# Computer simulation of solid C<sub>60</sub> using multiple time-step algorithms

Piero Procacci<sup>a)</sup> and B. J. Berne

Department of Chemistry, Columbia University, New York, New York 10027

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The reversible reference system propagator algorithm (*r*-RESPA), based on a Trotter factorization of the classical propagator, is tested in a molecular dynamics simulation of solid  $C_{60}$ . We show how, with an appropriate subdivision of the interaction potential and with a careful balancing of the integration parameters, one can adopt large time steps and impressively efficient *r*-RESPA integrators which yield the same dynamics obtained by means of the small time-step Verlet algorithm. The results presented here show that the use of *r*-RESPA integrators speeds up the simulation by a factor of between 20–40 with respect to the standard Verlet algorithms.

## I. INTRODUCTION

Molecular dynamics (MD) simulations of molecular systems based on the numerical integration of Newton's equations of motion are routinely used to elucidate the structural and dynamical behavior of condensed phases at the microscopic level. Molecular systems, however, are often characterized by having stiff intramolecular degrees of freedom (e.g., high-frequency intramolecular motions) evolving under the action of forces that can be decomposed into rapidly varying intramolecular forces and soft or slow intermolecular forces so that numerical stability in the stepwise integration of the equations of motion can be achieved only by imposing very short time steps. In standard methods, the intermolecular forces are computed after each of the short time steps, and a very large number of time steps must be generated to follow the motion of the whole system. A case in point is that of a crystal of fullerene molecules, C<sub>60</sub>. The intramolecular vibrations are very stiff (300-1600 cm<sup>-1</sup>) compared to the intermolecular vibrations  $(20-50 \text{ cm}^{-1})$  and librations  $(10-30 \text{ cm}^{-1})$ . It is of considerable interest to simulate the lattice dynamics of this system including intramolecular motion, but until recently such simulations have been impractical. Using standard integrators it would take several CPU weeks on a fast IBM/Risc 6000-370 workstation to determine the IR and Raman spectra of the crystal for a given thermodynamic state even for a crystal of only 32 flexible C<sub>60</sub> molecules.

Recently Tuckerman *et al.*<sup>1</sup> have devised a reversible and symplectic integration scheme, the reversible reference system propagator algorithm (*r*-RESPA), which makes it possible to efficiently treat the separation of time scales inherent in the motion of molecular assembles. The *r*-RESPA algorithm has been applied to a variety of systems<sup>2,3</sup> where there is a clear separation between "fast" and "slow" dynamics and to systems where the force can be further subvided into long- and short-range components.<sup>4</sup> Application of the *r*-RESPA propagator to simulations of flexible molecules have already started to emerge.<sup>5,6</sup> In a paper contemporaneous with this paper, Humphreys *et al.*<sup>6</sup> have successfully applied *r*-RESPA to the simulation of the small protein, Crambin, including in the model all atoms and all bond-stretching, bond-bending, and torsion-angle degrees of freedom. The speedups reported are completely consistent with those reported here. The *r*-RESPA method has also been applied to *ab initio* molecular dynamics using the Carr–Parrinello and generalized valence bond (GVB) scheme.<sup>7</sup>

In the present paper we apply *r*-RESPA to the simulation of the solid phase of flexible  $C_{60}$ . Experimental studies of intramolecular dynamics in solid  $C_{60}$  using high-resolution Fourier transform infrared (FTIR) techniques,<sup>8–10</sup> reveal complex details of the absorption pattern showing strong solid state effects on the internal motions of the  $C_{60}$  cage. Molecular dynamics simulations<sup>11–13</sup> of rigid  $C_{60}$  molecules based on simple interaction potentials, have successfully predicted the structural properties of the solid phase of  $C_{60}$  but, due to the assumed rigidity of  $C_{60}$  molecule, these simulations obviously cannot give information about crystal field effects on intramolecular dynamics. The new *r*-RESPA integrator enables us to simulate a crystal of flexible  $C_{60}$  molecules using accurate intramolecular<sup>14–16</sup> and intermolecular potentials<sup>12</sup> on a time scale of 12 CPU hours rather than the several CPU weeks required by the standard integrators.

In previous applications of r-RESPA, the dynamical variables of interest were calculated only after each large time step. Autocorrelation functions and averages of these dynamical variables were thus determined using only the large time-step data. For the case of solid fullerene at low temperature we show here that r-RESPA allows to use time steps as large as 25 fs. The largest frequency resolvable corresponding to the time step  $\Delta t = 25$  fs is approximately 800  $cm^{-1}$ . Given the frequency range of the intramolecular vibrations  $(300-1600 \text{ cm}^{-1})$  in C<sub>60</sub>, this means that the recording of dynamical variables must be done much more often than each large time step. In this paper, we show that even the values of the dynamical properties determined after each small time step can be used to accurately determine the autocorrelation functions and energy records. In fact, comparisons between r-RESPA using the small time-step data and pure velocity Verlet with a very small time step show that the

<sup>&</sup>lt;sup>a)</sup>Permanent address: Laboratorio di Spettroscopia Molecolare, Dipartimento di Chimica, Universita' di Firenze, 50121 Firenze, Italy.

IR and raman spectra, as well as the intramolecular energy record, give almost identical results.

The solid fullerene system is ideally suited to the application of *r*-RESPA. The time scale for the intramolecular motion is separated from the time scale of the librations and translations by a large gap. The highest intermolecular vibrational frequency is about eight times larger than the lowest intramolecular vibration. Moreover the long-range behavior of the intermolecular interaction potential allows a further separation of the slow intermolecular dynamics into shortand long-range forces.

In the present paper we demonstrate the power of the r-RESPA integrator scheme in the simulation of molecular systems comparing its performances with the standard single step integrators. Extensive numerical tests have been performed for the case of solid  $C_{60}$  at low and high temperature, and the resulting speedup for a triple time-step r-RESPA scheme with respect to a simple velocity Verlet integrator has been found to be of the order of 20-40. Our results show how the use of multiple time-step r-RESPA algorithms, based on an appropriate choice of the interaction potential subdivision, opens the way for computer simulations of systems of great complexity, hitherto beyond the reach of single time-step standard molecular dynamics. In a subsequent publication, the multiple time-step methodology discussed here is applied to study the effect of the crystal field on the intramolecular dynamics both in the low-temperature ordered phase and in the high-temperature orientationally disordered phase of solid C<sub>60</sub>.

This article is organized as follows: In Sec. II we present a brief review of the *r*-RESPA integration method focusing on its application to the dynamics of flexible molecules. In Sec. III we discuss the application of the *r*-RESPA scheme specifically to the solid phase of flexible  $C_{60}$  molecules, illustrating the use of a triple time-step integrator, based on the subdivision of the interaction potential into intramolecular and short- and long-ranged intermolecular contributions. The potential breakup is compared to previous approaches using a force breakup. In Sec. IV we present numerical tests performed on a periodic sample of 32 molecules, aimed at assessing the numerical accuracy and computational efficiency of the *r*-RESPA integrator for different choices of integration parameters.

A detailed study of the solid state spectra from detailed simulations of completely flexible  $C_{60}$  molecules in the solid state at different temperatures is presented in the accompanying paper.<sup>17</sup>

## **II. THEORY**

The classical propagator is defined as

$$U(t) = e^{iLt}. (2.1)$$

L is the Liouville operator for a system of N particles in Cartesian coordinates, and is defined as

$$iL = \{\dots, H\} = \sum_{i=1,n} \left[ \dot{x}_i \frac{\partial}{\partial x_i} - \frac{\partial V(\mathbf{x})}{\partial x_i} \frac{\partial}{\partial p_i} \right], \quad (2.2)$$

where  $\{x_i, p_i\}$  denote the positions and conjugate momenta of the N particles and  $V(\mathbf{x})$ , the interaction potential, depends only on the 3N-dimensional coordinate vector  $\mathbf{x}$ . If the system contains stiff degrees of freedom driven by a shortranged intramolecular potential, the potential function  $V(\mathbf{x})$ can be subdivided into

$$V(\mathbf{x}) = V_I(\mathbf{x}) + V_M(\mathbf{x}), \qquad (2.3)$$

where  $V_I(\mathbf{x})$  and  $V_M(\mathbf{x})$  are the intra- and intermolecular potentials, respectively. The intermolecular potential  $V_M$ , in the present treatment, is assumed to be a superposition of spherical atom-atom two-body interactions of the form  $V(r_{ij})$ , where  $r_{ij}$  denotes the distance between the two interacting atoms belonging to two different molecules. Each two-body atom-atom potential term, V(r), is further subdivided by arbitrarily subdividing the distance r into m subsegments of length  $r_1, r_2 - r_1, \dots, r_k - r_{k-1}$ , such that

$$V(r) = S_{1}(r)V(r) + [S_{2}(r) - S_{1}(r)]V(r) + \dots + [S_{k}(r) - S_{k-1}(r)]V(r) + \dots + [1 - S_{m-1}]V(r)$$
$$= \sum_{k=1}^{m} [S_{k}(r) - S_{k-1}(r)]V(r). \qquad (2.4)$$

The switching functions  $S_k(r)$  are defined as

$$S_0(r) \equiv 0, \quad S_m(r) \equiv 1,$$
 (2.5)

and

$$S_{k}(r) = \begin{cases} 1, & 0 \leq r < r_{k} - \lambda_{k} \\ 1 + R^{2}(2R - 3), & r_{k} - \lambda_{k} \leq r < r_{k} \\ 0, & r_{k} \leq r \end{cases}$$
(2.6)

with  $R = [r - (r_k - \lambda_k)]/\lambda$ ,  $r_0 = 0$ , and  $r_m = \infty$ . The analytical form of the switching function (in our case taken to be the Watanabe and Reinhardt function<sup>18</sup>) is arbitrary, the only requirement is that it and its first derivative is continuous. The continuity of the first derivative implies that  $S'_k$  is zero at  $r_k$ and  $r_k - \lambda_k$ . Using Eqs. (2.3) and (2.4), the total potential function can be written as

$$V(\mathbf{x}) = V_{l}(\mathbf{x}) + \sum_{k=1}^{m} V_{k}(\mathbf{x}), \qquad (2.7)$$

where in the kth intermolecular term,

$$V_{k}(\mathbf{x}) = \sum_{i < j} \left[ S_{k}(r_{ij}) - S_{k-1}(r_{ij}) \right] V(r_{ij}), \qquad (2.8)$$

only the pairwise interactions with  $r_{k-1} < r \le r_k$  yield a nonzero contribution. Given the subdivision, Eq. (2.7), we now write down the Liouville operator in the form

$$iL = iG_{m-1} + iL_m \tag{2.9}$$

with

and

$$iG_{m-1} = \sum_{i=1}^{N} \left[ \dot{x}_i \frac{\partial}{\partial x_i} - \frac{\partial V_I}{\partial x_i} \frac{\partial}{\partial p_i} - \sum_{k=1}^{m-1} \frac{\partial V_k}{\partial x_i} \frac{\partial}{\partial p_i} \right] \quad (2.10)$$

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$$L_m = -\sum_{i=1}^{N} \frac{\partial V_m}{\partial x_i} \frac{\partial}{\partial p_i}.$$
 (2.11)

According to the Trotter theorem,  $^{19,20}$  the associated propagator for this subdivision of the Liouvillian, Eq. (2.9), can be written as

$$e^{iLt} = [e^{iL_m \Delta t_m/2} e^{G_{m-1} \Delta t_m} e^{iL_m \Delta t_m/2}]^{P_m} + O(\Delta t_m^3),$$
(2.12)

where  $\Delta t_m = t/P_m$  is a discretization for  $\exp(iL_m t)$ , the external propagator, involving the slowly varying long-range pairwise interactions. The middle propagator generates the (faster) dynamics of the so-called "reference system" of order (m-1). During the time  $\Delta t_m$ , the (m-1)th reference system evolves freely with respect to the  $L_m$  propagator, i.e., without experiencing the force due to the interactions at interatomic distance within the outermost shell  $r_m \leq \infty$ . The above procedure differs from previous applications of *r*-RESPA in that here the potential function rather than the force is subdivided into short- and long-range components, as shown in Eq. (2.4).

It is important to note the similarities and differences of the potential breakup and the force breakup.

(a) Both breakups give reversible and symplectic integrators.

(b) Both breakups equally conserve the energy after each complete propagation step.

(c) Each breakup has its own constant of the motion for the intermediate time steps  $\Delta t_k$ . The energy  $KE + V_k$  is conserved during the short time steps of the potential breakup whereas the energy  $KE + V_k^*$  is conserved during the short time steps of the force breakup where  $V_k^*$  is so defined that  $F_k = -\nabla V_k^*$ . Thus to determine the latter constant of the motion one has to solve a differential equation.

Of course the the two breakups give equally accurate and stable integrators; nevertheless, if the conservation of the energy KE+V is used as a measure of the accuracy during the short time steps it might appear that the force breakup is less accurate than the potential breakup. This would be an erroneous conclusion. Anticipating the results of Sec. IV, numerical tests clearly demonstrate that equilibrium thermodynamic properties and dynamical properties, such as power spectra and correlation functions, do not depend appreciably on the switching method used.

We now proceed with the expansion of the middle propagator of Eq. (2.12) depending on the "faster" Liouvillian  $G_{m-1}$ :

$$e^{iG_{m-1}\Delta t_m} = e^{i(L_{m-1} + G_{m-2})\Delta t_m},$$
(2.13)

where

$$iG_{m-2} = \sum_{i=1}^{N} \left[ \dot{x}_i \frac{\partial}{\partial x_i} - \frac{\partial V_i}{\partial x_i} \frac{\partial}{\partial p_i} - \sum_{k=1}^{m-2} \frac{\partial V_k}{\partial x_i} \frac{\partial}{\partial p_i} \right] \quad (2.14)$$

and

$$L_{m-1} = -\sum_{i=1,n} \frac{\partial V_{m-1}}{\partial x_i} \frac{\partial}{\partial p_i}.$$
 (2.15)

Again applying the Trotter factorization to the right-hand side of Eq. (2.13) gives

$$e^{i(L_{m-1}+G_{m-2})\Delta t_{m}}$$
  
=  $[e^{iL_{m-1}\Delta t_{m-1}/2}e^{iG_{m-2}\Delta t_{m-1}}e^{iL_{m-1}\Delta t_{m-1}/2}]^{P_{m-1}}$   
+  $O(\Delta t_{m-1}^{3}).$  (2.16)

This approximate propagator has the same structure as the one in Eq. (2.12) with the time step associated with the operator in Eq. (2.15),

$$\Delta t_{m-1} = \frac{t_m}{P_{m-1}} = \frac{t}{P_m P_{m-1}} \,. \tag{2.17}$$

Inserting Eq. (2.16) into Eq. (2.12) yields

$$e^{iLt} = [e^{iL_m(\Delta t_m/2)} \\ \times [e^{iL_{m-1}(\Delta t_{m-1}/2)}e^{iG_{m-2}\Delta t_{m-1}}e^{iL_{m-1}(\Delta t_{m-1}/2)}]^{P_{m-1}} \\ \times e^{iL_m(\Delta t_m/2)}]^{P_m} + O(\Delta t_m^3) + O(\Delta t_{m-1}^3).$$
(2.18)

It is clear that such a procedure can be repeatedly applied until one exhausts all of the m terms of the intermolecular potential in the summation of Eq. (2.7). In order to remove all the excess baggage from the formalism we now define the following propagators:

$$f_k \equiv e^{iL_k \Delta t_k/2}, \quad g_{k-1} \equiv e^{iG_{k-1} \Delta t_k},$$
 (2.19)

where the kth time step is given by

$$\Delta t_k = \frac{t \prod_{j=0}^k P_j}{\prod_{j=0}^m P_j} \,. \tag{2.20}$$

Using the definitions [Eq. (2.19)] and repeatedly expanding the  $g_k$  propagator as in Eq. (2.13) one obtains

$$e^{iLt} = [f_m [f_{(m-1)...} [... [f_1 g_0 f_1]^{P_1}...]^{P_{m-k}}$$
$$...f_{(m-1)}]^{P_{m-1}} f_m]^{P_m} + \sum_{k=1}^m O(\Delta t_k^3)$$
(2.21)

with

$$g_0 = e^{iG_0 \Delta t_1} = \exp\left[\sum_{i=1}^N \dot{x}_i \frac{\partial}{\partial x_i} - \frac{\partial V_I}{\partial x_i} \frac{\partial}{\partial p_i}\right].$$
 (2.22)

The error in the above factorization is still of order  $O(\Delta t^3)$ as in the Verlet integrator. The choice of the constants  $\lambda_k$  and  $r_k$  in the switching functions, Eq. (2.6), together with the selection of the integers  $P_k$  must be tuned such that all the terms in the error summation  $\sum_k O(\Delta t_k^3)$  in Eq. (2.21) are approximately of the same order of magnitude. The  $g_0$ propagator [Eq. (2.22)] contains only the intramolecular potential and corresponds to the zeroth order reference system (the intramolecular reference system). Again using the Trotter formula, the intramolecular propagator  $g_0$  of Eq. (2.22) can be written as 2424

$$g_{0} = \left\{ \exp\left[\frac{\Delta t_{0}}{2} \sum_{i=1}^{n} \frac{\partial V_{I}}{\partial x_{i}} \frac{\partial}{\partial p_{i}}\right] \exp\left[\Delta t_{0} \sum_{i=1}^{n} \dot{x}_{i} \frac{\partial}{\partial x_{i}}\right] \\ \times \exp\left[\frac{\Delta t_{0}}{2} \sum_{i=1}^{n} \frac{\partial V_{I}}{\partial x_{i}} \frac{\partial}{\partial p_{i}}\right] \right\}^{P_{0}} + O(\Delta t_{0}^{3}), \quad (2.23)$$

where  $\Delta t_0 = t/\prod_{i=0}^m P_i$  [see Eq. (2.20)] is the shortest time step for the intramolecular dynamics. As shown in Ref. 1, the above factorization leads to the velocity Verlet integrator. Substitution of Eq. (2.23) into Eq. (2.20) yields the final propagator for an arbitrary subdivision of the intermolecular potential into m components. Of course, the intramolecular potential can be further subdivided into stretching, bending, and torsional components. Generally, however, the expensive task in the simulation of a molecular system is the force loop involving the intermolecular interactions (or nonbonded interactions for protein dynamics), so that a breakup of the intramolecular potential does not lead to an appreciable saving of CPU time. The time-advancing recipes for the propagator [Eq. (2.21)], with  $g_0$  factorized as in Eq. (2.23), can be trivially obtained by using the property of the exponential operators,  $\exp(a\partial/\partial x)f(x) = f(x+a)$ , in Eq. (2.21) and by applying these to the initial state  $\{\mathbf{x}(0), \mathbf{p}(0)\}$  at t=0.<sup>1</sup> The implementation of the resulting integration algorithm on a computer is straightforward. In the Appendix we give an example of FORTRAN code for a four time-step integrator for a molecular system. The great advantage of the method lies in the fact that the most expensive force routines, involving the larger number of pairwise interactions in the external shells, are those which are called less often during the simulation. Moreover during the execution of, say, the kth force routine, at virtually no cost, a neighbor list for the next (k-1)th force routine can be constructed. As we shall see, for the specific case of solid fullerene, this method allows dramatic savings in CPU time.

# III. APPLICATION OF r-RESPA TO SOLID C60

C<sub>60</sub>, a cage-like molecule with icosahedral symmetry, has stimulated an impressive number of experimental and theoretical interest since its discovery<sup>21</sup> and synthesis.<sup>22</sup> At least two crystalline phases are known from x-ray scattering: a low-temperature orientationally ordered phase with cubic symmetry and a high-temperature orientationally disordered plastic phase, also belonging to the cubic system.<sup>23-25</sup> The intramolecular potential for C<sub>60</sub> used in the present study is a slightly modified version of a previous force field.<sup>14</sup> The force field has been refit to the experimental frequencies of the isolated molecule<sup>22</sup> by excluding the three  $1-\hat{4}$  stretching constants as was done in the modeling of  $C_{70}$ .<sup>26</sup> The resulting intramolecular potential is a superposition of harmonic terms depending on a total of six parameters: two stretching force constants for the bonded atoms, two 1-3 stretching force constants for the nonbonded atom (meta position), and two bending force constants. We adopt the intermolecular potential function of Sprik et al.<sup>12</sup> This potential consists of a superposition of Lennard-Jones interactions with atom-atom centers placed on the carbon atoms and additional interaction sites placed midway along the "short bonds" (for a total of 90 interaction centers per molecule), plus an electrostatic term modeled by point charges placed on the same centers. In the present study the electrostatic term has been omitted since, as will be exhaustively discussed in a forthcoming paper,<sup>17</sup> its contribution to the dynamical and structural properties is negligible. The potential subdivision adopted in the present study of solid C<sub>60</sub> is therefore given by Eq. (2.3) in which the intermolecular potential  $V_M$  is subdivided into only two parts [m=2 in Eq. (2.7)] such that

$$V_{M}(r) = S(r)V(r) + [1 - S(r)]V(r) = V_{1}(r) + V_{2}(r).$$
(3.1)

The optimum choice of intermolecular potential breakup in Eq. (2.4) (i.e., of the integer m), depends on the analytical form of the intermolecular potential itself and on the density and size of the sample.<sup>4</sup> To the best of our knowledge, a multiple subdivision (m>2) has not yet been implemented in computer simulations of a molecular system. For maximum efficiency, this technique requires careful memory and data flow management when dealing with the neighbor lists and poses several subtle programming problems due to the extensive use of indirect addressing.

For  $C_{60}$ , we have adopted a simple short/long-range subdivision of the intermolecular potential (m=2) because the size of the sample is relatively small (32 molecules) and the intermolecular potential decays quickly as  $r \rightarrow \infty$ . Nevertheless, such a simple subdivision enables us to obtain remarkable computational efficiency. The computer time required for evaluating the intramolecular contribution force field for  $C_{60}$  is practically insignificant compared to the time needed for computing the intermolecular contribution. Therefore, in our *r*-RESPA implementation for  $C_{60}$  we choose not to break up the intramolecular potential.

According to Eqs. (2.20) to (2.23), the *r*-RESPA propagator associated with the subdivision given in Eq. (3.1) is a triple time-step integrator with  $\Delta t_2 = t/P_2$ ,  $\Delta t_1 = t/(P_2P_1)$ , and  $\Delta t_0 = t/(P_2P_1P_0)$ , satisfying the relations

$$\Delta t_2 = P_1 \Delta t_1; \quad \Delta t_1 = P_0 \Delta t_0. \tag{3.2}$$

The best choice of  $\Delta t_0$ ,  $\Delta t_1$ , and  $\Delta t_2$  must be such that the resulting multiple time-step integrator fulfills both the requirements of computational efficiency and numerical stability. Computational efficiency will be measured in CPU time per ps of simulation, whereas numerical stability will be quantified by R, the ratio of the standard deviation of the total energy to the standard deviation of the kinetic energy, i.e.,

$$R = \left(\frac{\sum_{i} (E_{i}^{\text{Tot}} - \langle E^{\text{Tot}} \rangle)^{2}}{\sum_{i} (E_{t}^{\text{Kin}} - \langle E^{\text{Kin}} \rangle)^{2}}\right)^{(1/2)}.$$
(3.3)

## **IV. NUMERICAL RESULTS**

All the tests reported in the tables and figures referred to in this section were performed at the temperature T=10 K for a system containing 32 molecules with cubic periodic

TABLE I. Numerical tests for the *r*-RESPA and Verlet integrators. The tests were carried out for 1 ps with a sample of 32 molecules at 10 K.  $\Delta t_0$ , the time step for the intramolecular reference system, is expressed in fs,  $P_0$ ,  $P_1$  are integers [see Eq. (3.3)] (for the velocity Verlet  $P_0 = P_1 = 1$ ), *R* is the dimensionless ratio defined in Eq. (3.4), *t*(CPU) is the CPU time in seconds per ps of simulation, measured on a RISC6000/370 workstation,  $\langle K \rangle$  is the average kinetic energy in KJ/mol, and  $r_1$  is the break-up distance (in units of  $\sigma$ ) for the intermolecular potential.

$\Delta t_0$	P <sub>0</sub>	<i>P</i> <sub>1</sub>	R	t(CPU)	$\langle K \rangle$	<i>r</i> <sub>1</sub>
0.25	1	1	0.0012	7.47×10 <sup>5</sup>	8.568	
0.50	1	1	0.0047	$3.70 \times 10^{5}$	8.554	
1.00	1	1	0.0192	$1.85 \times 10^{5}$	8.498	•••
2.00	1	1	0.0802	0.92×10 <sup>5</sup>	8.275	
3.00	1	1	0.1710	$0.62 \times 10^{5}$	7.904	•••
4.00	1	1	0.2645	$0.46 \times 10^{5}$	7.380	•••
0.25	2	1	0.0012	3.73×10 <sup>5</sup>	8.568	
0.25	4	1	0.0012	$1.88 \times 10^{5}$	8.568	•••
0.25	6	1	0.0015	$1.26 \times 10^{5}$	8.568	•••
0.25	8	1	0.0022	0.95×10 <sup>5</sup>	8.568	•••
0.25	10	1	0.0032	$0.75 \times 10^{5}$	8.568	
0.25	8	2	0.0027	$0.54 \times 10^{5}$	8.568	1.80
0.25	8	4	0.0047	$0.31 \times 10^{5}$	8.568	2.00
0.25	8	6	0.0065	$0.25 \times 10^{5}$	8.569	2.20
0.25	8	8	0.0058	0.23×10 <sup>5</sup>	8.569	2.40
0.25	8	10	0.0052	$0.23 \times 10^{5}$	8.569	2.55
0.25	8	12	0.0089	$0.24 \times 10^{5}$	8.572	2.70
0.25	10	2	0.0036	0.43×10 <sup>5</sup>	8.568	1.80
0.25	10	4	0.0062	$0.25 \times 10^{5}$	8.567	2.00
0.25	10	6	0.0084	0.20×10 <sup>5</sup>	8.567	2.20
0.25	10	8	0.0088	0.19×10 <sup>5</sup>	8.565	2.40
0.25	10	10	0.0082	$0.19 \times 10^{5}$	8.564	2.55
0.25	10	12	0.0089	0.20×10 <sup>5</sup>	8.572	2.70

boundary conditions using an IBM RISC/370 workstation. At this temperature, the  $C_{60}$  crystal is in the (orientationally) ordered cubic phase. The simulation was carried out in the microcanonical ensemble on a cubic primary cell of edge 13.99 Å, a size chosen to be equal to the average cell size found in a previous constant pressure MD simulation<sup>12</sup> of a sample of the same size and temperature. Here, as in Sprik's simulation,<sup>12</sup> no cutoff was imposed so that each molecule interacts with all of the minimum images. The distance  $r_1$  at which the intermolecular potential breakup is performed was varied form 1.8 $\sigma$  to 2.55 $\sigma$  and the healing length  $\lambda_1 = 0.15\sigma$ in all cases. As already pointed out in Ref. 4, the choice of the short-range cutoff  $r_1$  is the result of a compromise: the greater the distance  $r_1$  the larger the number of time steps  $P_1$ needed to guarantee that there will be no degradation of the numerical accuracy of the time integration. This has the consequence that the expensive calculation of all interatomic distances in the simulation box need be performed less often. On the other hand, the choice of large  $r_1$  requires the computation of a large number of "short-ranged" interactions for which the forces must be frequently recomputed.

The detailed results of several numerical tests for various values of the integers  $P_1$  and  $P_0$ , the zeroth order reference system time step  $\Delta t_0$ , and the intermolecular break-up distance  $r_1$  are reported in Table I for a total simulation time of I ps. The pure velocity Verlet has only one time step that can be varied and hence  $P_0 = P_1 = 1$ . When  $P_0 \neq 1$  and  $P_1 = 1$  the breakup of the potential is achieved by subdividing the potential into intramolecular and intermolecular contribu-



FIG. 1. (a) Energy conservation ratio R vs overall time step for Verlet (solid line), double time-step *r*-RESPA (dotted line), and triple time-step *r*-RESPA (dashed lines) (see the text). The horizontal line at  $\log(R) = -2.30$  denotes the threshold tolerance for the energy conservation ratio R. (b) Speedup ratio of *r*-RESPA over the velocity Verlet integrator (see the text).

tions and the corresponding algorithm uses only two time steps  $\Delta t_0$ ,  $P_0 \Delta t_0$  (this is called the double time-step regime). Finally, when both  $P_0 \neq 1$  and  $P_1 \neq 1$ , the intermolecular potential is further subdivided into long- and short-range contributions and there are hence three time steps  $\Delta t_0$ ,  $P_0 \Delta t_0$ ,  $P_0 P_1 \Delta t_0$  (this is called the triple time-step regime).

It is of interest to compare the numerical stability R, defined in Eq. (3.3), for the different integrators. For r-RESPA, the ratio R was computed from the record of the total and kinetic energy at the end of each short time step  $\Delta t_1$ . The pure velocity Verlet integrator (i.e.,  $P_0 = P_1 = 1$ ) gives a value R = 0.005 for  $\Delta t = 0.5$  fs and a value of R = 0.0192 for  $\Delta t = 1.0$  fs, whereas all of the various parametrizations of r-RESPA reported in Table I have low values of R, even for large integer values of  $P_0$  and  $P_1$ .

An overall comparison between the the *r*-RESPA and velocity Verlet methods, based on the data of Table I, is shown in Figs. 1(a) and 1(b), where the numerical accuracy R, defined in Eq. (3.3), and the ratio of the computational efficiency in CPU ps of *r*-RESPA to velocity Verlet ( $\Delta t = 0.5$  fs) are, respectively, plotted as a function of the largest time step  $P_0P_1\Delta t_0$ . The solid line in Fig. 1(a) refers to the pure velocity Verlet integrator, as a function of time step  $\Delta t$ . The

TABLE II. Intra- and intermolecular energy deviations in KJ/mol as defined by Eq. (4.2) for a sample of 32 molecules at 10 K for different integrators. For *r*-RESPA the time step (in units of fs) refers to the full propagation time step  $\Delta t_2 = P_0 P_1 \Delta t_0$ . For all integrators the deviations are computed by sampling the energies each 10 fs.

Method	Time step	$\Delta V_{I}$	$\Delta V_M$
Verlet	0.5	6.9165×10 <sup>-2</sup>	1.3821×10 <sup>-3</sup>
Verlet	1.0	0.311 63	$6.8780 \times 10^{-3}$
Verlet	2.0	0.554 49	$2.7925 \times 10^{-2}$
r-RESPA	8.0	$3.5551 \times 10^{-3}$	$3.2312 \times 10^{-3}$
r-RESPA	16.0	4.1981×10 <sup>-3</sup>	$4.0414 \times 10^{-3}$
r-RESPA	20.0	$8.3417 \times 10^{-3}$	6.4604×10 <sup>-3</sup>
r-RESPA	25.0	$8.9287 \times 10^{-3}$	5.3767×10 <sup>-3</sup>

dotted line, below 2.5 fs, corresponds to the double time-step regime for the r-RESPA integrator, where the potential has been subdivided into intra- and intermolecular contributions and only  $P_0$  is varied with constant  $P_1 = 1$ . The dashed lines correspond to triple time-step r-RESPA integrators where the intermolecular potential has been further subdivided into . short- and long-range contributions. The short-dashed line starts from the double time-step curve at  $\Delta t_1 = 2.0$ , whereas the long-dashed line starts at  $\Delta t_1 = 2.5$ . For these two curves, only the value of  $P_1$  is increased while keeping the integers  $P_0$  fixed at the values of 8 and 10, respectively. The horizontal dashed line corresponding to log(R) = -2.30 and defines what is here called the threshold tolerance for energy conservation (R=0.005).<sup>27,28</sup> The pure velocity Verlet integrator steadily looses numerical accuracy, as the time step increases. Although far less dramatically, the r-RESPA integrator also undergoes a fast degradation in the double timestep regime. In the triple time-step regime, increases in  $P_1$ and, correspondingly, in the intermolecular break-up distance  $r_1$ , have been tuned so that, for large time step, the integrators reach a plateau slightly above the threshold tolerance  $(R \approx 0.005)$ . The stability of the triple time-step r-RESPA algorithms for large time steps is due to the increase of the break-up distance  $r_1$  with increasing  $P_1$ .

As pointed out previously, to achieve computational efficiency, a price must be paid to guarantee the stability of the integrators. Shifting to larger values of  $r_1$  requires the calculation of a larger number of pairwise interactions for each of the  $P_1$  time steps. Such an effect is illustrated in Fig. 1(b) where we report the speedup of *r*-RESPA over simple velocity Verlet ( $\Delta t = 0.5$  fs and  $R \approx 0.005$ ). In the double timestep regime (dots) the speedup is practically linear in the integer  $P_0$ . As the subdivision of the intermolecular potential is switched on (dashed curves), the speed-up rate decreases, and eventually the triple time-step r-RESPA curves reach a "saturation point." Beyond the saturation point (i.e., for larger  $P_1$ ) the speed-up rate decreases and the r-RESPA algorithms become increasingly less efficient. At the saturation point the r-RESPA integrator with  $P_0 = 8$ ,  $P_1 = 8$  is almost 16 times faster than the velocity Verlet integrator. The other r-RESPA integrator ( $P_0 = 10$ ,  $P_1 = 10$ ), although slightly less accurate, is approximately 20 times faster than the velocity Verlet.

We now examine the dynamical evolution of several

FIG. 2. Intramolecular potential energy records for *r*-RESPA (squares; lower curve) with  $\Delta t_2 = 25$  ( $P_0 = 10$ ,  $P_1 = 10$ ,  $\Delta t_0 = 0.25$  fs) and for velocity Verlet (circles; upper curve) with  $\Delta t = 0.5$  fs. The superimposed solid curves refer to the exact trajectory obtained with velocity Verlet using a time step of 0.25 fs.

properties generated using the r-RESPA algorithm. In particular, we determine the time evolution of the intra- and intermolecular potential energy and we compute the IR and Raman spectra of the solid. For comparison it is assumed that the "exact" trajectory is generated by a velocity Verlet algorithm with a time step of 0.25 fs. Let

$$\Delta V_{I,M} = \frac{1}{t_f} \int_0^{t_f} [V_{I,M}(t) - V_{I,M}^{(e)}(t)]^2 dt$$
(4.1)

(where  $t_f = 1.0$  ps) represent the deviation of either the intramolecular (I) or intermolecular (M) potential energy from the exact values  $V_I^{(e)}(t)$  and  $V_M^{(e)}(t)$ , respectively. In Table II we report these energy deviations, calculated recording the energies every 10 fs, for several integrators as a function of the time step. (For *r*-RESPA by "time step" we mean the long propagation time step,  $\Delta t = P_0 P_1 \Delta t_0$ .)

From inspection of Table II, it is evident that the r-RESPA integrators reproduce the exact intramolecular energy record accurately with a weak dependence on the time step. By contrast, the increasing step size for the velocity Verlet produces a dramatic increase of the calculated deviation. For  $\Delta t = 0.5$  fs (i.e., a time step only double that of the exact trajectory) the velocity Verlet gives a deviation which is about one order of magnitude larger than that calculated with r-RESPA using  $\Delta t_2 = 25$  fs. The visual effect of these deviations is displayed in Fig. 2 where the intramolecular energy records of r-RESPA with  $\Delta t_2 = 25$  fs and velocity Verlet integrator with  $\Delta t = 0.5$  and  $R \approx 0.005$  (see Table I) are compared to the exact trajectory produced by the velocity Verlet algorithm with  $\Delta t = 0.25$  fs. We see that, while r-RESPA is found to reproduce the reference trajectory with impressive accuracy, even though the energies are sampled at



FIG. 3. Infrared spectrum of  $C_{60}$  for triple *r*-RESPA using a full propagation time step  $\Delta t_2 = 25$  fs ( $P_0 = 10$ ,  $P_1 = 10$ ,  $\Delta t_0 = 0.25$  fs) and for velocity Verlet using a time step of 0.25 fs.

the end of the *short* time steps, the velocity Verlet gives a time evolution significantly different starting at  $t \approx 0.3$  ps. As for the intermolecular energy, the deviations  $\Delta V_M$  obtained with *r*-RESPA are again extremely small (see Table II) for all time steps and even for the largest time step this integrator



FIG. 4. Details of the far-infrared spectrum (a) and mid-infrared regions (b). The squares refer to the IR intensities calculated with *r*-RESPA (lower curve) with  $\Delta t_2 = 25$  fs and the circles to the IR intensities calculated with velocity Verlet with  $\Delta t = 0.5$  fs (upper curve). The superimposed solid lines refer to the exact spectrum calculated with velocity Verlet using a time step of 0.25 fs.



FIG. 5. The blue shift in the high-frequency region of the infrared spectrum for the velocity Verlet algorithm with increasing time step. The solid lines refer to the exact trajectory computed using the velocity Verlet integrator with a time step of 0.25 fs. The circles refer to calculations with time steps (from bottom to top) of  $\Delta t = 0.5$ , 1.0, and 2.0 fs.

still produces a trajectory practically indistinguishable from the exact one. As expected, for both velocity Verlet integrators ( $\Delta t = 0.25$  fs and  $\Delta t = 0.50$  fs) the intermolecular energy recors differ little in contrast to their intramolecular recors. The intermolecular energy record is rather insensitive to the time step  $\Delta t$  used in the velocity Verlet integrator and only when  $\Delta t \approx 2.0$  fs does one start to see large deviations. The good accuracy of the Verlet algorithm for the intermolecular motions at large time step is expected since the coupling between intra- and intermolecular dynamics is low and the intermolecular energy changes are mostly driven by the slowly varying intermolecular forces. Comparison for longer simulation times is feasible only for a smaller sample because the velocity Verlet integration with a time step of 0.25 fs requires approximately 10 CPU days on a dedicated RISC/ 370 workstation to generate 10 ps of trajectory for a sample of 32 molecules. Tests performed on a small sample of four molecules indicate that the intra- and intermolecular potential energies records produced by r-RESPA with large time step (16–20 fs) and the velocity Verlet algorithm with  $\Delta t$ =0.25 are practically identical for 10 ps.

A further example of the accuracy of the multiple timestep integrator is given in Fig. 3 where the infrared spectrum is calculated using the velocity Verlet, with  $\Delta t = 0.25$  and for the r-RESPA algorithm with  $P_0 = 10$ ,  $P_1 = 10$ ,  $\Delta t_0 = 0.25$ , and overall time step  $\Delta t_2 = 25$  fs. The infrared spectrum has been obtained by computing the autocorrelation function of the cell dipole vector. Details of the methodology for calculating the infrared and Raman spectra of solid  $C_{60}$  will be given in a forthcoming paper.<sup>17</sup> It should be noted (see Table I) that the cited r-RESPA algorithm is a factor of 40 times faster than velocity Verlet with  $\Delta t = 0.25$ fs. The two spectra are practically identical. The accuracy of the r-RESPA integrator can be appreciated by inspecting Figs. 4(a) and 4(b) where details of the far- and mid-infrared regions are shown. In Figs. 4(a) and 4(b), for comparison, we also report the infrared intensities calculated with the velocity Verlet integrator using a time step of 0.5 fs (i.e., twice as



FIG. 6. Energy conservation ratio (left scale) R vs overall time step for the force switching *r*-RESPA algorithm (dashed line) and the potential switching *r*-RESPA (dotted line). R is computed using KE+ $\Sigma_k V_k$  for both the force breakup and the potential breakup. The solid line refers to the break-up distance (units of  $\sigma$ ) in the intermolecular potential (right scale).

big as that used to compute the exact spectrum) for which R=0.005 {the tolerance threshold for energy conservation [see Table I and Fig. 1(a)]}. As one can see from Figs. 4(a) and 4(b), the *r*-RESPA algorithm yields an infrared spectrum which agrees, even with respect to minor details, to the exact one for the whole frequency range. Furthermore, the doubling of the time step for the pure velocity Verlet scheme produces appreciable differences, especially in the mid-infrared region where the band at about 1420 cm<sup>-1</sup> undergoes an intensity enhancement and a blue shift of one frequency channel. When the time step is further increased the spectrum calculated for pure velocity Verlet becomes dramatically blue-shifted. This effect is illustrated in Fig. 5.

As discussed in Sec. II, we use a potential switching rather than the force switching method used in earlier r-RESPA implementations.<sup>1,4</sup> It is of interest to compare the accuracy of the two switching methods with respect to both energy conservation and spectral properties. In Fig. 6, R [Eq. (3.3)] is plotted vs the time step, for two *r*-RESPA integrators with different switching methods. It is important to recognize that the numerical accuracy of r-RESPA, as measured by the ratio R, strongly depends on the method of choice and on how the energy is recorded during the multiple time-step propagation. As was pointed out before, the two different switching methods have the same constant of motion (i.e., the total energy KE+V if the time grid is taken to be that of the full propagation step (i.e., if the energy is recorded at integers multiple of the time  $P_0P_1\Delta t_0$ , but they have different constants of motion associated with the corresponding reference system for the intermediate time step  $\Delta t_1 = P_0 \Delta t_0$ .

Here we show what happens when the previous definition of R is used and the total energy is recorded with a much higher frequency than that corresponding to the inverse of the full propagation step. The full propagation time step  $P_0P_1\Delta t_0$  is changed, by varying only  $P_1$  while keeping  $P_0=8$  constant. The total energy is recorded each eight  $\Delta t_0$ steps, which means each 2 fs, i.e., each intermediate time step  $\Delta t_1$  (see Table I). The force switching *r*-RESPA algorithm gives systematically larger values of R at small time steps (and hence for short break-up distances  $r_1$ ). With increasing  $P_1$  and, correspondingly larger values of  $r_1$ , the two methods appear to converge to a similar result, with no significant differences in the energy ratio R. It should be noticed that the time step at which the two methods yield comparable values of R corresponds to the saturation point in Fig. 1(b). The "apparent" inaccuracy of the force switching method for short time step results from using  $KE+V_s$  rather than KE  $+ V_{r}^{*}$ . When R is determined from the energies at the end of each full propagation time step, the two methods agree no matter how we choose  $r_1$  and  $P_1$ . For example, for  $P_1 = 2$ the value of log(R) for the force switching method drops from -1.80 to -2.61, i.e., approximately the same value obtained with the potential switching technique (for the potential switching technique, the value of R remains approximately unchanged, irrespectively of how frequently the energy is recorded). Hence, the advantage of the potential switching over the force switching technique lies solely in the fact that the total energy  $KE + \Sigma_k V_k$  can also be safely monitored at the intermediate time steps. At the intermediate time steps the force switching method would require the knowledge of the potential  $V_k^*$  defined by the equation  $F_k$  $= -\nabla V_{k}^{*}$  in order to compute the correct constant of the motion. It is, however, very important to stress that the force switching technique, even for the intermediate time steps, generates trajectories as accurate as the potential switching method. For example, both breakups generate equally accurate spectra as we now show.

The determination of spectral densities (power spectra) of the high-frequency vibrational modes requires data acquisition of dynamical properties such as cell dipole or polarizability tensors after small time steps in order to avoid aliasing of the high intramolecular frequencies. For  $C_{60}$  the acquisition is performed each 6 fs, i.e., at every three intermediate time steps  $\Delta t_1$ . Because spectral densities are very sensitive to the step size, as we have already seen for the case of the infrared spectrum (Fig. 5), it is important to test the accuracy of different integration schemes.

In order to quantitatively measure the spectral accuracy for different integrators, for an N-point spectrum  $S = \{s_1, ..., s_N\}$  we calculate the quantity

$$D = \arccos\left(\frac{\mathbf{S} \cdot \mathbf{S}^{(\mathbf{e})}}{|\mathbf{S}||\mathbf{S}^{(\mathbf{e})}|}\right) = \arccos\left[\frac{\sum_{i=1}^{N} s_i s_i^{(e)}}{(\sum_{i=1}^{N} s_i^2 \sum_{i=1}^{N} s_i^{(e)})^{1/2}}\right],$$
(4.2)

where  $s_i^{(e)}$  are the intensities of the exact spectrum. (Here again the exact spectrum is taken to be that calculated with the velocity Verlet algorithm using a time step of 0.25 fs.) The quantity D of Eq. (4.2) may be viewed as the angle between the vectors  $\mathbf{S} = \{s_1, ..., s_N\}$  and  $\mathbf{S}^{(e)} = \{s_1^{(e)}, ..., s_N^{(e)}\}$ . Such a definition for the spectral accuracy has the advantage that the spectra need not be normalized and scale factors will not affect the measure whose range, irrespective of the total intensity and of the spectral resolution, varies between 0 (maximum accuracy) and  $\pi/2$  (for totally uncorrelated spectra).

TABLE III. Spectral deviations, as defined by Eq. (4.2), calculated for a sample of 32 molecules at 10 K for different integrators. The exact intensities  $s_1^{(e)}$  are taken to be those calculated with the velocity Verlet method using a time step of 0.25 fs. The spectral deviations obtained using the force switching method are reported in parentheses. The values at  $\Delta t = 0.5$  refer to the deviations of the spectra obtained from the standard velocity Verlet algorithm but using a time step of 0.5 fs. The spectral deviations are evaluated for three qualitatively different kinds of spectra: (S<sub>IR</sub>) the infrared spectrum with multiple bands in the entire frequency range 0–1700 cm<sup>-1</sup>; (S<sub>R</sub>), the isotropic Raman spectrum with only two strong bands at about 500 and 1500 cm<sup>-1</sup>; and S<sub>L</sub>, the power spectrum of the molecular orientation vector autocorrelation function with low-frequency bands ( $\leq 30$  cm<sup>-1</sup>).

$\Delta t$	S <sub>IR</sub>	S <sub>R</sub>	S <sub>L</sub>
0.5	6.76×10 <sup>-2</sup>	1.46×10 <sup>-2</sup>	1.34×10 <sup>-4</sup>
4.0	9.52×10 <sup>-5</sup> (9.99×10 <sup>-5</sup> )	$9.42 \times 10^{-5} (1.30 \times 10^{-3})$	$1.86 \times 10^{-4} (1.86 \times 10^{-4})$
8.0	$1.03 \times 10^{-4} (9.98 \times 10^{-5})$	$1.10 \times 10^{-3} (3.34 \times 10^{-3})$	$1.30 \times 10^{-4} (1.86 \times 10^{-4})$
12.0	$1.67 \times 10^{-4} (9.76 \times 10^{-5})$	$1.53 \times 10^{-3} (1.79 \times 10^{-3})$	$1.85 \times 10^{-4} (1.86 \times 10^{-4})$
16.0	$1.36 \times 10^{-4} (9.81 \times 10^{-5})$	$4.02 \times 10^{-3} (1.57 \times 10^{-3})$	$1.85 \times 10^{-4} (1.86 \times 10^{-4})$
20.0	$2.07 \times 10^{-4} (9.64 \times 10^{-5})$	$4.24 \times 10^{-3} (5.65 \times 10^{-4})$	$1.31 \times 10^{-4} (1.86 \times 10^{-4})$

In Table III we report the spectral deviation, calculated according to Eq. (4.2), for three different spectral densities:

 $S_{IR}$ : the infrared spectrum, obtained by Fourier transforming the autocorrelation function of the cell dipole.

 $S_R$ : the isotropic component of the Raman spectrum, obtained by Fourier transforming the autocorrelation function of the spherical part of the cell polarizability tensor  $\alpha_{xx} + \alpha_{yy} + \alpha_{zz}$ .

 $S_L$ : the "librational" power spectrum, obtained by Fourier transforming the autocorrelation function  $\langle \Sigma_i \mathbf{u}_i(t) \rangle$  $\sum_{i} \mathbf{u}_{i}(0)$ , where  $\mathbf{u}_{i}$  is the unit vector normal to the hexagon on  $(S_6)$  symmetry site of the *j*th molecule. As can be seen in Table III, the spectral deviation [Eq. (4.2)] for the *r*-RESPA integrators is extremely small for all time steps, especially when compared to that calculated for the velocity Verlet integrator with  $\Delta t = 0.5$  fs, no matter which switching method is adopted. For some of the calculated spectra, the force switching technique is even slightly more accurate than the potential switching technique. Since acquisition was performed for both methods at the end of each short time step  $\Delta t_1$ , the data of Table III are a clear demonstration of the accuracy of the force switching technique for the whole time span and not only at multiple integers of the full propagation time step  $\Delta t_2$ .

The velocity Verlet integrator with  $\Delta t = 0.50$  fs differs significantly from the corresponding exact spectra. Only for the last spectrum  $S_L$ , for which most of the intensity occurs at very low frequency, does the velocity Verlet with time step 0.5 fs give a spectral deviation comparable to that obtained with *r*-RESPA. This is consistent with the results obtained for the intramolecular and intermolecular energy deviation of Eq. (4.1) (see Table II).

It is evident from the calculations of the spectra that the large time-step *r*-RESPA integrators are equivalent in accuracy to the velocity Verlet integrator with the shortest time step ( $\Delta t = 0.25$  fs) and are far more accurate (see Table III) than the velocity Verlet integrator with a time step of 0.5 fs, despite the fact that, with respect to the latter, they have slightly worse energy conservation (measured by *R*). A similar result was also found when we determined the accuracy of the intramolecular energy records (see Fig. 2 and Table II). Hence if we choose dynamical properties other than *R*,

such as the spectral deviation of Eq. (4.2) or the intramolecular energy deviation (4.1), as the criterion for judging the accuracy of the integration algorithm, the CPU time ratio of velocity Verlet/*r*-RESPA increases to approximately 40.

Finally, numerical tests carried out for the orientationally disordered (plastic phase) at T=300 K gave results not differing significantly from those already shown here for the orientationally ordered phase at T=10 K. For the sake of completeness, in Table IV we summarize the results of several numerical experiments for the velocity Verlet and *r*-RESPA integrators performed at 300 K.

#### **V. CONCLUSIONS**

We have shown how the *r*-RESPA algorithm can be straightforwardly implemented for the simulation of molecular systems as complex as the solid phases of fullerene. Numerical tests on a periodic system with a primary cell containing 32 molecules of  $C_{60}$  were undertaken, in order to compare the performances of the *r*-RESPA multiple timestep integrators to the standard velocity Verlet integrator. The *r*-RESPA integrator, after a careful tuning of the integration parameters ( $r_1, \Delta t_0, P_0, P_1$ ) results in considerable speedups of the simulation by a factor of 16–20 over the pure velocity Verlet integrator for the same accuracy when that accuracy is

TABLE IV. Numerical tests of the r-RESPA and velocity Verlet integrators at 300 K for a sample of 32 molecules. The column labels have the same meaning as in Table I.

$\overline{\Delta t_0}$	P_0	P <sub>1</sub>	R	t(CPU)	$\langle K \rangle$	<i>r</i> <sub>1</sub>
0.20	1	1	0.0007	11.82×10 <sup>5</sup>	251.11	
0.40	1	1	0.0029	5.47×10 <sup>5</sup>	250.86	•••
0.80	1	1	0.0115	2.95×10 <sup>5</sup>	249.83	•••
1.60	1	1	0.0467	1.49×10 <sup>5</sup>	245.75	•••
0.20	8	1	0.0007	$1.51 \times 10^{5}$	251.12	•••
0.20	8	2	0.0008	$0.85 \times 10^{5}$	251.12	1.80
0.20	8	4	0.0009	$0.48 \times 10^{5}$	251.13	2.00
0.20	8	6	0.0009	0.39×10 <sup>5</sup>	251.12	2.20
0.20	8	8	0.0009	$0.37 \times 10^{5}$	251.12	2.40
0.20	8	10	0.0010	0.37×10 <sup>5</sup>	251.13	2.55

measured by the energy conservation R and by a factor of 35-40 when the accuracy is measured by the deviation of various spectral density functions from the exact spectral density. The analysis of the trajectories, both at low and high temperature, has shown that the *r*-RESPA method produces the same quality dynamics as generated by the velocity Verlet algorithm with a much smaller time step.

The effect of different breakups of the intermolecular Liovillian was also studied. It was found that the potential and force switching methods produce essentially the same dynamics for all time steps as expected. It has been shown that one must use different approximants to the energy to compare the accuracy of these two breakups, otherwise erroneous conclusions will be drawn. Both breakups will give the same energy conservation if they are applied to the usual Hamiltonian only after the largest time step.

The *r*-RESPA algorithm, by virtue of its simplicity and superior performance, can be extremely effective in the study of molecular system with low coupling between intra- and intermolecular dynamics. In a forthcoming paper we present results of an extensive molecular dynamics study based on *r*-RESPA of the lattice dynamics of solid  $C_{60}$ .

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# **APPENDIX**

In this Appendix we show a sample code for the r-RESPA integrator, based on the general propagator of Eq. (2.19) with m=4. The routine "fouter" computes the intermolecular forces in the fourth and outermost shell building up the neighbors list for the next inner shell. The routine "fshell" computes the forces in the kth shell (first argument), receiving as input the neighbors list of kth shell (arguments njk, jck) and building up the neighbors list for the next inner (k-1) shell [arguments nj(k-1), jc(k-1)]. The routine "fintra" computes the forces due to the intramolecular potential. The routine "correc" advances the velocities for half-time step, using the velocities and forces of the previous step. The routine "tores the positions of the particles for one time step using the coordinates, velocities, and forces of the previous step:

• • •

CALL fouter(3,nmol,nato,x,y,z,fx3,fy3,fz3,nj2,jc2)CALL fshell(2,nj2,jc2,ntot,x,y,z,fx2,fy2,fz2,nj1,jc1)CALL fshell(1,nj1,jc1,ntot,x,y,z,fx1,fy1,fz1,nj0,jc0)CALL fintra(nmol,nato,x,y,z,fx0,fy0,fz0) . . . t3 = timetotal/float(nstepmax)t2 = t3/float(m2)t1 = t2/float(m1)t0 = t1/float(m0) $1000 \quad nstep = nstep + 1$ CALL correc(nmol, nato, vx, vy, vz, xm1, fx3, fy3, fz3, t3)DO i2 = 1, m2CALL correc(nmol, nato, vx, vy, vz, xm1, fx2, fy2, fz2, t2) DO i1 = 1.m1call correc(nmol,nato,vx,vy,vz,xm1,fx1,fy1,fz1,t1) DO i0 = 1.m0CALL verlet(nmol, nato, x, y, z, vx, vy, vz, xm1, fx0, fy0, fz0, t0)CALL fintra(nmol,nato,x,y,z,fx0,fy0,fz0) CALL correc(nmol,nato,vx,vy,vz,xm1,fx0,fy0,fz0,t0) k0 = k0 + 1

# END DO

CALL fshell(1,nj1,jc1,ntot,x,y,z,fx1,fy1,fz1,e1,nj0,jc0)
call correc(nmol,nato,vx,vy,vz,xm1,fx1,fy1,fz1,t1)
c COMPUTE AVERAGES AND STORE DATA HERE

•••

#### END DO

CALL fshell(2,nj2,jc2,ntot,x,y,z,fx2,fy2,fz2,e2,nj1,jc1)

CALL correc(nmol, nato, vx, vy, vz, xm1, fx2, fy2, fz2, t2)

## END DO

CALL fouter(3,nmol,nato,x,y,z,fx3,fy3,fz3,e3,nj2,jc2)

CALL correc(nmol,nato,vx,vy,vz,xm1,fx3,fy3,fz3,t3)

•••

IF(nstep.lt.nstepmax) GO To 1000

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