

# Split Integration Symplectic Method for Molecular Dynamics Integration

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An explicit Split Integration Symplectic Method (SISM) for molecular dynamics (MD) simulations is described. This work is an extension of an efficient symplectic integration algorithm introduced by Janežič and Merzel (*J. Chem. Inf. Comput. Sci.* **1995**, 35, 321–326). SISM is based on splitting of the total Hamiltonian of the system into a harmonic part and the remaining part in such a way that both parts can be efficiently computed. The Hamilton equations of motion are then solved using the second order generalized leap-frog integration scheme in which the high-frequency motions are treated analytically by the normal mode analysis which is carried out only once, at the beginning of the calculation. SISM requires only one force evaluation per integration step; the computation cost per integration step is approximately the same as that of the standard leap-frog-Verlet (LFV) method, and it allows an integration time step up to an order of magnitude larger than can be used by other methods of the same order and complexity. The simulation results of selected examples—MD simulations of a model system of linear chain molecules of the form  $\text{H}-(\text{C}\equiv\text{C})_2-\text{H}$  and a model system of flexible  $\text{CO}_2$  molecules—show that the SISM possesses long term stability and the ability to use long time steps. The approach for MD simulations described here is general and applicable to any complex system.

## 1. INTRODUCTION

Molecular dynamics (MD) simulation, in which the classical equations of motion for all particles of a system are integrated over finite period of time, is one of the theoretical methods to investigate dynamical properties of complex systems.<sup>1,2</sup> For a given potential energy function the MD simulation is the most exact method since there is no analytical solution of the system of corresponding differential equations. The problem which arises in performing MD simulations of complex systems is that only short simulations can be performed due to the high frequency bond stretching motion which requires the use of a small step size in MD simulations.<sup>3,4</sup> This limitation frustrates long simulations and therefore the algorithm which is able to employ a long time step without loss of stability would increase the efficiency and the scope of the MD method.<sup>4,5</sup>

To perform MD simulation of a system with a finite number of degrees of freedom the Hamilton equations of motion

$$\frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i}, \quad \frac{dq_i}{dt} = \frac{\partial H}{\partial p_i}, \quad i = 1 \dots d \quad (1)$$

where  $H$  is the Hamiltonian,  $q_i$  and  $p_i$  are the coordinate and momentum, respectively, and  $d$  is the number of degrees of freedom are to be solved.

The problem of how to increase the time step in MD simulations can be overcome by use of symplectic methods.<sup>6–10</sup>

The fundamental property of the Hamiltonian system is that for each fixed value of  $t$  the corresponding  $t$ -flow  $\phi_{t,H}$  is a symplectic or canonical mapping.<sup>6</sup> A mapping is said to be symplectic or canonical if it preserves the differential form  $D = dp \wedge dq$  which defines the symplectic structure

in the phase space.<sup>11</sup> Differential forms provide a geometric interpretation of symplecticity in terms of conservation of areas which follows from Liouville's theorem. Integration of the Hamilton system requires the integrator to be symplectic.<sup>12</sup> Symplectic integration methods replace  $t$ -flow  $\phi_{t,H}$  in the phase space by the symplectic transformation  $\psi_{t,H}$ , which inherits the symplectic character of the Hamiltonian flow  $\phi_{t,H}$ .

We recently introduced a new efficient symplectic algorithm for MD simulations of a class of isolated molecules for which it can be assumed that bond stretching satisfactorily describes all vibrational motions for linear molecule.<sup>9</sup> The method allowed the use of a step size at least a factor of ten larger than the standard leapfrog-Verlet method.<sup>13</sup> In this paper we describe the extension of the method proposed in ref 9 by introducing the Split Integration Symplectic Method (SISM) for MD simulations. This approach uses the idea of composition methods, which are particularly useful for numerically integrating differential equations when the equations have some special structure which is advantageous to preserve.<sup>14</sup> Ideally one would like to know the fastest method for a given problem with a given accuracy. The SISM described in this paper is quite distinct from other approaches using fractional step methods<sup>15,16</sup> owing to the analytical treatment of high frequency motions. The SISM presented here allows the use of an integration time step up to an order of magnitude larger than possible with other methods of the same order and complexity. In Section 2, the details of the method are given. In Section 3, the simulation results of selected examples are given and discussed.

## 2. THEORY

The explicit symplectic integrator can be derived in terms of free Lie algebra in which Hamilton eq (1) can be written

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in the form

$$\frac{d\mathbf{x}}{dt} = \{\mathbf{x}, H\} = \hat{L}_H \mathbf{x} \quad (2)$$

where  $\{\mathbf{x}, H\}$  denotes the Poisson bracket,  $\hat{L}_H$  is the Poisson bracket operator, and  $\mathbf{x} = (\mathbf{q}, \mathbf{p})$  is a vector in phase space composed of the coordinates and momenta of all particles. The formula

$$\mathbf{x}|_{\tau_0+\Delta\tau} = \exp(\Delta\tau\hat{L}_H)\mathbf{x}|_{\tau_0} \quad (3)$$

provides a way for integrating the Hamiltonian system in terms of Lie operators.<sup>17</sup> It is the formal solution of Hamilton equations or the exact time evolution of trajectories in phase space from  $\tau_0$  to  $\tau_0 + \Delta\tau$ , and  $\Delta\tau$  is a time step. The trouble with it resides in impossibility of evaluating  $\exp(\Delta\tau\hat{L}_H)$ . The Lie formalism used is the key in the development of symplectic integration. Symplectic integration consists in replacing  $\exp(\Delta\tau\hat{L}_H)$  by a product of symplectic maps which approximate  $\exp(\Delta\tau\hat{L}_H)$  to a given order.<sup>18</sup>

The construction of an efficient algorithm rests on the ability to separate the Hamiltonian into parts which are themselves integrable and also efficiently computable. Suppose that the MD Hamiltonian  $H$

$$H = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + \sum_{bonds} k_b(b - b_0)^2 + \sum_{angles} k_\varphi(\varphi - \varphi_0)^2 + \sum_{dihed} k_\vartheta(1 + \cos(n\vartheta - \delta)) + \sum_{i>j} \frac{e_i e_j}{r_{ij}} + \sum_{i>j} 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (4)$$

where  $i$  and  $j$  run over all atoms,  $e_i$  denotes the charge on the  $i$ -atom, and  $r_{ij}$  is the distance between atoms  $i$  and  $j$ , is split into two parts

$$H = H_0 + H_r \quad (5)$$

where

$$H_0 = H^{harm}(m_i, b_0, \varphi_0, \delta, k_b, k_\varphi, k_\vartheta)$$

$$H_r = H - H^{harm}(m_i, b_0, \varphi_0, \delta, k_b, k_\varphi, k_\vartheta) \quad (6)$$

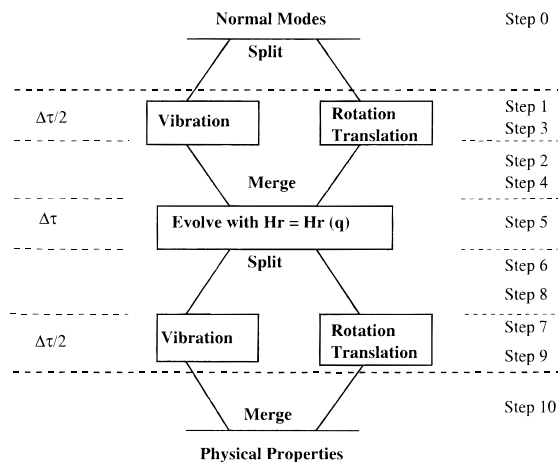
and  $H^{harm}$  denotes the harmonic approximation;  $m_i$  is the mass of the  $i$ -atom,  $b_0$ ,  $\varphi_0$ , and  $\delta$  are reference values for bond lengths, angles, and dihedral angles, respectively, and  $k_b$ ,  $k_\varphi$ , and  $k_\vartheta$  are corresponding force constants.

Then the following approximation for eq 3 can be used

$$\mathbf{x}|_{\tau_0+\Delta\tau} \approx \exp\left(\frac{\Delta\tau}{2}\hat{L}_{H_0}\right) \exp(\Delta\tau\hat{L}_{H_r}) \exp\left(\frac{\Delta\tau}{2}\hat{L}_{H_0}\right) \mathbf{x}|_{\tau_0} \quad (7)$$

which prescribes how to propagate from one point in phase space to another. First, the system is propagated a half step evolution with  $H_0$ , then a whole step with  $H_r$ , and finally another half step with  $H_0$ . This scheme is called the generalized leap-frog.<sup>19</sup> This integration scheme was used as a basis for the development of SISM, a second order symplectic integration algorithm for MD integration.

The Hamiltonian  $H_0$  describes the internal vibrational motion of the molecules and also the translation and rotation of molecules. It represents the dynamically leading contribution whose potential depends only on constant parameters of the simulation. This separation of the potential function



**Figure 1.** The Split Integration Symplectic Method (SISM) solution procedure.

allows to calculate normal modes only once, at the beginning of the calculation. In this term is in general, included all bonding, angle bending, and torsional angle interactions within the harmonic approximation. The dynamics driven by vibrational part of  $H_0$  is resolved analytically, by means of internal normal coordinates that rotate in phase space with the corresponding vibrational frequencies which are obtained by solving the secular equation at the outset of the calculation.<sup>20–22</sup> The analytical treatment of high frequency terms in the Hamiltonian permit the SISM to employ up to an order of magnitude larger integration step size than can be used by other methods of the same order and complexity.<sup>9,23</sup>

For the model Hamiltonian used in this study it was assumed that bond stretching satisfactorily describes all internal vibrational motions for a system of linear molecules and the split parts of the Hamiltonian were of the form

$$H_0 = i.p. \left( \sum_i \frac{\mathbf{p}_i^2}{2m_i} \right) + \sum_{bonds} k_b(b - b_0)^2 + H_{tran/rot} \quad (8)$$

$$H_r = \sum_{i>j} \frac{e_i e_j}{r_{ij}} + \sum_{i>j} 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (9)$$

and  $i.p.$  refer to the internal part of kinetic energy which corresponds to molecular vibrations,  $m_i$  is the mass of the  $i$ -atom,  $b_0$  is the reference value for bond length,  $k_b$  is the corresponding force constant,  $H_{tran/rot}$  corresponds to the translational and rotational part of kinetic energy,  $i$  and  $j$  run over all atoms,  $e_i$  denotes the charge on the  $i$ -atom and  $r_{ij}$  is the distance between atoms  $i$  and  $j$ ,  $\epsilon_{ij}$  and  $\sigma_{ij}$  are the corresponding constants of Lennard-Jones potential. The difference in the potential function compared to that used in the previous work<sup>9</sup> is that there was no  $H_{tran/rot}$  term.

Figure 1 displays the SISM solution procedure for MD integration which following the procedure defined by (7) can be written explicitly as follows:

**Step 0:** Perform normal mode calculation for the vibrational part of  $H_0$  of the Hamiltonian to get frequencies and normal modes of vibration. Normal modes are represented by internal normal coordinates, hereafter denoted  $P$  and  $Q$ , obtained by means of the transformational matrix  $\mathbf{S}$ . The columns of matrix  $\mathbf{S}$  are the normal mode vectors.

**Step 1:** Propagate by vibrational part of  $H_0$  for the time  $\Delta\tau/2$ . This corresponds to the rotation of internal normal

coordinates,  ${}^V_l P_i^0$  and  ${}^V_l Q_i^0$ , in the phase space by the corresponding vibrational frequency  $\omega_i$  (superscript  $V$  denotes vibrational part,  $i$  runs over all internal normal coordinates, and  $l$  runs over all molecules of the system).

$$\begin{bmatrix} {}^V_l P_i' \\ {}^V_l Q_i' \end{bmatrix} = \begin{bmatrix} \cos\left(\omega_i \frac{\Delta\tau}{2}\right) & -\omega_i \sin\left(\omega_i \frac{\Delta\tau}{2}\right) \\ (1/\omega_i) \sin\left(\omega_i \frac{\Delta\tau}{2}\right) & \cos\left(\omega_i \frac{\Delta\tau}{2}\right) \end{bmatrix} \begin{bmatrix} {}^V_l P_i^0 \\ {}^V_l Q_i^0 \end{bmatrix} \quad (10)$$

**Step 2:** Transformation from internal normal coordinates to internal displacement coordinates.

$${}^V_l p_k' = \sqrt{m_k} \sum_i S_{ki} {}^V_l P_i' \quad (11)$$

$${}^V_l q_k' = \frac{1}{\sqrt{m_k}} \sum_i S_{ki} {}^V_l Q_i' \quad (12)$$

$k$  runs over internal displacement coordinates of all atoms in the internal coordinate system).

**Step 3:** Translate the centers of molecular masses for the time  $\Delta\tau/2$ .

$$\mathbf{r}^* = \mathbf{r}_0^* + \mathbf{v}^* \frac{\Delta\tau}{2} \quad (13)$$

$\mathbf{r}^*$  is the center of mass,  $\mathbf{v}^*$  is the velocity of the center of mass. Rotate the molecules in the internal displacement coordinate system for an angle  ${}_l\Omega^*(\Delta\tau/2)$  about the angular velocity vector  ${}_l\Omega^*$

$$\mathbf{e}^* = \mathbf{R} \left( {}_l\Omega^* \frac{\Delta\tau}{2} \right) \mathbf{e}_0^* \quad (14)$$

where  $\mathbf{R}$  is the standard rotational matrix.<sup>17</sup>

**Step 4:** Transform the internal displacement coordinates ( ${}^V_l \mathbf{p}'$ ,  ${}^V_l \mathbf{q}'$ ) to Cartesian coordinates ( $\mathbf{p}'$ ,  $\mathbf{q}'$ ) taking into account the change of the centers of molecular masses and orientation of molecules ( $\mathbf{r}^*$ ,  $\mathbf{e}^*$ ).

**Step 5:** Evolve with  $H_r$  which means only a shift of all momenta for a corresponding impulse of force (SISM requires only one force evaluation per integration step)

$$p_j'' = p_j' - \Delta\tau \left( \frac{\partial H_r}{\partial q_j} \right)_{q_j=p_j'} \quad (15)$$

$$q_j'' = q_j' + \Delta\tau \left( \frac{\partial H_r}{\partial p_j} \right)_{p_j=p_j'} = q_j' \quad (16)$$

since  $H_r = H_r(\mathbf{q})$ ,  $[(\partial H_r / \partial p_j)_{p_j=p_j'} = 0]$ , only the momentum changes at this step ( $j$  runs over all three Cartesian components of each atom).

**Step 6:** Transformation of the new Cartesian coordinates ( $\mathbf{p}''$ ,  $\mathbf{q}''$ ) to internal displacement coordinates ( ${}^V_l \mathbf{p}''$ ,  ${}^V_l \mathbf{q}''$ ) by means of inverse transformation to the transformation used at Step 4.

**Step 7:** Translate the center of molecular masses and rotate the molecules for the time  $\Delta\tau/2$  (the same as Step 3).

**Step 8:** Back transformation from internal displacement coordinates to internal normal coordinates.

$${}^V_l P_i'' = \sum_k \frac{1}{\sqrt{m_k}} S_{ki}^T {}^V_l p_k'' \quad (17)$$

$${}^V_l Q_i'' = \sum_k \sqrt{m_k} S_{ki}^T {}^V_l q_k'' \quad (18)$$

**Step 9:** Again propagate by vibrational part of  $H_0$  for the time  $\Delta\tau/2$  in the phase space.

$$\begin{bmatrix} {}^V_l P_i'' \\ {}^V_l Q_i'' \end{bmatrix} = \begin{bmatrix} \cos\left(\omega_i \frac{\Delta\tau}{2}\right) & -\omega_i \sin\left(\omega_i \frac{\Delta\tau}{2}\right) \\ (1/\omega_i) \sin\left(\omega_i \frac{\Delta\tau}{2}\right) & \cos\left(\omega_i \frac{\Delta\tau}{2}\right) \end{bmatrix} \begin{bmatrix} {}^V_l P_i' \\ {}^V_l Q_i' \end{bmatrix} \quad (19)$$

**Step 10:** Return to **Step 1** until the desired number of calculation steps is completed.

SISM proposed here differs from the technique proposed in ref 9 in that new steps 3 and 7 are introduced. They are required to properly take into account the rotation and the translation of molecules. Additional intermediate steps 4 and 6 are added since extra transformations of coordinates are necessary in this case.

The analytical treatment of high frequency terms in Hamiltonian permits the SISM proposed in eqs 10–19 to use a much larger integration step size than the standard methods of the same order and complexity. This corresponds to the result obtained in the previous work<sup>9</sup> with an important difference that the technique proposed here is extended to a system of linear molecules.

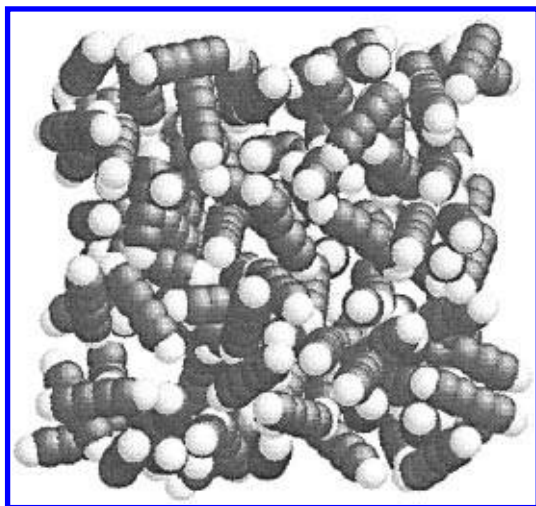
To test the efficiency of SISM it was compared to the second order LFV algorithm which is known to be symplectic and is of the same order and complexity as SISM. The Hamiltonian of the system was split to

$$H = T + V \quad (20)$$

$$T = \sum_i \frac{\mathbf{p}_i^2}{2m_i} \quad (21)$$

$$V = \sum_{bonds} k_b (b - b_0)^2 + \sum_{i>j} \frac{e_i e_j}{r_{ij}} + \sum_{i>j} 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (22)$$

where  $m_i$  is the mass of the  $i$ -atom,  $b_0$  is the reference value for bond length,  $k_b$  is the corresponding force constant,  $i$  and  $j$  run over all atoms,  $e_i$  denotes the charge on the  $i$ -atom and  $r_{ij}$  is the distance between atoms  $i$  and  $j$ , and  $\epsilon_{ij}$  and  $\sigma_{ij}$  are the corresponding constants of Lennard-Jones potential. The LFV integration method propagates coordinates and momenta



**Figure 2.** The model system of 128 H-(C≡C)<sub>2</sub>-H (butadiyne) molecules for  $\rho = 0.7364 \text{ g/cm}^3$ ,  $T = 300 \text{ K}$ , and  $L = 24.35 \text{ \AA}$  (dark are C atoms, white are H atoms).

on the basis of the equation of motion (1) by the following relations

$$q'_i = q_i + \frac{p_i}{m} \frac{\Delta\tau}{2} \quad (23)$$

$$p_{i+1} = p_i - \Delta\tau \left( \frac{\partial V}{\partial q} \right)_{q=q'_i} \quad (24)$$

$$q_{i+1} = q'_i + \frac{p_{i+1}}{m} \frac{\Delta\tau}{2} \quad (25)$$

where  $q_i$  is the coordinate,  $p_i$  is the momentum,  $\dim(p_i, q_i) = d$ ,  $d$  is the number of degrees of freedom,  $\Delta\tau$  is the time step, and  $m$  is the mass of the corresponding atom.

### 3. RESULTS

We shall illustrate the SISM described in Section 2 with two examples. As usual we use the total energy error as an

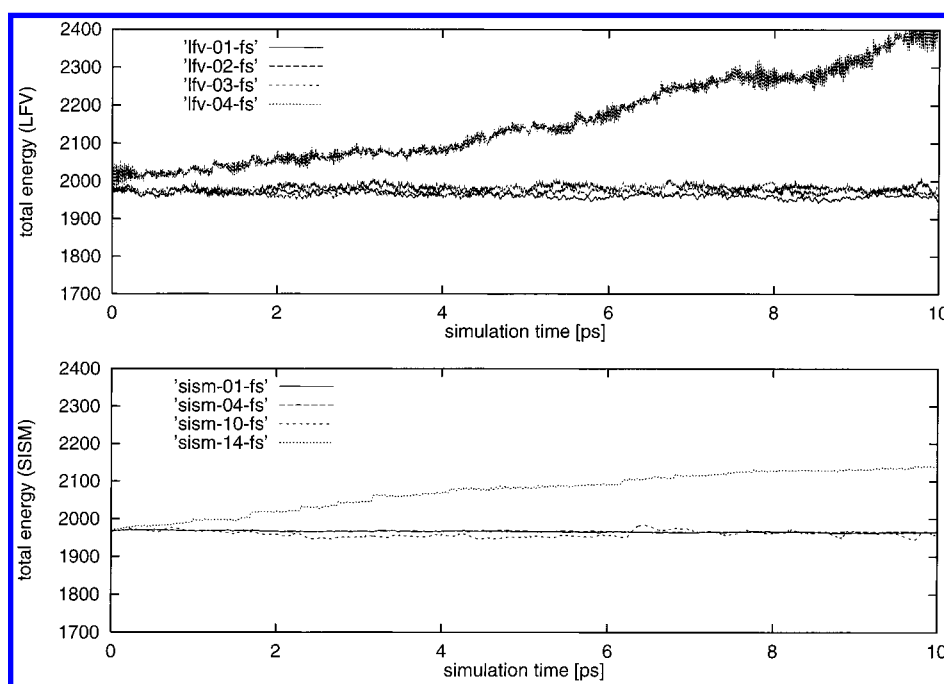
indicator of the degree to which phase space structures are preserved by the integrator. The aim of this type of calculation lays in the study of suitability of SISM for MD simulations.

The first evaluation model was composed of a system of  $N$  linear chain molecules of the form H-(C≡C)<sub>2</sub>-H, the total number of atoms in a molecule is six. The cube of the size  $L$  was chosen to give realistic merits of numeric accuracy and efficiency. The periodic boundary conditions were imposed to overcome the problem of surface effects.<sup>2</sup>

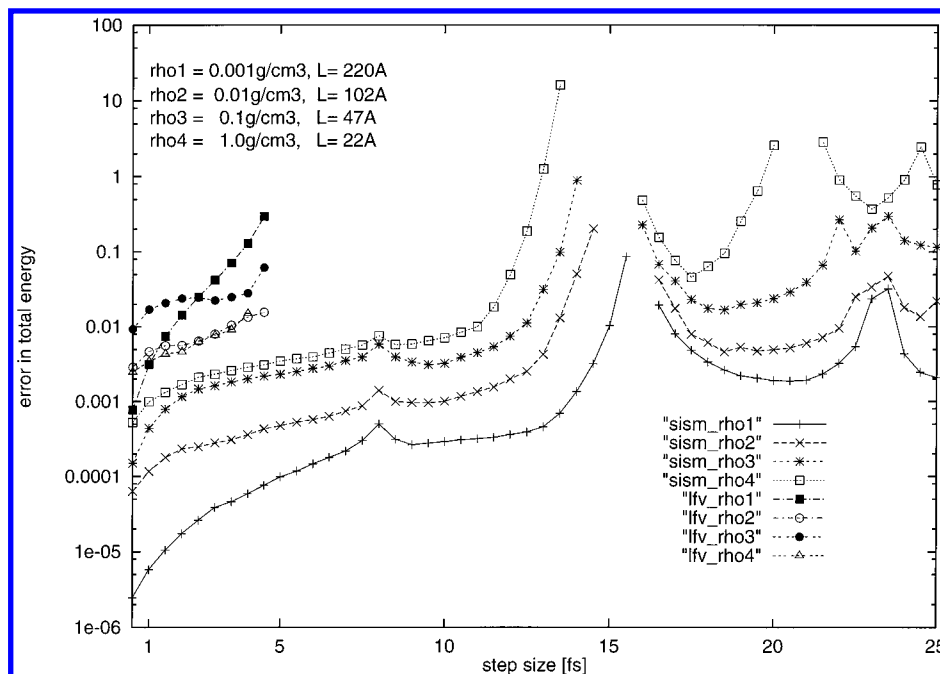
Initial conditions for coordinates and velocities of the system were obtained out of an initial MD run of randomly distributed molecules long enough to ensure Maxwell distribution of velocities according to the temperature  $T = 300 \text{ K}$ . The bond lengths and stretching constants were taken from van Gunsteren et al.<sup>24</sup> and Lennard-Jones parameters were taken from Allen et al.<sup>2</sup> Atomic charges of the linear molecules were calculated by fitting the point charges to the *ab initio* molecular electrostatic potential rather than Mulliken charges.<sup>25</sup>

Figure 2 displays the model system of 128 H-(C≡C)<sub>2</sub>-H (butadiyne) molecules; the box correspond to the experimental density of the liquid<sup>26</sup>  $\rho = 0.7364 \text{ g/cm}^3$ ,  $L = 24.35 \text{ \AA}$ , and  $T = 300 \text{ K}$ .

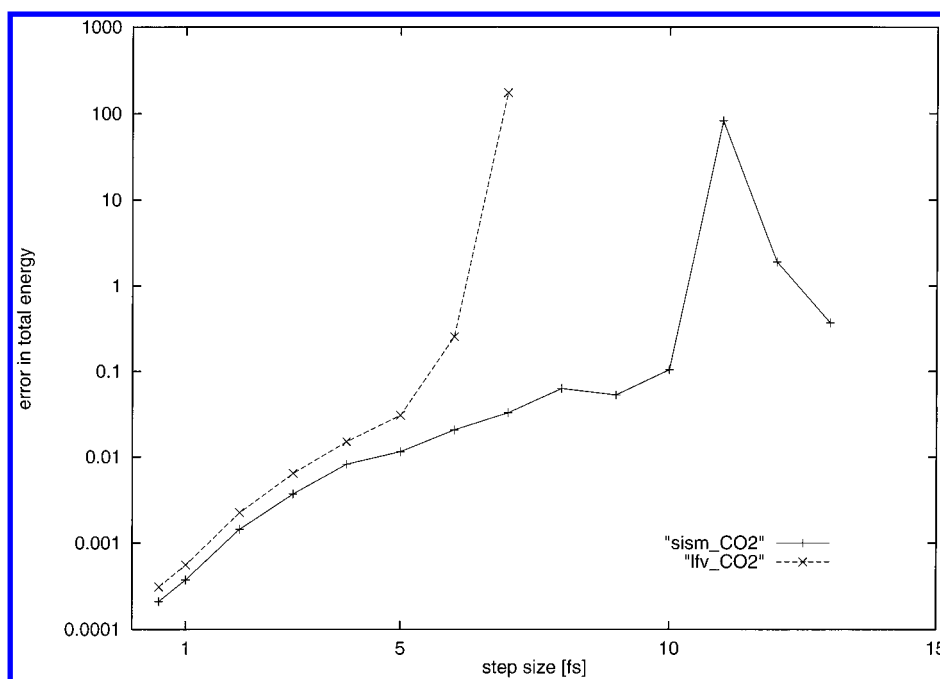
The primary metric used to quantify the accuracy of the results of a simulation is conservation of total energy. It is known that a good MD algorithm permits a large time step to be used while preserving acceptable energy conservation.<sup>2</sup> The long term stability for longer time steps is evident by the results shown in Figure 3, which depicts the time evolution of the total energy for the system of butadiyne molecules for various time steps and two different methods (LFV and SISM) for a trajectories of length of 10 ps. Using the LFV algorithm for time steps 1, 2, and 3 fs the total energy oscillates around its initial value without exhibiting growth, while for time step of 4 fs the excise growth is seen. In comparison with SISM the total energy is conserved for



**Figure 3.** The time history of the total energy for a system of 128 H-(C≡C)<sub>2</sub>-H (butadiyne) molecules obtained by leap-frog-Verlet (LFV) algorithm for time steps 1 fs, 2 fs, 3 fs, 4 fs, and Split Integration Symplectic Method (SISM) for time steps 1 fs, 4 fs, 10 fs, 14 fs for a trajectories of length of 10 ps.



**Figure 4.** Error in total energy for leap-frog-Verlet (LFV) algorithm and the Split Integration Symplectic Method (SISM) of a system of 128 H-(C≡C)<sub>2</sub>-H (butadiyne) molecules. Results are plotted for two different algorithms (LFV and SISM) and for four different system densities ( $\rho = 1.0, 0.1, 0.01, 0.001 \text{ g/cm}^3$ , corresponding to box size  $L = 22, 47, 102, 220 \text{ Å}$ ).



**Figure 5.** Error in total energy for leap-frog-Verlet (LFV) algorithm and Split Integration Symplectic Method (SISM) for a system of 40 flexible CO<sub>2</sub> molecules in a cubic box of  $L = 20 \text{ Å}$ . Results are plotted for two different algorithms (LFV and SISM).

time steps 1, 4, and 10 fs and no longer for the time step of 14 fs.

In order to compare the efficiency of the SISM with the standard LFV method, we compared computational performance for the same level of accuracy. To study the error accumulation and numerical stability we monitored the error in total energy,  $\Delta E$ , defined as

$$\Delta E = \frac{1}{M} \sum_{i=1}^M \left| \frac{E_0 - E_i}{E_0} \right| \quad (26)$$

where  $E_i$  is the total energy at step  $i$ ,  $E_0$  is the initial energy, and  $M$  is the total number of time steps.

The results of the errors in total energy for test molecules, a system of linear butadiyne molecules, for four different system densities ( $\rho = 1.0, 0.1, 0.01, 0.001 \text{ g/cm}^3$ , corresponding to box size  $L = 22, 47, 102, 220 \text{ Å}$ ) using two different methods (LFV and SISM) are presented on Figure 4. It can be seen that for the same level of accuracy, the time step in SISM can be up to an order of magnitude larger as in LFV. Also, LFV is stable for only very short time steps, up to 4 fs, while SISM is stable for much longer time steps, even for time steps larger than 25 fs. It should be noted that such large time steps no longer represent physical reality and are identified with linear molecules possessing no angle bending or torsional interactions. There are large

**Table 1.** CPU Time [s] for 1000 MD Steps of Box of  $\text{H}-(\text{C}\equiv\text{C})_2-\text{H}$  Molecules Using the Leap-Frog-Verlet (LFV) and the Split Integration Symplectic Method (SISM) for Equal Time Steps Computed on an HP C160 Workstation

no. of molecules	128	256
LFV	171.30	686.02
SISM	174.66	688.75

variations in total energy which might be due to the so called "step size resonances".<sup>27,28</sup> This phenomenon is due to the symplectic methods which seem to introduce artificial coupling among the motions associated with various frequencies leading to instability.<sup>29</sup>

In Table 1 the CPU time required by the two methods (LFV and SISM) for 1000 MD integration steps computed on an HP C160 workstation are compared for the same model system, a box of 128 and 256 butadiyne molecules, respectively. The computation cost per integration step is approximately the same for both methods so that the speed up of the SISM over the LFV algorithm is determined mainly by the difference in step size which is significant. Qualitatively the same result was obtained in the previous work<sup>9</sup> except that the CPU time performances for the calculation of an MD step are worse since there an isolated molecule was taken into account, while in the present work the system of interest is consisted of 128 and 256 molecules, respectively.

It can be seen that SISM can use much larger integration time step comparing to LFV for MD simulations of systems which have some particles which are significantly lighter than the others (e.g., hydrogen atoms). The method performs excellent when there is a great disparity in particle masses.

To study a system consisted of particles of similar masses with SISM the MD simulation of a model system of flexible  $\text{CO}_2$  molecules was performed. The model potential for this system was taken from ref 30. We performed the MD simulation of 40 flexible  $\text{CO}_2$  molecules in a cubic box of size  $L = 20 \text{ \AA}$  only to report the comparison with the SISM calculations. Results plotted on Figure 5 show that for this model system of  $\text{CO}_2$ , for the same level of accuracy, the time step in SISM can be approximately two times larger as in LFV algorithm. Again, a speed up of SISM over LFV, which is determined by the difference in step size, is gained even if it is not as significant as in the case of MD simulation of a system of butadiyne molecules.

## 5. CONCLUSIONS

The present work consists of the design and analysis of an explicit Split Integration Symplectic Method (SISM) for molecular dynamics (MD) simulations which uses an analytical treatment of high frequency motions within a second order generalized leap-frog scheme. SISM is up to an order of magnitude faster than the commonly used leap-frog-Verlet algorithm which is of the same order and complexity as SISM. The main restriction on step size in the general MD simulations, which stems from the high-frequency motion, is, to a large extent, overcome in this approach.

Much work remains to be done in the development of this approach to explore the advantages and limitations of the method. The method will be extended to force fields that include angle bending and torsional terms; large systems such as biological macromolecules will also be treated. The

application of SISM to MD simulation of liquid water is under way to explore this intriguing observations.

Further improvements in efficiency were achieved by implementing the method on computers with highly parallel architecture.<sup>31</sup>

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