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Published in:
Journal of Chemical Physics

DOI:
10.1063/1.4726728

Publication date:
2012

Document Version
Publisher's PDF, also known as Version of record

Citation for published version (APA):
Toxværd, S., Heilmann, O., & Dyre, J. C. (2012). Energy conservation in molecular dynamics simulations of classical systems. *Journal of Chemical Physics*, *136*(22), 224106-1 til 224106-8. https://doi.org/10.1063/1.4726728

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Citation: J. Chem. Phys. **136**, 224106 (2012); doi: 10.1063/1.4726728
View online: http://dx.doi.org/10.1063/1.4726728
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v136/i22
Published by the American Institute of Physics.

Energy conservation in molecular dynamics simulations of classical systems

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(Received 28 February 2012; accepted 23 May 2012; published online 12 June 2012)

Classical Newtonian dynamics is analytic and the energy of an isolated system is conserved. The energy of such a system, obtained by the discrete "Verlet" algorithm commonly used in molecular dynamics simulations, fluctuates but is conserved in the mean. This is explained by the existence of a "shadow Hamiltonian" $\tilde{H}$ [S. Toxvaerd, Phys. Rev. E **50**, 2271 (1994)], i.e., a Hamiltonian close to the original H with the property that the discrete positions of the Verlet algorithm for H lie on the analytic trajectories of $\tilde{H}$. The shadow Hamiltonian can be obtained from H by an asymptotic expansion in the time step length. Here we use the first non-trivial term in this expansion to obtain an improved estimate of the discrete values of the energy. The investigation is performed for a representative system with Lennard-Jones pair interactions. The simulations show that inclusion of this term reduces the standard deviation of the energy fluctuations by a factor of 100 for typical values of the time step length. Simulations further show that the energy is conserved for at least one hundred million time steps provided the potential and its first four derivatives are continuous at the cutoff. Finally, we show analytically as well as numerically that energy conservation is not sensitive to round-off errors. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4726728]

I. INTRODUCTION

Classical Newtonian dynamics is time reversible and the energy of an isolated system is conserved. Newton formulated his dynamics as an analytic dynamics with continuous time and space variables, and although quantum dynamics introduces discreteness in energies, continuity is maintained. In numerical solutions of classical dynamics all variables are discretized, however. In principle this could destroy the energy conservation. Nevertheless, one observes that the mean energy is conserved in time-reversible discrete dynamics.[1] This is explained by the existence of a *shadow Hamiltonian* $\tilde{H}$,[2] i.e., a Hamiltonian for which the numerical algorithm's discrete positions lie on its analytic trajectories.

Simulations of systems with discrete dynamics are generally performed by using symplectic (i.e., phase-space volume conserving) and time-reversible algorithms. For these algorithms there exists a shadow Hamiltonian $\tilde{H}$, which can be obtained from an asymptotic expansion of the original analytic Hamiltonian H.[3–6] Below we use this expansion to obtain an improved estimate of the discrete values of the energy for a Lennard-Jones fluid. Already the second non-trivial term in the expansion is quite complicated, and our investigation is limited to the first term in the series. Inclusion of this term reduces the standard deviation of the energy fluctuations by a factor of 100 for typical values of the discrete time-increment.

Besides the problem of obtaining the energy by discretizing the analytic equations of motion, computer simulations suffer from (at least) two shortcomings: The arithmetic operations are performed with finite accuracy (typically in double precision with relative accuracy of the order 10^{-16}). A second shortcoming appears in the calculation of the forces, which usually ignores interactions beyond a cutoff, r_c. This means that the forces are not exactly correct; moreover the cutoff is usually implemented such that it corresponds to a potential that is not analytic at r_c. Both shortcomings affect the energy conservation in molecular dynamics (MD) simulations. We have investigated the effects of the round-off errors and the non-analyticity of the potential on the energy conservation during long simulations. The round-off errors do not accumulate and the energy is not sensitive to round-off errors. This is consistent with the detailed analytic treatment given in Appendix B. As regards the role of the cutoff we find that the energy is conserved for at least one hundred million time steps provided the potential and its first four derivatives are continuous at r_c. This confirms the proof given by Hairer.[5]

The paper is organized as follows. Section II presents the MD algorithm(s) for the reversible discrete dynamics. The expression for the first term in the asymptotic expansion in powers of the time step, where the zeroth order term is the original Hamiltonian H, is given in Sec. III. Section IV describes MD of a Lennard-Jones fluid with the discrete values of the energy obtained by including the first term in the asymptotic expansion. The investigation is divided into short-time energy conservation (Sec. IV A) and long-time stability (Sec. IV B). Section V gives a brief discussion. Appendix A gives the expression for the first term in the asymptotic expansion, whereas the effect of round-off errors on the energy conservation is derived in Appendix B.

II. TIME-REVERSIBLE DISCRETE DYNAMICS OF CLASSICAL MECHANICAL SYSTEMS

The most commonly used algorithm in MD simulations of systems with classical dynamics is the so-called Verlet

algorithm,[7]

$$\mathbf{r}_i(t+h) = 2\mathbf{r}_i(t) - \mathbf{r}_i(t-h) + \frac{h^2}{m_i}\mathbf{f}_i(t), \tag{1}$$

where a new position $\mathbf{r}_i(t+h)$ at time $t+h$ of particle i with mass m_i is obtained from the two previous discrete positions, $\mathbf{r}_i(t)$, $\mathbf{r}_i(t-h)$, and $\mathbf{f}_i(t)$ is the force acting on the particle at time t. This algorithm is the *central-difference* expression for Newton's second law equating mass times acceleration to the force on a particle.[8] The Verlet algorithm has two fundamental properties:

1. It is time reversible[9] and symplectic.[10]
2. The positions are the only dynamic variables, i.e., the momenta, $\mathbf{p}$, are not dynamic variables. Consequently, an expansion of an analytic Hamiltonian, $H(\mathbf{q}, \mathbf{p})$, requires a choice of an expression for $\mathbf{p}$ in terms of the positions.

The Verlet algorithm appears in many different contexts and formulations with different names: Nyström-,[5] Störmer-,[9] Verlet-, position-Verlet-, velocity-Verlet-, leap-frog-,[1] isochronous leapfrog-,[10] and symplectic Euler algorithm.[11] According to Ref. 9, Delambre[12] have been the first (1791) to publish the algorithm, although it presumably was used already at Newton's time.

The leap-frog algorithm is the Lagrange-Hamilton formulation of the Verlet algorithm

$$\mathbf{r}_i(t+h) = \mathbf{r}_i(t) + \frac{h}{m_i}\mathbf{p}_i(t+h/2), \tag{2}$$

$$\mathbf{p}_i(t+h/2) = \mathbf{p}_i(t-h/2) + h\mathbf{f}_i(t), \tag{3}$$

where the momenta $\mathbf{p}_i$ or "velocities," $\mathbf{v}_i(t+h/2)$, $\mathbf{v}_i(t-h/2)$, are introduced as "help" variables that have no impact on the evolution of the system. This avoids subtractions (with inevitable loss of numerical accuracy) and for this reason we used this version of the algorithm in our investigation of energy conservation.

MD simulations using the Verlet algorithm present a fundamental problem: How to determine the total energy, $E(t) = U(t) + K(t)$, of the system. As mentioned, the Verlet algorithm is expressed exclusively in terms of the particle coordinates, there is no obvious expression for the momenta and thereby for the kinetic energy. A natural choice of the velocity at time t is

$$\mathbf{v}_i(t) = \frac{\mathbf{r}_i(t+h) - \mathbf{r}_i(t-h)}{2h}, \tag{4}$$

which is the mean velocity in the time interval $[t-h, t+h]$. If one uses this expression to obtain the kinetic energy $K(t)$ at time t, the total energy $E(t) = U(t) + K(t)$ is observed to fluctuate sizable, but it is constant in the mean even for very long simulations.[13] The origin of the fluctuation is clearly the use of Eq. (4). The main purpose of this paper is to show that one can do much better than this.

III. THE SHADOW HAMILTONIAN OBTAINED BY AN EXPANSION IN THE TIME-STEP INCREMENT

The shadow Hamiltonian $\tilde{H}$ for a symplectic and time-reversible algorithm can be obtained from H by an asymptotic expansion in the time step increment h if the potential energy is analytic. Griffiths and Sanz-Serna in 1986 (Ref. 3) were the first to suggest using "Modified Equations" (also called "Backward Error Analysis") for studying numerical methods of integration applied to ordinary differential equations. They gave several references to earlier works where the method is used for various partial differential equations. Sanz-Serna in 1992 (Ref. 4) stressed the importance of using symplectic methods of integration when integrating Hamiltonian systems. In 1994, Hairer[5] gave general formulas for systematically calculating the expansion of what became known as the "shadow Hamiltonian"[2,14] when using symplectic Rung-Kutta or Nyström methods (leap-frog). Hairer proved that such an expansion only exists if the integration method is symplectic. Reich in 1999 (Ref. 6) further advanced the theory in a paper where an extensive reference list can also be found. In 2000, Gans and Shalloway[15] gave an explicit expression for the first term in the expansion of the shadow Hamiltonian. The expansion was used for investigations of the errors introduced by the discretization of analytic (first-order) differential equations and to obtain "interpolatory shadow Hamiltonians."[15,16]

The Verlet algorithm is symplectic and time reversible. In Ref. 2, the first non-trivial term in the asymptotic expansion was obtained for the LJ system from consecutive sets of positions using the expression obtained from the expansion of H for a one-dimensional harmonic oscillator. Reference 15 gives the general expression for this using the method of modified equations derived in Refs. 3–6,

$$\tilde{H} = H + \frac{h^2}{2!}g(\mathbf{q}, \mathbf{p}) + \mathcal{O}(h^4), \tag{5}$$

with position $\mathbf{q}$ and momentum $\mathbf{p}$ in the Lagrange-Hamilton equations. For a system with potential energy $U(\mathbf{q})$, using Eq. (4) for $\mathbf{p}$ the first non-trivial term in the expansion is[15]

$$g(\mathbf{q}, \mathbf{p}) = \frac{1}{6}\mathbf{p}^T m^{-1}\frac{\partial^2 U(\mathbf{q})}{\partial \mathbf{q}^2}m^{-1}\mathbf{p} - \frac{1}{12}[\nabla U(\mathbf{q})]^T m^{-1}\nabla U(\mathbf{q}), \tag{6}$$

for a system of N particles with identical masses m.

We denote the Hessian, $\partial^2 U(\mathbf{q})/\partial \mathbf{q}^2$, of the potential energy function $U(\mathbf{q})$ by $\mathbf{J}$, the velocity of the N particles by $\mathbf{V}_n \equiv (\mathbf{v}_1, \ldots, \mathbf{v}_N)$, and the force with position $\mathbf{R} \equiv (\mathbf{r}_1, \ldots, \mathbf{r}_N)$ by $\mathbf{F}(\mathbf{R}) \equiv (\mathbf{f}_1(\mathbf{R}), \ldots, \mathbf{f}_N(\mathbf{R}))$. Using Eq. (4) for $\mathbf{V}$, Eq. (6) can be expressed in Cartesian coordinates as

$$E_n \simeq U(\mathbf{R}_n) + \frac{1}{2}m\mathbf{V}_n^2 + \frac{h^2}{12}\mathbf{V}_n^T\mathbf{J}(\mathbf{R}_n)\mathbf{V}_n - \frac{h^2}{24m}\mathbf{F}_n(\mathbf{R}_n)^2 \tag{7}$$

for the energy, E_n, at the nth time step. The first two terms are the standard expression for the discrete value of the total energy,

$$E_{disc,n} = U(\mathbf{R}_n) + \frac{1}{2}m\mathbf{V}_n^2. \tag{8}$$

The quantity $E_{disc,\,n}$ fluctuates with n but is conserved in the mean with a standard deviation (SD) of order h^2. According to Theorem 9 of Ref. 5 by including the next two terms in Eq. (7) the energy is conserved to fourth order in h, i.e.,

$$E_n - \langle E_n \rangle \sim h^4 . \tag{9}$$

Equation (9) includes the contribution to the energy from the first non-trivial term in the asymptotic expansion. The shadow energy $\tilde{E}_n$ obtained by using instead the full asymptotic expansion obeys[17] (where $a > 0$)

$$\tilde{E}_n - \langle \tilde{E}_n \rangle = \mathcal{O}(he^{-a/h}) . \tag{10}$$

There is a subtle difference between Eqs. (9) and (10). The condition for the existence of an asymptotic expansion and thus for Eq. (10) is that the potential is analytic. In contrast, the proof of Eq. (9) (Ref. 5) only requires that the first five derivatives of the potentials are continuous.

IV. MD SIMULATION OF THE LENNARD-JONES FLUID

We have analyzed the time dependence of the energy for a fluid of N particles in volume V interacting via the well-known Lennard-Jones (LJ) pair potential between particles with distance r and energy- and length units ϵ and σ, respectively:[18]

$$u_{\mathrm{LJ}}(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]. \tag{11}$$

The system's potential energy is given by

$$U = \frac{1}{2}\sum_{i\neq j} u_{\mathrm{LJ}}(r_{ij}) . \tag{12}$$

We simulated $N = 2000$ LJ particles at density $\rho = 0.8$ and temperature $T = 1.00$, a typical moderate-pressure liquid state. The dynamics was simulated in double-precision arithmetic with the leap-frog version of the Verlet algorithm.

In MD one usually ignores interactions beyond a certain "interaction range," r_c, which is for LJ particles traditionally taken to be $r_c = 2.5\sigma$. A standard shifted-potential (SP) cutoff introduces, however, an artificial force discontinuity at the truncation. This can be removed by using instead a shifted-forces (SF) cutoff, where one shifts the force below r_c such that it goes continuously to zero at r_c. In both cases $E_{disc,\,n}$ and E_n fluctuates, but in contrast to what is the case for a SP cutoff, the energy is stable over millions of time steps for a SF cutoff.[13]

As mentioned, the proof of Eq. (10) requires analytic potentials whereas Eq. (9) only requires that the first five derivatives of the potential are continuous[5] (actually it is enough that the fifth derivative is piecewise continuous and bounded). This difference is important when one truncates the potential because it is not possible to truncate a potential without violating analyticity. The potential can be smoothed in different ways.[13] The SP potential with a cutoff at r_c is simply $u(r) = u_{LJ}(r) - u_{LJ}(r_c)$ for $r < r_c$ ($u(r) = 0$ for $r > r_c$). We smooth it by the following replacement:

$$u(r) = (u_{LJ}(r) - u_{LJ}(r_c))\frac{(r_c - r)^n}{(r_c - r)^n + \alpha^n} \quad (r < r_c), \tag{13}$$

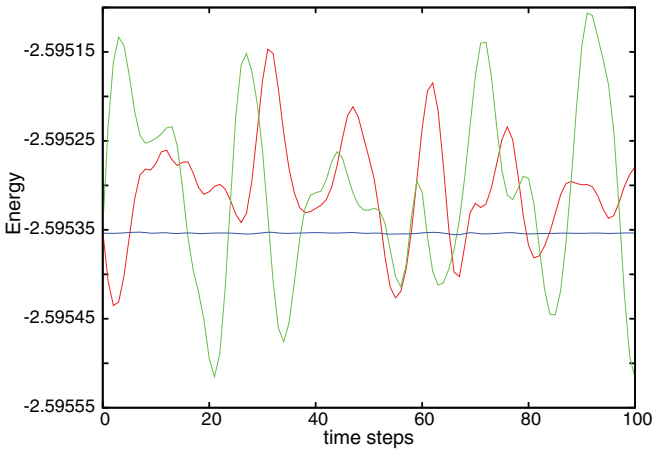

FIG. 1. The evolution of the energy per particle over short times for a LJ fluid at $T = 1.00$ and $\rho = 0.80$, with cutoff $r_c = 2.5\sigma$ and time-step increment $h = 0.005$. Red: $E_{disc,\,n}/N$ for a shifted-forces (SF) cutoff and green: $E_{disc,\,n}$ for a shifted-potential (SP) cutoff. With blue is shown E_n for SF obtained by Eq. (7) (the $E_{disc,\,n}$ energies are shifted such that the three energies are identical at the start).

where $\alpha > 0$. This smoothing ensures that the nth derivative of $u(r)$ is continuous at r_c. The parameter α gives the effective range of the smoothing; in the simulations we used $\alpha = 0.1$.

We performed MD with SF, SP, smoothed SP with $n = 2$ ("SP2"), and smoothed SP with $n = 4$ ("SP4"). The investigation of energy conservation below is divided into studies of the short-time behavior of the energy fluctuations (Sec. IV A) and studies of the long-time stability of the energy (Sec. IV B). Appendix A details the calculation of the Hessian matrix $\mathbf{J}$ for the LJ system.

A. Short-time behavior of energy fluctuations in MD

The energies $E_{disc,\,n}$ and E_n fluctuate with n. For the LJ system the short-time behavior and the standard deviations of these fluctuations were calculated for 10 000 steps for the different ways of smoothing of the energy function at the cutoff introduced above. The energy evolution for the first hundred time steps is shown in Fig. 1. The time increment is $h = 0.005$ and $r_c = 2.5\sigma$ (standard LJ values). The red line shows $E_{disc,\,n}$ for a SF cutoff and the green line is the corresponding energy evolution with a SP cutoff. In both cases the SD is 6.5×10^{-5}. With blue line is shown the SD for the E_n of Eq. (7) resulting in an improved SD of 6.5×10^{-7}, i.e., an improvement of a factor of 100.

In Ref. 2, we obtained an expression (Eq. (20) in Ref. 2) equivalent to Eq. (6) for the first non-trivial term in the asymptotic expansion. We determined E_n, not from $\mathbf{J}(t)$, but from three consecutive positions $\mathbf{R}(t-h)$, $\mathbf{R}(t)$, $\mathbf{R}(t+h)$ of the particles. For small time increments this should be comparable, but in fact it only improved the energy estimate of $\tilde{H}$ by a factor of four.

The dependence of the SD on the magnitude of the time increment h is studied in Fig. 2. According to Eq. (9) the SD of the energy fluctuations with the improved estimate of the energy of Eq. (7) is proportional to h^4; in contrast, the SD for $E_{disc,\,n}$ is proportional to h^2. Figure 2 shows the SD of the

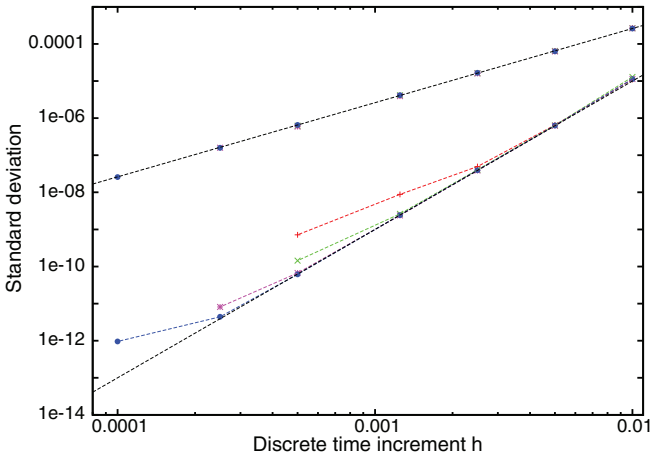

FIG. 2. Standard deviations (SD) of the energy per particle as a function of the time increment h. The upper points are for E_{disc}/N, the lower points are obtained from Eq. (7). The SD is obtained for different ranges of interaction r_c with a SF cutoff. Red dashes and +: $r_c = 2.5\sigma$; green and ×: 3.5σ; magenta and *: 4.5σ; and blue and filled circles: 5.5σ. The two black straight lines with dashes have the theoretically predicted slopes of two and four, respectively.

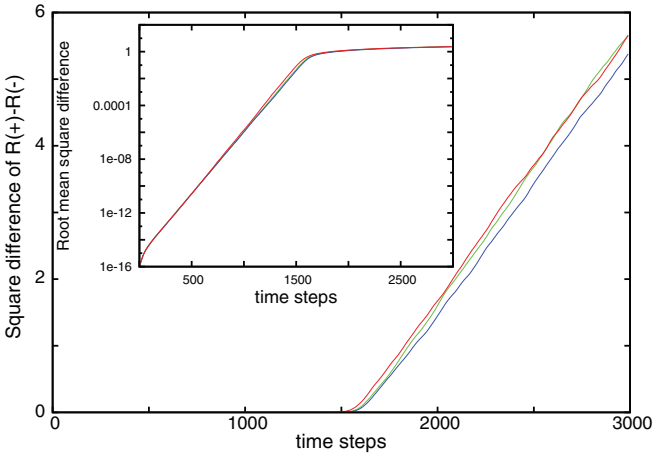

FIG. 3. Mean-square difference $\Delta\mathbf{R}^2/N = (\mathbf{R}_{M-n}(+) - \mathbf{R}_{M+n}(-))^2/2000$ of the positions at forwards (+) and backwards (–) simulations. The green line is for SP, the blue line for SP2, and the red line for SP4 (all for $r_c = 2.5\sigma$). The Lyapunov instability region (see insert) is not visible on the main figure. The inset shows $log[\sqrt{\Delta\mathbf{R}^2/N}]$ for the same time interval, but in a logarithmic plot.

energy fluctuations obtained from 10 000 steps with a SF cutoff for various values of h. The SD is improved by a factor of 10 000 for the smallest time increments. The dependence of h follows the predictions with minor deviations as h becomes very small. This deviations are not caused by numerical inaccuracies, but is due to the truncation of the force field at r_c. For $h = 0.00025$, for instance, it is necessary to extend the cutoff to $r_c = 4.5\sigma$ in order to obtain the predicted h^4 dependence.

According to Eq. (B13) in Appendix B the effect of the round-off error on energy conservation is diffusive-like. It does not accumulate provided the leading source originates from calculating the forces. The results shown in Fig. 2 demonstrate not only that the non-analyticity of the potential at r_c affects the energy conservation but also that the round-off errors do not affect energy conservation over 10 000 steps. We conclude this by noting that extending the range of attraction from $r_c = 2.5\sigma$ to $r_c = 4.5\sigma$—thereby reducing the effect of the discontinuities—does not affect the h^4 dependence despite the fact that one, by extending the range of attraction, includes many more attractions. The extension of r_c to 4.5σ increases the number of arithmetic operations and the round-off errors (with a factor of five) but does not ruin the h^4 dependence.

As mentioned, the proof of Eq. (9) requires that the first five derivatives are continuous at r_c. Although using a SF cutoff ensures that the forces are continuous at r_c and reduces the effect of the truncation on the higher-order derivatives of the potential at the cutoff, the results in Fig. 2 where only the first derivative of the potential is continuous, indicate that the energy conservation is sensitive to the truncation of the force field. This affects the long time stability of MD (see Sec. IV B).

The effect of the round-off errors on time reversibility and energy conservation can be investigated by stopping the forward simulation at some time, t_M, subsequently reversing time to retrace the steps.[9] Figure 3 shows as a function of the number of time steps the mean-square difference $\Delta\mathbf{R}^2/N = (\mathbf{R}_{M-n}(+) - \mathbf{R}_{M+n}(-))^2/N$ of the $N = 2000$ particles positions at a forwards (+) simulation, $\mathbf{R}_{M-n}(+)$ and "backwards" simulation (–), $\mathbf{R}_{M+n}(-)$. After 1500 steps there is a linear growth in the "diffusive regime." In this regime all particles have lost their memory about the origin positions and diffuse with a linearly growth of $\Delta\mathbf{R}^2/N$ equal to the corresponding growth of a random walk with a slope proportional to the self-diffusion constant (the "Einstein relation").[20] The transition from perfect time reversibility to the uncorrelated regime is not visible on the main figure. The inset shows $log[\sqrt{\Delta\mathbf{R}^2/N}]$ in a logarithmic plot in order to show this transition. The round-off errors result in an exponential Lyapunov instability,[21,22] which within 1500 steps results in a total loss of correlation between $\mathbf{R}_{M-n}(+)$ and $\mathbf{R}_{M+n}(-)$ and the memory about their common origin. The exponential growth of the mean distance (insert) is due to the Lyapunov exponents with the dominating effect caused by the most negative exponent.[21] The green line in the figure is for SP, the blue line for SP2, and the red line for SP4. The three behaviors are qualitatively the same. This demonstrates that the Lyapunov instability is caused by the round-off errors, not by discontinuities in the potential or its higher-order derivatives.

The round-off errors destroy time reversibility whereby also the observed energy $E_{M-n}(+)$ of the forward simulation deviates from the energy $E_{M+n}(-)$ of the backwards simulation. This is shown in Fig. 4. After 1500 steps where the trajectories are uncorrelated (Fig. 3), the energy difference $E_{M-n}(+) - E_{M+n}(-)$ fluctuates with the same mean amplitude as the discrete energies E_n. The inset shows the deviation in the Lyapunov instability regime ($n < 1500$) where the round-off errors destroy the correlation between $E_{M-n}(+)$ and $E_{M+n}(-)$.

The effect of the round-off error on time reversibility and energy conservation can be amplified by changing from double- to single-precision. Single-precision simulations rapidly violate time reversibility, and the energy

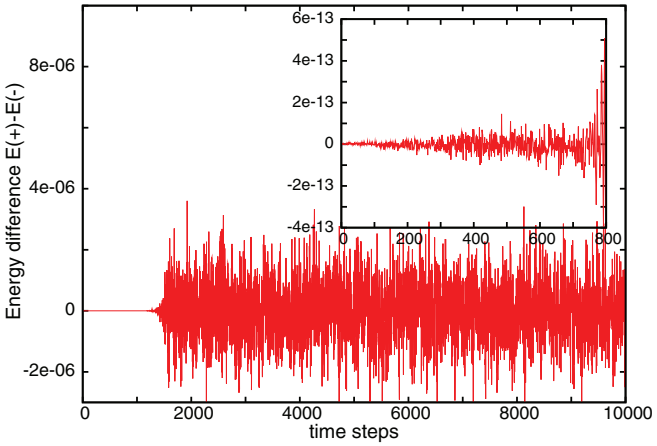

FIG. 4. Short-time behavior of $(E(+) - E(-))/N$ for SP4 with $r_c = 2.5\sigma$. The first 800 steps are shown in the inset.

difference $E_{M-n}(+) - E_{M+n}(-)$ fluctuates with an amplitude similar to the amplitude of the energy for double-precision simulations. Figure 5 shows the mean amplitude of the energy fluctuations for SP4 with $r_c = 2.5\sigma$ with single (green) and double precision (red). Our findings of the effect of round-off errors are consistent with the results of Levesque and Verlet[9] and Komatsu and Abe.[23] Levesque and Verlet[9] introduced an integer-arithmetic version of MD with the leap-frog algorithm free of round-off errors and showed that this algorithm is exactly time reversible down to the last bit and exhibits no long-time drift of the energy. Komatsu and Abe[23] used this method to show that the sequence of round-off errors is well modeled by a sequence of independent, identically distributed random variables.

In order to obtain a more precise determination of the effect of round-off errors on time reversibility and energy conservation we obtained the mean fluctuations for one hundred independent simulations of $E_{M-n}(+) - E_{M+n}(-)$. The result is shown in the inset in Fig. 5. The mean amplitude exhibits three different regimes for both single- and double-precision

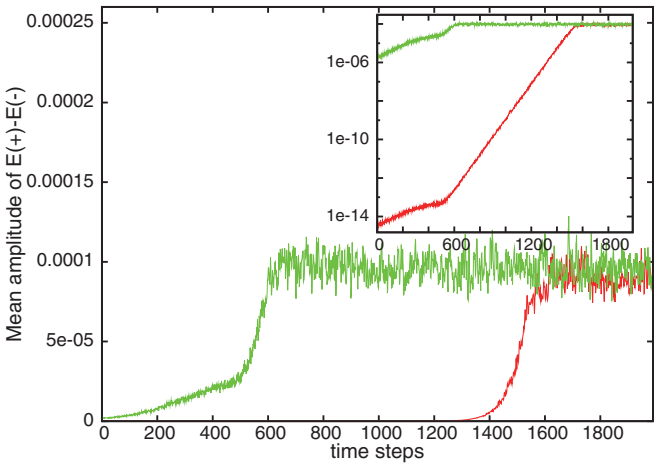

FIG. 5. Mean amplitude in the fluctuations in $(E(+) - E(-))/N$ for SP4 with cutoff $r_c = 2.5\sigma$ (the energies are obtained as $E_{disc,n}$). The green curve gives single-precision results and the red curve is for double-precision. The inset with a logarithmic ordinate reveals the short time behavior; it represents an average of 100 independent simulations.

simulations. The amplitude increases slowly the first ≈500 steps where the single-precision mean amplitude as expected is 10^8 times larger than the double-precision mean amplitude. In this region the Lyapunov instability affects the trajectories, but not the energies to the extent that their fluctuations are uncorrelated. In the next regime the two energies begin to uncorrelated. This is almost invisible in single precision where the two energies are uncorrelated after just ≈600 steps, whereas the double-precision energy difference first becomes uncorrelated after ≈1500 steps. The result is not sensitive to where the potential is truncated and the two mean amplitudes are similar after ≈1500 steps. This demonstrates that it is the imprecise determination of the discrete energy that determines the mean amplitude of the energy fluctuations, not the precision of the arithmetic nor the non-analyticity of the potential.

B. Long-time stability of the energy

The existence of a shadow Hamiltonian for discrete classical dynamics obtained by the Verlet algorithm implies that there is no drift in the energy, $E_{disc,n}$, nor in E_n, obtained from Eqs. (7) and (8). Because the differences between exact and approximated Hamiltonians are of order h^2 for $E_{disc,n}$ and h^4 for E_n, one observes corresponding energy fluctuations in the zeroth and first-order estimate of the conserved shadow energy. In order to obtain long-time conservation of the energy, however, it is necessary to ensure continuity of higher-order derivatives of the potential. We demonstrate this below by using different smoothing function in order to study the effect of the truncation. To enhance the effect, the potential is truncated already at $r_c = 1.5\sigma$ whereby the discontinuity in the LJ potential is increased by a factor of 20. By this truncation one includes only the interactions from the particles within the first coordination shell,[19] but the structure of the fluid as well as its dynamics are still maintained, also by using differently smoothed energy functions. The long-time stability of the discrete dynamics is, however, affected by the truncation at this short distance.

Figure 6 shows the energy evolution for SP and smoothed potentials (Eq. (13) with $n = 2$ (SP2) and $n = 4$ (SP4)) for 10^8 time steps. The SP is the traditional MD dynamics, which is known not to conserve the energy due to the fact that the truncation at r_c ignores the force discontinuity at the cutoff. SP2 (blue curve) represents a dramatic improvement (inset in the figure), but the energy is only conserved for SP4 (red curve), consistent with the analysis in Ref. 5. The lilac curve is SP4 with single-precision arithmetic. The round-off errors in double-precision arithmetic do not destroy the energy conservation for 10^8 time steps. The round-off errors' effect on MD with the Verlet algorithm is analyzed in Appendix B. According to Eq. (B13) the effect is diffusive-like and does not accumulate. This is why there is no observable drift in the SP4 energy even for many time steps. In single precision, as well as for long double-precision simulations, the round-off errors affect the dynamics and result in an "entropic drift." This term refers to the drift due to the random round-off errors, a drift that unavoidably takes the system to higher energies for the

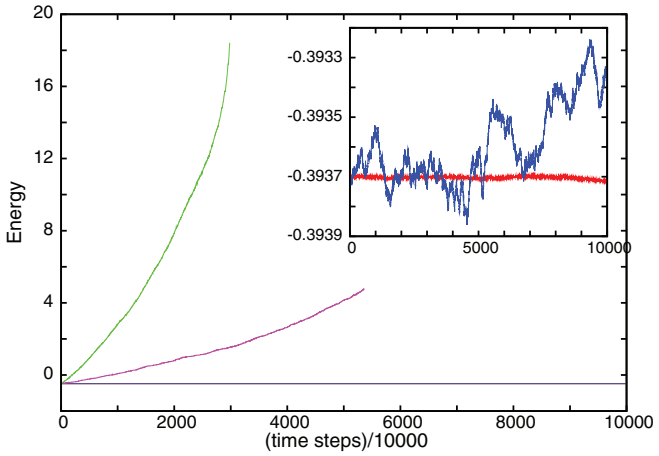

FIG. 6. One hundred million time steps with $h = 0.005$ and $r_c = 1.5\sigma$. Green: SP potential without smoothing; with smoothing (Eq. (13)) blue (SP2): $n = 2$, i.e., with the first and second derivatives continuous at r_c; and red (SP4): $n = 4$ for a smoothed LJ potential with the first four derivatives continuous at r_c. The lilac is SP4 with single-precision MD. The difference between the SP2 and SP4 energies are not visible on the figure; the inset shows E_n for SP2 and SP4 with a smaller energy unit on the ordinate. The "entropic" drift to higher energies reflect the fact that there are more energy states here.

simple reason that there are many more such states than low energy states—an entropic effect.[24]

We performed a similar set of simulations with smoothed SF-LJ functions and with the same conclusion (results not shown). In general, a SF cutoff conserves the energy much better than SP (Ref. 13) due to the continuity of the force at the cutoff. One expects that the discontinuities in the higher-order derivatives (from 5th order and upwards) of the potential, Eq. (13), with $n = 4$ result in a long-time drift in the energy; this effect, however, is not apparent for 10^8 time steps.

V. CONCLUSIONS

The central-difference Verlet algorithm is a time-reversible and symplectic discrete "propagator" in the **q**-space, and the dynamics does not depend on the momenta. According to the result of an asymptotic expansion from the Hamiltonian, H, of the corresponding analytic classical dynamics,[3–6] the discrete points lie on the analytic trajectory of a shadow Hamiltonian $\tilde{H}$.[2] Inclusion of the first non-trivial term in this expansion in the estimate of the (shadow) energy reduces the fluctuation in the energy by a factor of 100 for the LJ fluid for typical values of the time increment.

Time reversibility and energy conservation are affected by round-off errors in the arithmetic, as well as by the discontinuity in the potential and its derivatives. The round-off errors destroy time reversibility within a few thousand time steps, but do not affect the energy conservation even for many millions of time steps (Appendix B). The first term in the asymptotic expansion requires that the potential and the first four derivatives are continuous functions,[5] and only if this is the case does the energy remain constant for long simulations. With a potential function where the first four derivatives are continuous, the discrete dynamics of the LJ system is stable over at least one hundred million time steps.

In summary, our investigations show that the energy can be determined accurately already by including the first non-trivial term in the asymptotic expansion of the shadow Hamiltonian.

ACKNOWLEDGMENTS

The centre for viscous liquid dynamics "Glass and Time" is sponsored by the Danish National Research Foundation (DNRF).

APPENDIX A: $\mathbf{V}_n^T \mathbf{J}(\mathbf{R}_n)\mathbf{V}_n$ IN EQ. (7)

1. The term in Eq. (7) with the matrix J for a system of *N* particles with pair-interactions

The vectors in Eq. (7) are vectors with N components, each of which is a three-dimensional vector, so that, e.g., $\mathbf{v}_n(i)$ is a vector with components which represent the components of a velocity of the ith particle at the nth step. The potential is given by Eq. (12) as a sum over pair-potentials between particle i and j with radial distance r_{ij}. Using x_i, y_i, and z_i for the 3 components of the coordinates of the ith particle we have

$$\frac{\partial U}{\partial x_i} = \sum_{j \neq i} u'(r_{ij})(x_i - x_j)/r_{ij}, \tag{A1}$$

and similarly for y_i and z_i. We introduce the short-hand notation

$$u2(r_{ij}) = [u''(r_{ij}) - u'(r_{ij})/r_{ij}]/r_{ij}^2. \tag{A2}$$

The contributions to the third term in Eq. (7) from differentiating $u(r_{ij})$ come from four different parts of **J**. There are two "diagonal" parts where one differentiates twice with respect to the coordinates of either particle i or particle j, and two "off-diagonal" parts where one differentiates once with respect to a coordinate of particle i and once with respect to a coordinate of particle j. With the notation in Eq. (A2) we have, e.g.,

$$\frac{\partial^2 U}{\partial x_i^2} = \sum_{j \neq i} [u2(r_{ij})(x_i - x_j)^2 + u'(r_{ij})/r_{ij}], \tag{A3}$$

$$\frac{\partial^2 U}{\partial x_i \partial y_i} = \sum_{j \neq i} u2(r_{ij})(x_i - x_j)(y_i - y_j), \tag{A4}$$

$$\frac{\partial^2 U}{\partial x_i \partial x_j} = -(u2(r_{ij})(x_i - x_j)^2 + u'(r_{ij})/r_{ij}), \ (i \neq j), \tag{A5}$$

$$\frac{\partial^2 U}{\partial x_i \partial y_j} = -u2(r_{ij})(x_i - x_j)(y_i - y_j), \ (i \neq j). \tag{A6}$$

Combining it all, one gets the i, jth contribution to the third term in Eq. (7)

$$[(\mathbf{v}_i - \mathbf{v}_j)^T \mathbf{r}_{ij})]^2 u2(r_{ij}) + (\mathbf{v}_i - \mathbf{v}_j)^T (\mathbf{v}_i - \mathbf{v}_j) u'(r_{ij})/r_{ij}. \tag{A7}$$

APPENDIX B: EFFECTS OF THE ROUND-OFF ERRORS

1. Round-off errors of the Verlet algorithm

The starting point is the basic equation of the Verlet algorithm, Eq. (1), for the progression of the positions $\mathbf{R}$ of the N particles with equal mass m. For simplicity we take the time increment h in unit of $\sqrt{m}$.[18] The VA algorithm is

$$\mathbf{R}_{n+1} = 2\mathbf{R}_n - \mathbf{R}_{n-1} + h^2\mathbf{F}_n, \tag{B1}$$

where the force is given by $\mathbf{F}_n = -\nabla U(\mathbf{R}_n)$. Let $\mathbf{R}_n$ be the positions after n steps without round-off errors and introducing $\Delta\mathbf{R}_n$ as the accumulated effect of the round-off errors on $\mathbf{R}_n$, the positions after the n steps is $\mathbf{R}_n + \Delta\mathbf{R}_n$ and the VA for the actual computations becomes

$$\mathbf{R}_{n+1} + \Delta\mathbf{R}_{n+1} = 2(\mathbf{R}_n + \Delta\mathbf{R}_n) - (\mathbf{R}_{n-1} + \Delta\mathbf{R}_{n-1}) - h^2\nabla(U(\mathbf{R}_n + \Delta\mathbf{R}_n)) + h^2\Delta_n, \tag{B2}$$

where Δ_n is the round-off error from computing the force at the nth step. Most "floating-point" arithmetic operations in the MD are performed when the forces are calculated, and Δ_n is the dominating source to the round-off errors.

Expanding the force to first order in $\Delta\mathbf{R}_n$ and subtracting Eq. (B1) yields the difference equation for the accumulated error, $\Delta\mathbf{R}_n$,

$$\Delta\mathbf{R}_{n+1} = 2\Delta\mathbf{R}_n - \Delta\mathbf{R}_{n-1} - h^2\mathbf{J}(\mathbf{R}_n + \Delta\mathbf{R}_n) + h^2\Delta_n, \tag{B3}$$

where the matrix of the second derivatives of $U(\mathbf{R})$ at the point $\mathbf{R}_n$ is denoted by $\mathbf{J}(\mathbf{R}_n)$. If the matrix $\mathbf{J}$ has negative eigenvalues, the behavior along the corresponding eigenvectors is chaotic. Since $\mathbf{J}$ in general depends on $\mathbf{R}_n$, the eigenvectors mix and the chaotic behavior might spread to all degrees of freedom, except for the possible existence of an invariant subspace which is independent of $\mathbf{R}_n$ (see below).

If $\mathbf{J}$ depends only weakly on the way the cutoff of the potential is done, the chaotic behavior of the trajectory should be almost the same for all types of cutoff. If the potential, $U(\mathbf{R}_n)$, is a quadratic function of the coordinates (a harmonic potential), $\mathbf{J}$ is constant and there is no coupling between the eigenvectors. That is, the chaotic behavior might be very different in this case, and it is not possible to use a harmonic potential to investigate the general behavior of the Verlet algorithm for complex systems.

The VA dynamics implies four kinds of invariance of the computations: *time-reversibility, conservation of total momentum, conservation of total angular momentum,* and *conservation of the total energy* discussed above.

2. Time reversibility

The effect of the round-off errors on the time reversibility can be investigated by stopping the forward simulation at some time, t_M, reverse the time and retrace the steps.[9] The results are shown in Fig. 3 and the effect on the energy conservation in Figs. 4 and 5.

3. Conservation of total momentum and angular momentum

The components of $\mathbf{R}$ which pick out the three coordinates of the center of mass are $\mathbf{X}$, $\mathbf{Y}$, and $\mathbf{Z}$. If there are no external forces, it follows from Newton's third law that the three vectors are orthogonal to $\mathbf{F}$ at all values of $\mathbf{R}$. Consequently, they are eigenvectors to $\mathbf{J}$ at all values of $\mathbf{R}$ with the eigenvalue zero, and we have found an invariant subspace of $\mathbf{J}$. This implies that center-of-mass moves like a Brownian particle without friction under the influence of the round-off errors. The motion of the center of mass cannot be used to check whether the system is chaotic in general. The mean velocity of the center of mass after the 10^8 time steps is $\approx 10^{-14}$ and this has no impact on the conservation of the energy.

The total angular momentum, obtained by Eq. (1), is conserved for an isolated system, but not for a system with periodic boundaries.

4. The effect of round-off errors on the conservation of the energy

We use the notation

$$\tilde{\mathbf{V}} \equiv \langle \mathbf{V} \rangle \tag{B4}$$

for the time average of the velocity. The velocity, $\mathbf{V}_n$ in Eq. (8) can be written as the average of the mean velocity, $\tilde{\mathbf{V}}_{n+1}$ in the time interval $[t_n, t_{n+1}]$ and the mean velocity, $\tilde{\mathbf{V}}_n$, in the time interval $[t_{n-1}, t_n]$

$$\mathbf{V}_n = (\tilde{\mathbf{V}}_{n+1} + \tilde{\mathbf{V}}_n)/2 \tag{B5}$$

and the energy as

$$E_{disc,n} = U(\mathbf{R}_n + \Delta\mathbf{R}_n) + (1/8)(\tilde{\mathbf{V}}_{n+1} + \tilde{\mathbf{V}}_n)^2, \tag{B6}$$

where

$$\tilde{\mathbf{V}}_n = (\mathbf{R}_n + \Delta\mathbf{R}_n - \mathbf{R}_{n-1} - \Delta\mathbf{R}_{n-1})/h. \tag{B7}$$

Equation (B3) can be rewritten as

$$\tilde{\mathbf{V}}_{n+1} = \tilde{\mathbf{V}}_n - h\nabla U(\mathbf{R}_n + \Delta\mathbf{R}_n) + h\Delta_n. \tag{B8}$$

To find the progression of errors in $E_{disc,\,n}$ we compute

$$E_{disc,n} - E_{disc,n-1} = U(\mathbf{R}_n + \Delta\mathbf{R}_n) - U(\mathbf{R}_{n-1} + \Delta\mathbf{R}_{n-1}) + \frac{1}{8}(\tilde{\mathbf{V}}_{n+1} + \tilde{\mathbf{V}}_n)^2 - \frac{1}{8}(\tilde{\mathbf{V}}_n + \tilde{\mathbf{V}}_{n-1})^2. \tag{B9}$$

Expanding the potential energy yields

$$U(\mathbf{R}_n + \Delta\mathbf{R}_n) - U(\mathbf{R}_{n-1} + \Delta\mathbf{R}_{n-1}) = h\tilde{\mathbf{V}}_n^T\nabla U(\mathbf{R}_n + \Delta\mathbf{R}_n) - \frac{1}{2}h^2\tilde{\mathbf{V}}_n^T\mathbf{J}(\mathbf{R}_n + \Delta\mathbf{R}_n)\tilde{\mathbf{V}}_n + O(h^3). \tag{B10}$$

The part with the kinetic energy yields

$$\frac{1}{8}(\tilde{\mathbf{V}}_{n+1} + \tilde{\mathbf{V}}_n)^2 - \frac{1}{8}(\tilde{\mathbf{V}}_n + \tilde{\mathbf{V}}_{n-1})^2 = \frac{1}{8}[(2\tilde{\mathbf{V}}_n - h\nabla U(\mathbf{R}_n + \Delta\mathbf{R}_n) + h\Delta_n)^2 - (2\tilde{\mathbf{V}}_n + h\nabla U(\mathbf{R}_{n-1} + \Delta\mathbf{R}_{n-1}) - h\Delta_{n-1})^2]$$

$$= \frac{1}{8}(4h\tilde{\mathbf{V}}_n^T(-\nabla U(\mathbf{R}_n + \Delta\mathbf{R}_n) - \nabla U(\mathbf{R}_{n-1} + \Delta\mathbf{R}_{n-1}) + \Delta_n + \Delta_{n-1}) + h^2(\nabla U(\mathbf{R}_n + \Delta\mathbf{R}_n) + \Delta_n)^2 - h^2(\nabla U(\mathbf{R}_{n-1} + \Delta\mathbf{R}_{n-1}) + \Delta_{n-1})^2)$$

$$= -h\tilde{\mathbf{V}}_n^T\nabla U(\mathbf{R}_n + \Delta\mathbf{R}_n) + \frac{1}{2}h^2\tilde{\mathbf{V}}_n^T\mathbf{J}(\mathbf{R}_n + \Delta\mathbf{R}_n)\tilde{\mathbf{V}}_n + \frac{1}{2}h\tilde{\mathbf{V}}_n^T(\Delta_n + \Delta_{n-1}) + \frac{1}{4}h^2(\nabla U(\mathbf{R}_n + \Delta\mathbf{R}_n)^T\Delta_n - \nabla U(\mathbf{R}_{n-1} + \Delta\mathbf{R}_{n-1})^T\Delta_{n-1}) + O(h^3), \quad \text{(B11)}$$

where we have left out terms which are quadratic in the round-off errors, Δ_n. Combining Eqs. (B10) and (B11) we get

$$E_{disc,n} - E_{disc,n-1} = \frac{1}{2}h\tilde{\mathbf{V}}_n^T(\Delta_n + \Delta_{n-1}) + \frac{1}{4}h^2(\nabla U(\mathbf{R}_n + \Delta\mathbf{R}_n)^T\Delta_n - \nabla U(\mathbf{R}_{n-1} + \Delta\mathbf{R}_{n-1})^T\Delta_{n-1}) + O(h^3). \quad \text{(B12)}$$

Summing up from $i = 1$ to n the second term in Eq. (B12) almost cancels and we have

$$E_{disc,n} = E_{disc,0} + \frac{1}{2}h\sum_{i<n}\tilde{\mathbf{V}}_i^T(\Delta_i + \Delta_{i-1}), \quad \text{(B13)}$$

i.e., the round-off errors effect on the (shadow) energy at the nth step is a sum of projected random (and uncorrelated) round-off errors for the n steps. Since $\sum_{i<n}\Delta_i \approx 0$ this implies a diffusive-like behavior of the error of the energy. This fact explains why the energy in double-precision arithmetic is unaffected by the round-off errors even after 10^8 time steps.

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