INRODUCTION

Nowadays Molecular Dynamics (MD) approach is widely applied in many areas of physics, chemistry and biochemistry. The MD is based on solution of second order differential equations of motion, this is why the integration algorithm is a cornerstone of the MD method. The Newtonian equations of motion are time-reversible and it would be reasonable to preserve this essential property in our integration schemes. Since 1990 there are many nice symplectic integrators were invented, mainly in force-gradient form but none with higher-order gradient operators. In this short report we derive a new time-reversible explicit integrator on the basis of second order Taylor expansion of force. There is good reason to think the new method will be easy-to-use for MD and, possibly, celestial mechanics applications.

IDEA OF A NEW METHOD

Consider the second order differential equation:

\[ x = f(x) \]  

It is useful to introduce the function \( s(t) \):

\[ s(t) = 1 + t = h; \quad h < t < 0 \]

By using Eq. (1) one may integrate by parts the integral

\[ Z_h \int x(t) s(t) dt = x(0) s(0) + \int x(t) s(t) dt = x(0) s(0) + \int x(t) s(t) dt = (x(0) s(t))_h^z + (x(t) s(t))_h^z \]

and finally

\[ x(t) = x(0) + \int x(t) s(t) dt \]  

A proper approximation of the function \( f(x) \) in the Eq. (5) within the segment \( t \in [h; h] \) may give us difference schemes for numerical integration of Eq. (1). For instance, by assuming \( f(x) = f(0) \), the exact formula immediately gives the explicit Verlet integrator:

\[ x(0) + \int x(t) s(t) dt = x(0) + \int x(0) s(t) dt \]

It is convenient to introduce notations:

\[ x_0 = x(0); \quad x_h = x(h); \quad x_h = x(h) \]

\[ v(t) = x(t); \quad a(t) = x(t); \quad h(t) = h(t) \]

\[ f_0 = f(x_0); \quad f_h = f(x_h); \quad f_h = f(x_h) \]

Second order Taylor approximation of \( f(x) \):

\[ f(x) = f(0) + f_0 x_0 + f_0 x_0 x_0 + f_0 x_0 x_0 = 2 + f_0 (x_0 x_0) = 6 + \cdots \]  

Thus the Verlet method is given by

\[ x_h = x_0 + a_0 h^2 + O(\Omega h^4) \]  

Expand \( f(x) \) in the vicinity of \( x = x_0 \) and \( x(t) \) at a point \( t = 0 \) in a Taylor series

\[ f(x) = f_0 + f_0 x_0 + f_0 x_0 x_0 = 2 + f_0 (x_0 x_0) = 6 + \cdots \]  

Substitute \( x(t) \) from Eq. (5) to Eq. (8) and hold only the even terms so one may find that the function along the trajectory of motion around \( t = 0 \) is

\[ f_{\text{even}}(t) = f_0 + (a_0 f_0 + v_0 f_0) h^2 = 2 + O(\Omega h^4) \]

Substitute Eq. (10) to Eq. (11) and integrate the latter:

\[ \int x(t) s(t) dt = h^2 = 6 \]

and

\[ c_0 = a_0 f_0 + v_0 f_0 \]

The explicit integrator is time-reversible likewise the Verlet method. The important difference of Eq. (11) from Verlet formula is a velocity and acceleration dependencies in the \( c_0 \) coefficient.

How to evaluate velocity \( v_h \)?

First way. By using the same approach as above for derivation of (11) one may deduce a formula

\[ v_h = v_0 + f(x) dt \]

Therefore the time-reversible velocity formula is

\[ v_h = v_0 + f_0 h^2 + (a_0 f_0 + v_0 f_0) h^4 = 3 + O(\Omega h^4) \]

The main disadvantage of Eq. (13) is a poor accuracy.

Second way. Assume that in the vicinity of \( t = 0 \) the \( x(t) \) can be represented by polynomial interpolation:

\[ x(t) = x_0 + v_0 t + a_0 t^2 = 2 + c_0 t^2 + c_0 t^4 + c_0 t^6 \]

By using the known positions, velocities, and accelerations at points \( t = [h/2; h] \) (see Table 1) one can derive a
Table 1 The source data for the time-reversible interpolation formula of velocity (14)

| t  | h  | 0   | h  |
|----|----|-----|----|
| x  | x h | x0  | x h |
| v  | v h | v0  | v h |
| a  | a h | a0  | a h |

Table 2 Algorithm of integrator based on formulae (11,15).
Here K is a time-step number and L is a logical step number within the given time-step. The first time-step $0_0$ ! $1_0$ has to be done by using another integrator.

| K  | L  | 0  | 1  | 2  | 3  | 4  | 5  |
|----|----|----|----|----|----|----|----|
| x  | x0 | x1 | x2 | x3 | x4 | x5 | x6 |
| v  | v0 | v1 | v2 | v3 | v4 | v5 | v6 |
| a  | a0 | a1 | a2 | a3 | a4 | a5 | a6 |
| c  | c0 | c1 | c2 | c3 | c4 | c5 | c6 |

time-reversible formula for evaluation of velocity at time point $t=h$:

$$v_h = v_0 + (x_h - x_0) \frac{8}{3h} + (a_h + a_0) \frac{h}{9} + o(h^6)$$

(14)

Eq. (14) is more accurate than Eq. (13), but it requires the knowledge of position and acceleration at $t=h$. The general scheme of the new integrator on the basis of formulae (11,14) is presented in the Table 2. The first time-step has to be done by using another integrator.

3rd way. One may obtain even more precise velocity formula by using correction term $c_0$ of Eq. (11):

$$v_h = v_0 + (x_h - x_0) \frac{48}{13h} + (a_h + a_0) \frac{24a_0}{13} \frac{h}{13} + c_0 \frac{8h^3}{12} + o(h^6)$$

(15)

It should be noted the precision of estimate of velocity by Eq. (15) exceeds the precision of coordinate evaluation, therefore the energy conservation can not be improved considerably by this way.

VECTOR FORMULAE

Again let us consider the second order differential equation in vector notation:

$$\ddot{r} = f(\dot{r}) = m = a$$

(16)

Eqs. (28,29) can be rewritten as vector equations:

$$\ddot{v} = f(\dot{v})$$

(17)

$$f(x_0 + r) = f_0 + (a_0 + \dot{v} x) r + O(h^2)$$

(18)

$$r = v_0 t + a_0 t^2 = 2 + b_0 t^3 = 6 + O(h^4)$$

(19)

As it was for Eq. (16), substitute $r$ from Eq. (19) to Eq. (18) and hold only the even terms

$$f(x_0 + r)_{\text{even}} = f_0 + (a_0 + \dot{v}) (x_0 + r) + O(h^2)$$

(20)

and finally

$$c_0 = (a \cdot x) + (v \cdot \ddot{x}) = m$$

(21)

For evaluation of velocity one may again use Eq. (15) and the general scheme of integration (see Table 2).

1st example

Consider the forces depending only on distance $r = r \cdot j$

$$f(r) = f(v) = r$$

We need the following vector identities

$$(\overrightarrow{w} \cdot r) f = f(r) \overrightarrow{w} + f(\overrightarrow{w} \cdot r) r$$

(22)

$$2 \left( \overrightarrow{w} \cdot r \right) f = 2 f(\overrightarrow{w} \cdot r) \overrightarrow{w} + f(\overrightarrow{w} \cdot r) r + f(\overrightarrow{w} \cdot r) r$$

(23)

where $w = \text{const}$.

Applying Eqs. (22,23) to the general integration formula Eq. (21)

$$c_0 = f(r) x + f(\overrightarrow{w} \cdot r) v + f(\overrightarrow{w} \cdot r) \overrightarrow{w} + f(\overrightarrow{w} \cdot r) r$$

(24)

$$x_i = x_0 + a_0 h^2 + c_0 h^4$$

(25)

2nd example

Let us consider the Molecular Dynamics system of $N$ particles with pair-wise interaction. In the vector notation $N$ equations of motion are given by

$$m_i \ddot{r}_i = \sum_{j \neq i} f(\overrightarrow{r}_{ij})$$

(26)

Represent the relative positions $r_{ij}$ in a Taylor series about $t=0$

$$r_{ij} = r_{ij}(t) = r_{ij}(0) + (v_{ij} \cdot t) + (a_{ij} \cdot t^2) + \cdots$$

(27)

and expand the pair-wise forces $f_{ij}$ in the vicinity of $r_{ij}(0)$

$$f_{ij}(r_{ij}(0) + x_{ij}) = f_{ij}(0) + (x \cdot \dot{r}_{ij}) = f_{ij}(0) + (x \cdot \dot{r}_{ij})$$

(28)
By substitution \( r_{ij} \) from Eq. (27) to Eq. (28) one may obtain

\[
r_{ijh} = r_{ij0} + \frac{X}{\sum_{i,j} h_{ij0}} + \frac{h^2}{12m_i} \]

(29)

Then, by substitution \( a_{ij} = (a_i, a_j) \) and so on into Eqs. (24,25) it is easy to derive the final formula:

\[
c_{ij0} = \frac{f(x)}{r} + 2 \frac{g_0}{r} (v \cdot r) + v^2 + (a \cdot r) r + \frac{f_0}{r^2} \frac{v^2}{r^2} r = m_i
\]

(30)

\[
r_{ijh} = r_{ij0} + a_{ij0} h^2 + \frac{X}{\sum_{i,j} c_{ij0}} h^4 = 12
\]

(31)

**MOLECULAR DYNAMICS TESTING**

We have performed a practical test of the new method to estimate its applicability for MD simulation problem. The pair potential for our model system is described by the quasi-Lennard-Jones (qLJ) potential with cut-off distance \( r_c^2 = 5 \sigma_0^2 \), where \( \sigma_0 = 2 \). In reduced MD units with LJ parameters \( = 1, = 1 \) it is given by

\[
q_{LJ}(r) = \frac{\sigma_0^2}{r^2} - \frac{\sigma_0^4}{r^4} \quad r < 2.51 \quad r \geq 2.51
\]

(32)

Unlike to standard LJ potential function the qLJ potential Eq. (32) has “good” properties at cut-off radius \( r = r_c \). The mass is assumed to be \( m = 48 \). Number of atoms is fixed \( N = 3375 \) and all of them are located inside the MD simulation cube \( L = 17 \) MD units with imposed periodical conditions. Before testing the MD system is thermalized at \( T = 1.2 \) and stored on disk. This thermodynamically equilibrium state is a starting point of all testing runs.

For comparison purposes we choose Verlet algorithm in the coordinate form Eqs. (33-34):

\[
x_i(t) = x_i(0) + \alpha_i h^2 + O(\alpha_i^4)
\]

(33)

\[
x_i = x_i + \alpha_i h
\]

(34)

\[
\alpha_i = f(x_i) = m
\]

(35)

\[
\alpha_i = (x_i + x_i) = 2h + (a_i + 2a_i)h = 3 + O(\alpha_i^4)
\]

(36)

To improve the local energy conservation in the Verlet scheme the particle velocity \( v_i \) is evaluated by using accurate Eq. (36) which does not affect the trajectory evaluation (see 3).

The new integrator is chosen in the form of Eqs. (33-36) with step-by-step algorithm from the Table 2. Unfortunately, the new method requires, in principle, the double run over all \( i,j \) particles to evaluate \( a_i \) and \( c_{ij} \). According to our simulations it takes approximately 2 (from 1.8 to 2.2 on different machines) times more computer time than it takes for the Verlet scheme.

Figures 1, 2 show the timing data of several simulation runs for different time steps. Fig. 1 indicates that root-mean-square accuracy of the new method is the superior, but the new method takes almost twice as much of CPU time. We evaluate the relative efficiency of the method by comparing timings required for simulation of the same MD time by the new method and Verlet method at given accuracy. The results are demonstrated in Fig. 2. For given test the new integrator becomes more efficient if the desired accuracy is better than \( 5 \times 10^{-5} \). For instance, at the pre-
scribed accuracy $10^6$ the new method takes 4 times less computer time than the Verlet algorithm.

CONCLUSION

We have demonstrated that the new integrator is time-reversible and very accurate. It can be efficiently applied for highly precise MD simulations. The new method is expected to be useful for simulation of celestial mechanics problems too.

It should be noted that Eq. (31) was obtained first in [4], but it was used in a time-irreversible algorithm.

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