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Cristiano De Michele ✉ ; Giovanni Ciccotti

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Cristiano De Michele[1,a)] and **Giovanni Ciccotti**[1,2,3]

AFFILIATIONS

[1] Department of Physics, "Sapienza" University of Rome, Piazzale Aldo Moro N. 2, Rome, Italy
[2] Insitute for Applied Computing "Mauro Picone" (IAC), CNR, Via dei Taurini 19, Rome 00185, Italy
[3] School of Physics, University College of Dublin, Belfield, Dublin 4, Ireland

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[a)] **Author to whom correspondence should be addressed:** cristiano.demichele@uniroma1.it

ABSTRACT

Symplectic integrators are largely employed in MD due to their long-term stability and near conservation of invariants. Their numerical robustness can be rationalized by the existence of a *shadow Hamiltonian* H_{sh}, exactly conserved by symplectic integrators and expressible as an asymptotic expansion with respect to the integration time steps δt around the physical Hamiltonian H. In this work, we suggest not attaching any physical meaning to H_{sh}, based on theoretical analysis and MD simulations of a standard LJ system using the velocity-Verlet algorithm. We do not intend to optimize symplectic algorithms. Instead, we claim that the existence of H_{sh} cannot provide better observables to estimate statistical properties. For that reason, we will also examine the behavior of trajectories integrated with large δt that are always exact integrations of their corresponding $H_{\text{sh}}(\delta t)$. To these trajectories, of course, we do not attach a physical meaning. Note that the stability of the energy cannot be enough to guarantee accurate estimates of statistical properties. Although symplectic integrators yield, within numerical accuracy, exact trajectories of H_{sh}, thermodynamic quantities derived from H_{sh} deviate from the physical ones when δt is too large. Indeed, the conventional kinetic temperature of H is wrongly estimated for large δt, while "shadow" temperature becomes unphysical for the same large δt, despite its exact meaning for H_{sh}. We conclude that H_{sh} lacks physical relevance for large δt, and the only remedy to perform simulations by standard integrators, such as the velocity-Verlet, is to use a short enough δt, in which case the estimated physical properties coincide.

I. INTRODUCTION

Simulations in molecular dynamics generally refer to systems modeled using Hamilton's equations of motion derived from a time-independent Hamiltonian,

$$H(\mathbf{Q},\mathbf{P}) = \frac{1}{2}\mathbf{P}^T M\ \mathbf{P} + V(\mathbf{Q}) \tag{1}$$

with $\mathbf{P} = (\mathbf{p}_{1,}\ \ldots, \mathbf{p}_N)$ and $\mathbf{Q} = (\mathbf{q}_{1,}\ \ldots, \mathbf{q}_N)$, where $\mathbf{q}_i$ and $\mathbf{p}_i$ with $i = 1, \ldots, N$ are the positions and momenta, respectively; M is the diagonal mass tensor; and $V(\mathbf{Q})$ is the potential energy function often coming from additive pair forces but also derived from *ab initio* calculations. The dimensionality of the configuration space is dN, with d being the space dimensions and N being the number of particles. The trajectory $\mathbf{Q}(t;\ \mathbf{Q}_0, \mathbf{P}_0)$, with $(\mathbf{Q}_0, \mathbf{P}_0)$ being the initial conditions, is determined by

$$\begin{aligned}\dot{\mathbf{Q}} &= \frac{\partial H}{\partial \mathbf{P}},\\ \dot{\mathbf{P}} &= -\frac{\partial H}{\partial \mathbf{Q}}.\end{aligned} \tag{2}$$

A numerical integrator of these equations that generates a sequence of phase-space points $(\mathbf{Q}_n, \mathbf{P}_n)$ at discrete time points $t_n = n\delta t$ is defined as symplectic if

$$M^T J M = J, \tag{3}$$

where M is the Jacobian of the mapping induced by the solution of the equation of motion going from $(\mathbf{Q}_n, \mathbf{P}_n)$ to $(\mathbf{Q}_{n+1}, \mathbf{P}_{n+1})$, i.e.,

$$M = \begin{pmatrix} \dfrac{\partial \mathbf{Q}_{n+1}}{\partial \mathbf{Q}_n} & \dfrac{\partial \mathbf{Q}_{n+1}}{\partial \mathbf{P}_n} \\ \dfrac{\partial \mathbf{P}_{n+1}}{\partial \mathbf{Q}_n} & \dfrac{\partial \mathbf{P}_{n+1}}{\partial \mathbf{P}_n} \end{pmatrix}, \tag{4}$$

with

$$J = \begin{pmatrix} 0 & I \\ -I & 0 \end{pmatrix} \tag{5}$$

and I being the $3N \times 3N$ identity matrix. Symplectic integrators are widely used in simulations due to their remarkable stability at relatively large time steps and their ability to approximately conserve invariants quite well over long timescales. The absence of significant violations of conserved quantities even at relatively large integration time steps may appear unexpected at first. This property arises because the phase-space points $(\mathbf{Q}_n, \mathbf{P}_n)$ generated by a symplectic integrator lie exactly, of course, within the numerical accuracy, on the trajectory $[\mathbf{Q}(t), \mathbf{P}(t)]$ of the exact solution to Eq. (2) corresponding to a different Hamiltonian called the *shadow Hamiltonian* H_{sh}, which can be represented as an asymptotic expansion in the time step δt around the original Hamiltonian H so that

$$\begin{aligned} \mathbf{Q}_n &= \mathbf{Q}(n\,\delta t), \\ \mathbf{P}_n &= \mathbf{P}(n\,\delta t). \end{aligned} \tag{6}$$

Note that H_{sh} is generally not separable in the simple form given by Eq. (1). Symplectic integrators, such as the velocity-Verlet, sample positions and momenta almost exactly from a trajectory generated by the shadow Hamiltonian. This new Hamiltonian can be formally derived as an asymptotic expansion if the potential energy is an analytic function of positions and momenta. The concept of employing modified equations—also referred to as backward error analysis—to study numerical integration methods for ordinary differential equations was first proposed by Griffiths and Sanz-Serna in 1986.[1] Their work also cited earlier applications of this methodology to partial differential equations. Subsequently, Sanz-Serna[2] emphasized the critical importance of employing symplectic integrators for Hamiltonian dynamics. In 1994, Hairer[3] derived general formulas enabling the systematic computation of the shadow Hamiltonian expansion when applying symplectic Runge–Kutta or Nyström (leap-frog) schemes and rigorously proved that such an expansion exists exclusively for symplectic methods. Reich[4] further developed the theoretical framework and provided a comprehensive set of references. Later, Gans and Shalloway presented an explicit formula for the leading-order term of the shadow Hamiltonian expansion, which they employed to analyze discretization errors in analytic first-order differential equations and to construct shadow Hamiltonians.[5–7]

In Ref. 8, the first non-trivial contribution to the asymptotic expansion was explicitly obtained for the Lennard-Jones system by evaluating consecutive sets of positions, using the expression previously derived from the expansion of H for the one-dimensional harmonic oscillator. The general form of this result, grounded in the modified equation approach of Refs. 1–4, is given in Ref. 5,

$$H_{\text{sh}}(\mathbf{Q}, \mathbf{P}, \delta t) = H + \frac{\delta t^2}{2} g_2(\mathbf{Q}, \mathbf{P}) + \frac{\delta t^4}{4!} g_4(\mathbf{Q}, \mathbf{P}) + \mathscr{O}(\delta t^6). \tag{7}$$

For a system with potential energy $U(\mathbf{q})$, the first non-trivial term in the expansion, i.e., $g_2(\mathbf{q}, \mathbf{p})$, has been calculated,[9] and it turns out to be

$$g_2(\mathbf{Q}, \mathbf{P}) = \frac{1}{6} \mathbf{P}^T M^{-1} \frac{\partial^2 V}{\partial \mathbf{Q}^2} M^{-1} \mathbf{P} - \frac{1}{2} [\nabla V]^T M^{-1} \nabla V. \tag{8}$$

Symplectic integrators do not exhibit energy drift, since they integrate exactly, i.e., without algorithmic errors, the equations of motion associated to H_{sh}. In Ref. 5, it has been suggested (as we will see with little use) that derivatives of interpolated position trajectories, rather than velocity-Verlet "velocities," should be used for computing energy fluctuations and physical velocity-dependent observables, e.g., diffusion constants. While this suggestion[5] can be useful and even please numerical analysts, it will pay nothing to molecular simulators,[10] because no physical meaning can be attached to them, as discussed in Sec. II. To have the physical meaning, the two estimated properties computed with appropriately short integration time steps should simply coincide. Accurate determination and control of temperature are then critical in molecular dynamics (MD) simulations. In the microcanonical ensemble, where temperature is calculated by using the kinetic energy of the system, standard analyses of equilibrium simulations for too large integration time steps can yield different temperatures when estimated for classes of different degrees of freedom, seemingly violating the equipartition theorem. This fact is discussed extensively in Ref. 10, where such discrepancies are correctly ascribed to algorithmic integration errors, since for large time steps symplectic integrators do not integrate the Hamiltonian equations of motion exactly anymore. In Ref. 10, it has been argued that Tolman's generalized equipartition theorem[11,12] holds for long, stable simulations with symplectic integrators since they provide exact trajectories for the equations of motion associated with the shadow Hamiltonians (remember that the shadow Hamiltonian depends on the integration time step). Based on this principle, in Ref. 10, a new temperature estimator, based on $p\dot{q}$ (not $p^2/2m$, which depends on the mass), where $\dot{q}$ is the time derivative of interpolated positions, has been suggested. The new estimator is shown in Fig. 2 of Ref. 10, and it is supposed to eliminate the apparent temperature variations observed with standard temperature estimators $(p^2/2m)$. The proposed use of velocities calculated from interpolated position trajectories is based on the fact that positions are exact solutions of the equations of motion associated with the shadow Hamiltonians. The assumption to be confuted in this claim is that H_{sh} possesses a physical meaning identical to that of the original Hamiltonian. Instead, for large δt, H_{sh} is no longer representative of the physical properties of H. This is exactly the point we want to address in the present paper, where we used the velocity-Verlet algorithm, as in Refs. 5 and 10. In other words, are the statistical properties of a correct integration of the trajectory generated by $H_{\text{sh}}(\delta t)$ (a function of the integration time step δt) providing us with a better evaluation of statistical properties of the original Hamiltonian? The answer is no. The absence of energy drift for the symplectic integrators does not give correct properties of H unless the time step δt is small enough to guarantee reliability of the statistical analysis. The guarantee is given by the fact that the computed properties of H coincide with the ones of H_{sh}. Any attempt to evaluate the properties of H through the ones of H_{sh} is doomed to fail. In Ref. 10, it is observed that one can be tempted to use very large integration time steps as long as equipartition related to H_{sh} holds, as previously suggested with insufficient ground in Refs. 13 and 14. This suggestion is misleading and pernicious. On one hand, increasing the integration time step δt, the accuracy of physical properties obtained from H through a symplectic integrator degrades due to integration errors; on the other hand, physical properties obtained from the shadow Hamiltonian lose relevance due to the fact that H_{sh}, with its statistical properties, is increasingly different from the Hamiltonian H. In Sec. II, we recall some theoretical results. Section III defines the model on which we intend to illustrate and check our claim and present our results. Section IV is devoted to some concluding remarks.

II. THEORY

Given a generic Hamiltonian system of N particles enclosed in a volume V, as in Eq. (1), whose equations of motion are given in Eq. (2), the microcanonical partition function Q reads

$$Q(N, V, E) = \int \delta(\mathscr{H} - E) d\mathbf{Q}\, d\mathbf{P}. \tag{9}$$

If we define

$$\Gamma(t) = \begin{pmatrix} \mathbf{Q}(t) \\ \mathbf{P}(t) \end{pmatrix}. \tag{10}$$

The exact evolution of the system is given by

$$\Gamma(t) = e^{i\mathscr{L}t}\Gamma(0), \tag{11}$$

where

$$i\mathscr{L} = \sum_{i=1}^{N} \dot{\mathbf{q}}_i \frac{\partial}{\partial \mathbf{q}_i} + \dot{\mathbf{p}}_i \frac{\partial}{\partial \mathbf{p}_i}. \tag{12}$$

With a system described by a separable Hamiltonian, as in Eq. (1), a symplectic integrator can be obtained by a suitable factorization of the evolution operator $e^{i\mathscr{L}\delta t}$ over a small time step δt. A possible choice is a symmetric factorization based on Trotter's theorem, i.e.,

$$e^{i\mathscr{L}\delta t} = e^{i\mathscr{L}_p \delta t/2} e^{i\mathscr{L}_q \delta} e^{i\mathscr{L}_p \delta t/2} + \mathscr{O}(\delta t^3) = e^{iL_{vv}\delta t} + \mathscr{O}(\delta t^3), \tag{13}$$

where $i\mathscr{L}_q = \sum_i \frac{\mathbf{p_i}}{m_i}\frac{\partial}{\partial q_i}$ and $i\mathscr{L}_p = -\sum_i \frac{\partial V}{\partial \mathbf{q}_i}\frac{\partial}{\partial \mathbf{p}_i}$. The factorization in Eq. (13) yields the well-known velocity-Verlet algorithm, whose accuracy degrades on increasing δt. At the same time, if one considers the shadow Hamiltonian for this system, the evolution of positions and momenta provided by Eq. (13) is exact, i.e., H_{sh} is exactly conserved,

$$e^{iL_{vv}\delta t} H_{\text{sh}} = e^{i\left(\sum_i^N \frac{\partial H_{\text{sh}}}{\partial \mathbf{p}_i}\frac{\partial}{\partial \mathbf{q}_i} - \frac{\partial H_{\text{sh}}}{\partial \mathbf{q}_i}\frac{\partial}{\partial \mathbf{p}_i}\right)\delta t} H_{\text{sh}} = H_{\text{sh}}. \tag{14}$$

An important physical property to be calculated for H and H_{sh} is the temperature. The generalized equipartition theorem states (for a derivation, see Refs. 11 and 12) that

$$\left\langle x_i \frac{\partial H}{\partial x_i} \right\rangle = k_B T, \tag{15}$$

where x_i indicates an element of either position or a momentum component. If, in Eq. (15), x_i represents the momentum, by summing over all particles, one obtains

$$\left\langle x_i \frac{\partial H}{\partial x_i} \right\rangle = \frac{1}{3N}\left\langle \sum_i \mathbf{p}_i \cdot \dot{\mathbf{q}}_i \right\rangle = k_B T. \tag{16}$$

For a separable Hamiltonian, such as the one in Eq. (1), one finds

$$\left\langle \frac{\mathbf{p}_i^2}{2m_i} \right\rangle = \frac{k_B T_{p^2}}{2}, \tag{17}$$

which can be rewritten by summing over all degrees of freedom of the N particles, as

$$\langle K \rangle = \left\langle \sum_i \frac{\mathbf{p}_i^2}{2m_i} \right\rangle = \frac{3Nk_B T_{p^2}}{2}, \tag{18}$$

where K is the kinetic energy of the system, the standard estimator of temperature in molecular dynamics simulations. For a non-separable Hamiltonian, such as the shadow Hamiltonian, one has

$$\left\langle \sum_i x_i \frac{\partial H_{\text{sh}}}{\partial x_i} \right\rangle = \left\langle \sum_i \mathbf{p}_i \cdot \dot{\mathbf{q}}_i \right\rangle = 3Nk_B T_{pv}, \tag{19}$$

which is a good estimator of temperature for H_{sh}, since the bare mass does not intervene. In general, for $\delta t \neq 0$, T_{pv} has not to be equal to T_{p^2}; indeed, from a thermodynamic point of view, with $S(N, E, V) = k_B \ln(Q)$, the temperature of a Hamiltonian H is defined as

$$T = \left(\frac{\partial S}{\partial E}\right)^{-1} \tag{20}$$

and for the shadow Hamiltonian with $S_{\text{sh}}(N, E, V) = k_B \ln(Q_{\text{sh}})$, we have

$$T_{\text{sh}} = \left(\frac{\partial S_{\text{sh}}}{\partial E}\right)^{-1}. \tag{21}$$

It could appear obvious, but we believe it is important to stress this point: the entropy S and the corresponding family of $S_{\text{sh}}(\delta t)$ depending on δt have no reason to generate the same thermodynamics; therefore, we can only use one for the other when they give identical results. This trivial observation has motivated our attempt to falsify physically meaningless differences in the estimation of temperature.[10] As shown above, T_{p^2} and T_{pv} can be estimators of these two temperatures, which should coincide only in the limit $\delta t \to 0$. For any positive and sufficiently large δt, T_{pv} is not necessarily equal to T_{p^2}. In the following, we explain, through computer simulations by going up to clearly unphysically large time steps δt ($\delta t \approx 0.012$), the meaning of the discrepancy that shows up. In fact, by the unphysical trajectories produced by too large δt, the time averages cannot be used to estimate properly T [Eq. (20)]. The same trajectories are instead, by construction, exact, referring to $H_{\text{sh}}(\mathbf{Q}, \mathbf{P}, \delta t)$, and therefore can be used to estimate the thermodynamic properties of H_{sh}, including T_{sh} [Eq. (21)]. In conclusion, as obvious, trajectories with large δt are useless if you want to study H, as variously suggested.[10,13,14] This is the main, restricted scope of our paper.

III. MODEL AND NUMERICAL RESULTS

We studied a system of $N = 1000$ atoms of mass m in a cubic box of volume V with periodic boundary conditions interacting through a Lennard-Jones (LJ) potential, i.e.,

$$v_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{22}$$

with a cutoff $r_c = 3.5\sigma$. We carried out simulations at $T = 0.722\frac{\varepsilon}{k_B}$ and $\rho = N/V = 0.8422\sigma^{-3}$, which is a state close to the LJ triple point.[15] To integrate the equations of motion, we used, as usual, reduced units, i.e., the lengths are expressed in units of σ ($\sigma = 3.405$ Å for argon), the energies in units of ε ($\varepsilon/k_B = 119.8$ K for argon), and the mass in units of m ($m = 39.948$ Dalton for argon). Hence, the time unit is $\tau = \sqrt{m\sigma^2/\varepsilon}$ ($\tau = 2.16 \times 10^{-12}$ s). The thermodynamic quantities will be measured in reduced units.

To eliminate the effects of cutoff on energy conservation, it is advisable to employ a suitable smoothing of the potential at r_c. A convenient approach, proposed in Ref. 9, to avoid the discontinuity at $r = r_c$, consists in replacing the LJ potential with the following equation:

$$u(r) = \begin{cases} [v_{LJ}(r) - v_{LJ}(r_c)]\dfrac{(r_c - r)^n}{(r_c - r)^n + \alpha^n}, & r < r_c, \\ 0, & \text{otherwise}, \end{cases} \tag{23}$$

where the derivatives up to the nth order are continuous, $\alpha > 0$ sets the range of smoothing, and r_c is the cutoff radius. In our simulations, we set $n = 4$ so that the interaction potential is continuous up to the fourth order at $r = r_c$ ($r_c = 3.5$) and $\alpha = 0.1$ as in Ref. 9. We were content to use for all our simulations only the velocity-Verlet algorithm as in Ref. 10 in discussing the issue: our interest is not in optimizing the symplectic integrator but rather to discuss the physical meaning of the H_{sh} with respect to H. All simulations were started from the same initial configuration, which we obtained after a suitable equilibration. Equilibration was achieved by employing a standard Nose–Hoover thermostat initially in order to set the desired temperature $T = 0.722$ and performing afterward a microcanonical simulation to further equilibrate the system. Starting from this final configuration, we carried out 14 distinct simulations where we used different integration time steps ranging from $\delta t = 0.001$ to $\delta t = 0.014$, which for liquid argon correspond to 2.2 and 25.9 fs, respectively.

The shadow temperature in our computer simulations is calculated by performing the time derivative of the interpolated positions. Interpolation is carried out by employing a standard polynomial interpolation based on Neville's algorithm as discussed in Ref. 16. Given M points (t_i, x_i) with $i = 1, \dots, M$, where x_i is a component of position $\mathbf{r_j}$ of particle j at time t_i, an interpolating polynomial of degree $M - 1$ can be built by the following procedure. Let $P_i(t)$ be the unique polynomial of degree 0, i.e., a constant, passing through the point (t_0, x_0); then $P_0(t) = x_0$ [similarly, the polynomials $P_1(t), P_2(t), \dots, P_{M-1}(t)$ could be defined]. Now, let $P_{01}(t)$ be the unique polynomial of degree one passing through both points (t_0, x_0) and (t_1, x_1) [similarly, $P_{12}(t)$, $P_{23}(t)$, $\dots, P_{(M-2)(M-1)(t)}$ could be defined]. Then, we can do the same for higher order polynomials, so after $P_{012}(t)$, the unique third order polynomial passing through points (t_0, x_0), (t_1, x_1), and (t_2, x_2), one could also define $P_{123}(t), \dots, P_{[(M-3)(M-2)(M-1)](t)}$. Eventually, one defines $P_{012,\dots,(M-1)}(t)$, the unique polynomial of degree $M - 1$, which interpolates all the given M points. Neville's algorithm is a strategy to build recursively the above polynomials based on the following recursive relations:

$$P_{i(i+1)\dots(i+m)} = \frac{(t - t_{i+m})P_{i(i+1)\dots(i+m-1)} + (t_i - t)P_{(i+1)(i+1)\dots(i+m)}}{t_i - t_{i+m}}, \tag{24}$$

where $i = 0, \dots, M - 1$ and $m = 1, \dots, M - 1$, with $i < m$. In other words, through this recursive relation, the polynomial $P_{(012,\dots,M-1)}(t)$ of degree $M - 1$ is finally expressed in terms of the polynomials $P_i(t)$, i.e., polynomials of degree 0. The final expression for the interpolated position $x(t)$ is

$$x(t) = P_{(012\ \dots M-1)}(t). \tag{25}$$

In the present work, we used tenth degree polynomials, i.e., $M = 11$, and we carefully checked that by employing higher order polynomials, no further improvement in the calculation of velocities is achieved. Figure 1 shows the velocity p_x/m and the time derivative of its positions $\dot{x}_i$ along the x-axis for the smallest integration time step used, i.e., $\delta t = 0.001$ and for $\delta t = 0.012$. It can be seen that for the smallest integration time step, time derivatives of interpolated positions are essentially identical to velocities, while at $\delta t = 0.012$ they become significantly different, although their difference remains bounded over time. That clearly indicates that, for $\delta t = 0.012$, the

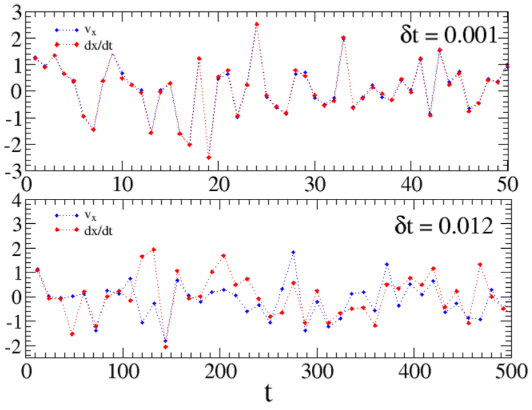

FIG. 1. Velocity $v_x = p_x/m$ and time-derivative of positions (dx/dt) as a function of time of a particle over a simulation time equal to 50 and 500 r.u. for $\delta t = 0.001$ (top) and $\delta t = 0.012$ (bottom), respectively. The time-derivative of positions has been calculated by deriving the described tenth order polynomial (25), which interpolates $x(t)$. If two points coincide, only red symbols are shown.

physics of H_{sh} has become different from that of H and that the latter has become unreliable.

In order to check the stability of the integrator and verify that for all simulations the thermodynamic state point remains the same during the run, we calculated the total energy for all the studied integration time steps. The results are shown in Fig. 2. It can be seen that, over the time range simulated, the energy is still reasonably well conserved up to $\delta t = 0.012$, whereas for $\delta t = 0.013$ and 0.014, the drift is already significant and starts to set in soon. Since all simulations started from the same initial configuration, their thermodynamic state (N, V, E) has to be the same, and so will be any physical observables.

Hence, we estimated the temperatures T_{p^2} related to H and T_{pv} related to H_{sh}, and we plotted T_{p^2}/T_0 and T_{pv}/T_0 for all integration time steps, with T_0 being the temperature for $\delta t = 0.001$, as reported in Fig. 3. We note that within numerical errors for $\delta t = 0.001$, one has $T_{p^2} = T_{pv}$. As expected, both temperatures start deviating from the correct value, and even if the deviation is less than 1%, being errors much less than the symbols, it can be concluded that neither T_{p^2} nor T_{pv} is any longer the correct physical temperature of the system. T_{p^2} differs from the *exact* value due to the algorithmic integration errors, while T_{pv} is the correct temperature of the shadow Hamiltonian H_{sh}, which is different from H [see Eqs. (20) and (21)]. In Ref. 10, the claim is somehow subtler. They notice that for molecular systems temperature can be measured by only considering translational, vibrational, or rotational degrees of freedom. They find already for simple diatomic systems that the equipartition theorem related to vibrational or translational kinetic energy breaks on increasing δt (see Fig. 3 of Ref. 10). There is, however, a difference between H_{sh} and H in an intermediate range of δt. In this range, the two temperatures coincide for H_{sh}, but they are already different for H. They conclude that this intermediate range of δt is usable assuming that one computes the temperature as the average of $\dot{q}p$ instead of the average of $\frac{p^2}{2m}$. This argument is clearly wrong since the condition of a valid choice of δt is only the coincidence of p/m and $\dot{x}$. The relatively larger stability of the shadow results is easily explained by the fact that the trajectories for each δt are exact for H_{sh}. The statistical results produced by these trajectories correspond, however, to the physics generated by H_{sh} and no more to the one generated by H. To illustrate this, it is instructive to plot as a function of δt the relative fluctuations of the total energy, $\sigma_H/|H|$, where σ_H is the standard deviation of H, alongside those of the potential energy, $\sigma_V/|V|$, as shown in Fig. 4. Note that $\sigma_H/|H|$ and $\sigma_V/|V|$ are calculated directly from values of total energy H and potential energy V saved every 1000 integration time steps, respectively. Indeed, the degradation of the conservation is monotonic, and for larger integration time steps, the relative fluctuations of the total energy become comparable to, and eventually larger than, those of the total potential energy. This raises concerns about the physical reliability of mechanical properties obtained from the simulated trajectories, despite the exact conservation of H_{sh}. In Fig. 5, we show the average potential energy $\langle V\rangle$ and the pressure $P = T\left.\frac{\partial S}{\partial V}\right|_E$ of the system, estimated as usual by the virial, as a function of δt. It can

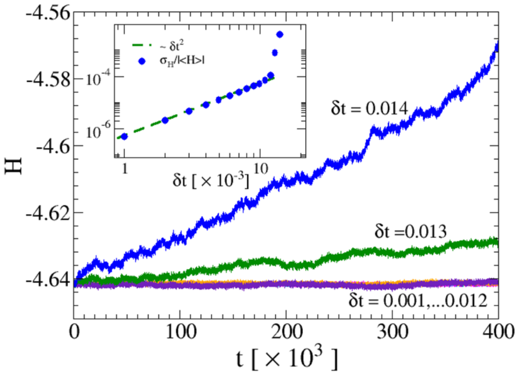

FIG. 2. Total energy H of the system as a function of time for all integration time steps δt studied over a total simulation time equal to 4×10^5. Blue and green lines correspond to $\delta t = 0.014$ and $\delta t = 0.013$, respectively. All other integration time steps, i.e., $\delta t = 0.001$, 0.002, 0.003, 0.004, 0.005, 0.006, 0.007, 0.008, 0.009, 0.010, 0.011, and 0.012, overlap. The inset shows $\sigma(H)/|\langle H\rangle|$, i.e., the standard deviation of energy divided by its average value, and the dashed green line indicates, for reference, a quadratic behavior.

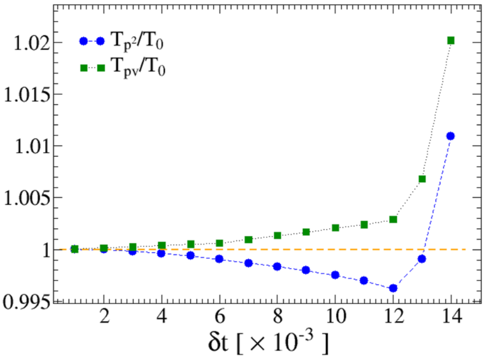

FIG. 3. Scaled temperatures T_{p^2}/T_0 and T_{pv}/T_0, where T_{p^2} and T_{pv} are defined in Eqs. (19) and (20), respectively, plotted as a function of integration time step δt. T_0 is the temperature of the system for $\delta t = 0.001$. The dashed orange line is just for reference. We estimated errors by reblocking analysis,[17] and the error for each point is smaller than 2×10^{-4}, i.e., always smaller than the symbol size.

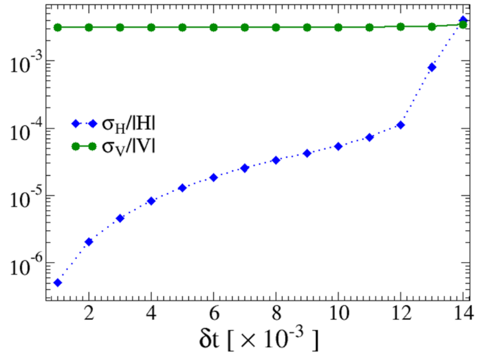

FIG. 4. Standard deviation σ of $H(t)$ over its absolute average value $(\sigma_H/|\langle H\rangle|)$ and standard deviation of potential energy over value $(\sigma_V/|\langle V\rangle|)$.

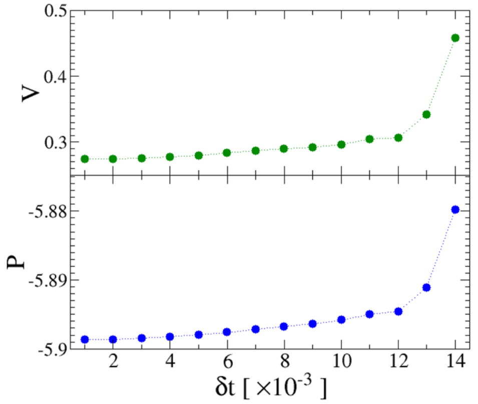

FIG. 5. Average potential energy $\langle V \rangle$ and pressure P as a function of the integration time δt. Errors for $\langle V \rangle$ and P are for each point smaller than 10^{-3} and 10^{-4} r.u., respectively, i.e., they are smaller than symbol size.

be seen that, as δt increases, they both deviate from their exact values. One can expect the same behavior for analogous macroscopic quantities. This indicates that all the thermodynamic properties of the system are not correctly captured by either H or H_{sh} if the integration time step is even moderately too large. Note that $\langle V \rangle$ can be trivially obtained from total energy and temperature; nevertheless, being a macroscopic observable, it is worth showing that its trend, on increasing the integration time step, confirms the ones of T and P.

IV. CONCLUSIONS

We are now in the position to conclude. In past papers, it has been attempted to attribute a physical significance to the shadow Hamiltonian, which, as we have shown, it does not possess. The shadow Hamiltonian is a useful tool to understand the absence of drift in symplectic integrators but not to obtain values of observables more accurate than those which can be obtained from H. It is a long story that the original (equivalent) Verlet and velocity Verlet algorithms were very stable and convenient in molecular dynamics simulations. The notion of symplecticity helped clarify the reason behind those remarkable performances but did not create special hopes. In the meantime, applied mathematicians took the lead and clarified many aspects of these specific integrators. In particular, they came out with the discovery of the shadow Hamiltonian defined implicitly, introducing new problems such as the notion of an effective mass very different from the bare mass of the physical Hamiltonian. That introduced a question about the potential difference between the momentum and the physical velocity of the particles composing the statistical system. The question raised in Ref. 5 brought about a discussion of the proper way to treat observables depending on momenta, since the claim was that p/m, with m being the bare mass of a particle, is not the actual velocity, v, of it, since the "true" velocity must be computed directly as dr/dt. Indeed, that is true if you want to compute the velocity of the "particle" corresponding to the shadow Hamiltonian but not for the real particle, which at most is badly computed unless the two coincide, a fact that is certain in the $\delta t \to 0$ limit (the corrections start at the order of δt^2). Despite that trivial observation in Ref. 5, in 2000, Gans and Shalloway insisted that "[...] velocities derived from interpolated positions, rather than conventional velocity-Verlet velocities, should be used to compute physical properties." We believe that we have convincingly proved that, to obtain the correct macroscopic physical properties of the system H, we have to work in the δt region where the two quantities coincide. Thus, the question of the existence of the shadow Hamiltonian, while important for understanding the stability of the integrator, is not particularly interesting as a tool for improving anything, apart from providing an extra criterion for proving that we are integrating the equations of motion correctly, namely, the identity of p/m and dr/dt. That is the major result of our paper: to kill any special interest in this very interesting mathematical fact in molecular dynamics applications. Second and also important, there have been attempts to show that the difference in the estimation of the velocities can create opportunities for the simulators. Indeed, in molecular simulations where you have molecules with internal degrees of freedom, there can be many different estimators for the same observable velocity depending on, e.g., the temperature. These different observables can be sensitive to the way they are computed. In 2010, in Ref. 10, Eastwood *et al.* claimed that, by using the T_{pv} temperature estimator, which is obtained from the generalized equipartition theorem and which they consider a "new temperature estimator," equipartition for different degrees of freedom in a simulated system is recovered. Again, the claim is unjustified since, as we have shown, as soon as the new observable gives different values from the more traditional ones, we happen to be measuring the pseudo-physical properties of the shadow system and no longer the ones of the real simulated system. Summing up, our main result is that either p/m and dr/dt are equal to the chosen integration step or we are entering a no man's land since we are starting to sample the microcanonical ensemble of H_{sh} (a system of no physical interest) and no more of H. Our Fig. 3 gives clear evidence for that. A positive side of the discussion raised by the existence of the shadow Hamiltonian conservation, in our mind, is that even a quite stable conservation of energy (in δt) can be not enough to guarantee the correct integration of the equations of motion, a fact necessitated by the need to get the correct physics since the energy can be reasonably conserved (see Figs. 3 and 5 together), and the properties between H and H_{sh} have already started to diverge. The only way, as correctly stated in Ref. 10, is to find more powerful symplectic algorithms capable of permitting larger time steps at similar cost (a very nice example being r-Respa[18]). We wish to conclude by saying that we hope to have convinced you that the rumor generated by the quoted paper[10] has been no more than much ado about nothing.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Cristiano De Michele: Conceptualization (equal); Investigation (equal); Methodology (equal); Software (lead); Supervision (equal); Writing – original draft (lead); Writing – review & editing (lead). **Giovanni Ciccotti**: Conceptualization (equal); Investigation (equal); Methodology (equal); Supervision (equal); Writing – original draft (supporting); Writing – review & editing (supporting).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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