\epsilon \left[ \left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6} \right], \tag{1}$$

where $\phi(r_{ij})$ is the potential energy between molecules $i$ and $j$, separated by distance $r_{ij}$, and $\epsilon$ and $\sigma$ are the usual energy and length parameters. The method is easily extended to systems of non-spherical molecules.

The instantaneous force on molecule $i$ is a vector ;

$$\mathbf{F} = \sum_{j \neq i} - \left[ \frac{\mathbf{r}_{ij}}{r_{ij}} \frac{d\phi(r_{ij})}{dr_{ij}} \right]_{r_{ij} \leqslant r_c} . \tag{2}$$

Here $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, where $\mathbf{r}_i$ is the position vector of molecule $i$ and $r_{ij} = |\mathbf{r}_{ij}|$. The summation is over all neighbours, $j$, lying within a sphere of radius $r_c$ centred on $i$, that is, over all $ij$ pairs that are members of the cardinal set. We call these the cardinal neighbours of molecule $i$. If the sphere of radius $r_c$ centred on $i$ is divided in two by a smaller sphere of radius $r_a$, also centred on $i$ (figure 1), the cardinal neighbours of $i$ are divided into two sets : primary neighbours, whose centres lie inside the smaller sphere, and secondary neighbours, whose centres lie between the two spheres. Then the total force $\mathbf{F}$ on molecule $i$, given by equation (2), can be separated into a primary force $\mathbf{F}_p$ and a secondary force $\mathbf{F}_s$, produced by these two sets of neighbours :

$$\mathbf{F} = \mathbf{F}_p + \mathbf{F}_s = \sum_j \left[ -\frac{\mathbf{r}_{ij}}{r_{ij}} \frac{d\phi(r_{ij})}{dr_{ij}} \right]_{r_{ij} \leqslant r_a} + \sum_k \left[ -\frac{\mathbf{r}_{ik}}{r_{ik}} \frac{d\phi(r_{ik})}{dr_{ik}} \right]_{r_a \leqslant r_{ik} \leqslant r_c} . \tag{3}$$

We have calculated these components of the force for LJ systems at liquid-like densities, with $r_c = 2{\cdot}5\ \sigma$ and $\sigma \leqslant r_a \leqslant 1{\cdot}5\ \sigma$ (thus treating as primary neighbours most of the pairs responsible for the first peak in the radial distribution function) and have found that, on average,

$$|\mathbf{F}_p| > |\mathbf{F}_s|. \tag{4}$$

Similar inequalities hold for the time derivatives of these quantities. Indeed, this is precisely what the physics of the problem suggests : the motion of a molecule is dominated by a rapidly changing primary force resulting from collisions with a cage of nearest neighbours, the primary neighbours. The longer-ranged secondary force is smaller, and changes more slowly with distance and time.

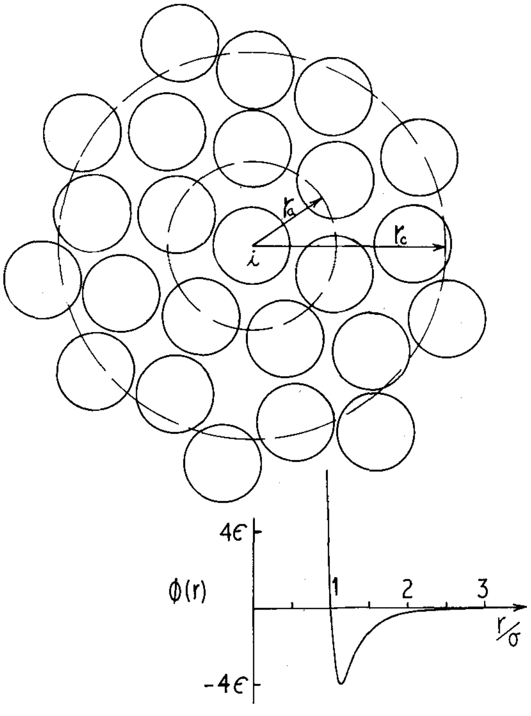

Figure 1. Primary and secondary neighbours of molecule $i$. In this diagram the ' diameter ' of each molecule is $\sigma$, and the radii $r_a$ and $r_c$ are 1·5 $\sigma$ and 2·5 $\sigma$ respectively. Below is a graph of the potential function drawn to scale using the same value of $\sigma$ as in the figure above.

It is the rapidly changing primary force that imposes an upper limit on the time step in MD simulations. If the time step is too long, the algorithm used to solve the equations of motion predicts unrealistic overlaps between molecules in successive time steps, leading to progressive, often catastrophic, numerical failure. In conventional MD methods no distinction is made between primary and secondary forces ; the intermolecular forces for all pairs in the cardinal set are recalculated at every time step. In the MTS method, however, only the primary force is recalculated at every step, while time steps ten to twenty times longer are used to calculate the time evolution of the secondary force. The average computing time per step is thereby greatly reduced.

### 2.2. *Outline of the MTS method*

At time $t_0$ the primary and secondary forces on molecule $i$, $\mathbf{F}_p(t_0)$ and $\mathbf{F}_s(t_0)$, are calculated from equation (3). Concurrently the time derivatives $\mathbf{F}_s'(t_0)$, $\mathbf{F}_s''(t_0)$, . . ., of the secondary force are calculated (the expressions are given in the Appendix), and a list is compiled of the primary neighbours. At each of the next $n-1$ time steps, the primary force is determined in the usual way, by calculating and summing the forces exerted on $i$ by its primary neighbours ; however, the secondary force is calculated from a Taylor series expansion, using information available at $t_0$ :

$$\mathbf{F}_s(t_0+K\Delta t)=\mathbf{F}_s(t_0)+\mathbf{F}_s'(t_0)\frac{K\Delta t}{1\,!}+\dots\,\mathbf{F}_s^{(m)}(t_0)\frac{(K\Delta t)^m}{m\,!}$$
$$+K=1,\,2,\,\dots,\,n-1. \qquad (5)$$

We refer to the series truncated after $m$ terms as the $m$th-order Taylor series. The list of primary neighbours compiled at $t_0$ is used to calculate the primary force at each of the succeeding $n-1$ time steps. The boundary between primary and secondary neighbours is gradually distorted from its original shape ; however, at step $n+1$ the list of primary neighbours is recompiled and the primary and secondary forces are recalculated from equation (3). The time derivatives of the secondary force are also recalculated, and that step becomes the new $t_0$. In this way time steps of length $\Delta t$ and $n\Delta t$ are used for the primary and secondary forces, respectively ; hence the name multiple time-step method.

To calculate the contributions to the configurational internal energy $U$, and the total virial $W$ (used to calculate pressure) at each time step, the expressions for these properties must be separated into contributions from primary and secondary neighbours and calculated in an analogous way. The necessary equations are given in the Appendix.

The use of the MTS method requires additional computer storage of the order of $10N$ to $15N$ words of memory.

### 2.3. *Time evolution of the secondary force in a system of LJ molecules*

We have made a detailed study of the time evolution of the primary and secondary forces on several molecules in a 256-molecule LJ system. (In this work we used a modified LJ potential, called the shifted force potential [11], which eliminates the step discontinuity in the force associated with the cut-off in the potential at $r=r_c$.) Figure 2 shows how the secondary forces estimated from first, second, and third-order Taylor series depart from the true secondary force

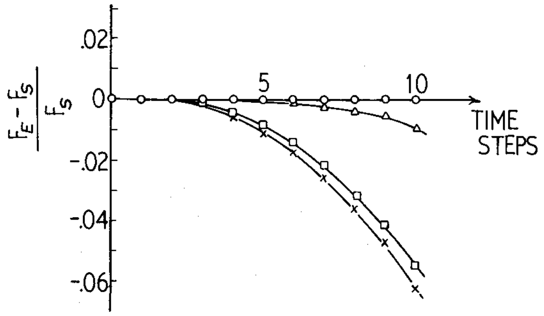

Figure 2. Examples of differences between the exact secondary force, $F_S$ and the value $F_E$ estimated from several versions of the MTS method. Legend : — × — : first-order Taylor series ; —△— ; second-order Taylor series ; —○— : third-order Taylor series ; —□— ; linear predictor method (Appendix, A 3).

over ten time steps, for a state at liquid-like density. Also included is a comparison with an alternative first-order method, called the linear predictor MTS method, described in the Appendix. The linear predictor method is of marginally better accuracy than the first-order Taylor series. It is important to point out that the secondary force is typically about an order of magnitude smaller than the primary force under these conditions ; hence the maximum errors shown in figure 2 are less than 1 per cent of the total force on a molecule. Errors of this magnitude are averaged out in this simulation, and do not significantly affect the energy conservation. (They are the same order of magnitude as the discontinuity in force associated with truncation of the potential at $r_c = 2.5\ \sigma$.) The second-order Taylor series leads to errors almost an order of magnitude smaller, while the third order is exact to five significant figures.

### 2.4. *Comparison with results from conventional MD programs*

A program with a third-order Taylor series has been used to calculate more than 50 state points in the Lennard-Jones system, at reduced densities $0{\cdot}35 \leqslant \rho^* \leqslant 1{\cdot}20$, and reduced temperatures $0{\cdot}6 \leqslant T^* \leqslant 6{\cdot}0$ [11]. As a check on the accuracy of the MTS method, several points were also calculated using a conventional MD program. A comparison of reduced pressures and energies for these points is shown in the table below.

Comparison of pressures and energies for several state points in the LJ system, calculated from conventional and MTS molecular dynamics programs.

| Conventional MD | | | | MTS method | |
|---|---|---|---|---|---|
| $\rho^*$ | $T^*$ | $P^*$ | $U^*$ | $P^*$ | $U^*$ |
| 0·9 | 4·66 | 21·08 | −2·904 | 20·92 | −2·908 |
| 1·0 | 3·50 | 24·46 | −3·480 | 24·43 | −3·471 |
| 1·05 | 2·50 | 23·21 | −4·278 | 23·14 | −4·283 |

Radial distribution functions calculated from two programs agree to within three significant figures.

## 3. INCREASES IN COMPUTING SPEED

The increase in computing speed over conventional MD methods is a function of the lengths $r_a$ and $r_c$ (figure 1) and the parameters $m$ and $n$ (equation (5)). In most of our work on LJ systems we have used $m = 3$, $n = 10$, $r_c = 2{\cdot}50\ \sigma$, and $r_a = 1{\cdot}1\ \sigma$. At a reduced density $\rho\sigma^3 = 0{\cdot}8$, the average numbers of primary and secondary neighbours in this case are 1·4 and 24, respectively ; at $\rho\sigma^3 = 1{\cdot}05$ (a high density) the numbers are 3·1 and 29. Thus at these two densities, for nine out of ten steps the average numbers of pair interactions evaluated per molecule are reduced by factors of $24/1{\cdot}4 = 17{\cdot}1$ and $29/3{\cdot}1 = 9{\cdot}4$, respectively, compared to conventional MD simulations. We have found that for systems of 256 molecules, our program using the MTS method is three to five times faster than a conventional MD program that uses Verlet neighbour lists [2], and seven to ten times faster than one that does not.

The limiting values of $r_a$, $m$, and $n$ are strongly interdependent, and are mildly dependent on density, temperature, and the length of the time step. We have successfully carried out simulations for a system of 256 LJ molecules, with $r_c = 2{\cdot}5\ \sigma$, $\sigma \leqslant r_a \leqslant 1{\cdot}5\ \sigma$, $1 \leqslant m \leqslant 4$, and $5 \leqslant n \leqslant 20$. A run was considered successful if the resulting particule trajectories were essentially the same as those obtained in a conventional MD run started from the same point in phase space. In most cases the difference in positions and velocities were about one part in $10^5$ after 1000 time steps.

We have applied the MTS method to systems of diatomic and tetrahedral molecules governed by atom–atom potentials, with comparable increases in computing speed.

The MTS method can be used to best advantage with time steps of about $5 \times 10^{-15}$ s or less. With larger time steps it is necessary to adjust the parameters $r_a$ and $n$ to less favourable values ($r_a$ increased, $n$ decreased), with the result that the computing speed increase may be only marginal. In simulations of LJ molecules time steps of order $10^{-14}$ s have traditionally been used [1, 2], and in cases where it is desirable to cover the greatest possible real time with a given amount of computing time, such as in simulations of inhomogeneous systems [13] or in calculating time-dependent properties over periods in excess of $10^{-12}$ s, little can be gained by using the MTS method with a shorter step. However, it is our experience that equilibrium properties of the homogeneous LJ fluid can be computed with comparable precision in several thousand time steps of either $10^{-14}$ s or $5 \times 10^{-15}$, in which case the MTS using the shorter time step is superior. It is in simulations of polyatomic liquids that the MTS method offers clear advantages over conventional molecular dynamics methods. In these systems, time steps of order $10^{-15}$ s are required to cope with rotational motion [4–6], and we have found that no further decrease in step length is required by the MTS method.

The MTS method can be generalized to a hierarchy of time steps of different lengths, applied to components of the force produced by neighbours located in progressively larger spherical shells centred on each molecule ; but the gains in going beyond two shells are small in the cases we have studied.

## 4. Discussion and conclusions

The essence of the MTS method is the use of time steps of different lengths to calculate the time evolution of rapidly and slowly varying forces in a molecular dynamics simulation. In a limited sense it is the dynamic analogue of the method used by Weeks *et al.* [12] to separate the effects of repulsive and attractive forces in static structure and equilibrium thermodynamic properties. Just as these authors have shown that equilibrium structure is dominated by short-ranged forces which vary rapidly with distance, we have shown here that dynamic behaviour is dominated by short-ranged forces which vary rapidly in time ; and just as they have shown that the equilibrium effects of the longer-ranged attractive forces can be calculated by a simple perturbation method, we have shown that the dynamic effects of the longer-ranged, slowly varying forces can be calculated with less computational effort by the use of a longer time step than that used for the rapidly varying forces. The analogy is not complete, however, since (so far as we know) one cannot separate the effects of the rapidly and slowly varying forces on the time-dependent properties in the same way that the effects of repulsive and attractive forces on the equilibrium properties can be separated.

In principle the MTS method is compatible with any of the conventional MD methods with which we are familiar, including the central force method [16] and the method of constraints [17]. The only disadvantage of the MTS method is that it requires a considerably larger programming effort.

The MTS method is a significant advance in the technique of molecular dynamics simulations. A *sine qua non* of the method is the deterministic nature of motion in a system governed by the laws of classical mechanics ; therefore, it does not appear to have a counterpart in the Monte Carlo method.

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## APPENDIX

### A 1. *Expressions for time derivatives of the secondary force*

The secondary force on molecule $i$ at time $t_0$ is given by the second expression in equation (3). Since the terms in the summation can be differentiated separately, we need here consider only one of them, which we write as

$$\mathbf{F} = -\frac{\mathbf{r}}{r}\frac{d\phi}{dr}. \qquad \text{(A 1)}$$

Noting that the potential $\phi$ is a function only of $r$, we define $A = -r^{-1}(d\phi/dr)$ and reduce equation (A 1) to

$$\mathbf{F} = A\mathbf{r}. \qquad \text{(A 2)}$$

Differentiating with respect to time gives

$$\mathbf{F}' = A\mathbf{r}' + B(\mathbf{r} \,.\, \mathbf{r}')\mathbf{r}, \qquad \text{(A 3)}$$

where $B = r^{-1}(dA/dr)$. The second and third derivatives are

$$\mathbf{F}'' = [B(\mathbf{r} \,.\, \mathbf{r}'' + \mathbf{r}' \,.\, \mathbf{r}') + C(\mathbf{r} \,.\, \mathbf{r}')^2]\mathbf{r} + 2B(\mathbf{r} \,.\, \mathbf{r}')\mathbf{r}' + A\mathbf{r}'' \qquad \text{(A 4)}$$

and

$$\begin{aligned}\mathbf{F}''' = {} & \{B(\mathbf{r} \,.\, \mathbf{r}''' + 3\mathbf{r}' \,.\, \mathbf{r}'') + 3C[(\mathbf{r} \,.\, \mathbf{r}')(\mathbf{r} \,.\, \mathbf{r}'') + (\mathbf{r} \,.\, \mathbf{r}')(\mathbf{r}' \,.\, \mathbf{r}')] + D(\mathbf{r} \,.\, \mathbf{r}')^3\}\mathbf{r} \\ & + 3[B(\mathbf{r} \,.\, \mathbf{r}'' + \mathbf{r}' \,.\, \mathbf{r}') + C(\mathbf{r} \,.\, \mathbf{r}')^2]\mathbf{r}' + 3B(\mathbf{r} \,.\, \mathbf{r}')\mathbf{r}'' + A\mathbf{r}''', \qquad \text{(A 5)}\end{aligned}$$

where

$$\left.\begin{aligned} \mathbf{r} &= \mathbf{r}_i - \mathbf{r}_j, \\ \mathbf{r}' &= \mathbf{r}_i' - \mathbf{r}_j' \\ &\text{etc.} \end{aligned}\right\} \qquad \text{(A 6)}$$

and $C = r^{-1}(dB/dr)$ and $D = r^{-1}(dC/dr)$. If the LJ potential is used, the expressions for $A$, $B$, $C$ and $D$ are

$$\left.\begin{aligned} A &= -\frac{1}{r}\frac{d\phi}{dr} = 48(r^{-14} - 0{\cdot}5r^{-8}) \\ B &= \frac{1}{r}\frac{dA}{dr} = 192(-3{\cdot}5r^{-16} + r^{-10}) \\ C &= \frac{1}{r}\frac{dB}{dr} = 1920(5{\cdot}6r^{-18} - r^{-12}) \\ D &= \frac{1}{r}\frac{dC}{dr} = 23040(-8{\cdot}4r^{-20} + r^{-14}) \end{aligned}\right\} \tag{A 7}$$

(distances and energies are expressed in units of $\sigma$ and $\epsilon$ respectively).

Since derivatives of $\mathbf{r}_i$ to second order are often routinely calculated in carrying forward a MD simulation, the MTS method can be readily incorporated at this level and should increase the speed of computation by a factor of 3 or more. To achieve greater speed it may be necessary to use a higher-order Taylor series. The additional effort required to calculate the higher order derivatives of $\mathbf{r}_i$ depends mainly on the type of numerical algorithm used to solve the equations of motion. If a predictor–corrector algorithm of order $m$ is used, the derivatives of $\mathbf{r}_i$ to order $m$ are routinely calculated, hence third and higher-order MTS methods are facilitated by these algorithms.

### A 2. *Time derivatives of thermodynamic functions*

In molecular dynamics simulations, the equilibrium thermodynamic properties are calculated from time averages over the states generated at each time step. For example, the internal energy $U$ and pressure $P$ in a system of simple molecules are calculated (in part) from

$$U = \langle \sum_i \sum_{j>i} \phi(r_{ij}) \rangle_{r_{ij} \leqslant r_c} \tag{A 8}$$

and

$$\frac{P}{\rho kT} = 1 - \frac{1}{3NT} \left\langle \sum_i \sum_{j>i} r_{ij} \frac{d\phi(r_{ij})}{dr_{ij}} \right\rangle_{r_{ij} \leqslant r_c}, \tag{A 9}$$

where the angular brackets indicate time averages and the double sums are over all pairs in the cardinal set. When the MTS method is used, two alternatives are available for calculating thermodynamic properties : (1) include the contributions to the averages only at intervals of $n$ time steps, when all pair interactions in the cardinal set are evaluated, or (2) calculate the contributions to the averages at the intervening steps from Taylor series expressions similar to equation (5). The latter alternative requires expressions for the time derivatives of those terms in the double sums in (A 8) and (A 9) that represent interactions with secondary neighbours ($r_a < r_{ij} \leqslant r_c$). The first three derivatives are

$$\left.\begin{aligned}
\phi' &= -A(\mathbf{r} \, . \, \mathbf{r}'), \\
\phi'' &= -B(\mathbf{r} \, . \, \mathbf{r}')^2 - A(\mathbf{r} \, . \, \mathbf{r}'' + \mathbf{r}' \, . \, \mathbf{r}') \\
\phi''' &= -C(\mathbf{r} \, . \, \mathbf{r}')^3 - 3B[(\mathbf{r} \, . \, \mathbf{r}')(\mathbf{r} \, . \, \mathbf{r}'' + \mathbf{r}' \, . \, \mathbf{r}')] \\
&\qquad - A(\mathbf{r} \, . \, \mathbf{r}''' + 3\mathbf{r}' \, . \, \mathbf{r}''), \\
[r(d\phi/dr)]' &= -X(\mathbf{r} \, . \, \mathbf{r}'), \\
[r(d\phi/dr)]'' &= -Y(\mathbf{r} \, . \, \mathbf{r}')^2 - X(\mathbf{r} \, . \, \mathbf{r}'' + \mathbf{r}' \, . \, \mathbf{r}'), \\
[r(d\phi/dr]''' &= -Z(\mathbf{r} \, . \, \mathbf{r}')^3 - 3Y[(\mathbf{r} \, . \, \mathbf{r}')(\mathbf{r} \, . \, \mathbf{r}'' + \mathbf{r}' \, . \, \mathbf{r}')] \\
&\qquad - X(\mathbf{r} \, . \, \mathbf{r}''' + 3\mathbf{r}' \, . \, \mathbf{r}''),
\end{aligned}\right\} \qquad \text{(A 10)}$$

where $X \equiv -(d\phi/dr)$, $Y \equiv r^{-1}(dX/dr)$, and $Z \equiv r^{-1}(dY/dr)$.

### A 3. *The linear extrapolation method*

We have tested an alternative scheme for estimating the first time derivative of the secondary force, $\mathbf{F}_s'(t_0)$, for use with a first-order MTS method. In lieu of equation (A 3), a finite difference formula is used :

$$\mathbf{F}_s'(t_0) \approx \frac{\mathbf{F}_s(t_0 + \Delta t) - \mathbf{F}_s(t_0)}{\Delta t}. \qquad \text{(A 11)}$$

In this case all pairs in the cardinal set are explicitly evaluated at each of the first two steps in each block of $n$ time steps, and a linear extrapolation of $\mathbf{F}_s(t)$ is carried out over the next $n-2$ steps. This method is marginally more accurate than the first-order Taylor series based on equation (A 3), but slightly less efficient. In some respects it is easier to apply to systems governed by complex intermolecular potential functions. We have used it in simulations of 108 methane molecules, modelled by a tetrahedral atom–atom potential [14], and have realized a factor of 4 increase in computing speed over a conventional MD simulation of the same system [15].

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