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Some Multistep Methods for Use in Molecular Dynamics Calculations

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Some multistep methods are presented that are particularly well suited for integrating the equations of motion describing the molecular dynamics of liquids and dense gases. Some tests and comparisons with other methods are described which demonstrate that a combination of a third-order explicit method for the calculation of positions and an implicit method for the calculation of velocities is particularly stable when used in computations of this type.

In the computer simulation of the molecular dynamics of simple liquids, one must numerically solve the second-order differential equation

$$\ddot{\mathbf{r}} = \mathbf{a}(\mathbf{r}), \tag{1}$$

finding $\mathbf{r}(t)$ and $\mathbf{v}(t)$. Here, $\mathbf{r}$, $\mathbf{v}$, and $\mathbf{a}$ are vectors with $3N$ components, representing the x, y, and z components of the position, velocity, and acceleration of each of N molecules, where N is typically on the order of 1000. The acceleration of the ith molecule, at position $\mathbf{r}_i$, is given by $\mathbf{a}_i(\mathbf{r}_i) = -\nabla V(\mathbf{r}_i)/m$, where m represents the molecular mass. The potential energy of the ith molecule, $V(\mathbf{r}_i)$, is often approximated by the Lennard–Jones potential,

$$V(\mathbf{r}) = 4\epsilon \sum_{j=1}^{N} (\sigma/R_{ij})^{12} - (\sigma/R_{ij})^{6}, \tag{2}$$

where R_{ij} represents the distance between the ith and jth molecules.

For argon, $\epsilon/k_B = 119.8$°K, and $\sigma = 3.4$ Å. As the evaluation of $\mathbf{a}(\mathbf{r})$ involves, in principle, a double summation over the N molecules, one wishes to minimize the number of times that $\mathbf{a}(\mathbf{r})$ must be calculated for each time step in the numerical integration of Eq. (1). For this reason, multistep methods, which make use of the evaluation of $\mathbf{a}(\mathbf{r})$ at previous time steps, are to be preferred over those methods that make successive approximations to $\mathbf{a}(\mathbf{r})$ or that require the calculation of derivatives of $\mathbf{a}(\mathbf{r})$. On the other hand, due to the size of the vectors $\mathbf{r}$, $\mathbf{v}$, and $\mathbf{a}$

and the use of double precision arithmetic, core limitations may prevent the retention of information from very many previous steps.

In his simulation of liquid argon, Rahman [1] used the midpoint method predictor,

$$\mathbf{r}_{n+1} = \mathbf{r}_{n-1} + 2h\mathbf{v}_n \tag{3}$$

and the second-order Moulton's corrector,

$$\mathbf{v}_{n+1} = \mathbf{v}_n + (\mathbf{a}_{n+1} + \mathbf{a}_n)h/2, \tag{4a}$$

$$\mathbf{r}_{n+1} = \mathbf{r}_n + (\mathbf{v}_{n+1} + \mathbf{v}_n)h/2. \tag{4b}$$

Here, h represents the size of the time step, $h = t_{n+1} - t_n$. Typically, two iterations of the corrector cycle were performed. This method will be referred to here as a $P(\mathbf{r})(E(\mathbf{a})\ C(\mathbf{v})\ C(\mathbf{r}))^2$ method, meaning that a predictor is used to calculate $\mathbf{r}$ and that there are two iterations of the sequence: evaluation of $\mathbf{a}$, calculation of $\mathbf{v}$ using a corrector, and calculation of $\mathbf{r}$ using a corrector. This method suffers from the disadvantage that it requires the simultaneous storage of six vectors and yet is only of second-order accuracy.

One could extend this procedure to higher order by using the third-order Adams–Bashforth predictor,

$$\mathbf{r}_{n+1} = \mathbf{r}_n + (23\mathbf{v}_n - 16\mathbf{v}_{n-1} + 5\mathbf{v}_{n-2})h/12 \tag{5}$$

and the third-order Adams–Moulton correctors,

$$\mathbf{v}_{n+1} = \mathbf{v}_n + (5\mathbf{a}_{n+1} + 8\mathbf{a}_n - \mathbf{a}_{n-1})h/12, \tag{6a}$$

$$\mathbf{r}_{n+1} = \mathbf{r}_n + (5\mathbf{v}_{n+1} + 8\mathbf{v}_n - \mathbf{v}_{n-1})h/12. \tag{6b}$$

For n iterations of the corrector cycle, the sequence of operations would be described as $P(\mathbf{r})(E(\mathbf{a})\ C(\mathbf{v})\ C(\mathbf{r}))^n$. Unfortunately, this method requires the simultaneous storage of eight vectors. A fourth-order Adams predictor–corrector would require ten.

The storage requirements for higher-order methods may be substantially reduced by going to direct methods for integrating Eq. (1) in one operation, rather than treating it as a system of two first-order equations. Verlet [2] has used Störmer's third-order explicit formula,

$$\mathbf{r}_{n+1} = 2\mathbf{r}_n - \mathbf{r}_{n-1} + h^2\mathbf{a}_n, \tag{7}$$

and the midpoint evaluation of $\mathbf{v}$,

$$\mathbf{v}_n = (\mathbf{r}_{n+1} - \mathbf{r}_{n-1})/(2h). \tag{8}$$

The use of this comparatively crude first-order method of calculating the velocities does not threaten the stability of the procedure because the velocities do not appear in Eq. (7). As it only requires the storage of three vectors, it represents a considerable advantage over the use of Eqs. (5) and (6). On the other hand, with a large integration step, the error in $\mathbf{v}_n$ may be quite large. If it is necessary to know the velocities of the molecules as well as the positions, this error may be excessive. Furthermore, it is often desirable to have $\mathbf{v}_n$ appear in the predictor used to calculate $\mathbf{r}_{n+1}$, so that the temperature of the system may be adjusted by scaling the velocities of the molecules up or down by a constant factor.

The advantages of Rahman's procedure may be combined with those of Verlet's by the use of a predictor of order q of the form

$$\mathbf{r}_{n+1} = \mathbf{r}_n + h\mathbf{v}_n + h^2 \sum_{p=1}^{q-1} b_p \mathbf{a}_{n-q+1} \tag{9a}$$

and the position and velocity correctors

$$\mathbf{r}_{n+1} = \mathbf{r}_n + h\mathbf{v}_n + h^2 \sum_{p=1}^{q-1} c_p \mathbf{a}_{n-q+2}\,, \tag{9b}$$

$$h\mathbf{v}_{n+1} = \mathbf{r}_{n+1} - \mathbf{r}_n + h^2 \sum_{p=1}^{q-1} d_p \mathbf{a}_{n-q+2}\,. \tag{9c}$$

For a given order q, the coefficients b_p, c_p, and d_p may be found by expanding all quantities in Eqs. (9a), (9b), and (9c) in a Taylor series about t_n.

For $q = 3$, one finds the predictor,

$$\mathbf{r}_{n+1} = \mathbf{r}_n + h\mathbf{v}_n + (h^2/6)(4\mathbf{a}_n - \mathbf{a}_{n-1}) + (1/8)\, h^4 \mathbf{r}_n^{(4)}, \tag{10a}$$

and the correctors

$$\mathbf{r}_{n+1} = \mathbf{r}_n + h\mathbf{v}_n + (h^2/6)(\mathbf{a}_{n+1} + 2\mathbf{a}_n) - (1/12)\, h^4 \mathbf{r}_n^{(4)}, \tag{10b}$$

$$h\mathbf{v}_{n+1} = \mathbf{r}_{n+1} - \mathbf{r}_n + (h^2/6)(2\mathbf{a}_{n+1} + \mathbf{a}_n) - (1/24)\, h^4 \mathbf{r}_n^{(4)}. \tag{10c}$$

The last term on the right-hand side of Eqs. (10a), (10b), and (10c) represents the truncation error, where $\mathbf{r}_n^{(4)}$ is the fourth time derivative of $\mathbf{r}$, evaluated at t_n. In a similar manner, one finds for $q = 4$,

$$\mathbf{r}_{n+1} = \mathbf{r}_n + h\mathbf{v}_n + (h^2/24)(19\mathbf{a}_n - 10\mathbf{a}_{n-1} + 3\mathbf{a}_{n-2}) + (19/180)\, h^5 \mathbf{r}_n^{(5)}, \tag{11a}$$

$$\mathbf{r}_{n+1} = \mathbf{r}_n + h\mathbf{v}_n + (h^2/24)(3\mathbf{a}_{n+1} + 10\mathbf{a}_n - \mathbf{a}_{n-1}) - (7/360)\, h^5 \mathbf{r}_n^{(5)}, \tag{11b}$$

and

$$h\mathbf{v}_{n+1} = \mathbf{r}_{n+1} - \mathbf{r}_n + (h^2/24)(7\mathbf{a}_{n+1} + 6\mathbf{a}_n - \mathbf{a}_{n-1}) - (1/45)\, h^5 \mathbf{r}_n^{(5)}. \tag{11c}$$

For $q = 5$, one obtains

$$\mathbf{r}_{n+1} = \mathbf{r}_n + h\mathbf{v}_n + (h^2/360)(323\mathbf{a}_n - 264\mathbf{a}_{n-1} + 159\mathbf{a}_{n-2} - 38\mathbf{a}_{n-3}) + (135/1440)\, h^6\mathbf{r}_n^{(6)}, \tag{12a}$$

$$\mathbf{r}_{n+1} = \mathbf{r}_n + h\mathbf{v}_n + (h^2/360)(38\mathbf{a}_{n+1} + 171\mathbf{a}_n - 36\mathbf{a}_{n-1} + 7\mathbf{a}_{n-2}) - (17/1440)\, h^6\mathbf{r}_n^{(6)}, \tag{12b}$$

$$h\mathbf{v}_{n+1} = \mathbf{r}_{n+1} - \mathbf{r}_n + (h^2/360)(97\mathbf{a}_{n+1} + 114\mathbf{a}_n - 39\mathbf{a}_{n-1} + 8\mathbf{a}_{n-2}) - (19/1440)\, \mathbf{r}_n^{(6)}. \tag{12c}$$

If Eqs. (10a) and (10c) are used in the sequence $P(\mathbf{r})\, E(\mathbf{a})\, C(\mathbf{v})$, and $\mathbf{v}_{n+1}$ and $\mathbf{r}_n$ are equivalenced so as to occupy the same storage location, four vectors are needed. The sequences $P(\mathbf{r})\, E(\mathbf{a})\, C(\mathbf{r})\, C(\mathbf{v})$ and $P(\mathbf{r})\, E(\mathbf{a})\, C(\mathbf{r})\, E(\mathbf{a})\, C(\mathbf{v})$ do not allow equivalencing of $\mathbf{v}_{n+1}$ and $\mathbf{r}_n$ and thus require five vectors. Similarly, the fourth-order direct method requires five vectors if only the predictor is used to calculate positions and requires six vectors if Eq. (11b) is used to correct the positions. The fifth-order direct method of Eq. (12) makes use of six vectors if the positions are not corrected and requires seven vectors if the position corrector is used.

It may be shown [4, 5] that the Nordsieck method [6] of solving first-order ordinary differential equations (ODEs) is fully equivalent to the Adams methods. The Nordsieck method has been extended to higher order ODEs by Gear [4, 5], and has been used in molecular dynamics calculations [7]. It is of interest to determine what relationship Eqs. (10)–(12) might have to the Nordsieck method.

In the Nordsieck formulation, the solution for an ODE involving the variable y is expressed in terms of higher derivatives of y at the current time step, rather than in terms of y and its derivative evaluated at previous time steps. For a method that expresses y_{n+1} in terms of $q + 1$ quantities, one defines the column vector

$$\mathbf{a}_n = (y_n\,,\ hy_n',\ h^2y_n''/2, \ldots,\ h^qy_n^{(q)}/q!). \tag{13}$$

The predicted values of y_{n+1} and its derivatives are given by

$$\mathbf{a}_{n+1}^{(p)} = A\mathbf{a}_n\,, \tag{14}$$

where A is the Pascal triangle matrix. The corrector is

$$\mathbf{a}_{n+1}^{(c)} = \mathbf{a}_{n+1}^{(p)} + lF(\mathbf{a}_{n+1}^{(p)}). \tag{15}$$

For the second-order ODE $y'' = f(y)$, the correction term is

$$F(\mathbf{a}_{n+1}^{(p)}) = h^2[f(y_{n+1}^{(p)}) - y_{n+1}^{\prime\prime(p)}]/2.$$

The column vector l gives the coefficients of the correction term. For $q = 3$, $l = (1/6, 5/6, 1, 1/3)$. For $q = 4$, $l = (19/120, 3/4, 1, 1/2, 1/12)$, and for $q = 5$, $l = (3/20, 251/360, 1, 11/18, 1/6, 1/60)$. By a straightforward application of the transformation discussed in [5, Chap. 9], one may find an equivalent representation of Eqs. (14) and (15) in terms of y_n, y_n', y_n'', and past values of y''. For $q = 3$, 4, and 5, the predictor yields $y^{(p)}_{n+1}$ of the form of Eqs. (10a), (11a), and (12a). On the other hand, the corrector gives, for these three cases,

$$y^{(c)}_{n+1} = y_n + hy_n' + (h^2/12)(f_{n+1} + 6f_n - f_{n-1}) + (h^4/24) f_n^{(4)}, \tag{16}$$

$$\begin{aligned} y^{(c)}_{n+1} = y_n + hy_n' &+ (h^2/240)(19f_{n+1} + 133f_n - 43f_{n-1} + 11f_{n-2}) \\ &+ (19/720)\, h^5 y^{(5)}, \end{aligned} \tag{17}$$

$$\begin{aligned} y^{(c)}_{n+1} = y_n + hy_n' &+ (h^2/360)(27f_{n+1} + 215f_n - 102f_{n-1} + 51f_{n-2} - 11f_{n-3}) \\ &+ (3/160)\, h^6 f_n^{(6)}. \end{aligned} \tag{18}$$

For $q = 3$, $y'^{(c)}_{n+1}$ is of the form of Eq. (6a), the third-order Adams–Moulton corrector. Similarly, $q = 4$ and 5 yield the fourth- and fifth-order Adams–Moulton expressions.

Reference [4] presents an alternate choice for l_0, the first component of l. For $q = 4$, $l_0 = 19/90$ may replace 19/120, and for $q = 5$, one may use $l_0 = 3/16$ in place of 3/20. With $q = 4$ and $l_0 = 19/90$, one obtains the position corrector, Eq. (12b). The Adams–Moulton velocity corrector remains unchanged. Although the local truncation error of Eq. (12b) is one order higher than that of Eq. (17), the global error of the method is of one order lower than with $l_0 = 19/120$ [4]. In molecular dynamics simulations of water, Rahman and Stillinger [7] have used $l_0 = 3/16$ with $q = 5$. This results in a position corrector of the form of Eq. (9b) with $q = 6$. Again, a smaller local truncation error is achieved at the cost of a larger global error.

The third-order direct method algorithm $P(\mathbf{r})\,E(\mathbf{a})\,C(\mathbf{v})$ was used by the author in molecular dynamics simulations of liquid argon performed at Harwell [3]. The method seemed unusually stable compared to other algorithms, but at the time, no detailed comparisons were made. Recently, a series of tests was performed in order to compare the third-, fourth-, and fifth-order direct methods given above, with and without position corrector, Rahman's method, Verlet's method, the third-order Adams predictor–corrector, and the Nordsieck method for second-order ODEs.

A system of 108 atoms was used. The interaction was given by Eq. (2), with parameters appropriate to liquid argon. The density of the system was set at 0.9418 g/cm^3, and the velocities were adjusted so that the system reached equilibrium at a temperature of about 140°K. Under these conditions, the average energy per atom was approximately −227°K. This corresponds to a point on the argon vapor pressure curve near the critical point, but sufficiently removed so as to avoid the large statistical fluctuations encountered at the critical point. In the first test, 60 integration steps with $h = 1.0 \times 10^{-14}$ sec were used with the third-, fourth-, and fifth-order direct method (Eqs. (10), (11), and (12), respectively) in both the sequence $P(\mathbf{r})\,E(\mathbf{a})\,C(\mathbf{v})$ and $P(\mathbf{r})\,E(\mathbf{a})\,C(\mathbf{r})\,E(\mathbf{a})\,C(\mathbf{v})$. For comparison, the computation was also carried out using one, two, three, and four iterations of both Rahman's predictor–corrector (Eqs. (3) and (4)) and the third-order Adams predictor–corrector (Eqs. (5) and (6)). Note that Eq. (10c), which gives $h\mathbf{v}_{n+1}$ to third-order accuracy, is of the same order of accuracy as Eqs. (10a) and (10b), although it gives $\mathbf{v}_{n+1}$ to only second-order accuracy. It would seem reasonable that the accuracy of the third-order $P(\mathbf{r})\,E(\mathbf{a})\,C(\mathbf{v})$ algorithm could be improved by using the third-order Adams–Moulton velocity corrector, Eq. (6a), instead of Eq. (10c). Accordingly, this sequence was also tried, in spite of the fact that it requires the storage of an additional vector. The average energy per atom was calculated at each integration step. For each method, this information was used to calculate the standard deviation in energy over the 60 steps, σ_E; the mean of the absolute values of the energy change at each step, $\langle|\Delta E|/\text{step}\rangle$; and the mean rate of energy change per step, $\langle\Delta E/\text{step}\rangle$, obtained from the slope of a linear least squares fit to the energy per atom as a function of the number of integration steps. The results of this test are summarized in Table I.

As one might expect, all of the higher-order direct methods had a smaller mean absolute value of energy change per step than the third-order $P(\mathbf{r})\,E(\mathbf{a})\,C(\mathbf{v})$. With the exception of the fourth-order $P(\mathbf{r})\,E(\mathbf{a})\,C(\mathbf{v})$, they also had a smaller standard deviation in average energy per atom, and a smaller drift in energy, as measured by $\langle\Delta E/\text{step}\rangle$. Rahman's procedure required at least two iterations of the corrector cycle for reasonable energy conservation, but with two or more iterations, it seemed to perform better than the direct methods. The Adams third-order predictor–corrector showed the best energy conservation of all the methods tested, even with only one corrector cycle. The $P(\mathbf{r})\,E(\mathbf{a})\,C(\mathbf{v})$ sequence using the third-order position predictor of Eq. (10a) and the Adams–Moulton velocity corrector of Eq. (6a) was slightly inferior to the sequence using Eqs. (10a) and (10c).

Because of the hardness of the repulsive interaction of Eq. (2) and the high temperature used, it was suspected that the lower-order methods might perform better when a large time step was used. In this case, the information provided by the acceleration at previous integration steps would be of lesser relevance. To test this hypothesis, h was increased to 3.0×10^{-14} sec, and 30 integration steps were performed. The same algorithms were tested, as well as the third-order direct method, $P(\mathbf{r})\,E(\mathbf{a})\,C(\mathbf{r})\,C(\mathbf{v})$. It was hoped that this last method would provide

TABLE I

Sixty Steps with $h = 1.0 \times 10^{-14}$ sec

Algorithm	σ_E(°K)	$\langle \lvert \Delta E \rvert /\text{step}\rangle$(°K)	$\langle \Delta E/\text{step}\rangle$(°K)
Equation			
(10) 3rd-order $P(\mathbf{r})E(\mathbf{a})C(\mathbf{v})$	0.086	0.0068	−0.0045
(10) 3rd-order $P(\mathbf{r})E(\mathbf{a})C(\mathbf{r})E(\mathbf{a})C(\mathbf{v})$	0.056	0.0058	−0.0035
(11) 4th-order $P(\mathbf{r})E(\mathbf{a})C(\mathbf{v})$	0.092	0.0063	−0.0057
(11) 4th-order $P(\mathbf{r})E(\mathbf{a})C(\mathbf{r})E(\mathbf{a})C(\mathbf{v})$	0.052	0.0056	−0.0031
(12) 5th-order $P(\mathbf{r})E(\mathbf{a})C(\mathbf{v})$	0.086	0.0058	−0.0041
(12) 5th-order $P(\mathbf{r})E(\mathbf{a})C(\mathbf{r})E(\mathbf{a})C(\mathbf{v})$	0.080	0.0056	−0.0040
Rahman method (iterations)			
1	0.229	0.0116	−0.0130
2	0.065	0.0056	−0.0032
3	0.061	0.0057	−0.0033
4	0.051	0.0057	−0.0033
Adams 3rd order (iterations)			
1	0.056	0.0059	−0.0029
2	0.033	0.0055	−0.0023
3	0.061	0.0055	−0.0023
4	0.065	0.0055	−0.0023
$P(\mathbf{r})E(\mathbf{a})C(\mathbf{v})$ with Eqs. (10a) and (6a)	0.092	0.0064	−0.0056

more accuracy than the third-order $P(\mathbf{r})\ E(\mathbf{a})\ C(\mathbf{v})$ sequence without the necessity of evaluating the accelerations twice. Table II summarizes the results of this test. As suspected, the higher-order algorithms show some stability problems with this large step size. Although the average magnitude of the energy change per step is smaller for the fourth- and fifth-order methods, only the fifth-order $P(\mathbf{r})\ E(\mathbf{a})\ C(\mathbf{r})\ E(\mathbf{a})\ C(\mathbf{v})$ method shows a smaller standard deviation in energy than the third-order $P(\mathbf{r})\ E(\mathbf{a})\ C(\mathbf{v})$, with a comparable mean rate of energy change per step. The third-order $P(\mathbf{r})\ E(\mathbf{a})\ C(\mathbf{r})\ C(\mathbf{v})$ method was substantially worse. Although the third-order $P(\mathbf{r})\ E(\mathbf{a})\ C(\mathbf{r})\ E(\mathbf{a})\ C(\mathbf{v})$ sequence showed the best energy conservation of any of the algorithms tested, it was only slightly better than the third-order $P(\mathbf{r})\ E(\mathbf{a})\ C(\mathbf{v})$ method and required twice as many evaluations of $\mathbf{a}$. Although the Adams predictor–corrector was also of third-order accuracy, it showed a large variation in energy as well as a sizable drift, even after three or four corrector cycles. Rahman's method required three evaluations of $\mathbf{a}$ to obtain the accuracy of the third-order direct method, $P(\mathbf{r})\ E(\mathbf{a})\ C(\mathbf{v})$. With this step size, the $P(\mathbf{r})\ E(\mathbf{a})\ C(\mathbf{v})$ sequence with Eqs. (10a) and (6a) showed severe stability problems.

TABLE II

Thirty Steps with $h = 3.0 \times 10^{-14}$ sec

Algorithm	σ_E(°K)	$\langle \lvert \Delta E \rvert$/step$\rangle$(°K)	$\langle \Delta E$/step$\rangle$(°K)
Equation			
(10) 3rd-order $P(\mathbf{r})E(\mathbf{a})C(\mathbf{v})$	0.237	0.130	−0.019
(10) 3rd-order $P(\mathbf{r})E(\mathbf{a})C(\mathbf{r})C(\mathbf{v})$	0.685	0.114	−0.075
(10) 3rd-order $P(\mathbf{r})E(\mathbf{a})C(\mathbf{r})E(\mathbf{a})C(\mathbf{v})$	0.219	0.077	+0.014
(11) 4th-order $P(\mathbf{r})E(\mathbf{a})C(\mathbf{v})$	1.218	0.167	−0.137
(11) 4th-order $P(\mathbf{r})E(\mathbf{a})C(\mathbf{r})E(\mathbf{a})C(\mathbf{v})$	0.692	0.091	+0.076
(12) 5th-order $P(\mathbf{r})E(\mathbf{a})C(\mathbf{v})$	0.463	0.123	−0.047
(12) 5th-order $P(\mathbf{r})E(\mathbf{a})C(\mathbf{r})E(\mathbf{a})C(\mathbf{v})$	0.191	0.047	+0.020
Rahman method (iterations)			
1	4.970	0.560	−0.563
2	0.596	0.104	+0.061
3	0.262	0.076	+0.021
4	0.292	0.078	+0.024
Adams 3rd order (iterations)			
1	1.479	0.218	−0.166
2	1.455	0.176	+0.164
3	1.256	0.150	+0.142
4	1.270	0.152	+0.143
$P(\mathbf{r})E(\mathbf{a})C(\mathbf{v})$ with Eqs. (10a) and (6a)	1.192	0.145	−0.133

Although the test just described is suggestive, the fact that an algorithm may appear fairly stable over 30 integration steps is no guarantee that it will perform equally well over the much longer time spans used in molecular dynamics calculations. Therefore, more extended tests were made on those algorithms that performed well on the test with $h = 3.0 \times 10^{-14}$ sec. In this series, the Nordsieck methods were also included for comparison. Table III summarizes the results of runs of 300 integration steps with $h = 3.0 \times 10^{-14}$ sec for the third- and fifth-order direct methods and the Nordsieck methods discussed above. The superiority of the third-order $P(\mathbf{r})\,E(\mathbf{a})\,C(\mathbf{v})$ sequence to the other direct methods is clearly evident. Not only does it have the smallest standard deviation in energy, but the energy drift is barely larger than the statistical uncertainty in the drift. This result is consistent with the author's experience with this algorithm in more extended molecular dynamics calculations. A system of 500 argon-like atoms with a density of 1.266 gm/cm^3 and temperature of 108.3°K showed no discernible drift in energy over 2000 integration steps with $h = 3.0 \times 10^{-14}$ sec. The Nordsieck

TABLE III

Three Hundred Steps with $h = 3.0 \times 10^{-14}$ sec

Algorithm	σ_E(°K)	$\langle \Delta E/\text{step} \rangle$(°K)
Equation		
(10) 3rd-order $P(\mathbf{r})E(\mathbf{a})C(\mathbf{v})$	0.324	-0.0008 ± 0.0007
(10) 3rd-order $P(\mathbf{r})E(\mathbf{a})C(\mathbf{r})C(\mathbf{v})$	10.587	-0.1200 ± 0.0013
(10) 3rd-order $P(\mathbf{r})E(\mathbf{a})C(\mathbf{r})E(\mathbf{a})C(\mathbf{v})$	0.636	-0.0060 ± 0.0007
(12) 5th-order $P(\mathbf{r})E(\mathbf{a})C(\mathbf{v})$	6.614	-0.0750 ± 0.0009
(12) 5th-order $P(\mathbf{r})E(\mathbf{a})C(\mathbf{r})E(\mathbf{a})C(\mathbf{v})$	3.022	$+0.0342 \pm 0.0005$
Nordsieck method		
$q = 3, l_0 = 1/6$	5.973	-0.0674 ± 0.0008
$q = 4, l_0 = 19/120$	0.277	$+0.0015 \pm 0.0005$
$q = 5, l_0 = 3/20$	3.756	$+0.0424 \pm 0.0008$
$q = 4, l_0 = 19/90$	3.074	$+0.0347 \pm 0.0007$
$q = 5, l_0 = 3/16$	4.532	$+0.0513 \pm 0.0009$

methods all had a much larger standard deviation in energy and energy drift than the third-order $P(\mathbf{r})\,E(\mathbf{a})\,C(\mathbf{v})$ sequence, with the exception of the case, $q = 4$, $l_0 = 19/120$. This case showed a slightly smaller standard deviation in energy, with a larger drift in energy. As the method requires the storage of one more vector than the third-order $P(\mathbf{r})\,E(\mathbf{a})\,C(\mathbf{v})$ sequence, there would be no advantage in its use. The higher accuracy associated with the values of l given in [5] ($l_0 = 19/120$ instead of 19/90 for $q = 4$, and $l_0 = 3/20$ instead of 3/16 for $q = 5$) is also evident from these tests.

In addition to the tests described above, 30 integration steps with $h = 3.0 \times 10^{-14}$ sec were performed with the combination of Eqs. (7) and (8) used by Verlet. Although there was little overall drift in energy, there were significant deviations in energy and temperature at each step from the values calculated using the third-order $P(\mathbf{r})\,E(\mathbf{a})\,C(\mathbf{v})$ direct method. The average energy calculated over the 30 steps differed by about 1.0°K for the two methods. The average magnitude of the temperature difference at each step was 1.3°K. This was not considered to be a fair test of the accuracy of the method, because the variations in energy of the system were primarily due to the inaccuracy of Eq. (8), which is used to calculate the velocities. As Eq. (7), which calculates the positions, does not make use of the velocities, these errors are not propagated. In order to provide a better test of Eq. (7), 300 integration steps were performed with $h = 3.0 \times 10^{-14}$ sec, using Eq. (7) to calculate the positions, but using Eq. (10c) to calculate the velocities. When this was done, all measurements of the energy and its variation were the same as those listed in Table I for the direct third-order $P(\mathbf{r})\,E(\mathbf{a})\,C(\mathbf{v})$ method. The positions calculated by the two algorithms showed differences of about one part in 10^6 by the end of 300 steps. This very slight discrepancy is evidently due to roundoff error, as Eqs. (10a) and (10c) may be combined to give Eq. (7), with the same truncation error. (All calculations were carried out using double-precision arithmetic.)

From these tests, one may conclude that the combination of Eqs. (10a) and (10c) provides a very stable and efficient method of integrating the equations of motions of particles interacting with steeply repulsive forces. Although the method is equivalent to the third-order Störmer method of Eq. (7), it is much more useful for calculations of this type because it permits an accurate determination of velocities with a large integration step. It offers the additional convenience of using the velocities in a way that facilitates the adjustment of the temperature of the system. As the fourth- and fifth-order algorithms of Eqs. (11) and (12) have smaller truncation errors and show better energy conservation from step to step, it is possible that they may be useful for systems involving more slowly varying potentials. A possible application might be the study of a collection of bodies at low density interacting via coulombic or gravitational forces.

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