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A Multiple Time-Step Method for Molecular Dynamics Simulations of Fluids of Chain Molecules

R. D. SWINDOLL* AND J. M. HAILE

Department of Chemical Engineering,
Clemson University, Clemson, South Carolina 29631

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The implementation of a multiple time-step method that produces factors of 1.5 to 2.5 decrease in the computer time needed for performing molecular dynamics simulations of fluid alkanes is reported. The simulation method has been used to obtain a pair distribution function for *n*-butane that is compared with recent x-ray diffraction data.

1. INTRODUCTION

The study of fluids by computer simulation has assumed an important role that complements traditional theoretical and experimental studies. In recent years, computer simulations by Monte Carlo, molecular dynamics, and Brownian dynamics have been applied to fluids of increasing complexity, including those composed of molecules having internal degrees of freedom. There is vast literature on the use of Monte Carlo to study such problems as excluded volume effects in polymeric-type systems. However, it is only in the last several years that molecular and Brownian dymanics methods have been devised for simulating such complicated systems. The Brownian dynamics method treats a single chain molecule immersed in a continuum solvent and is, therefore, appropriate for study of single molecule properties, such as conformational dynamics. Molecular dynamics treats all molecules as explicit entities and, therefore, is appropriate for study of collective properties, such as intermolecular distribution functions. A coherent review of these methods and recent results for short chain molecules has been given by Evans [1].

Because molecular dynamics simulates systems with large numbers of degrees of freedom, it is much more expensive to perform than Brownian dynamics. In this paper we report the successful implementation of a multiple time-step (MTS) method into the molecular dynamics algorithm for fluids of straight chain molecules. We have tested the MTS method on fluid *n*-butane and find that the method provides a substantial reduction in the computer time needed to perform simulations of such systems.

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* Present address: Linear Polyethylene and Derivatives Technology Center, Dow Chemical USA, Plaquemine, La. 70764.

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Previous molecular dynamics simulations of alkane fluids include the work of Ryckaert *et al.* [2–5], Weber [6, 7], and Szczepanski and Maitland [8]. In the work reported here we have adopted the skeletal model of alkanes used by Weber. In this model methyl and methylene groups are represented as soft spheres whose intermolecular interactions are assumed to be Lennard-Jones (6, 9) potentials. Intramolecular interactions include harmonic potentials for bond vibration and bond angle bending plus a bond rotation potential. The rotational potential is dependent upon the dihedral angle about the bond, but also involves a Lennard-Jones (6, 9) interaction between methyl–methylene groups that are separated by two or more groups. Detailed expressions for these potential models and values for the potential parameters are given in [6, 9].

Weber's potential model offers the advantage of complete chain flexibility, thereby promoting a more realistic sampling of phase space [10, 11] than the Ryckaert model, which contains rigid bond lengths and bond angles. However, the presence of vibratory motion in the bond lengths and bond angles of Weber's model necessitates use of a smaller integration time-step to maintain stable solutions to the equations of motion. The MTS method applied to Weber's model partially compensates for the computational disadvantage of the smaller time-step.

2. MULTIPLE TIME-STEP METHOD

Multiple time-step methods are variants of the usual molecular dynamics method and typically execute considerably faster than the usual method without compromising the accuracy of the simulation results. The physical idea behind the method is that the force on a particle i, $\mathbf{F}_i$, can be separated into two components whose rates of change are significantly different from one another. The rapidly varying component is due to interactions with nearest neighbors and is referred to as the primary force, $\mathbf{P}_i$. The more slowly varying component is due to interactions with secondary neighbors, $\mathbf{S}_i$. We therefore write

$$\mathbf{F}_i = \mathbf{P}_i + \mathbf{S}_i, \tag{1}$$

$$\mathbf{P}_i = -\sum_{j \neq i} \frac{du(r_{ij})}{d\mathbf{r}_i}, \qquad r_{ij} < r_a, \tag{2}$$

and

$$\mathbf{S}_i = -\sum_{j \neq i} \frac{du(r_{ij})}{d\mathbf{r}_i}, \qquad r_a \leqslant r_{ij} \leqslant r_c, \tag{3}$$

where $\mathbf{r}_i$ is a location vector for particle i, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, $u(r_{ij})$ is the pair potential acting between particles i and j separated by distances r_{ij}, r_c is the distance at which the potential is truncated, and r_a is the radius of a sphere centered at particle i and enclosing the nearest neighbors of i.

During an MTS simulation, the primary force on particle i is calculated from (2) by sampling nearest neighbors in the usual way. However, the secondary force is calculated from (3) only at intervals of k time-steps. During the interim, $\mathbf{S}_i$ is estimated by a Taylor series,

$$\mathbf{S}_i(t + m\,\Delta t) = \mathbf{S}_i(t) + \dot{\mathbf{S}}_i(t)\, m\,\Delta t + \ddot{\mathbf{S}}_i(t)(m\,\Delta t)^2/2! + \text{etc.}, \qquad m = 1,\ldots, k, \tag{4}$$

where the dots indicate time derivatives and Δt is the size of the integration time-step. Expressions for the first three time derivatives of a Lennard-Jones (6, 9) force are given in [9].

Since the calculation of the forces is by far the most time consuming portion of a molecular dynamics simulation, the decrease in computing time realized by the MTS method depends on the amount of computation that is avoided by using (4) instead of (3) for evaluating the secondary forces. Decreases in execution time by factors of two to five have been realized by applying the MTS method to atomic fluids at liquid densities [12]. Versions of the MTS method have also been developed for fluids composed of rigid nonspherical molecules [13] and for fluids containing three-body interactions [14]. The MTS method can be made more elaborate by dividing the region from r_a to r_c into a series of concentric spherical shells of secondary, tertiary, etc., neighbors and calculating the force in each on a different time scale, k_1, k_2, etc. [12].

In molecular dynamics simulations of fluids composed of chain molecules with a total of N interacting sites in the system, the evaluation of the intermolecular forces requires calculation time proportional to N^2, whereas the time needed for evaluation of intramolecular forces is proportional to N. Thus, we have applied the MTS method to the evaluation of the intermolecular forces and leave the calculation of intramolecular forces undisturbed. The procedure is exactly that outlined above in (1)–(4), with each methyl–methylene group designated by a subscript i in (1)–(4) and the $\mathbf{F}_i$ on the l.h.s. of (1) now representing only the Lennard-Jones intermolecular interaction. Hence, the total force on the ith methyl–methylene group is

$$\mathbf{F}_i = \mathbf{F}_i^{(\mathrm{intra})} + \mathbf{P}_i + \mathbf{S}_i. \tag{5}$$

For skeletal models of chain molecules, therefore, the MTS method represented by (2)–(5) differs from that for atomic fluids only by the presence of the intramolecular forces in (5).

We have tested the MTS method on simulations of fluid n-butane and compared the results with our version of a "standard" molecular dynamics program (i.e., one not containing the MTS method) and with Weber's published results [6] for n-butane. Our simulations of n-butane were carried out on systems of 64 molecules interacting via Weber's inter- and intramolecular potentials with the following modifications. We truncated the Lennard-Jones potential at $r/r_m = 2.5$, whereas Weber used $r/r_m = 5$. Here, r_m is the value of r at which the potential is a minimum, $r_m = 4$ Å. With this shorter cutoff distance, impulse forces due to particles crossing the cutoff disrupt the energy conservation of the simulation. To remove these spurious impulses, we modified the Lennard-Jones truncated potential to a shifted-force potential given by [15]

$$\begin{aligned} u(r) &= u_{\mathrm{LJ}}(r) - u_{\mathrm{LJ}}(r_{\mathrm{c}}) - F_{\mathrm{LJ}}(r_{\mathrm{c}})[r - r_{\mathrm{c}}], \qquad && r < r_{\mathrm{c}}, \\ &= 0, && r \geqslant r_{\mathrm{c}}, \end{aligned} \tag{6}$$

where, for notational simplicity, we have written r for r_{ij}, u_{LJ} is the (6, 9) Lennard-Jones potential, and $\mathrm{F}_{\mathrm{LJ}}(r_{\mathrm{c}})$ is the Lennard-Jones force at the cutoff distance. Static properties obtained from simulations using (6), as opposed to a simple truncated potential, can be readily corrected for the presence of the shift [15].

3. RESULTS

Our molecular dynamics program solves the Newtonian equations of motion for each methyl and methylene group using a fifth-order predictor–corrector algorithm due to Gear [16]. Periodic boundary conditions and the minimum image criterion were applied on a methyl–methylene particle basis. Initial conditions were assigned as follows. One methyl group of each molecule was assigned to an FCC lattice site; the remaining methyl and methylene groups on each molecule were assigned positions at the equilibrium values for all bond lengths and bond angles with initial values for the dihedral angles randomly assigned. The initial values of the molecular velocities were randomly assigned, with each methyl and methylene group on the same molecule given the same initial velocity. These initial velocities were adjusted so the total linear momentum of the system was zero and the velocities were then scaled to produce the desired value of the kinetic temperature.

The system was allowed to relax from these initial conditions by running the simulation over an equilibration period of about 2500 time-steps. During this equilibration the particle velocities were continually rescaled to maintain the desired temperature. At the end of this equilibration, the velocity scaling was terminated and a further 300 time-steps were executed and discarded before the production phase of the simulation began.

The MTS method contains three parameters whose values can be adjusted to obtain the maximum increase in execution speed for an allowed tolerance in some measure of the accuracy of the algorithm. The three parameters are r_a, the radial distance at which primary and secondary neighbors are separated; n, the order of the Taylor series (4) used to estimate the secondary forces; and k, the interval at which the secondary forces are explicitly evaluated by (3) rather than by (4). We determined optimal values of these three parameters by studying the average fractional deviation $\langle \Delta S \rangle$ in the secondary force estimated by the Taylor series (4), $\mathbf{S}^{\mathrm{E}}$, as compared to the true value given by (3), $\mathbf{S}^{\mathrm{T}}$,

$$\langle \Delta S \rangle = \frac{1}{3N} \sum_{i=1}^{N} \sum_{a=x,y,z} |(S_{ia}^{\mathrm{T}} - S_{ia}^{\mathrm{E}})/S_{ia}^{\mathrm{T}}|. \tag{7}$$

In our opinion using $\langle \Delta S \rangle$ as a criterion for selecting values for the MTS parameters is a more direct and restrictive approach than making the choice based merely on considerations of total energy conservation. To initiate the procedure, we rather arbitrarily decided to choose MTS-parameter values such that the maximum $\langle \Delta S \rangle$ value was about 0.05 (recalling that for dense fluids the secondary force is a small portion of the total force on each particle). We subsequently confirmed that in fact this is a conservative choice since energy conservation is maintained to a high degree, and property values from the MTS method are in satisfactory agreement with those from a standard simulation.

Values of $\langle \Delta S \rangle$ were obtained from test runs on 64 *n*-butane molecules at a density of 579 kg/m^3 and a temperature of 750° K. The results are shown in Figs. 1 and 2. Figure 1 shows that the fractional deviation $\langle \Delta S \rangle$ decreases in an expected fashion with increasing order of the Taylor series. We judged that slight gains in accuracy provided by a Taylor series of order $n > 3$ would not be sufficient to justify the deriving, coding, and storing of additional derivatives of the secondary force. In contrast, Fig. 2 indicates that for a given number of time-steps $\langle \Delta S \rangle$ goes through a minimum as r_a is increased. For small values of r_a (< 1.1) there are quickly varying, first neighbor contributions to the secondary force, which lead to large errors in the Taylor series estimate. For large values of r_a(> 1.3) the magnitude of the secondary force S^{T} is small, so the fractional deviation $\langle \Delta S \rangle$ defined by (7) is again large. The presence of these two effects leads to optimal values for r_a in the range $1.1 < r_a < 1.2$. We find that the optimal values of r_a and n are weak functions of the fluid state condition, so, based on Figs. 1 and 2, we used $n = 3$ and $r_a/r_m = 1.1$ in all our butane simulations. The optimum value of k is more dependent on state condition than n or

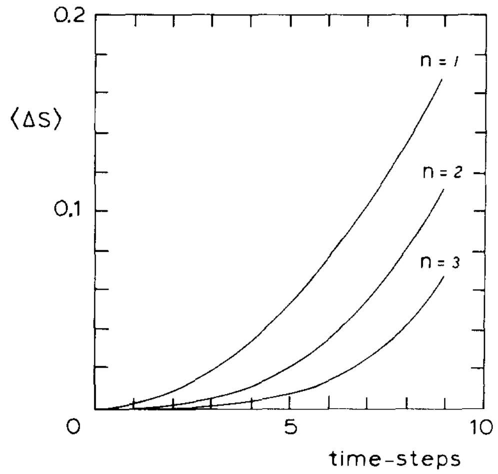

FIG. 1. Effect of the order n of the Tylor series (4) on the accuracy of the MTS algorithm as measured by the average fractional deviation in the secondary force (7). This figure is from a simulation of *n*-butane at 579 kg/m^3 and 750° K.

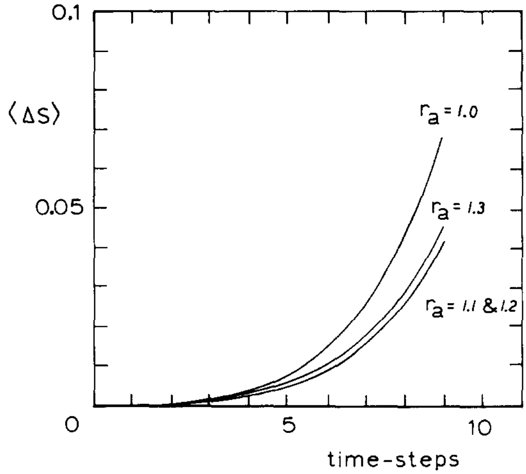

FIG. 2. Effect of the value of the distance r_a (at which primary and secondary neighbors are separated) on the accuracy of the MTS algorithm. Fluid same as in Fig. 1.

r_a; hence, we determined a value of k from a figure such as Fig. 2 for each state condition simulated. Typically, $5 < k < 15$, in units of integration time-steps. For the state condition of Fig. 1, we chose a conservative value of $k = 5$ time-steps.

In Table I a sampling of properties from the MTS program is compared with results from our standard molecular dynamics program and with the published results of Weber [6]. Both the standard and MTS versions of our molecular dynamics program used neighbor lists to improve the execution speed of the simulations. In the standard version the neighbor list was constructed for all pairs having $r_{ij} < 2.8r_m$, while in the MTS version the list was maintained on the primary neighbors only. The standard program showed a drift of 0.02% in the total energy over one psec, while the drift was twice that large in the MTS program. Our experience is that the drift in total energy may be as large as 0.1% over one psec without detrimental effects on resulting property values.

The results from the MTS program are in satisfactory agreement with the standard program results. The slight deviations are attributable to the difference in temperatures of the two runs. The results from the MTS program are in reasonable agreement with Weber's, except for the pressure. The discrepancy in the values of the pressure is due to the difference in state condition, to the use of different values for the potential cutoff r_c, and to the difference in run duration. Our values for the internal energy and the pressure shown in Table I include estimates for the long-range contribution beyond the cutoff r_c. These estimates were obtained by making the usual uniform fluid approximation for $r > r_c$; however, the pressure is more sensitive to this type of an approximation than is the internal energy. In addition to the properties shown in Table I, the inter- and intramolecular pair distribution functions from the three simulations are all in excellent agreement.

TABLE I

MTS Simulation Results for *n*-Butane Compared with Our Standard Molecular Dynamics Program and with the Results of Weber [6]

	Weber	Std MD	MTS[a] MD
Number butane molecules	100.	64.	64.
LJ cutoff, r_c/r_m	5.	2.5	2.5
Run duration, psec	12.	8.	8.
Time-step, psec	0.002	0.002	0.002
Density, kg/m^3	578.	579.	579.
Temperature, °K	745.	767.	750.
Internal energy, kJ/mol	48.0	48.9	48.8
Pressure, MPa	100.	140.	130.
Diffusion coefficient, 10^8 m^2/sec	3.3	3.7	3.6
Average % trans	42.	50.	47.
CPU time, min[b]	—	54.6	37.1

[a] $r_a = 1.1 r_m$, $n = 3$, $k = 5$.

[b] On an IBM 370/3033, FORTRAN IV-G compiler, double precision arithmetic.

We have also used the MTS method in a simulation of *n*-butane and compared the resulting pair distribution function with the x-ray diffraction results of Narten *et al.* [17]. The x-ray experiment was performed at 605 kg/m^3 and 275° K. For this state condition we determined an optimum value of the MTS parameter $k = 8$ time-steps with $n = 3$ and $r_a = 1.1 r_m$. An 8 psec production run under these conditions required 21.7 min of central processor time on an IBM 370/3033.

The simulation and x-ray results for the distribution function are compared in Fig. 3. In the figure, both the simulation results (solid line) and the x-ray data (points) contain the end-to-end (1)–(4) intramolecular contribution to $g(r)$, as well as the intermolecular contribution from methyl and methylene groups on different molecules. The (1)–(2) and (1)–(3) contributions have been suppressed in the figure since they are merely sharp Gaussian functions centered at positions corresponding to the equilibrium bond lengths and bond angles. To help distinguish the intra- from the intermolecular contributions in Fig. 3, we also show the (1)–(4) contribution obtained from the simulation (broken line). Thus, the simulation leads us to interpret the bump in the x-ray data at $r \cong 3.1$ Å as due to gauche conformations and the first half of the double peak, at $r \cong 4.2$ Å as due to trans conformations. The second half of the double peak, at $r \cong 5.1$ Å, is actually the first main peak in the intermolecular part of the distribution function. The simulation qualitatively reproduces these details, although the gauche bump near $r = 3.1$ Å is overshadowed by the leading edge of the

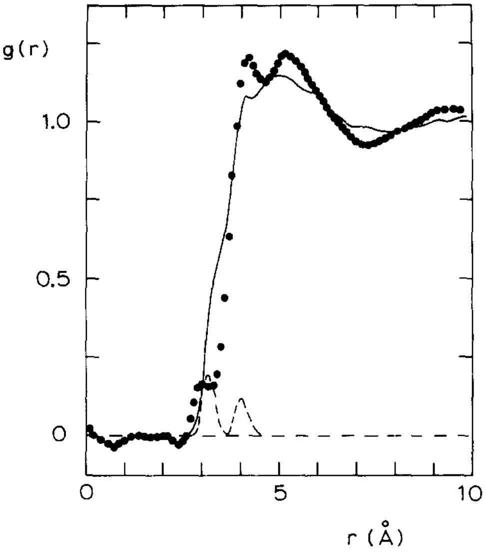

FIG. 3. Pair distribution function for methyl–methylene groups in fluid *n*-butane at 650 kg/m^3. Points are x-ray diffraction data from Narten *et al.* [17] at 267° K. Lines are MTS–MD results at 275° K. Solid line is the inter- plus (1)–(4) intramolecular distribution function. Broken line is the (1)–(4) intramolecular distribution function only.

main peak in the intermolecular part of the distribution function. A slightly larger value for the potential parameter r_m in the Lennard-Jones model and a weaker (1)–(4) interaction in the intramolecular potential would improve the simulation result compared to the x-ray data.

4. DISCUSSION

We have shown that a multiple time-step method executes about a factor of two faster than a standard molecular dynamics algorithm for simulating fluid *n*-butane. The optimal speed increase depends somewhat on fluid state condition, but in any case the method introduces no error, within the statistical precision of the calculations, into values for macroscopic properties. Our tests of the method were performed on Weber's skeletal model of alkanes and the increased execution speed provided by the MTS method helps compensate for the small integration time-step required by the model's vibratory internal motions. The MTS method could also be applied to alkane models that use rigid bond lengths and bond angles. Indeed, the application of the MTS method to rigid polyatomic fluids has already been discussed in general terms in [13].

In the algorithm described here the MTS method is applied only to the calculation of intermolecular forces; intramolecular forces are determined by the same procedure as used in a conventional molecular dynamics program. Thus, this version of the method can, without modification, be applied to solutions of a chain-molecule solute in a solvent of spherical molecules. Further, for chains containing up to, say, eight or ten methylene groups, we expect the fractional savings in execution time to be only weakly dependent on the molecular chain length. For longer molecules, particularly for densities at which the molecules tend to entangle themselves, the present version of the MTS method may be less effective since a smaller fraction of first and second neighbors will be intermolecular methylene groups.

One could contemplate extending the present method to include intramolecular forces in the MTS algorithm. This would be a possibility for Weber's model, which has a direct Lennard-Jones interaction between methyl–methylene groups that are third neighbors and beyond. For such a model third neighbor interactions would have to be included in the primary not secondary forces, since conformational transitions, while infrequent, take place relatively rapidly. Further, if the Lennard-Jones potential were truncated at $r_c/r^* = 2.5$, then neighbors beyond the eighth would not contribute to the intramolecular force in any case. Thus, the secondary forces would contain intramolecular contributions only from fourth through eighth neighbors. For short chains, such as hexane, there would probably be little speed advantage to including intramolecular forces in the MTS method. However, for longer molecules, such as approximations to polymeric materials, the inclusion of intramolecular interaction could be of substantial benefit.

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