# Energy, temperature, and heat capacity in discrete classical dynamics

Søren Toxvaerd
*Department of Science and Environment, Roskilde University, Post Box 260, DK-4000 Roskilde, Denmark*

(Received 24 August 2023; accepted 18 December 2023; published 24 January 2024)

Simulations of objects with classical dynamics are in fact a particular version of discrete dynamics, since almost all the classical dynamics simulations in natural science are performed with the use of the simple "leapfrog" or "Verlet" algorithm. It was, however, Newton who in *Principia*, *Proposition I* in 1687 first formulated the discrete algorithm, which much later in 1967 was rederived by L. Verlet. Verlet also formulated a first-order approximation for the velocity $\mathbf{v}(t)$ at time $t$, which has been used in simulations since then. The approximated expressions for $\mathbf{v}(t)$ and the kinetic energy lead to severe errors in the thermodynamics at high densities, temperatures, strong repulsive forces, or for large discrete time increments used in discrete "molecular dynamics" (MD) simulations. Here we derive the exact expressions for the discrete dynamics, and show by simulations of a Lennard-Jones system that these expressions now result in equality between temperatures determined from the kinetic energies and the corresponding configurational temperatures determined from the expresssion of Landau and Lifshitz, derived from the forces.

DOI: 10.1103/PhysRevE.109.015306

## I. INTRODUCTION

Simulations of objects with classical dynamics are in fact a particular version of discrete dynamics. since almost all the classical dynamics simulations in natural science are performed with the use of a simple algorithm, first formulated by Newton [1,2]. A new position in Newton's discrete dynamics, $\mathbf{r}_i(t+\delta t)$, at time $t+\delta t$ of an object $i$ with the mass $m_i$ is determined by the force $\mathbf{f}_i(t)$ acting on the object at the discrete position $\mathbf{r}_i(t)$ at time $t$ together with the position $\mathbf{r}_i(t-\delta t)$ at $t-\delta t$ as

$$m_i\frac{\mathbf{r}_i(t+\delta t)-\mathbf{r}_i(t)}{\delta t}=m_i\frac{\mathbf{r}_i(t)-\mathbf{r}_i(t-\delta t)}{\delta t}+\delta t\mathbf{f}_i(t), \quad (1)$$

where the velocities $\mathbf{v}_i(t+\delta t/2)=[\mathbf{r}_i(t+\delta t)-\mathbf{r}_i(t)]/\delta t$ and $\mathbf{v}_i(t-\delta t/2)=[\mathbf{r}_i(t)-\mathbf{r}_i(t-\delta t)]/\delta t$ and corresponding momenta are constant in the time intervals in between the discrete positions. Newton begins *Principia* by postulating Eq. (1) in *Proposition I*, and he obtained his second law as the limit $\lim_{\delta t\to 0}$ of the equation. For Newton's derivation of his second law and his discrete algorithm in *Proposition I* see Ref. [3], Chap. 2.

The algorithm, Eq. (1), is usually presented as the Leapfrog algorithm

$$\mathbf{v}_i(t+\delta t/2)=\mathbf{v}_i(t-\delta t/2)+\delta t/m_i\mathbf{f}_i(t) \quad (2)$$

$$\mathbf{r}_i(t+\delta t)=\mathbf{r}_i(t)+\delta t\mathbf{v}_i(t+\delta t/2), \quad (3)$$

where the positions are obtained from the discrete values of the velocities. The rearrangement of Eq. (1) gives the Verlet algorithm [4]

$$\mathbf{r}_i(t+\delta t)=2\mathbf{r}_i(t)-\mathbf{r}_i(t-\delta t)+\delta t^2\mathbf{f}_i(t)/m_i. \quad (4)$$

The algorithm is used in almost all discrete "molecular dynamics" (MD) simulations and with Verlet's expression for the velocity at the discrete time $t$,

$$\mathbf{v}_0(t)=\frac{\mathbf{r}(t+\delta t)-\mathbf{r}(t-\delta t)}{2\delta t}. \quad (5)$$

The approximation (5) for the velocity $\mathbf{v}(t)$ is the first term in a symmetrical Taylor expansion from the position $\mathbf{r}(t)$ on the classical analytic trajectory, but the discrete dynamics trajectory is not analytic. Furthermore, there are times for an analytic trajectory where a Taylor expansion is very slowly converging, e.g., at particle collisions or for fast vibrations of atoms in molecules with covalent bonds. The velocity is, however, as Newton noticed in *Principia*, constant in time except at the discrete times where it is exposed to an impulsive force (see next section), and it is given by Eq. (2). Verlet's inaccurate expression for the velocity results in a corresponding inaccurate measure of the energy, temperature, and heat capacity.

The purpose of the article is to show that Newton's discrete dynamics has the same properties as his analytic classical mechanics, and to correct the expressions for the energy, temperature, and heat capacity in MD simulations [3].

In Sec. II we first present Newton and Verlet's formulation of the discrete classical dynamics and derive the energy invariance. The connections between the "Verlet" expressions for the energy, temperature, and heat capacity and the corresponding exact Newtonian discrete dynamic expressions are derived in Sec. III. In Sec. IV we determine the differences between the traditional (Verlet) values of the temperature and heat capacities, and the corresponding Newtonian values for a system of $N=2000$ particles with Lennard-Jones (LJ) interactions. Section V summarizes the results.

## II. DISCRETE NEWTONIAN DYNAMICS

The classical discrete dynamics between $N$ spherically symmetrical objects with masses $m^N=m_1,m_2,\ldots,$

 

$m_i, \ldots, m_N$ and positions $\mathbf{r}^N(t) = \mathbf{r}_1(t), \mathbf{r}_2(t), \ldots, \mathbf{r}_i(t), \ldots, \mathbf{r}_N(t)$ is obtained by Eq. (1). Let the force $\mathbf{f}_i(t)$ on object $i$ be a sum of pairwise forces $\mathbf{f}_{ij}(t)$ between pairs of objects $i$ and $j$:

$$\mathbf{f}_i(t) = \sum_{j \neq i}^{N} \mathbf{f}_{ij}(t). \tag{6}$$

### A. Newton's formulation of discrete classical dynamics

Newton begins *Principia* by postulating Eq. (1) in *Proposition I*. The English translation of *Proposition I* is

*Of the Invention of Centripetal Forces.*

PROPOSITION I. Theorem I.

The areas, which revolving bodies describe by radii drawn to an immovable centre of force do lie in the same immovable planes, and are proportional to the times in which they are described.

For suppose the time to be divided into equal parts, and in the first part of time let the body by its innate force describe the right line AB. In the second part of that time, the same would (by Law I.), if not hindered, proceed directly to c, along the line Bc equal to AB; so that the radii AS, BS, cS, drawn to the centre, the equal areas ASB, BSc, would be described. But when the body is arrived at B, *suppose that a centripetal force acts at once with a great impulse*, and, turning aside the body from the right line Bc, compels it afterwards to continue its motion along the right line BC. Draw cC parallel to BS meeting BC in C; and at the end of the second part of the time, the body (by Cor. I of Laws) will be found in C, in the same plane with the triangle ASB. Join SC, and, because SB and Cs are parallel, the triangle SBC will be equal to the triangle SBc, and therefore also to the triangle SAB. By the like argument, if the centripetal force acts successively in C, D, E, & c., and makes the body, in each single particle of time, to describe the right lines CD, DE, EF, & c., they will all lie in the same plane; and the triangle SCD will be equal to the triangle SBC, and SDE to SCD, and SEF to SDE. And therefore, in equal times, equal areas are described in on immovable plane: and, by composition, any sums SADS, SAFS, of those areas, are one to the other as the times in which they are described. Now let the number of those triangles be augmented; and their breadth diminished in infinitum; and (by Cor. 4, Lem III) their ultimate perimeter ADF will be a curve line: and therefore the centripetal force, by which the body is perpetually drawn back from the tangent of this curve, will act continually; and any described areas SADS, SAFS, which are always proportional to the times of description, will, in this case also, be proportional to those times. Q.E.D.

*Proposition I* in *Principia* is illustrated with a figure (Fig. 1). The assumption *suppose that a centripetal force acts at once with a great impulse* in *Proposition I* is highlighted here. It is the central part in *Principia* (Fig. 1). Newton's second law is derived from his discrete dynamics, where the time, forces, and the change in momenta are quantized and the velocities are constant in between the discrete times. Newton's discrete dynamics in *Proposition I* is in fact classical quantum dynamics [3].

Nobel Laureate T. D. Lee was perhaps the first to suggest that difference equations are to be preferred in the foundation

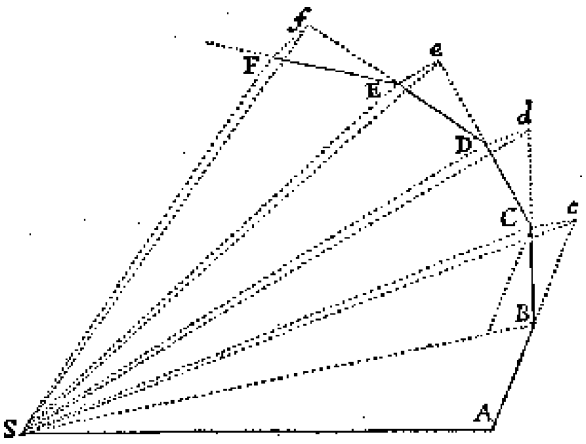


FIG. 1. Newton's figure at *Proposition I* in *Principia*, with the formulations of the discrete dynamics. The discrete positions are A: $\mathbf{r}(t - \delta t)$; B: $\mathbf{r}(t)$; C: $\mathbf{r}(t + \delta t)$, etc. The deviation cC from the straight line ABc (Newton's first law) is caused by a force from the position S at time $t$.

of dynamics, and with a classical difference equation as the classical limit path of Feynman's quantum paths [5]. This classical limit path is Newton's discrete dynamics in *Proposition I*. Our classical world is of course analytic. The difference between analytic and discrete dynamics is proportional to the square of $\delta t$ = Planck time ($\approx 10^{-43}$ s), and negligible. But one can say that Newtonian discrete dynamics simulations with time increments $\delta t \approx 10^{-14}$ s, used in many MD simulations, is in the same "universality class" as the analytic dynamics, and exact in the same manner as classical analytic dynamics. If so it places Newtonian discrete dynamics as a remarkably useful scientific tool.

### B. The Verlet algorithm

Loup Verlet (1931–2019) published in 1967 the article *Computer "Experiments" on Classical Fluids. I. Themodynamical Properties of Lennard-Jones Molecules* [4], where Newton's discrete algorithm with the formulation by Eq. (4) was introduced. The algorithm was derived by a forward and backward Taylor expansion [6]

$$\begin{aligned}
\mathbf{r}(t + \delta t) &= \mathbf{r}(t) + \delta t \frac{\partial \mathbf{r}(t)}{\partial t} + \frac{1}{2}\delta t^2 \frac{\partial^2 \mathbf{r}(t)}{\partial t^2} \\
&\quad + \frac{1}{6}\delta t^3 \frac{\partial^3 \mathbf{r}(t)}{\partial t^3} + \cdots \\
\mathbf{r}(t - \delta t) &= \mathbf{r}(t) - \delta t \frac{\partial \mathbf{r}(t)}{\partial t} + \frac{1}{2}\delta t^2 \frac{\partial^2 \mathbf{r}(t)}{\partial t^2} \\
&\quad - \frac{1}{6}\delta t^3 \frac{\partial^3 \mathbf{r}(t)}{\partial t^3} + \cdots ,
\end{aligned} \tag{7}$$

and the algorithm was obtained from the sum $\mathbf{r}(t + \delta t) + \mathbf{r}(t - \delta t)$ and $\delta t^2 \partial^2 \mathbf{r}(t)/\partial t^2 = \frac{\delta t^2}{m}\mathbf{f}(t)$. All the odd terms in the sum cancel, and the Verlet algorithm was formulated as a fourth-order time symmetric predictor of the positions at the analytic trajectories. The velocity is correspondingly derived from the difference $\mathbf{r}(t + \delta t) - \mathbf{r}(t - \delta t)$; all even terms

cancel, and it is

$$\mathbf{v}(t) = \frac{\mathbf{r}(t+\delta t) - \mathbf{r}(t-\delta t)}{2\delta t} + \frac{1}{6}\frac{\delta t^2}{m}\mathbf{f}'(t) + \cdots . \quad (8)$$

The scientific community and Verlet were much later aware that it actually was Newton who first published the geometric formulation of the algorithm in *Proposition I* [7].

### C. The energy invariance in discrete Newtonian dynamics

Newton's algorithm is a symmetric time centered difference whereby the dynamics is time reversible and symplectic. The conservation of momentum and angular momentum for a conservative system follows directly from Newton's third law for a conservative system with the forces $\mathbf{f}_{ij}(t) = -\mathbf{f}_{ji}(t)$ between objects $i$ and $j$, but the energy invariance is not so obvious.

The energy in a system with analytic dynamics is the sum of potential energy $U(\mathbf{r}^N(t))$ and kinetic energy $K(t)$, and it is time invariant for a conservative system. The kinetic energy in the discrete dynamics at time $t$ is, however, not well defined since the velocities change at $t$. Traditionally one uses Verlet's first-order expression for the velocity at time $t$, Eq. (5), obtained by the symmetric Taylor expansion, and

$$K_0(t) = \sum_i^N \frac{1}{2} m_i \mathbf{v}_{0,i}(t)^2, \quad (9)$$

$$E_0(t) = U(\mathbf{r}^N(t)) + K_0(t). \quad (10)$$

The energy $E_0$ obtained by using the approximation (5) and with $K(t) = K_0(t)$ for the kinetic energy fluctuates with time, although it is constant when averaged over long time intervals.

The velocities are, however, constant in between the discrete times in Newton's discrete dynamics, and the energy invariance can be obtained by considering the energy in the time interval $[t - \delta t/2, t + \delta t/2]$ and dividing the interval into two subintervals $[t - \delta t/2, t]$ and $[t, t + \delta t/2, t]$. The energy invariance $E_D$ in Newton's discrete dynamics (D) can then be obtained by considering the change in kinetic energy, $\delta K_D$, the change in potential energy, $\delta U_D$, and the work $W_D$ done by the forces in the time interval $[t - \delta t/2, t + \delta t/2]$.

The loss in potential energy, $-\delta U_D$, is defined as the work done by the forces for a change of positions [8]. The work $W_D$ done in the time interval by the discrete dynamics from the position $[\mathbf{r}_i(t) + \mathbf{r}_i(t-\delta t)]/2$ at $t - \delta t/2$ to the position $[\mathbf{r}_i(t+\delta t) + \mathbf{r}_i(t)]/2$ at $t + \delta t/2$, and with the change $\delta\mathbf{r}_i$ of the position $\delta\mathbf{r}_i = [\mathbf{r}_i(t+\delta t) - \mathbf{r}_i(t-\delta t)]/2$, is [3]

$$-\delta U_D = W_D = \sum_i^N \mathbf{f}_i(t)[(\mathbf{r}_i(t+\delta t) - \mathbf{r}_i(t-\delta t)]/2. \quad (11)$$

By rewriting Eq. (4) to

$$\mathbf{r}_i(t+\delta t) - \mathbf{r}_i(t-\delta t) = 2[\mathbf{r}_i(t) - \mathbf{r}_i(t-\delta t)] + \frac{\delta t^2}{m_i}\mathbf{f}_i(t) \quad (12)$$

and inserting Eq. (11) one obtains an expression for the total work in the time interval:

$$-\delta U_D = W_D = \sum_i^N \left[ [(\mathbf{r}_i(t) - \mathbf{r}_i(t-\delta t)]\mathbf{f}_i(t) + \frac{\delta t^2}{2m_i}\mathbf{f}_i(t)^2 \right]. \quad (13)$$

The mean kinetic energy $K_D$ of the discrete dynamics in the time interval $[t - \delta t/2, t + \delta t/2]$ is

$$\begin{aligned} K_D &= \frac{1}{2}\sum_i^N \frac{1}{2} m_i \left[ \frac{[\mathbf{r}_i(t+\delta t/2) - \mathbf{r}_i(t)]^2}{\delta(t/2)^2} \right. \\ &\quad \left. + \frac{[\mathbf{r}_i(t) - \mathbf{r}_i(t-\delta t/2)]^2}{\delta(t/2)^2} \right] \\ &= \frac{1}{2}\sum_i^N \frac{1}{2} m_i \left[ \frac{[\mathbf{r}_i(t+\delta t) - \mathbf{r}_i(t)]^2}{\delta t^2} \right. \\ &\quad \left. + \frac{[\mathbf{r}_i(t) - \mathbf{r}_i(t-\delta t)]^2}{\delta t^2} \right], \end{aligned} \quad (14)$$

with the change

$$\begin{aligned} \delta K_D = \sum_i^N \frac{1}{2} m_i \left[ \frac{[\mathbf{r}_i(t+\delta t) - \mathbf{r}_i(t)]^2}{\delta t^2} \right. \\ \left. - \frac{[\mathbf{r}_i(t) - \mathbf{r}_i(t-\delta t)]^2}{\delta t^2} \right]. \end{aligned} \quad (15)$$

By rewriting Eq. (4) to

$$\mathbf{r}_i(t+\delta t) - \mathbf{r}_i(t) = \mathbf{r}_i(t) - \mathbf{r}_i(t-\delta t) + \frac{\delta t^2}{m_i}\mathbf{f}_i(t) \quad (16)$$

and inserting the squared expression for $\mathbf{r}_i(t+\delta t) - \mathbf{r}_i(t)$ in Eq. (15), the change in kinetic energy is

$$\delta K_D = \sum_i^N \left[ [\mathbf{r}_i(t) - \mathbf{r}_i(t-\delta t)]\mathbf{f}_i(t) + \frac{\delta t^2}{2m_i}\mathbf{f}_i(t)^2 \right]. \quad (17)$$

The energy invariance from the a discrete change of time from $t - \delta t/2$ to $t + \delta t/2$ in Newton's discrete dynamics is expressed by Eqs. (13) and (17) as [3]

$$\delta E_D = \delta U_D + \delta K_D = 0. \quad (18)$$

## III. THE KINETIC ENERGY, TEMPERATURE, AND HEAT CAPACITY IN A NEWTONIAN DISCRETE CONSERVATIVE SYSTEM

The constant velocities in the time intervals between force impulses at time $t$ are related. It is easy to derive the relation [9]

$$\mathbf{v}_{0,i}(t)^2 = \frac{1}{2}\mathbf{v}_i(t+\delta t/2)^2 + \frac{1}{2}\mathbf{v}_i(t-\delta t/2)^2 - \frac{1}{4}\left(\frac{\delta t}{m_i}\mathbf{f}_i(t)\right)^2 \quad (19)$$

from Eq. (4) between the square of the first term in Verlet's Taylor expansion $\mathbf{v}_{0,i}(t)^2$, Eq. (5), for the velocity at time $t$ and Newton's exact expression for the square of the constant velocities in the time intervals $[t - \delta t, t]$ and $[t, t + \delta t]$. The

corresponding expression for the kinetic energy, $K_0(t)$, and the traditional value for the temperature used in MD simulations,

$$T_0 = \frac{\langle 2K_0(t)\rangle}{N_f}, \tag{20}$$

used in MD simulations for a system with $N_f$ degrees of freedom is less than the mean kinetic energy $K_{\rm D}$ and the temperature $T_{\rm D}$. In the discrete time interval $[t-\delta t/2, t+\delta t/2]$ the relation is

$$K_0(t) = K_D(t) - \sum_i^N \frac{1}{8}\frac{\delta t^2}{m_i}\mathbf{f}_i(t)^2, \tag{21}$$

and the systematic difference $T_D - T_0$ in the time interval by using Verlet's first-order approximation is

$$T_{\rm D}(t) - T_0(t) = \sum_i^N \frac{1}{4}\frac{\delta t^2}{m_i}\mathbf{f}_i(t)^2/N_f. \tag{22}$$

Newton's discrete dynamics depends purely on the positions and the forces. The momenta are not dynamic variables, but only "bookkeeping" expressions in the dynamics [3]. Therefore, the configurational temperature

$$T_{\rm Conf}(t) = \langle \nabla^2 U(\mathbf{r}^N)\rangle = \frac{\sum_i^N \mathbf{f}_i(t)^2}{-\sum_i^N \boldsymbol{\nabla}\cdot\mathbf{f}_i(t)} \tag{23}$$

could be a more relevant expression for the temperature since it depends purely on the forces. Equation (23) is derived from the average of the Laplacian of the potential energy $\nabla^2 U(\mathbf{r}^N)$, and is obtained from canonical averaging in the configurational phase space [10,11]. The value of $T_{\rm Conf}(t)$ fluctuates with time, but its mean value obtained from long simulations agrees with the corresponding temperatures $T_{\rm D}$ obtained from the kinetic energy.

The heat capacity $C_V = 3/2R + C_V^i$ consists of two terms: the term from the kinetic energy and the term $C_V^i$ from the interactions. The heat capacity can be determined either from numerical differentiation of the energy $U(T,\rho)$ or from the mean square fluctuation $\langle K(t)^2\rangle - \bar{K}^2$ of the kinetic energy [12]. The term $K_{\rm D}(t) - K_0(t) = \sum_i^N \frac{\delta t^2}{8m}\mathbf{f}_i^2$ in the kinetic energy $K_0(t)$ is important at high densities with hard particle collisions, and it affects $C_V^i$. The ratio

$$\Delta C_V^i = \frac{\langle (K_{\rm D}(t) - \bar{K}_{\rm D})^2\rangle - \langle (K_0(t) - \bar{K}_0)^2\rangle}{\langle (K_{\rm D}(t) - \bar{K}_{\rm D})^2\rangle} \tag{24}$$

is a measure of the relative error in $C_V^i$ by using Eq. (9) for the kinetic energy.

## IV. SIMULATIONS

Verlet used Lennard-Jones (LJ) forces to simulate argon, and his force field (FF) has been a standard used in many simulations, e.g., simulations of organic molecules to describe the atom-atom FF in the molecules together with the stronger FF, e.g., for covalent bonds. The errors $T_D - T_0$, $E_D - E_0$, and in the heat capacities by using Verlet's first-order approximation for the velocity are biggest for strong force fields, and especially at collisions where the FF is strongly repulsive. So the errors for systems with strong intramolecular FF and by using Eq. (20) are bigger than for an LJ system.

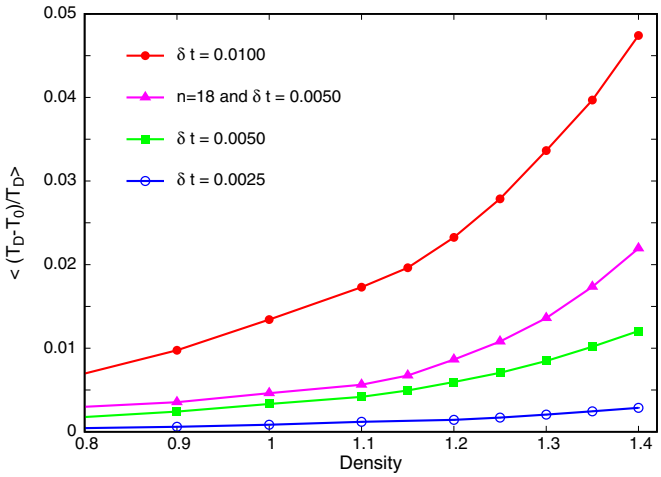


FIG. 2. The relative mean difference $\langle (T_D - T_0)/T_D\rangle$ between $T_D$ and $T_0$ as a function of the density for an LJ fluid system at $T_D = 1$.

LJ systems with $N = 2000$ LJ particles were simulated at $T_D = 1.00$ for different densities, temperatures, strength of the repulsive forces, and time increments. The differences between $T_D$ and $T_0$ at $T_D = 1.00$ as a function of density for $10^6$ time steps are shown in Fig. 2 for different time increments $\delta t$ and repulsive forces given by the exponent $n$ in the $n-6$ LJ potential [13]. The differences increase with density, temperature, the strength of the repulsive forces, or the discrete time step $\delta t$, but they are relatively small at state points with low densities. But the differences are significant for state points with high densities, systems with stronger forces, and for large time increments $\delta t$.

Most MD simulations are with a thermostat ($NVT$ and $NPT$ ensemble MD) and with the thermostat temperature $T(\text{thermostat}) = T_0$. We have performed $NVT$ simulations with a Nosé-Hover thermostat [14,15] and with $T(\text{thermostat}) = T_0$ as well as $T(\text{thermostat}) = T_{\rm D}$. The results from the $NVT$ simulations agree with the $NVE$ data. So the $NVE$ results in Fig. 2 are also valid for the other ensemble simulations.

The fluctuations of the temperatures $T_{\rm D}(t)$, $T_0(t)$, and $T_{\rm Conf}(t)$ in the time interval $t \in [4000\delta t, 4300\delta t]$ for the MD are shown in Fig. 3. The temperatures are obtained for $N = 2000$ LJ particles at $(T_D,\rho) = (1.00, 1.40)$, and with $\delta t = 0.010$. The red curve is for 300 time steps for $T_D(t)$, and the green curve is $T_{\rm Conf}(t)$. The mean temperatures $T_{\rm D}$ and $T_{\rm Conf}$ from $10^6$ time steps are approximately equal, $T_{\rm D} = 0.999 \pm 0.011$ and $T_{\rm Conf} = 1.008 \pm 0.020$, and higher than the mean $T_0 = 0.954 \pm 0.011$ for $T_0(t)$ shown in blue. The temperatures in Fig. 3 show that the temperature $T_{\rm D}$ in Newtonian discrete dynamics is consistent with the otherwise obtained configurational temperature $T_{\rm Conf}$, but is not consistent with $T_0$.

The relative difference between fluctuations in the square of the excess kinetic energies $\Delta C_V^i$ for a few hundred time steps is shown in Fig. 4 for the LJ system, and with the corresponding fluctuations $K_D(t)^2 - \bar{K}_D^2$ and $K_0(t)^2 - \bar{K}_0^2$ in the inset in the figure. The fluctuations are for the LJ system at $(T_D,\rho) = (1.00, 1.40)$ with the corresponding temperature fluctuations shown in Fig. 3. At first glance, the fluctuations

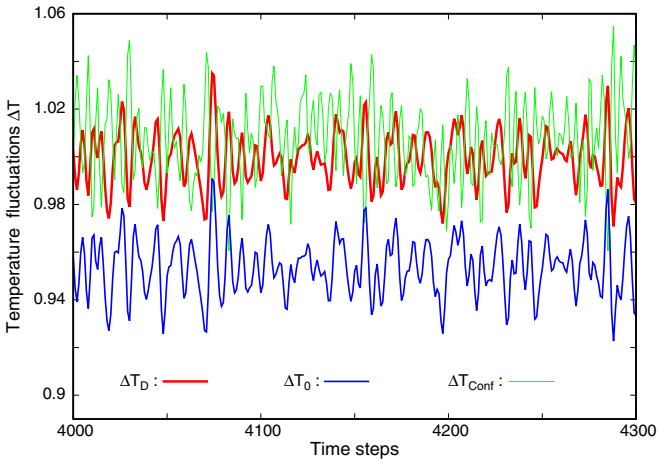


FIG. 3. Temperature fluctuations in a $NVE$ system of $N = 2000$ LJ particles at the density $\rho = 1.40$, temperature $T_D = 1$, and with $\delta t = 0.010$. The red plot is $T_D(t)$, blue is the traditional expression $T_0(t)$ for the temperature, and green is the configurational temperature $T_{\rm Conf}(t)$.

are synchronous (Fig. 3 and the inset in Fig. 4), but a closer examination reveals that there are significant differences of the order of 12% for the state point with relatively high density $\rho = 1.40$ and for the time increment $\delta t = 0.010$.

The relative difference in $C_V^i$ with $10^6$ time steps for the system at $T_{\rm D} = 1.00$ and at different densities and time increments is shown in Fig. 5. (The corresponding relative temperature differences are shown in Fig. 2.) The differences between $C_V^i$ obtained by fluctuations in $K_{\rm D}(t)$ and $K_0(t)$, respectively, increase with increasing density, temperature, strength of the repulsive forces, or time increment.

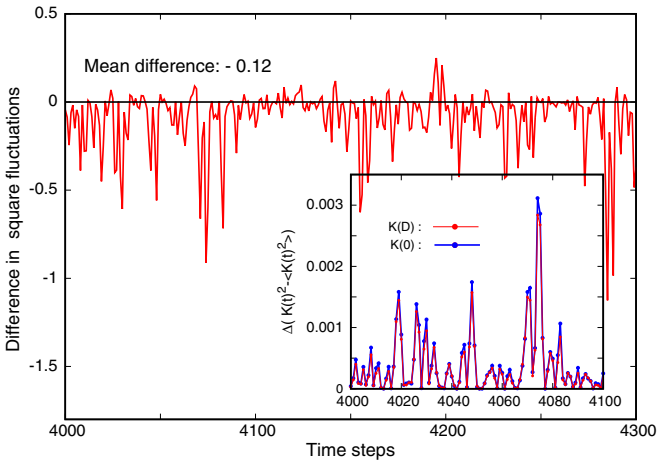


FIG. 4. The relative difference in the time interval $t \in [4000\delta t, 4300\delta t]$ between the fluctuations in the square of the excess kinetic energies $\Delta C_V^i$ for the LJ system at $(T, \rho) = (1.00, 1.40)$ and with $\delta t = 0.010$. The mean of the difference of the square excess kinetic energies [Eq. (24)] is $-0.12$. The inset shows the two excess squared kinetic energies per particle: red is $K_D(t)^2 - \bar{K}_D^2$ and blue is $K_0(t)^2 - \bar{K}_0^2$.

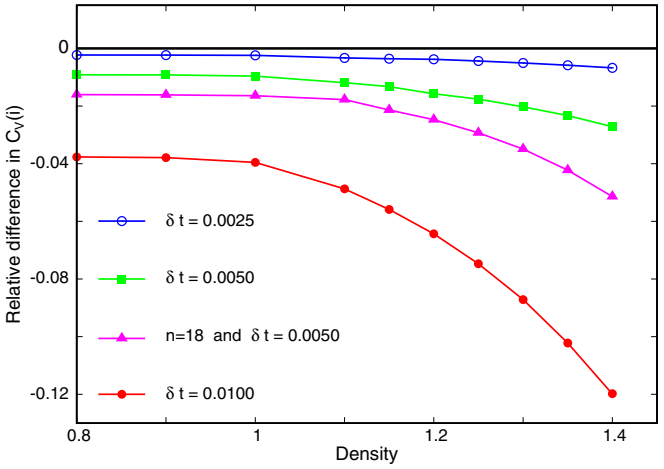


FIG. 5. The relative difference between the fluctuations in the square of the excess kinetic energies $\Delta C_V^i$ for the LJ system at $T = 1.00$ for different densities and time increments. The corresponding relative differences in temperatures are shown in Fig. 2.

## V. CONCLUSION

Newton published his discrete algorithm in *Principia Proposition I*, and the algorithm is now used everywhere in natural science disciplines ranging from simulations of planetary systems to simulations of atoms, molecules, and systems with complex proteins. L. Verlet rederived in 1967 the algorithm from a forward and backward Taylor expansion [6] and performed his MD simulations with Eq. (5) for the velocity and Eq. (9) for the kinetic energy. Discrete dynamics with Newton's algorithm has been further developed and is now a standard tool used in natural science, and MD work resulted in a Nobel Prize in 2013.

Newton's discrete dynamics has the same properties as his analytic classical mechanics: it is time reversible, symplectic, and has the same invariances for a conservative system [3]. Furthermore, there exists a shadow Hamiltonian where the positions of the discrete dynamics are located on the analytical trajectories for the shadow Hamiltonian [3,16,17]. This means that there is no qualitative difference between the analytical and the discrete dynamics, and MD with the Newton-Verlet algorithm is the exact generation of positions for the discrete dynamics.

Verlet's approximative expression for the velocity at time $t$, Eq. (5), which is used in MD simulations, does not affect the discrete dynamics and the discrete positions, but it is an unnecessary approximation. It is the first term in his Taylor expansion, and the corresponding expression for the kinetic energy, Eq. (9) ought to be replaced with the exact expression, Eq. (14). Doing so, one achieves an agreement between the kinetic and configurational temperatures (Fig. 3). Potential energy fluctuations $\delta U$ should be obtained by Eq. (11) or (13), and velocities and their time correlations by the (constant) velocities in the respective time intervals. Most MD simulations are canonical $NVT$ ensemble or $NPT$ ensemble simulations with the thermostat temperature $T$(thermostat) $= T_0$, and not only are the $NVT_0$ and $NPT_0$ temperatures wrong, so are also the values of $C_V^i$. The errors caused by using Eq. (5) for the velocity and Eq. (9) for the kinetic energy might only be a few

percent for systems with relatively weak forces. But the errors increase according to Eq. (22) with the strength of the forces and the time increment $\delta t$ used in the simulations, and can lead to severe errors for systems with strong forces such as full-atomic models of e.g. biomolecules with fast intramolecular vibrations.

The biggest challenge with an MD simulation of a real system, however, is to formulate a correct force field, and also for this reason it is important to use the correct expression for the kinetic energy, whereby one avoids introducing a systematic error in the calculated energies. The public software used for MD simulations should be corrected.


[1] I. Newton, *Philosophiæ Naturalis Principia Mathematica, Londini, Anno MDCLXXXVII* (Benediction Classics, Oxford, 2020).
[2] S. Toxvaerd, Eur. Phys. J. Plus **135**, 267 (2020).
[3] S. Toxvaerd, *Comprehensive Computational Chemistry* (Elsevier, Amsterdam, 2023), Vol. 3, p. 32.
[4] L. Verlet, Phys. Rev. **159**, 98 (1967).
[5] T. D. Lee, J. Stat. Phys. **46**, 843 (1987).
[6] See Appendix in [3].
[7] M. Nauenberg, Am. J. Phys. **86**, 765 (2018), see Ref. [7].
[8] H. Goldstein, *Classical Mechanics*, 2nd ed. (Addison-Wesley, Reading, MA, 1980), Chap. 1.
[9] S. Toxvaerd, J. Chem. Phys. **139**, 224106 (2013).
[10] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, Oxford, 1958), Eq. (33.14).
[11] H. H. Rugh, Phys. Rev. Lett. **78**, 772 (1997).
[12] J. L. Lebowitz, J. K. Percus, and L. Verlet, Phys. Rev. **153**, 250 (1967).
[13] D. Heyes and J. Powels, Mol. Phys. **95**, 259 (1998).
[14] W. G. Hoover, Phys. Rev. A **31**, 1695 (1985).
[15] S. Toxvaerd (unpublished).
[16] S. Toxvaerd, Phys. Rev. E **50**, 2271 (1994).
[17] S. Toxvaerd, O. J. Heilmann, and J. C. Dyre, J. Chem. Phys. **136**, 224106 (2012).