TASK QUARTERLY 6 No 3 (2002), 461–468

INFLUENCE OF STEP ERRORS (TRUNCATION ERRORS) ON RESULTS OF MOLECULAR DYNAMICS SIMULATIONS

MAREK LITNIEWSKI

Institute of Physical Chemistry of the Polish Academy of Sciences,
Kasprzaka 44/52, 01-224 Warsaw, Poland
mark@ichf.edu.pl

(Received 21 March 2002)

Abstract: Step errors (local errors, called also truncation errors) of the algorithms used in molecular dynamics simulations may result in non-physical correlations between particle velocities, as well as in errors of thermodynamic properties of simulated systems (energy, pressure). The simulations of the Lennard-Jones liquid showed, that the influence is especially high for the Verlet velocity algorithm. Beeman's technique decreases the correlations between the velocities, but at high densities the values of the errors of general averages are close to that of the Verlet method. The influence of step errors can be decreased by about two orders of magnitude by applying the Cowell-Numerov 4^{th} order implicit method (equivalent to the Gear 4^{th} order method treated as an implicit one). The method is very stable (more stable than the Verlet one), and can be highly optimized by restricting iteration to the closest neighbors of a given particle. As a result, the method becomes more efficient than the higher order explicit symplectic methods.

Keywords: error, molecular dynamics, symplectic, Verlet, Beeman, Cowell-Numerov

1. Introduction

The most popular and widely used method of integrating the equations of motion is the Verlet algorithm [1–3] called also the leap-frog scheme. The algorithm is time-reversible and symplectic [4], which is important from theoretical point of view. The method is very stable and has excellent energy conserving properties [2]. It is also simple and very easy to apply. However, as will be shown, it has an important disadvantage. A high step error (local error) of the main formula of the method, (Equation (1) below), generates noticeable errors in the properties of the simulated systems.

The formulas of the Verlet algorithm used for evaluating the $3N$-dimensional vector of the coordinates ($\mathbf{q}$) and momenta ($\mathbf{p}$) of an N-particle system at the time $t+\Delta t$ are as follows:

$$\mathbf{q}(t+\Delta t) = 2\mathbf{q}(t) - \mathbf{q}(t-\Delta t) + \frac{\Delta t^2}{m}\mathbf{F}(t) + O(\Delta t^4), \tag{1}$$

$$\mathbf{p}(t+\Delta t)=\frac{m}{\Delta t}\left[\mathbf{q}(t+\Delta t)-\mathbf{q}(t)\right]+\frac{\Delta t}{2}\mathbf{F}(t+\Delta t)+O(\Delta t^2), \tag{2}$$

where $\mathbf{F}(t)$ denotes the force, and m the particle mass.

The system (1)–(2) is equivalent to so called velocity Verlet algorithm. If $\mathbf{F}$ is independent of $\mathbf{p}$, Equation (1) can be solved independently and Equation (2) may be treated as a definition of momentum. The error of this "definition" is quite high ($-(\Delta t^2/6)d\mathbf{F}/dt$), and the averages $\langle \mathbf{p}_i d\mathbf{F}_i/dt\rangle$, $(i=1,\ldots,N)$ are non-zero. As a result, individual errors of $\mathbf{p}_i$ accumulate, shifting the average value of the total kinetic energy (E_k) by:

$$\Delta E_k \cong \left\langle \sum_{i=1}^{N} \mathbf{p}_i \mathbf{Err}(\mathbf{p}_i)/m_i \right\rangle. \tag{3}$$

In the case of Equation (2), ΔE_k is of order $O(\Delta t^2)$, and it may considerably influences the simulations results.

The mentioned effect is known [5], and a way to decrease its influence is to replace Equation (2) by a better approximation, for example:

$$\mathbf{p}(t+\Delta t)=\frac{m}{\Delta t}\left[\mathbf{q}(t+\Delta t)-\mathbf{q}(t)\right]+\frac{\Delta t}{6}\left[2\mathbf{F}(t+\Delta t)+\mathbf{F}(t)\right]+O(\Delta t^3). \tag{4}$$

Equations (1) and (4) are equivalent to the so called Beeman's technique [6], which is recommended [5, 7] as the most accurate of all the methods based on or equivalent to (1). ΔE_k resulting from Equation (4) is of order $O(\Delta t^4)$ (the contributions from $d^2\mathbf{F}_i/dt^2$ nullify), but the step error of Equation (1) is still not changed and it propagates as $O(\Delta t^2)$. Therefore, the Beeman method is of the same order (the second one) as the Verlet velocity one and would be more accurate only if the influence of the error of Equation (1) can be neglected when compared to the influence of the error resulting from Equation (2).

The other family of integrators applied for molecular dynamics simulations is the set of the Gear predictor-corrector methods [1]. The most known of them is the fourth order one. The method has an important property: its final (corrected) formula is time-reversible. The corrected formulas of the method are equivalent to Equation (4) and the fourth order Cowell-Numerov formula for a second order differential equation [8]:

$$\mathbf{q}(t+\Delta t)=2\mathbf{q}(t)-\mathbf{q}(t-\Delta t)+\frac{\Delta t^2}{12m}\left[\mathbf{F}(t+\Delta t)+10\mathbf{F}(t)+\mathbf{F}(t-\Delta t)\right]+O(\Delta t^6). \tag{5}$$

Recently, it has been shown [9] that the Cowell-Numerov method is also symplectic.

The main problem of Equation (5) is that usually $\mathbf{F}(t)=\mathbf{F}(\mathbf{q}(t))$, and the time-reversibility requires iterative solving of the equation, which is very time-consuming. Fortunately, for a vast majority of potentials used in simulations the iteration can be restricted only to the closest neighbors of a given molecule. Application of the restricted iteration significantly decreases the time required for performing a single time step.

Since Equation (5) is independent of momenta, similarly as in the case of Equation (1), we can use much more accurate formula to define the momentum. For example:

$$\begin{aligned}\mathbf{p}(t) = {} & \frac{m}{\Delta t}\left[\mathbf{q}(t+\Delta t)-\mathbf{q}(t)\right] \\ & -\frac{\Delta t}{360}\left[38\mathbf{F}(t+\Delta t)+171\mathbf{F}(t)-36\mathbf{F}(t-\Delta t)+7\mathbf{F}(t-2\Delta t)\right]+O(\Delta t^5)\end{aligned} \tag{6}$$

can be used. At typical conditions the error of Equation (6), and the resulting value of ΔE_k (3) is much lower than that of Equation (4). The only disadvantage is that the formula (6) gives the momentum at time t but not $t+\Delta t$ (like Equation (4)). As a consequence, the total energy can not be evaluated before the next step is performed. In this work the method of iterative solving of Equation (5) with momenta evaluated from Equation (6) is called simply the Cowell-Numerov (CN) method.

2. Computer simulations, results and discussion [10]

Computer simulations were performed using standard molecular dynamics (MD) method [1, 2] in a cube with the periodic boundary conditions. The constant parameters of each run were: the number of particles, N, always equal to 32768, volume V, and the total energy, E. The particles interacted with specially truncated Lennard-Jones [2] (LJ) potential:

$$u_{ij} = \begin{cases} 4\varepsilon\left[\left(\dfrac{\sigma}{r_{ij}}\right)^{12}-\left(\dfrac{\sigma}{r_{ij}}\right)^{6}\right]+A & \text{for } r_{ij}/\sigma < R_S = 1.60, \\ B\left(r_{ij}/\sigma - R_C\right)^3\left[1+C\left(r_{ij}/\sigma-R_C\right)\right] & \text{for } R_S \le r_{ij}/\sigma \le R_C, \\ 0 & \text{for } r_{ij}/\sigma > R_C = 2.0, \end{cases} \tag{7}$$

where ε and σ are the LJ energy and length parameters, respectively, and the A, B, and C constants were adjusted to make the second derivative of u a continuous function for all interparticle distances, r_{ij}. All numerical values presented further are expressed in reduced LJ units (*i.e.* $\sigma=\varepsilon=m=1$).

The total momentum of the simulated system was always equal to zero. For such a case, for an infinite system at the equilibrium state, the average value of scalar product of velocities should be zero for all r_{ij}. In our case of not very large N, and because of the periodic boundary conditions used, some non-zero values can appear. But, possible non-physical correlations between particle velocities can be also due to a method applied for solving the equations of motion.

The effect is presented in Figure 1, which shows the average value of scalar product of velocities ($\mathbf{v}$) of a pair of particles (i,j) as a function of the interparticle distance (r_{ij}). The simulations were performed for the number density $\rho=0.67$ and the reduced temperature $k_BT\approx 2.5$. Most of the simulations were performed using Equation (1). These results are presented as triangles (for $\Delta t=0.0075$) and circles (for $\Delta t=0.0025$). The momenta of particles were evaluated form Equation (2) (empty symbols), and Equation (4) (filled symbols). The crosses represent the results obtained by iterative solving of Equation (5) for $\Delta t=0.005$. For this case the particle velocities were exceptionally evaluated from Equation (4).

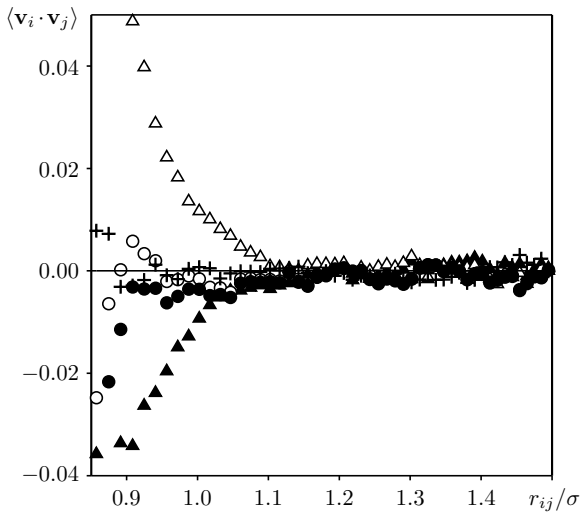

Figure 1. The dependence of the average value of scalar product of velocities $\langle \mathbf{v}_i \cdot \mathbf{v}_j \rangle$ of a pair of particles (i,j) as a function of the interparticle distance (r_{ij}); triangles – Equation (1) for $\Delta t = 0.0075$, circles – Equation (1) for $\Delta t = 0.0025$; empty symbols – velocities from Equation (2), filled symbols – velocities from Equation (4); crosses – iterative solving of Equation (5) with the velocities from Equation (4), for $\Delta t = 0.005$

At typical thermodynamic conditions the error of Equation (4) is much lower than that of Equation (2). As a result, the particle velocities obtained from Beeman' technique should be less correlated than the velocities resulted from the standard Verlet formula. This is seen by comparing the results for $\Delta t = 0.0075$ (filled and empty triangles). For the velocity Verlet method the results are reasonable for $r_{ij} > 1.1$, whereas for Beeman's formula the lower limit of r_{ij} amounts to about 1.02. For very low interparticle distances both methods give strongly non-physical result also for $\Delta t = 0.0025$ (circles). But in this case, the reason of the non-physical effect is the step error of Equation (1). This arises from the results obtained using Equations (5) and (4) (crosses). The obtained values are reasonable (taking into account the errors) in the whole range of r_{ij} in spite of $\Delta t = 0.005$, and the formula for velocities is the same as that for Beeman's technique.

The presented results show that the Beeman method can be better than the velocity Verlet one only when the interparticle interactions are sufficiently weak. Therefore, especially at high densities or/and high temperatures the errors resulting from the two methods should be comparable. This agrees with the results presented in Figure 2. The figure presents the potential energy density, U/N, as a function of the length of the time step Δt for various algorithms at the state point: $\rho = 0.75$, $E/N = -1.17620 \pm 0.00002$ ($k_B T \approx 1.26$). The tested algorithms were as follows: the velocity Verlet method (Equations (1) and (2), empty circles), Beeman's technique (Equations (1) and (4), filled circles), the Gear 4^{th} order predictor-corrector [2, 3] (empty triangles), the CN method (Equations (5) and (6), squares), and the Calvo and Sanz-Serena (CSS) 4^{th} order method [11, 12] (filled triangles). The latter method is recommended as the most efficient of all the explicit symplectic integrators [12]. The dependence of the virial function $\phi = \langle \sum \mathbf{r}_{ij} (\partial u_{ij} / \partial \mathbf{r}_{ij}) \rangle$ from Δt was very similar to that from Figure 2.

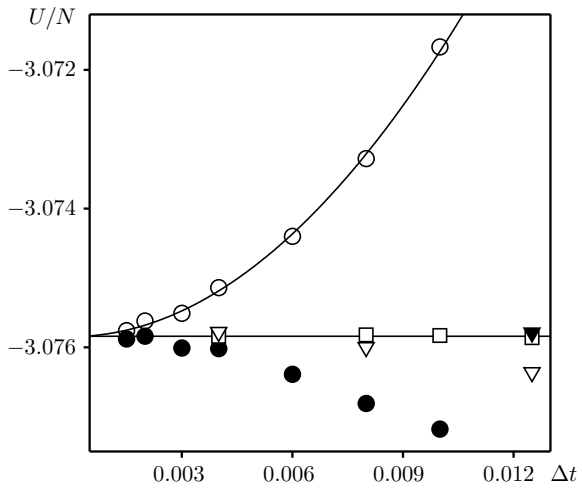

Figure 2. Potential energy density, U/N, as a function of Δt for various algorithms: empty circles – Verlet velocity, filled circles – Beeman, empty triangles – Gear 4^{th} order predictor-corrector, empty squares – Cowell-Numerov, filled triangle – Calvo and Sanz-Serena. The curve was fitted by the least squares method. The horizontal line corresponds to the value of U_0/N resulting from the fit

The values of U and ϕ obtained by the second order methods (Equations (1) and (2) or (4)) were fitted to the curves of the form $X = X_0 + A_X(\Delta t)^2$ (X_0 and A_X are constants) by using the least squares method. The values of χ^2 were close to 1 for both U and ϕ. For example, the U/N curve for the velocity Verlet method is presented in Figure 2. In order to compare the results of the simulations we assumed that the values of U_0 and ϕ_0 obtained from the minimizations are very close (for our purposes the difference can be neglected) to the real values (*i.e.* obtained from an exact solution of the equations of motion). This assumption is in full agreement with the results of the remaining methods (see Figure 2, the horizontal line corresponds to U_0/N).

Table 1. The deviations of U and ϕ obtained from the simulations from the hypothetical real values (U_0 and ϕ_0) for several selected runs

Method	Δt	$(U-U_0)/N$	$(\phi-\phi_0)/3V$
velocity Verlet	0.010	0.00417(6)	-0.01481(33)
Beeman	0.010	-0.00139(6)	0.00900(30)
Gear pred-corr 4^{th} order	0.0125	-0.00052(6)	0.00084(33)
Cowell-Numerov	0.0125	-0.00002(4)	0.00019(17)
Calvo and Sanz-Serena	0.0125	0.00005(4)	-0.00018(15)

The deviations of U from U_0 and ϕ from ϕ_0 for the runs performed with the highest Δt are presented in Table 1. The numbers in parenthesis are the errors in units of the last digit of the corresponding value. Table 1, as well as Figure 2, clearly show that at the given state point the Beeman method is only slightly better than the Verlet one. According to the interpretation of Figure 1 a decrease of the density, which results in a decrease of the rate of strong collisions, should decrease the deviations of U and ϕ and the effect should be stronger for Equation (4) than for (2). This was

confirmed by additional simulations for $\rho = 0.50$ and $\Delta t = 0.01$. For Beeman's method the obtained deviations were over 5 times lower than those from Table 1. For the velocity Verlet method the ratio amounted to about 2.

Figure 2 and Table 1 show a great advantage of the higher order methods as compared with the methods based on formula (1). For the CN and the CSS method the advantage is evident. The deviations of U and ϕ from the reference values are nearly two orders of magnitude lower than those for the second order methods, although the time step applied for the fourth order methods is longer. For the Gear predictor-corrector method the deviation of U for $\Delta t = 0.0125$ is only about three times lower than that for the Beeman method, but this is due not to the step error, but rather to the scaling of the velocities. The scaling is necessary to keep the total energy constant. The Gear method merely approximates the solution of Equation (5). This leads to a considerable inconsistency between the left and the right hand side of Equation (5) and, as a consequence, to the drift of the energy. The drift sharply increases with increasing Δt.

The method applied to solving of Equation (5) was also an approximate one. The iterations were restricted to the closest surrounding of a given particle ($r_{ij} < 1.25$). As a result, there appeared a drift of the energy, which forced us to scale the velocities. But in this case, the influence of the velocity scaling on the obtained results was negligible. For the method of restricted iteration the inconsistency between both sides of Equation (5) and the resulting drift was many orders of magnitude lower than that for the Gear method. For example, the drift for $\Delta t = 0.0125$ was over 10 times lower than that for the Gear predictor-corrector method for $\Delta t = 0.004$.

In the case of exact solving of Equation (5) (iterations for all $r_{ij} < R_C$), the CN method becomes more stable even than the Verlet one. Additional simulations gave for $\Delta t = 0.0125$ the drift of E/N per time unit equal to $5 \cdot 10^{-7}$ for the exact CN, and to $3 \cdot 10^{-6}$ for Equation (1).

The presented methods were additionally tested by performing series of central collisions of a pair of particles interacting by potential (7). The Newton equation of motion was solved numerically by applying, for various time steps: Equation (1), Equation (5), and the CSS method. U and ϕ were measured at the same time intervals always equal to the maximal time step $\Delta t_{\max} = 0.01$. In order to eliminate the influence of initial conditions the results were averaged over $n_s = 100$ collisions, each for the initial distance $r_0^i = R_C + (i-1)|v_0|\Delta t_{\max}/n_s$ for $i = 1, \ldots, n_s$, where v_0 – the initial velocity. The test was performed for $v_0 = -3.0$ and -5.0. The results are presented in Table 2.

The results from Table 2 fully confirm the superiority of the higher order methods. The errors of the methods are over two orders of magnitude lower than the errors resulted from the application of Equation (1). The results presented in Table 1 and 2 also show that the accuracy of the CN method is very close to that of the CSS one. High values of the errors (see the brackets) from Table 1 as well as an approximated character of the test (Table 2) do not allow us to judge which of the two methods is more accurate. Therefore, the only thing we can say, is that the accuracies of the two methods are approximately the same.

The main problem of the higher order explicit integrators is the time of performing a single time step. The methods require several (for CSS – four) evaluations

Table 2. The deviations of the average potential energy (u) and the virial function ($r\partial u/\partial r$) as a function of Δt for central collisions of a pair of LJ particles for three various methods. $\delta\langle x\rangle$ is the deviation of the measured values from the value evaluated for $\Delta t = 0.0003125$

		$v_0 = -3.0$		$v_0 = -5.0$	
Method	Δt	$\delta\langle u\rangle$	$\delta\langle r\partial u/\partial r\rangle$	$\delta\langle u\rangle$	$\delta\langle r\partial u/\partial r\rangle$
Verlet	0.00125	$1.3\cdot10^{-5}$	$3.8\cdot10^{-5}$	$3.3\cdot10^{-5}$	$2.1\cdot10^{-4}$
	0.0025	$5.5\cdot10^{-5}$	$1.6\cdot10^{-4}$	$1.4\cdot10^{-4}$	$8.9\cdot10^{-4}$
	0.0050	$2.2\cdot10^{-4}$	$6.5\cdot10^{-4}$	$5.6\cdot10^{-4}$	$3.6\cdot10^{-3}$
	0.010	$9.0\cdot10^{-4}$	$2.6\cdot10^{-3}$	$2.3\cdot10^{-3}$	$1.5\cdot10^{-2}$
Cowell-Numerov	0.00125	$1.5\cdot10^{-9}$	$6.8\cdot10^{-9}$	$8.1\cdot10^{-9}$	$8.5\cdot10^{-8}$
	0.0025	$2.4\cdot10^{-8}$	$1.1\cdot10^{-7}$	$1.3\cdot10^{-7}$	$1.4\cdot10^{-7}$
	0.0050	$3.8\cdot10^{-7}$	$1.8\cdot10^{-6}$	$2.1\cdot10^{-6}$	$2.2\cdot10^{-5}$
	0.010	$6.2\cdot10^{-6}$	$2.8\cdot10^{-5}$	$3.4\cdot10^{-5}$	$3.6\cdot10^{-4}$
Calvo and Sanz-Serena	0.00125	$1.1\cdot10^{-9}$	$-2.1\cdot10^{-8}$	$1.7\cdot10^{-8}$	$-2.6\cdot10^{-7}$
	0.0025	$1.8\cdot10^{-8}$	$-3.4\cdot10^{-7}$	$2.7\cdot10^{-7}$	$-4.1\cdot10^{-6}$
	0.0050	$3.0\cdot10^{-7}$	$-5.4\cdot10^{-6}$	$4.3\cdot10^{-6}$	$-6.6\cdot10^{-5}$
	0.010	$4.8\cdot10^{-6}$	$-8.8\cdot10^{-5}$	$7.0\cdot10^{-5}$	$-1.1\cdot10^{-3}$

of the total force to perform one time step. An exact iterative solving of Equation (5) would be an equally inefficient procedure. The method of approximated solving makes the CN method much more efficient than the higher order explicit methods. For the simulations performed here ($R_C = 2.0$; iterations restricted to $r_{ij} < 1.25$) the ratio of the time of performing one time step to the time of evaluation of the total force amounted to about 1.6. The value of the ratio strongly depends on the cut-off distance. An additional simulation for $R_C = 3.0$ gave the ratio close to 1.2. For comparison, for the CSS method this ratio amounts to about 4.0.

3. Summary and concluding remarks

In this work the influence of the step error of several popular algorithms on the results of simulations was presented. It was shown that in the case of the most widely used formula (1) the influence is quite high even if we apply Beeman's technique to reduce ΔE_k as much as possible. The obtained result (the shift of pressure by nearly 0.01 for $\Delta t = 0.01$) shows that the methods based on Equation (1) can be used only to qualitative simulations. A higher order algorithm is necessary if we are interested in quantitative simulations. The proposed implicit method based on approximated solving of Equation (5) is much more efficient than the higher order explicit symplectic methods. The approximation applied to solve Equation (5) bases on the assumption that we can divide the interparticle interactions into strong (and/or rapidly varying) and weak (and/or slowly varying). Such a division is almost always possible (maybe except for ion interactions) subject to the condition that the cut-off distance is not very low.

The main problem of the CN method with the proposed iteration scheme is high complexity of the procedure. Thus, the quantitative simulations are very time consuming processes. They require many tests (*e.g.* the effect of "shifting" the results presented in this work), and the final simulations are usually performed for a very long time. As a result, the time used to implement the procedure of restricted iteration is

short when compared to the total time devoted to the problem. The procedure, once written, can be easily adapted to another interparticle potential. The CN method can be also useful in the case of qualitative simulations, especially if we deal with a new problem. In such a case it is very often not sure whether the problem is only a qualitative or rather a quantitative one.

References

[1] Verlet L 1967 *Phys. Rev.* **159** 98
[2] Allen M P and Tildesley D J 1987 *Computer Simulations of Liquids*, Clarendon Press, Oxford
[3] Berendsen J C and van Gunsteren W F 1986 *Proc. Enrico Fermi Summer School* (Ciccotti G and Hoover W G , Eds.), Varenna 1985, North Holland, New York
[4] Isbister D J, Searles D J and Evans D J 1997 *Physica* **A240** 105
[5] MacGowan D and Heyes D M 1988 *Mol. Simul.* **1** 277
[6] Beeman D 1976 *J. Comput. Phys.* **20** 130
[7] Rodger P M 1989 *Mol. Simul.* **3** 263
[8] Dahlquist G and Bjorck A 1974 *Numerical Methods*, Prentice-Hall, New York
[9] Skeel R D, Zhang G and Schlick T 1997 *SIAM J. Sci. Comput.* **18** 203
[10] The results of this section, except for those concerning Figure 1, will be published in *Molecular Simulation*
[11] Okunbor D I and Skeel R D 1992 *J. Comput. Chem.* **15** 72
[12] Gray S K, Noid D W and Sumpter B G 1994 *J. Chem. Phys.* **101** 4062