Implicit Runge-Kutta Method for Molecular Dynamics Integration

Dušanka Janežič*

National Institute of Chemistry, Hajdrihova 19, 61115 Ljubljana, Slovenia

Bojan Orel

FER and IMFM, University of Ljubljana, Tržaška 25, 61000 Ljubljana, Slovenia

Received July 20, 1992

An implicit Runge-Kutta (RK) integration scheme, the two-stage 4th order Gauss-Legendre Runge-Kutta (GLRK) method, for numerical solution of molecular dynamics equations is described. An estimate of the initial guess for the starting value of the fixed-point iteration is based on the typical particle frequency. The algorithm was applied to the harmonic oscillator and compared to various algorithms for numerical integration of equations of motion. The algorithm was also applied to a complex system of 256 particles interacting through a Lennard-Jones potential, and compared to a summed form of the Verlet algorithm. The proposed implicit RK method, which permits a wide range of time steps, is highly accurate and stable and is thus suitable for the molecular dynamics integration.

I. INTRODUCTION

Computer simulation is a widely used tool in many fields of science.[1,2] These methods made possible the study of systems not tractable by analytical methods, and they also gave insight into the behavior of the systems. The major obstacle that reduces the efficiency of computer simulation methods of complex systems, such as proteins and nucleic acids, lays in the inability to sample sufficient portions of the phase space. The efficiency of the molecular dynamics (MD) method would be enhanced by the introduction of more stable algorithms for the numerical integration of equations of motion. Several algorithms for MD integration have been proposed.[1-6] The simplest and most commonly used is that of Störmer-Verlet,[7] which is an explicit method. Explicit methods, although simple to use, are less accurate and less stable than implicit methods. The application of explicit methods to MD problems of large size leads to severe restrictions on the step size. They tend to quickly become unstable as the integration time step is increased.[8] However, for studies of dynamics of large molecular systems, larger time steps in the MD integration procedure are needed. The problem of how to increase the time step in the integration procedure for stiff problems, such as MD integration, can be overcome by the use of implicit methods.[9-11]

The important property of Hamiltonian systems is that the flow in the phase space is symplectic, a fact which implies the existence of the phenomenon of the Poincaré recurrence.[12] Therefore, the numerical methods for solving these systems are expected to reproduce this property.[13] In this context, specific Runge-Kutta methods appear to be most promising. In 1988, it was discovered that implicit Runge-Kutta (RK) methods are symplectic, subject to a simple algebraic test.[14-16] Such methods are difficult to implement, which means that special implicit Runge-Kutta methods have to be designed in a computationally less demanding way while retaining symplecticity. There exist unique s-stage ($s \geq 1$) implicit Runge-Kutta methods of maximal order $2s$, the Gauss-Legendre schemes which are symplectic.

The best-known example of a Hamiltonian system is the harmonic oscillator which can be exactly solved. In the example of complex systems, e.g., liquids and biological macromolecules, the equations of motion for N particles have to be solved numerically on the basis of postulated atom-to-atom potentials. The MD method calculates static as well as dynamic properties of the system for a constant number of particles, volume and energy (*NVE* ensemble) by integrating the equations of motion numerically.[1-4] These techniques are easily extendable to a canonical ensemble (*NVT*) and also to isothermal-isobaric ensembles (*NPT*).[17] If high accuracy of MD simulation is required, e.g., near the phase change[18] or in a stochastic simulation,[19] a higher order algorithm has to be chosen to avoid accumulating errors and the instability of the solution.

In this paper, we describe the two-stage 4th order Gauss-Legendre Runge-Kutta (GLRK) method for MD integration, an implicit RK method. GLRK methods were so far used mainly for solving stiff initial value problems.[20] Application of the two-stage 4th order GLRK method to molecular dynamics integration leads to a nonlinear system of algebraic equations. For solving the resulting nonlinear system of equations, the alternatives are the Newton-Raphson method and the fixed-point iteration. If the nonlinear system of equations is solved by an iterative technique, the initial guess for the starting value of the fixed-point iteration should be made. When solving Hamiltonian systems, the fixed-point iteration converges for stepsizes acceptable from the accuracy point of view. Since the number of fixed-point iterations depends strongly on the starting point of the iteration, an initial guess for the starting value of the fixed-point iteration is made on the basis of the typical frequency of the particle. In Section II, the details of the method are given. In Section III, the results obtained for the harmonic oscillator and a system of 256 particles in a box with periodical boundaries interacting through a Lennard-Jones potential are given and discussed. A comparison with other methods is also presented.

II. THEORY

The system to be considered here is described by a set of Hamilton equations; the energy $H = V + T$ is the sum of potential energy V and kinetic energy T, where $V = V(x_1, x_2, \ldots, x_d)$ and depends only on the positions of the different

* Author to whom correspondence should be addressed.

0095-2338/93/1633-0252$04.00/0

particles and where the kinetic energy is

$$T = 1/2\sum_{i=1}^{d}(m_i\dot{x}_i^2) \qquad (m_i = \text{mass of particle } i) \quad \text{(II.0.1)}$$

Using Newton's law, the equation of motion for a system of particles assumes the form

$$\ddot{\mathbf{x}} = \mathbf{f}(\mathbf{x}) \quad \text{(II.0.2)}$$

for a unit mass ($m_i = 1$), $\mathbf{x} = \mathbf{x}(t)$ is the position of the particle at time t, $\ddot{\mathbf{x}}$ is the acceleration, and $\mathbf{f}$ is the force acting on it. The force $\mathbf{f}$ is determined by the assumed potential $V(\mathbf{x})$

$$\mathbf{f} = -\nabla V(\mathbf{x}) \quad \text{(II.0.3)}$$

The implicit RK method requires the equation of motion to be written as a system of first-order differential equations

$$\dot{\mathbf{x}} = \mathbf{v} \quad \text{(II.0.4)}$$

$$\dot{\mathbf{v}} = \mathbf{f}(\mathbf{x}) \quad \text{(II.0.5)}$$

II.1. Runge–Kutta Method. The general implicit s-stage RK method for the solution of the first-order initial value problem

$$\mathbf{y}' = \mathbf{F}(\mathbf{y}) \qquad \mathbf{y}(0) = \mathbf{y}_0 \quad \text{(II.1.1)}$$

where $\mathbf{y}$ is a vector with d components, is determined by the matrix $A = [a_{ij}]_{i,j=1}^{s}$ and the vector $\mathbf{b} = [b_i]_{i=1}^{s}$. It can be written

$$Y_i = \mathbf{y}_n + h\sum_{j=1}^{s}a_{ij}\mathbf{F}(\mathbf{Y}_j) \qquad i = 1, ..., s \quad \text{(II.1.2)}$$

$$\mathbf{y}_{n+1} = \mathbf{y}_n + h\sum_{i=1}^{s}b_i\mathbf{F}(\mathbf{Y}_i) \quad \text{(II.1.3)}$$

where h is the time step. Equation II.1.2 implicitly defines internal quantities Y_i which can be interpreted as an approximation to the exact solution $\mathbf{y}(t)$ at the intermediate point $t = t_n + c_ih$. The coefficients of the method are collected in the form of Butcher's tableau that provides a condensed representation of the RK method[20]

$$\begin{array}{c|c} \mathbf{c} & A \\ \hline & \mathbf{b}^T \end{array}$$

where $\mathbf{c} = [c_i]_{i=1}^{s}$ and $c_i = \sum_{i=1}^{s}a_{ij}$.

According to Sanz–Serna,[15] a RK method, which is suitable for the solution of Hamiltonian systems, is symplectic, if it satisfies the condition

$$BA + A^TB - \mathbf{b}\mathbf{b}^T = 0 \quad \text{(II.1.4)}$$

where $B = \text{diag}(b_1, ..., b_s)$ is a diagonal matrix.

The unique s-stage RK method of order $2s$, the Gauss–Legendre (GL) scheme, obeys eq II.1.4 for every s. The two-stage 4th order GLRK method has the coefficients

$$\begin{array}{lc|cc} c_1 = \dfrac{3-\sqrt{3}}{6} & & \dfrac{1}{4} & \dfrac{3-2\sqrt{3}}{12} \\ c_2 = \dfrac{3+\sqrt{3}}{6} & & \dfrac{3+2\sqrt{3}}{12} & \dfrac{1}{4} \\ \hline & & \dfrac{1}{2} & \dfrac{1}{2} \end{array} \quad \text{(II.1.5)}$$

Algorithm. Application of the two-stage 4th order GLRK to MD integration problem (eqs II.0.4 and II.0.5) leads to the following relations

$$\mathbf{V}_1 = \mathbf{v}_n + h\left(\frac{1}{4}\mathbf{f}(\mathbf{X}_1) + \frac{3-2\sqrt{3}}{12}\mathbf{f}(\mathbf{X}_2)\right) \quad \text{(II.1.6)}$$

$$\mathbf{V}_2 = \mathbf{v}_n + h\left(\frac{3+2\sqrt{3}}{12}\mathbf{f}(\mathbf{X}_1) + \frac{1}{4}\mathbf{f}(\mathbf{X}_2)\right) \quad \text{(II.1.7)}$$

$$\mathbf{X}_1 = \mathbf{x}_n + h\left(\frac{1}{4}\mathbf{V}_1 + \frac{3-2\sqrt{3}}{12}\mathbf{V}_2\right) \quad \text{(II.1.8)}$$

$$\mathbf{X}_2 = \mathbf{x}_n + h\left(\frac{3+2\sqrt{3}}{12}\mathbf{V}_1 + \frac{1}{4}\mathbf{V}_2\right) \quad \text{(II.1.9)}$$

($\mathbf{V}_i$ and $\mathbf{X}_i$ correspond to $\mathbf{Y}_i$ from eq II.1.2 and $\mathbf{f}$ is the force (eq II.0.3)) which implicitly defines the *internal approximations* $\mathbf{V}_1$, $\mathbf{V}_2$, $\mathbf{X}_1$, and $\mathbf{X}_2$. These relations are used in a fixed-point iteration that results in accurate internal approximations if initiated with good starting values for $\mathbf{X}_1$ and $\mathbf{X}_2$. These starting values are based on the information from the previous step. Four approximants to the exact solution known at each step, $\mathbf{x}_{n-1}$, $\mathbf{X}_1$, $\mathbf{X}_2$, $\mathbf{x}_n$, are approximate values of the solution at points t_{n-1}, $t_{n-1} + c_1h$, $t_{n-1} + c_2h$, and $t_{n-1} + h$ (coefficients c_1, c_2 are those from the table in eq II.1.5). The starting values for the approximants to the exact solution in a fixed-point iteration are determined by means of an adequately chosen extrapolation function. There are a number of ways to determine this function. The extrapolation function $z^i(t)$ for the ith coordinate, imposed by the character of motion of the system considered, is chosen to be of the form

$$z^i(t) = s_1^i + s_2^i \sin\omega_i(t - t_{n-1}) + s_3^i \cos\omega_i(t - t_{n-1})$$

with s_1^i, s_2^i and s_3^i as free parameters and ω_i as the typical frequency of the particle.

In order to get the coefficients of the function $z^i(t)$ by the least-squares method, the following quantities have to be computed

$$\begin{aligned} S &= \sin\omega_ihc_1 + \sin\omega_ihc_2 + \sin\omega_ih \\ C &= 1 + \cos\omega_ihc_1 + \cos\omega_ihc_2 + \cos\omega_ih \\ S_2 &= \sin^2\omega_ihc_1 + \sin^2\omega_ihc_2 + \sin^2\omega_ih \\ C_2 &= 1 + \cos^2\omega_ihc_1 + \cos^2\omega_ihc_2 + \cos^2\omega_ih \\ S_C &= \sin\omega_ihc_1\cos\omega_ihc_1 + \sin\omega_ihc_2\cos\omega_ihc_2 + \\ &\quad \sin\omega_ih\cos\omega_ih \\ Z_1^i &= x_{n-1}^i + X_1^i + X_2^i + x_n^i \\ Z_2^i &= X_1^i\sin\omega_ihc_1 + X_2^i\sin\omega_ihc_2 + x_n^i\sin\omega_ih \\ Z_3^i &= x_{n-1}^i + X_1^i\cos\omega_ihc_1 + X_2^i\cos\omega_ihc_2 + x_n^i\cos\omega_ih \end{aligned}$$

Parameters s_1^i, s_2^i, and s_3^i for the ith coordinate are the solution of the following system of linear equations:

$$\begin{aligned} 4s_1^i + Ss_2^i + Cs_3^i &= Z_1^i \\ Ss_1^i + S_2s_2^i + S_Cs_3^i &= Z_2^i \\ Cs_1^i + S_Cs_2^i + C_2s_3^i &= Z_3^i \end{aligned} \quad \text{(II.1.10)}$$

Starting values for the fixed-point iteration (eqs II.1.6–II.1.9) can be written as

$$X_1^i = s_1^i + s_2^i\sin h\omega_i(1 + c_1) + s_3^i\cos h\omega_i(1 + c_1) \quad \text{(II.1.11)}$$

$$X_2^i = s_1^i + s_2^i\sin h\omega_i(1 + c_2) + s_3^i\cos h\omega_i(1 + c_2) \quad \text{(II.1.12)}$$

The new velocities and the new positions are given by

$$\mathbf{v}_{n+1} = \mathbf{v}_n + \frac{h}{2}(\mathbf{f}(\mathbf{X}_1) + \mathbf{f}(\mathbf{X}_2)) \quad \text{(II.1.13)}$$

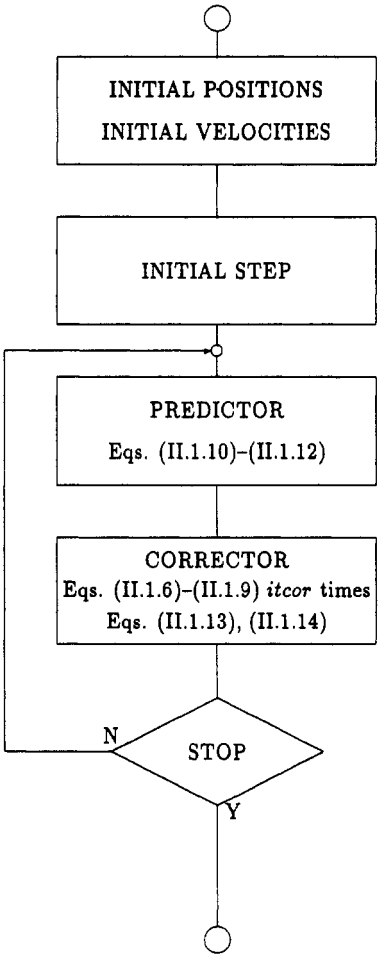

Figure 1. Scheme of the implicit Runge–Kutta algorithm for MD integration.

$$\mathbf{x}_{n+1} = \mathbf{x}_n + \frac{h}{2}(\mathbf{V}_1 + \mathbf{V}_2) \qquad \text{(II.1.14)}$$

and the procedure is repeated until the desired number of steps of calculation is performed.

III. RESULTS

The method described in Section II was tested on the harmonic oscillator and on a system of Lennard-Jones particles. A comparison with the summed form of the Verlet algorithm was performed. The aim of this type of calculation lays in the study of the suitability of implicit RK methods for MD integration.

Harmonic Oscillator. Any algorithm developed for solving second-order differential equations is easily judged on the simple example of the harmonic oscillator. The equations for the harmonic oscillator written in terms of the systems of first-order differential equations are

$$\dot{x} = v \qquad \text{(III.0.1)}$$

$$\dot{v} = -x \qquad \text{(III.0.2)}$$

Initial conditions $x(0) = 1$ and $v(0) = 0$ correspond to the exact solution

$$x(t) = \cos t \qquad v(t) = -\sin t$$

which represents an oscillation with period 2π. For this system, it is easy to calculate the quantities such as total error in x from the exact solution as well as drift and noise in energy, which show the quality of the solution.[5]

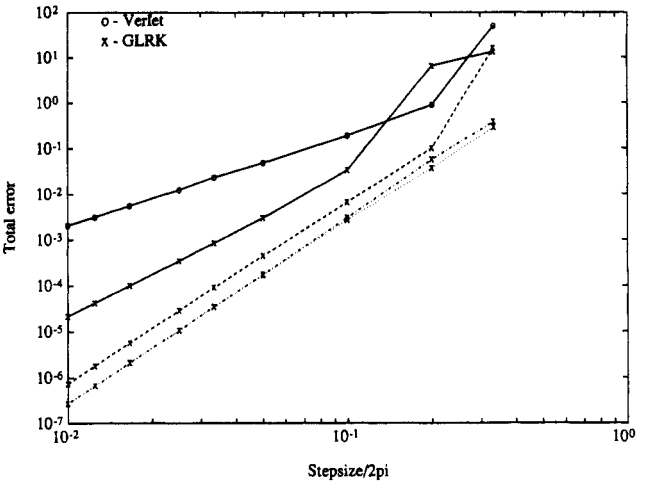

Figure 2. Total error in x from the exact solution for the harmonic oscillator as a function of stepsize. Results are plotted for two different algorithms (O, summed form of the Verlet algorithm, ×, the two-stage 4th order GLRK method) and for four different values of *itcor* parameter. In the case of the two-stage 4th order GLRK method, the solid line represents *itcor* = 1; the dashed line represents *itcor* = 2, the dotted line represents *itcor* = 3; and the dot-dash represents *itcor* = 4.

Figure 1 displays the scheme of the two-stage 4th order GLRK algorithm, explicitly written for harmonic oscillators as follows: at the initial step of the calculation, the initial positions and velocities are known only at the starting point; thus, some approximation about internal approximations have to be made. Starting values for X_1 and X_2 in the example of the harmonic oscillator can be taken as $X_1 = \cos c_1 t$ and $X_2 = \cos c_2 t$, and $f(X_1) = -X_1$ and $f(X_2) = -X_2$. In this way, in the first and all subsequent steps of the calculation, the values of x_{n-1}, X_1, X_2, and x_n from the previous step are known. The internal approximations V_1, V_2, X_1, and X_2 are obtained from eqs II.1.6–II.1.9 and are iterated *itcor* times according to the following iteration scheme:

$$V_1 = v_n - h\left(\frac{1}{4}X_1 + \frac{3-2\sqrt{3}}{12}X_2\right) \qquad \text{(III.0.3)}$$

$$V_2 = v_n - h\left(\frac{3+2\sqrt{3}}{12}X_1 + \frac{1}{4}X_2\right) \qquad \text{(III.0.4)}$$

$$X_1 = x_n + h\left(\frac{1}{4}V_1 + \frac{3-2\sqrt{3}}{12}V_2\right) \qquad \text{(III.0.5)}$$

$$X_2 = x_n + h\left(\frac{3+2\sqrt{3}}{12}V_1 + \frac{1}{4}V_2\right) \qquad \text{(III.0.6)}$$

The new velocity and position are computed as

$$v_{n+1} = v_n - \frac{h}{2}(X_1 + X_2) \qquad \text{(III.0.7)}$$

$$x_{n+1} = x_n + \frac{h}{2}(V_1 + V_2) \qquad \text{(III.0.8)}$$

which are subsequently used in the equations for the predictor (eq II.1.11) and (eq II.1.12) to calculate new values for internal approximations X_1 and X_2. This procedure is then repeated until the desired number of steps of the calculation was performed. If the system (eqs III.0.3–III.0.6) is solved using a direct method, e.g., Gauss elimination method, the drift and noise in energy for the harmonic oscillator equals zero within the limits of precision of the machine.

The results of the calculation of the total error in x, the drift, the noise in energy for the harmonic oscillator of the two-stage 4th order GLRK method, and the summed form of the Verlet method are displayed in Figures 2–4, respectively.

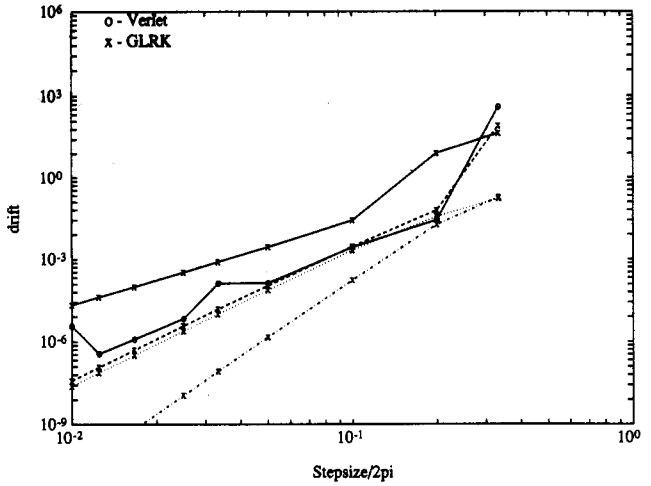

Figure 3. Drift in "energy" $x^2 + v^2$ for harmonic oscillator as a function of stepsize. See Figure 2 legend for the symbol key.

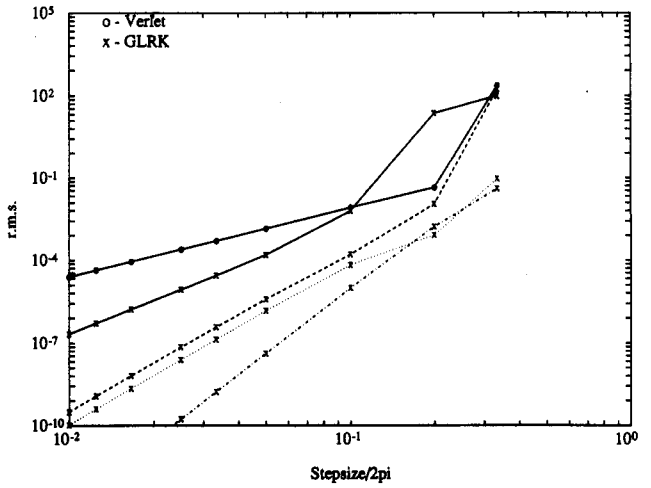

Figure 4. Noise or rms from the linear regression line to the "energy" $x^2 + v^2$ for harmonic oscillator as a function of stepsize. See Figure 2 legend for the symbol key.

The summed form of the Verlet method was chosen for comparison because it is the most commonly used method in MD simulations. It is also symplectic and time reversible as is the two-stage 4th order GLRK method.

In Figure 2, the total error in x from the exact solution of the harmonic oscillator as a function of stepsize for $t = 4\pi$ (over 2 cycles) for the summed form of the Verlet algorithm and the two-stage 4th order GLRK method are plotted. Also shown is the influence of the number of iterations of the corrector performed (*itcor* times) on the total error in x for the two-stage 4th order GLRK method. Obviously, the "best" value of the *itcor* parameter is 4, comparing the improvement of the numerical solution of the differential equation and the demand of calculation.

Figure 3 shows the plot of the drift in energy for the two methods presented as the *itcor* parameter is varying from 1 to 4. This is the drift in "energy" $x^2 + v^2$ over one period which has the "conserved" value of 1 for the harmonic oscillator.

Plots of root mean square (rms) or noise from the linear regression line to the "energy" $x^2 + v^2$ for the harmonic oscillator are depicted in Figure 4. Presented are the results for the summed form of the Verlet algorithm and the two-stage 4th order GLRK method with the *itcor* parameter changing from 1 to 4.

The results for the two-stage 4th order GLRK method as the *itcor* parameter equals 4 show the accumulation of error to be very small and the stability of the solution to be very good. In all the calculations using the two-stage 4th order GLRK method, the value of the typical frequency ω was 1, which is the exact value. As the value of ω is randomly altered between the values 0.5 and 1.5, the results are similar, supporting the results presented in Figures 2–4.

System of *N* Lennard-Jones Particles. A monoatomic system of 256 particles interacting by the Lennard-Jones potential

$$V(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

enclosed in a box of side L was considered. The values for ϵ (specifying the units of energy) and σ (specifying the units of length) were choosen as appropriate for argon, i.e., ϵ = 119.8 K and σ = 3.405 Å;[3] the periodic boundary conditions were imposed to conserve the density. This completely determines the point studied in the phase diagram. To perform the MD simulation of such a system the force acting on each particle must be known. The force in the x direction on the ith particle exerted by the jth particle is

$$f_x(r_{ij}) = 48\frac{\epsilon}{\sigma^2}(x_i - x_j)\left[\left(\frac{\sigma}{r_{ij}}\right)^{14} - \frac{1}{2}\left(\frac{\sigma}{r_{ij}}\right)^{8}\right]$$

and, similarly, for the y and z direction.

All the equations in computer simulation were rendered dimensionless by scaling time and positions by $(m\sigma^2/48\epsilon)^{1/2}$ and σ, respectively (m is the mass of argon atom). The time unit for argon is 3×10^{-13} s. The time step was taken to be $h = 0.064$ or 2×10^{-14} s. We studied the argon system in two points of the phase diagram: $(T^*,\rho^*) = (0.722, 0.83134)$ and $(T^*,\rho^*) = (2.53, 0.636)$ for which the linear MD cell sizes are $L = 6.75$ and $L = 7.38$, respectively.[1]

For MD integration of the argon system, we applied the two-stage 4th order GLRK method and also the summed form of the Verlet algorithm for comparison. In all calculations 5000 MD steps were performed. The MD simulation was carried out in the example $(T^*,\rho^*) = (0.722, 0.83134)$ by using the two-stage 4th order GLRK method for the time steps h, $2h$, $3h$, and $4h$, and in the example $(T^*,\rho^*) = (2.53, 0.636)$ for the time steps $h/2$, h, $2h$, and $3h$ for several different values of *itcor* parameter. The summed form of the Verlet algorithm was performed at the same points in the phase diagram for the time steps h and $2h$, and $h/2$ and h, respectively. MD simulation using the summed form of the Verlet algorithm for larger time steps is numerically not stable and, thus, cannot be performed.

The initial positions were taken at the nodes of a face-centered-cubic lattice. The initial values themselves were taken as starting points for the internal approximations and two times *itcor* successive corrector iterations were performed at the beginning of the calculation.

For the computation of forces, the potential was truncated at the cut-off values $r_c = 2.5$ and 3.6, respectively. Having specified the initial positions and the initial velocities and also the initial internal approximations for the two-stage 4th order GLRK method, the system was equilibrated during the first 500 MD steps. At each 50th MD step an ad hoc readjustment of the velocities was performed. The velocities were scaled by

$$\beta = \left(\frac{T^*(N-1)}{16\sum_i v_i^2}\right)^{1/2}$$

The main part of the computation concerns the study of error accumulation and numerical stability of the method

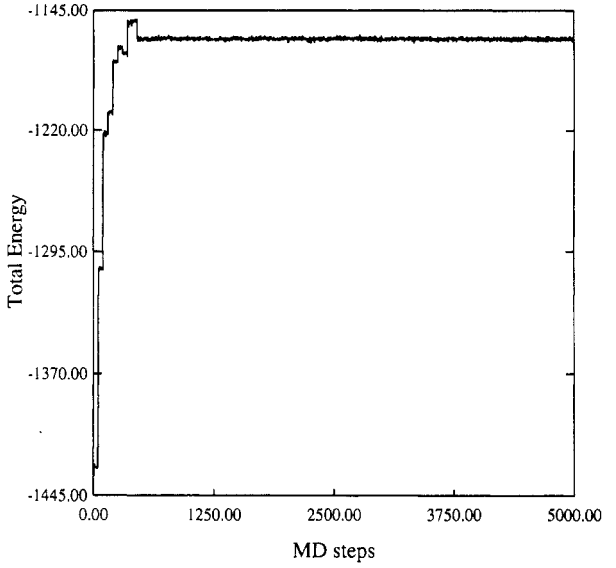

Figure 5. Evolution of 5000 MD steps of total energy for argon system for the example $(T^*,\rho^*) = (0.722, 0.83134)$ and $r_c = 2.5$ using the two-stage 4th order GLRK method and time step $h = 0.064$. The jumps in the energy are due to the rescaling of velocities during the first 500 MD steps.

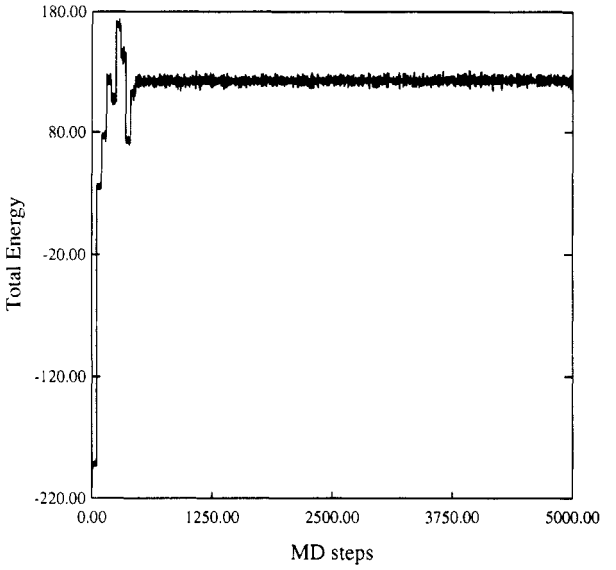

Figure 6. Same as Figure 5 for the example $(T^*,\rho^*) = (2.53, 0.636)$ and $r_c = 2.5$.

proposed, monitoring the conservation of the total energy of the system as well as the drift and the noise in the total energy of the system. The evolution of total energy of MD calculation of 5000 time steps for the example $(T^*,\rho^*) = (0.722, 0.83134)$ and $r_c = 2.5$ using the two-stage 4th order GLRK method for the time step $h = 0.064$ is presented in Figure 5. Figure 6 displays the evolution of the total energy of MD calculation of 5000 time steps for the example $(T^*,\rho^*) = (2.53, 0.636)$ and $r_c = 2.5$ using the two-stage 4th order GLRK method for the time step $h = 0.064$. During the first 500 MD steps, the velocities were scaled every 50th step to give the desired temperature. All quantities are given in reduced units. These results are in good agreement with the results obtained using the summed form of the Verlet algorithm.[1]

In Tables I and II, the results for the summed form of the Verlet algorithm and the two-stage 4th order GLRK algorithm for drift and noise in the total energy of the argon system for the two points in the phase space and different values of the time step and *itcor* parameter are presented. The effect of the different truncations of the range of interactions were also examined. The results collected in Table I show that for the example $(T^*,\rho^*) = (0.722, 0.83134)$ the summed form of the Verlet algorithm is not stable for time steps larger than $2h$ while the two-stage 4th order GLRK method is stable for time steps as large as $4h$. The summed form of the Verlet algorithm is stable only for time step h for the example $(T^*,\rho^*) = (2.53, 0.636)$ whereas the two-stage 4th order GLRK method is stable for time steps up to $3h$ (Table II).

In the MD simulation for argon, at two points of the space diagram, the value of the *itcor* parameter has to be increased with increasing value of the time step in order to obtain low values of the drift in the total energy. The cut-off of the potential function introduces a drift in the total energy. Obviously, the drift is lower for the larger cut-off, and this is also true for the more accurate method, i.e., with a larger value of *itcor* parameter. The values of rms increase with increasing time step or decreasing value of *itcor* parameter. This is due to the fixed-point iteration in solving the resulting system of nonlinear equations. The larger the value of the *itcor* parameter, the more iterations are performed and lead to a decrease of the rms value.

Data in Tables I and II lead to the conclusion that the two-stage 4th order GLRK algorithm is more stable and accurate than the Verlet algorithm. The former also allows for a larger time step to be used, and in practice it comes close to conserving the total energy. Hence, the GLRK algorithm is promising for MD simulation, especially when large-scale molecular motions are to be studied and larger time steps are required.

It is known that a good MD algorithm permits a large time step to be used while preserving acceptable energy conservation. An integration algorithm also should be simple.[2] The

Table I. Results for the Drift and Noise in Total Energy for Argon System of 256 Particles over 4500 MD Steps Using the Verlet and Two-Stage 4th Order GLRK Algorithms for Different Values of Time Step for the Case $(T^*,\rho^*) = (0.722, 0.83134)$

			drift		noise	
method	stepsize	*itcor*	$r_c = 2.5$	$r_c = 3.6$	$r_c = 2.5$	$r_c = 3.6$
Verlet	h		3.1×10^{-5}	2.3×10^{-5}	0.38	0.12
Verlet	$2h$		4.3×10^{-4}	2.8×10^{-4}	0.61	0.44
GLRK	h	2	3.2×10^{-2}	2.7×10^{-2}	4.14	2.88
GLRK	h	3	1.4×10^{-4}	9.3×10^{-5}	0.70	0.59
GLRK	h	4	4.4×10^{-5}	3.7×10^{-6}	0.68	0.62
GLRK	h	5	4.2×10^{-5}	1.1×10^{-6}	0.71	0.60
GLRK	h	6	1.8×10^{-5}	9.5×10^{-6}	0.72	0.60
GLRK	$2h$	3	1.6×10^{-3}	1.6×10^{-3}	1.19	1.27
GLRK	$2h$	4	6.7×10^{-4}	9.3×10^{-4}	1.23	1.28
GLRK	$2h$	6	-4.4×10^{-5}	1.7×10^{-6}	1.30	1.31
GLRK	$3h$	6	1.0×10^{-4}	3.7×10^{-5}	1.97	1.91
GLRK	$4h$	6	-7.7×10^{-3}	-4.7×10^{-3}	2.86	2.64
GLRK	$4h$	8	4.6×10^{-3}	3.6×10^{-3}	2.84	2.73

Table II. Results for Drift and Noise in Total Energy for Argon System of 256 Particles over 4500 MD Steps Using Verlet and Two-Stage 4th Order GLRK Algorithms for Different Values of Time Step for Case (T^*,ρ^*) = (2.53, 0.636)

			drift		noise	
method	stepsize	*itcor*	r_c = 2.5	r_c = 3.6	r_c = 2.5	r_c = 3.6
Verlet	$h/2$		2.9×10^{-5}	7.5×10^{-6}	0.42	0.15
Verlet	h		2.1×10^{-4}	-2.5×10^{-4}	0.73	0.60
GLRK	$h/2$	2	-2.5×10^{-2}	-2.5×10^{-2}	1.62	1.70
GLRK	$h/2$	4	5.3×10^{-6}	2.8×10^{-7}	1.23	1.16
GLRK	h	2	-1.3×10^{-1}	-1.3×10^{-1}	43.78	42.15
GLRK	h	3	8.7×10^{-4}	8.6×10^{-4}	2.41	2.23
GLRK	h	4	2.3×10^{-4}	2.6×10^{-4}	2.39	2.41
GLRK	h	5	-2.9×10^{-5}	-1.2×10^{-5}	2.42	2.45
GLRK	h	6	4.8×10^{-5}	-8.9×10^{-6}	2.40	2.41
GLRK	$2h$	4	1.1×10^{-1}	1.4×10^{-1}	33.13	42.98
GLRK	$2h$	6	-4.9×10^{-4}	6.9×10^{-4}	4.85	4.74
GLRK	$3h$	6	-4.5×10^{-2}	-5.9×10^{-2}	18.06	13.66

proposed two-stage 4th order GLRK algorithm corresponds to these demands except that $2(itcor + 1)$ force evaluations are necessary for one integration step, compared to one of the Verlet algorithm. One Verlet integration step takes in these particular MD calculations 0.99 CPU s on the HP 730 workstation[21] while the proposed two-stage 4th order GLRK method is by far $2(itcor + 1)$ computationally more demanding. The results of more detailed measurements of CPU seconds for MD simulation of argon system using the Verlet algorithm performed on different computers are given in ref 21. There are at least two possibilities to remedy this drawback of the proposed method. One is to introduce the neighbor lists to reduce the force calculation for particles separated by distances greater than the potential cutoff. Thus, when solving the system of nonlinear equations for internal approximations a very small, additional cutoff of the potential function may be introduced because in this case only a few nearest neighbors need to be considered in the force calculation. Since avoiding expensive calculations of forces, which actually do not change, the MD calculation will be faster. The other possibility lies in the development of better numerical methods for solving the system of nonlinear equations for internal approximations, e.g., Newton-like iteration. Further improvements could possibly be achieved by a parallel implementation of the method proposed to computers with highly parallel architecture. Although we have not tested these alternative strategies in the present paper, we believe that the proposed implicit RK method should become the choice for MD integration.

IV. CONCLUSIONS

The present work is a first attempt to design and analyze an implicit RK method, the two-stage 4th order GLRK method, for molecular dynamics integration. This method proved to be accurate and numerically stable for a wide range of time steps. The accuracy and numerical stability considerations are an important factor in the MD calculations. The more accurate calculation scheme is suitable at the phase transitions, and the related interfacial systems are suitable for long-term correlated properties.

The results of the present work are conclusive enough to allow a comparison with the wide range of method proposed for numerical integration of the equations of motion. The accumulation of errors in the two-stage 4th order GLRK method proposed is surprisingly small, and the stability of the solution is very good.

ACKNOWLEDGMENT

The authors thank Professors D. Hadži and S. P. Nørsett and Drs. B. R. Brooks, A. Miklavc, and R. W. Pastor for helpful discussions. This work was supported by the Ministry of Science and Technology of the Republic of Slovenia.

REFERENCES AND NOTES

(1) Heerman, D. W. *Computer Simulation Methods in Theoretical Physics*; Springer: New York, 1986.
(2) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Clarendon Press: Oxford, 1987.
(3) Verlet, L. Computer "Experiments" on Classical Fluids. I. Thermodynamical Properties of Lennard-Jones Molecules. *Phys. Rev.* **1967**, *159*, 98–103.
(4) Borštnik, B.; Pumpernik, D.; Janežič, D.; Ažman, A. In *Molecular Interactions: Molecular Dynamics Studies of Molecular Interactions*; Ratajczak, H., Orville-Thomas, W. J., Eds.; John Wiley and Sons: New York, 1980.
(5) Berendsen, H. J. C.; Gunsteren, W. F. van In *Molecular Dynamics of Statistical Mechanical Systems: Practical Algorithms for Dynamic Simulation*; Ciccotti, G., Hoover, W. G., Eds.; Proceedings of the International School of Physics, North Holland: Amsterdam, 1986.
(6) Beeman, D. Some Multistep Methods for Use in Molecular Dynamics Calculations. *J. Comput. Phys.* **1976**, *20*, 130–139.
(7) Henrici, P. *Discrete Variable Methods in Ordinary Differential Equations*; John Wiley: New York, 1962.
(8) Pastor, R. W.; Brooks, B. R.; Szabo, A. An Analysis of the Accuracy of Langevin and Molecular Dynamics Algorithms. *Mol. Phys.* **1988**, *65*, 1409–1419.
(9) Peskin, C. S.; Schlick, T. Molecular Dynamics by the Backward-Euler Method. *Commun. Appl. Math.* **1989**, *42*, 1001–1031.
(10) Schlick, T. New Approaches to Potential Energy Minimization and Molecular Dynamics Algorithms. *Comput. Chem.* **1991**, *15*, 251–260.
(11) Fincham, D. Leapfrog Rotational Algorithms. *Mol. Simul.* **1992**, *8*, 165–178.
(12) Arnold, V. I. *Mathematical Methods of Classical Mechanics*; Springer: New York, 1978.
(13) Iserles, A.; Nørsett, S. P. *Order Stars*; Chapman & Hall: London, 1991.
(14) Lasagni, F. Canonical Runge–Kutta Methods. *ZAMP* **1988**, *39*, 952–953.
(15) Sanz-Serna, J. M. Runge–Kutta Schemes for Hamiltonian Systems. *BIT* **1988**, *28*, 877–883.
(16) Suris, Y. B. Canonical Transformations Generated by Methods of Runge–Kutta Type for the Numerical Integration of the System $x'' = -\partial U/\partial x$. *Zh. Vychisl. Mat. Mat. Fiz.* **1989**, *29*, 202–211.
(17) Winkler, R. G.; Morawitz, H.; Yoon, D. Y. Novel Molecular Dynamics Simulations at Constant Pressure. *Mol. Phys.* **1992**, *75*, 669–688.
(18) Toxvaerd, S. J. A New Algorithm for Molecular Dynamics Calculations. *Comput. Phys.* **1982**, *47*, 444–451.
(19) van Gunsteren, W. F.; Berendsen, H. J. C. Algorithms for Brownian Dynamics. *Mol. Phys.* **1982**, *45*, 637–647.
(20) Butcher, J. *The Numerical Analysis of Ordinary Differential Equations, Runge–Kutta Methods and General Linear Methods*; Wiley: Chichester, 1987.
(21) Trobec, R.; Jerebic, I.; Janežič, D. Parallel Algorithm for Molecular Dynamics Integration. Submitted to *Parallel Comput.*