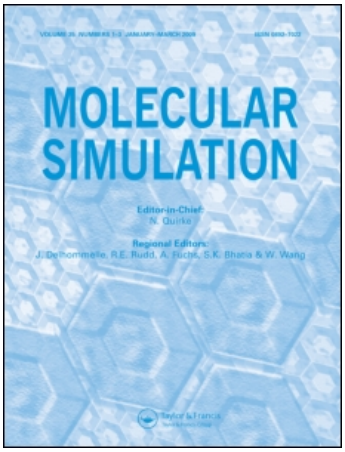

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Modified Velocity Scaling Scheme for Molecular Dynamics at Constant Temperature and/or Pressure

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Modified Velocity Scaling Scheme for Molecular Dynamics at Constant Temperature and/or Pressure

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A modified and generalized velocity scaling (VS) scheme to integrate equations of motion (EOM) for constant temperature and/or pressure molecular dynamics (MD) simulations in the framework of the leapfrog algorithm is presented. This modified VS scheme (MVS) enables us to integrate EOM with a velocity dependent force such as a friction term easily maintaining the accuracy of the leapfrog (Verlet) algorithm. The scaling factor in the MVS does not depend on the detailed expression of the friction term. Therefore, it can be incorporated in various constant temperature and/or pressure methods. The accuracy of integrations in the MVS and original VS was compared in a Lennard–Jones fluid. It is confirmed that the MVS holds the Verlet's accuracy, while original VS fails.

Keywords: Molecular dynamics; Velocity scaling; Leapfrog algorithm; Equations of motions

1 INTRODUCTION

Several extensions of molecular dynamics (MD) simulations have been proposed in the last 20 years. The constant temperature or constant pressure methods [1–5] are the most important progress in the methodology of MD simulations. The temperature or pressure controlling is desirable because it extends applicability of MD simulations.

In most constant temperature and/or pressure methods, we have to solve the equation of motion (EOM) just as the following:

$$m_i\ddot{x}_i = F_i - \zeta m_i\dot{x}_i, \tag{1}$$

where ζ is a kind of frictional coefficient (but not constant), $F_i = -\partial\Phi/\partial x_i$, and Φ is potential energy. This equation realizes energy dispersion and temperature of systems can be controlled. However, the right-hand side of Eq. (1) has a velocity dependent term. It prevents us from employing the leapfrog algorithm to integrate Eq. (1) in MD runs.

The leapfrog algorithm is equivalent to the Verlet algorithm [6] and is widely used in MD simulations. This is simple and offers good stability even with a relatively large time step (Δt). The following steps are performed in the leapfrog algorithm to integrate EOM without the energy dispersion term,

$$v_i(t + \Delta t/2) = v_i(t - \Delta t/2) + \Delta t\frac{F_i(t)}{m_i} + \mathrm{O}(\Delta t^3), \tag{2}$$

$$q_i(t + \Delta t) = q_i(t) + \Delta t v_i(t + \Delta t/2) + \mathrm{O}(\Delta t^4), \tag{3}$$

$$v_i(t) = [v_i(t + \Delta t/2) + v_i(t - \Delta t/2)]/2 + \mathrm{O}(\Delta t^2). \tag{4}$$

The position q_i and velocity $v_i(\dot{q}_i)$ of particle i are obtained at $t + \Delta t$ (or t) with the error of $\mathrm{O}(\Delta t^4)$ and $\mathrm{O}(\Delta t^2)$, respectively. It is easily recognized that v_i at t is calculated from v_i at preceding time step, $t + \Delta t/2$. Thus, the velocity dependent force in Eq. (1) cannot be incorporated directly in the leapfrog algorithm. In such cases, Gear's predictor–corrector algorithm is often used [6]. However, in this algorithm, we need more memory to deal with higher derivatives, $\dot{q}_i$, $\ddot{q}_i$, $\dddot{q}_i$..., and a smaller time step to realize good stability. These are the disadvantages especially for large systems such as protein.

In this study, we present a modification of the velocity scaling (VS) scheme in the leapfrog algorithm to overcome above problems. Velocity Scalings can be easily performed in the leapfrog algorithm. With specific scaling factors of velocity,

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they approximately correspond to Eq. (1) [9]. However, they lose the original accuracy of the leapfrog (Verlet) algorithm. In our modified VS scheme, Eq. (1) can be integrated with a generalized scaling factor maintaining the Verlet's accuracy. This scheme is available independently of the detailed expressions of the coefficient ζ in Eq. (1). Therefore, all EOM which has the energy dispersion term such as Eq. (1) can be handled only by replacing ζ with a corresponding one in each case.

In Section 2, the VS scheme in the leapfrog algorithm is briefly reviewed. The modified VS scheme is presented in Section 3 and algorithms with the modified VS for various constant temperature and/or pressure methods are given in Section 4. The accuracy of integrations in the modified VS is examined in a Lennard–Jones (LJ) fluid in Section 5 and we summarize the present work in Section 6. In the Appendix, an algorithm with the modified VS scheme for the isothermal–isobaric MD by Melchinna *et al.* [7] is presented.

2 VELOCITY SCALING IN THE LEAPFROG ALGORITHM

The leapfrog algorithm is described in Eqs. (2)–(4). The VS scheme is easily employed in this algorithm:

$$v_i(t+\Delta t/2) = v_i(t-\Delta t/2) + \Delta t \frac{F_i(t)}{m_i}, \tag{5}$$

$$v_i^*(t+\Delta t/2) = S v_i(t+\Delta t/2), \tag{6}$$

$$q_i(t+\Delta t) = q_i(t) + \Delta t v_i^*(t+\Delta t/2), \tag{7}$$

$$v_i^*(t) = [v_i^*(t+\Delta t/2) + v_i(t-\Delta t/2)]/2, \tag{8}$$

where S is a scaling factor. Without Eq. (6), above equations are the same as Eqs. (2)–(4). In Eq. (6), the velocity at $t+\Delta t/2$ is modified to control kinetic energy K of a particle system and the velocity at t is given in Eq. (8).

In most cases, the following simple scaling factor is used,

$$S = \sqrt{\frac{T_0}{T_+}}, \tag{9}$$

where T_0 is the pre-set temperature, $T_+ = \sum m_i v_i^2(t+\Delta t/2)/3Nk$, N is the number of particles, and k is Boltzmann's constant. The VS with this simple scaling factor is close to the Gaussian thermostat if the scaling is performed at every time step. The Gaussian thermostat was proposed by Hoover *et al.* and Evans [1,2] based on Gauss' principle of least constraint. In this thermostat, momentum p_i is forced to keep kinetic energy $K(=\sum p_i^2/2m_i)$ to a constant, so that the fluctuation of K is completely suppressed. It is known that this thermostat yields the canonical ensemble in the configurational space (q_i) [8,9]. The equations of motion (EOM) for the Gaussian thermostat are

$$\dot{q}_i = \frac{p_i}{m_i} = v_i, \tag{10}$$

$$\dot{p}_i = F_i - \zeta_G p_i, \tag{11}$$

where

$$\zeta_G = \frac{\sum v_i \cdot F_i}{3NkT_0}. \tag{12}$$

With S in Eq. (9), the VS in the leapfrog algorithm (Eqs. (5)–(8)) corresponds to the following EOM [9],

$$\ddot{q}_i = \frac{F_i(t)}{m_i} - \zeta_G v_i(t) + \mathrm{O}(\Delta t). \tag{13}$$

Therefore the Gaussian thermostat is approximately realized by the VS with Eq. (9). However, it should be noted that integrations are carried out with the error of $\mathrm{O}(\Delta t)$, whereas the accuracy in the Verlet algorithm is of $\mathrm{O}(\Delta t^2)$.

Another scaling factor is also available. For the weak coupling (WC) thermostat, which was proposed by Berendsen *et al.* [10], the corresponding scaling factor is

$$S_{WC} = \sqrt{1 + \frac{\Delta t}{\tau}\left(\frac{T_0}{T_+} - 1\right)}, \tag{14}$$

where τ is a coupling parameter which determines the strength of coupling with a heat bath. The EOM for the WC thermostat are formally the same as Eqs. (10) and (11) but ζ_G is replaced with ζ_{WC}:

$$\zeta_{WC} = -\frac{1}{2\tau}\left(\frac{T_0}{T} - 1\right), \tag{15}$$

where $T = 2K/3Nk$. This thermostat is derived by eliminating local disturbance from random noise in a Langevin equation. This results in relatively gentle temperature controlling. Recently, it is shown that the WC thermostat generate an intermediate statistical ensemble in the configurational space between the microcanonical and canonical ensemble [11]. Similar to the Gaussian thermostat, the VS with S_{WC} corresponds to the EOM for the WC thermostat with the error of $\mathrm{O}(\Delta t)$ [10,11].

With the specific scaling factors, the Gaussian and WC thermostats can be treated by the VS in the leapfrog algorithm. However, the corresponding EOM are under the accuracy of one order less than that of the Verlet algorithm. In addition, other thermostats or constant pressure schemes cannot be employed. In the next section, the modification of the VS scheme to integrate the general EOM for constant temperature and/or pressure MD (i.e. Eq. (1)) within the accuracy of the Verlet algorithm is shown. We will see algorithms to incorporate the Gaussian and

WC thermostats in the modified VS scheme in Section 4.

3 MODIFIED VELOCITY SCALING FOR CONSTANT TEMPERATURE AND/OR PRESSURE MD

The EOM corresponding to the VS in the leapfrog algorithm [9] is given as

$$\begin{aligned}\frac{\mathrm{d}^2 q_i}{\mathrm{d}t^2} = \frac{\mathrm{d}v_i}{\mathrm{d}t} &= [v_i^*(t+\Delta t/2) - v_i(t-\Delta t/2)]/\Delta t \\ &= [Sv_i(t+\Delta t/2) - v_i(t-\Delta t/2)]/\Delta t \\ &= \frac{F_i(t)}{m_i} + \frac{S-1}{\Delta t} v_i(t+\Delta t/2) + \mathrm{O}(\Delta t^2). \end{aligned} \tag{16}$$

In order to integrate the EOM for constant temperature and/or pressure MD (Eq. (1)) without reducing the accuracy of the Verlet algorithm ($\mathrm{O}(\Delta t^2)$), the following relation should be satisfied,

$$\frac{S-1}{\Delta t} v_i(t+\Delta t/2) = -\zeta(t) v_i^*(t) + \mathrm{O}(\Delta t^2). \tag{17}$$

The scaling factor S is to be determined to satisfy Eq. (17). We do not discuss detailed expressions of ζ in this section and assume that ζ (or $\zeta' = \zeta + \mathrm{O}(\Delta t^2)$) is known at t. If this assumption is held, the discussion in this section is valid independently of expressions of ζ.

Here, we define the form of the modified scaling factor S_i as

$$S_i \equiv 1 - \zeta(t)\Delta t + \alpha_i \Delta t^2. \tag{18}$$

The parameter α_i should be determined to satisfy Eq. (17), and the scaling factor can depend on each particle i. Using this form, the left-hand and right-hand sides of Eq. (17) can be written as

$$\begin{aligned}\frac{S-1}{\Delta t} v_i(t+\Delta t/2) = &-\zeta(t) v_i(t) - \zeta(t)\frac{F_i(t)\Delta t}{2m_i} \\ &+ v_i(t)\alpha_i \Delta t + \mathrm{O}(\Delta t^2), \end{aligned} \tag{19}$$

$$\begin{aligned}-\zeta(t) v_i^*(t) = &-\zeta(t)\left(v_i(t) - \zeta(t)\frac{v_i(t)}{2}\Delta t\right) \\ &+ \mathrm{O}(\Delta t^2), \end{aligned} \tag{20}$$

where $v_i(t)$ is "non-corrected" velocity at t:

$$v_i(t) = [v_i(t+\Delta t/2) + v_i(t-\Delta t/2)]/2. \tag{21}$$

From Eqs. (17), (19) and (20), α_i is determined as

$$\alpha_i = \frac{\zeta(t)^2}{2} + \frac{\zeta(t) F_i(t)}{2 m_i v_i(t)}. \tag{22}$$

Therefore,

$$S_i = 1 - \zeta(t)\Delta t + \left[\frac{\zeta(t)^2}{2} + \frac{\zeta(t) F_i(t)}{2 m_i v_i(t)}\right]\Delta t^2. \tag{23}$$

By the VS with this scaling factor, Eq. (16) becomes

$$\ddot{q}_i = \frac{F_i(t)}{m_i} - \zeta(t) v_i^*(t) + \mathrm{O}(\Delta t^2). \tag{24}$$

Consequently, the EOM for constant temperature and/or pressure MD can be numerically solved by this "modified" VS scheme in the leapfrog algorithm (MVS) within the accuracy of the Verlet algorithm.

Let us consider the Nosé–Hoover thermostat [3,12] as an example. In this thermostat, ζ is regarded as a dynamical variable and ζ at t is easily obtained. The EOM of ζ is

$$Q\dot{\zeta} = 2K - 3NkT_0, \tag{25}$$

where Q is a fictitious mass for ζ. The variable ζ at t is calculated in the leapfrog algorithm as

$$\zeta(t) = \zeta(t-\Delta t) + \Delta t(2K(t-\Delta t/2) - 3NkT_0)/Q. \tag{26}$$

Kinetic energy K at $t - \Delta t/2$ can be obtained from $v_i(t-\Delta t/2)$. From Eqs. (23) and (26), S_i for the Nosé–Hoover thermostat is obtained and the Nosé–Hoover MD can be performed by the MVS (Eqs. (5)–(8) and (23)). It is noted that the MVS scheme in the Nosé–Hoover thermostat is consistent with the algorithm by Toxvaerd [13] within the Verlet's accuracy.

4 ALGORITHMS FOR THE EOM WITH A VELOCITY DEPENDENT FRICTIONAL COEFFICIENT

In several constant temperature and/or pressure methods, frictional coefficients such as ζ depend on particles' velocity at t: $\zeta(v^*(t))$. In this section, algorithms incorporating the MVS scheme for these methods are shown. They are easily constructed by use of the following relation:

$$\begin{aligned} v_i^*(t) &= v_i(t-\Delta t/2) + \frac{\Delta t}{2m_i}[F_i(t) \\ &\quad - \zeta(v_i^*(t)) m_i v_i^*(t)] + \mathrm{O}(\Delta t^2) \\ &\simeq v_i(t-\Delta t/2) + \frac{\Delta t}{2m_i}[F_i(t) - \zeta(v_i(t \\ &\quad - \Delta t/2)) m_i v_i(t-\Delta t/2)] + \mathrm{O}(\Delta t^2). \end{aligned} \tag{27}$$

In the last approximate expression, we assume that $\zeta(v^*(t)) = \zeta(v^*(t-\Delta t/2)) + \mathrm{O}(\Delta t)$. This relation enables us to calculate $\zeta(v^*(t))$ and to obtain the MVS scaling factor S_i (Eq. (23)). In the following

subsections, we show algorithms for three constant temperature or pressure methods separately: the WC and Gaussian thermostats, and the Andersen's constant pressure method.

4.1 WC Thermostat

The frictional coefficient ζ_{WC} in the WC thermostat is already described in Eq. (15). We note that T in Eq. (15) is expressed as $T = \sum m_i v_i^{*2}(t)/3Nk$. In the original paper by Berendsen *et al.* [10], they introduced a simple VS algorithm (i.e. Eq. (14)) to incorporate the leapfrog algorithm. However, integrations are carried out with the accuracy of one order less than that of the Verlet algorithm as described in Section 2.

To maintain the accuracy of the Verlet algorithm, we can use the relation of Eq. (27) and calculate $\zeta'_{WC}(= \zeta_{WC} + \mathrm{O}(\Delta t^2))$ at t as

$$\zeta'_{WC}(t) = -\frac{1}{2\tau}\left[\frac{T_0}{T_- + \left(\frac{\sum v_{i-}\cdot F_{i0}}{3Nk} + \frac{1}{2\tau}(T_0 - T_-)\right)\Delta t} - 1\right], \tag{28}$$

where $T_- = \sum m_i v_{i-}^2/3Nk$, $v_{i-} = v_i(t - \Delta t/2)$, $F_{i0} = F_i(t)$, and T_0 is the pre-set temperature. It is easily confirmed that the difference between ζ_{WC} and ζ'_{WC} is of $\mathrm{O}(\Delta t^2)$. The modified scaling factor S_{iWC} for the WC thermostat is obtained by substituting ζ'_{WC} to Eq. (23). The MVS with S_{iWC} realizes the integration of the EOM for the WC thermostat under the accuracy of the Verlet algorithm.

4.2 Gaussian Thermostat

The frictional coefficient ζ_G in the Gaussian thermostat is described in Eq. (12). By use of Eq. (27), we obtain ζ'_G as

$$\zeta'_{\mathrm{G}} = \frac{\sum v_{i-}\cdot F_{i0}}{3NkT_0} + \frac{\Delta t}{3NkT_0}\left(\sum \frac{F_{i0}^2}{2m_i} - \frac{(\sum v_{i-}\cdot F_{i0})^2}{6NkT_0}\right). \tag{29}$$

From this, the MVS scaling factor S_{iG} for the Gaussian thermostat is obtained.

It is useful to remark that S_{iG} can be reexpressed as

$$S_{iG} = \sqrt{T_0/T_+} + B_i\Delta t^2, \tag{30}$$

where

$$B_i \equiv \frac{F_{i0}(\sum v_{i-}\cdot F_{i0})}{6NkT_0 m_i v_{i+}} - \frac{(\sum v_{i-}\cdot F_{i0})^2}{2(3NkT_0)^2}, \tag{31}$$

$T_+ = \sum m_i v_{i+}^2/3Nk$, and $v_i+ = v_i(t + \Delta t/2)$. In the Gaussian thermostat, kinetic energy K is forced to be a constant $(3NkT_0/2)$. If integrations of the EOM for the Gaussian thermostat are performed with the accuracy of the Verlet algorithm, the error of $\delta K(\equiv K(t + \Delta t) - K(t))$ should be of $\mathrm{O}(\Delta t^3)$. Using the MVS, K is conserved with this accuracy during simulations. However, the following relation is easily obtained,

$$\Delta t^2 \sum m_i v_{i-}^2 B_i \sim \mathrm{O}(\Delta t^3). \tag{32}$$

This means that the simple VS $(S = \sqrt{T_0/T_+})$ also conserves K within $\mathrm{O}(\Delta t^3)$. Therefore, the accuracy in the MVS and simple VS is the same with respect to the conservation of K. However, the corresponding EOM are different by $\mathrm{O}(\Delta t)$ (see Eqs. (13) and (24)).

4.3 Andersen's Constant Pressure Method

In the Andersen's constant pressure method [4], the volume V of a simulation cell can change and is regarded as a dynamical variable. For simplicity, we assume that a simulation cell is a cubic box (its edge length L is expressed as $V^{1/3}$). The coordinate q_i is scaled by L as

$$q_i = Ls_i, \tag{33}$$

where s_i is a scaled coordinate $(0 \le s_i \le 1)$ and velocity is defined as

$$v_i = L\dot{s}_i.$$

In this method, s_i and V are explicitly evolved and their EOM are the following:

$$m_i\ddot{s}_i = -V^{-1/3}\frac{\partial \Phi}{\partial q_i} - \frac{2\dot{V}}{3V}m_i\dot{s}_i, \tag{35}$$

$$W\ddot{V} = \left[\frac{1}{3V}\left(\sum m_i v_i^2 - \sum q_i\cdot\frac{\partial \Phi}{\partial q_i}\right)\right] - P_{\mathrm{ex}}, \tag{36}$$

where W is a fictitious mass corresponding to the variable V and P_{ex} is the pre-set external pressure. Inside of [ ] in Eq. (36) corresponds to the instantaneous internal pressure. The constant pressure condition is realized by changing V to balance the internal and external pressure.

In the leapfrog algorithm, it is difficult to integrate Eqs. (35) and (36). The former has the same form as Eq. (1) (the corresponding term to ζ in Eq. (1) is $(2\dot{V}/3V)$), and the latter also has a force term depending on particles' velocity at t. These problems can be overcome by the use of Eq. (27) replacing v_i with $\dot{s}_i$ (F_i in Eq. (27) corresponds to the first term in the right-hand side of Eq. (35) and

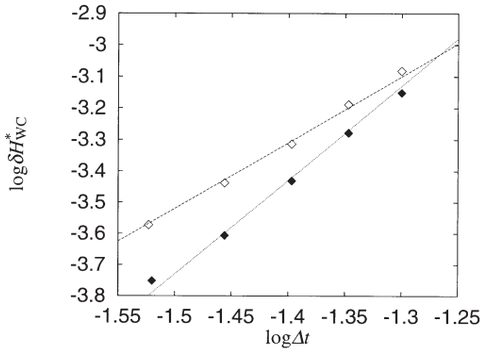

FIGURE 1 Relation between $\log \delta H^*_{WC}$ and $\log \Delta t$ obtained in a LJ fluid with the WC thermostat. Filled diamond denotes results by the MVS and open diamond denotes those by the original VS. Dotted and dashed lines have slope 3 and 2, respectively.

$2\dot{V}(t - \Delta t/2)/3V(t)$ is regarded as $\zeta(t - \Delta t/2)$). After calculating $s_i^*(t)$, $\dot{V}$ at t can be obtained as

$$\dot{V}(t + \Delta t/2) = \dot{V}(t - \Delta t/2) + \frac{\Delta t}{W}\left\{\left[\frac{1}{3V(t)}\left(\sum m_i v_i^{*2}(t) - \sum q_i \cdot \frac{\partial \Phi}{\partial q_i}\right) - P_{ex}\right\} + O(\Delta t^3), \quad (37)$$

$$\dot{V}(t) = [\dot{V}(t + \Delta t/2) + \dot{V}(t - \Delta t/2)]/2 + O(\Delta t^2), \quad (38)$$

where v_i^* is $V^{1/3}(t)\dot{s}_i^*(t)$. It is noted that V at t is already known just as q_i in the leapfrog algorithm. We can obtain the MVS scaling factor to integrate Eq. (35) by replacing $\zeta(t)$ in Eq. (23) with $(2\dot{V}(t)/3V(t))$. The variables s_i and $\dot{s}_i$ are calculated just as q_i and v_i in Eqs. (5)–(8) with the MVS scaling factor (Eq. (23)). The volume V is obtained in the same manner as scaled coordinates s_i:

$$V(t + \Delta t) = V(t) + \Delta t \dot{V}(t + \Delta t/2). \quad (39)$$

The "real" coordinate q_i at $t + \Delta t$ is obtained as $q_i(t + \Delta t) = V^{1/3}(t + \Delta t)s_i(t + \Delta t)$.

The combination of the Andersen's constant pressure method and constant temperature methods such as the Nosé–Hoover, Gaussian, and WC thermostats is straightforward. Melchinna *et al.* proposed the constant temperature and pressure method which realizes the exact NPT (isothermal–isobaric) ensemble [7]. In the Appendix, an algorithm with the MVS scheme to solve the EOM for this NPT MD is presented.

5 APPLICATION

Accuracy of integrations of EOM by the MVS scheme was examined in a LJ (12-6) fluid. In the MVS scheme, integrations are carried out maintaining the accuracy of the Verlet algorithm, while in the original VS such as Eqs. (9) and (14), it is of one order less than that of the Verlet algorithm. This is easily checked by the error of a conserved quantity H^*:

$$\delta H^* = \langle H^*(t + \Delta t) - H^*(t)\rangle, \quad (40)$$

where $\langle\ \rangle$ denotes time average. In the Verlet algorithm, it is shown that δH^* is of $O(\Delta t^3)$ (as an example, estimation of δH^* in the WC thermostat is given in the following). Therefore, we can obtain the following relation if EOM are integrated under the accuracy of the Verlet algorithm [6],

$$\log \delta H^* \propto 3 \log \Delta t. \quad (41)$$

In this section, accuracy of integrations by the MVS and original VS (Eq. (14)) is compared in simulations of a LJ fluid with the WC thermostat.

In the WC thermostat, the conserved quantity H^*_{WC} is

$$H^*_{WC} = K + \Phi - \int \frac{d\epsilon}{dt} dt, \quad (42)$$

where

$$\int \frac{d\epsilon}{dt} dt = -\frac{1}{2\tau}(2K - 3NkT_0). \quad (43)$$

With the leapfrog algorithm, Eq. (43) can be expressed as

$$\int_t^{t+\Delta t} \frac{d\epsilon}{dt} dt = \epsilon(t + \Delta t) - \epsilon(t) = -(2K(t + \Delta t/2) - 3NkT_0)\frac{\Delta t}{2\tau} + O(\Delta t^3). \quad (44)$$

The errors of K and Φ are easily estimated [6] and the following relation is obtained,

$$\delta K + \delta \Phi = \delta \epsilon + O(\Delta t^3). \quad (45)$$

Thus, H^*_{WC} is the conserved quantity of $O(\Delta t^3)$. On the other hand, in the original scaling scheme (Eq. (14)), δH^*_{WC} is of $O(\Delta t^2)$.

Simulations with the WC thermostat were carried out for 864 LJ particles using the MVS and original VS, respectively, with reduced density $\rho^* = 0.85$ and temperature $T^* = 0.87$. Errors of $H^*_{WC}(\delta H^*_{WC})$ were estimated in both simulations. Several MD runs with different time step Δt were performed and the relations of $\log \delta H^*_{WC}$ and $\log \Delta t$ were obtained.

In Fig. 1, the dependence of $\log \delta H^*_{WC}$ on $\log \Delta t$ is shown. Filled diamond denotes results by the MVS and open diamond denotes those by the original VS. Dotted and dashed lines have slope 3 and 2, respectively. It is clearly shown that the MVS scheme maintains the accuracy of the Verlet algorithm, while

the original VS is under the accuracy of $O(\Delta t^2)$. Integrations under the Verlet's accuracy in the MVS scheme are rigidly confirmed.

6 SUMMARY

The modified and generalized version of the VS scheme in the leapfrog algorithm is presented. This scaling method enables us to integrate EOM with the velocity dependent force such as Eq. (1) in the framework of the leapfrog algorithm. The leapfrog algorithm is the most widely used in MD simulations but not suitable for treating the velocity dependent force. Therefore, the modified VS extend the applicability of the leapfrog algorithm to constant temperature and/or pressure MD in which the velocity dependent force should be handled. It is also worthy to note that the VS in the leapfrog algorithm is more easily performed than other integration schemes such as the predictor–corrector algorithm especially for large systems. The expression of the modified scaling factor S_i is formally the same for all constant temperature and/or pressure methods described in the present study. Therefore, various methods are easily employed according to simulation conditions. Furthermore, the original accuracy of integrations in the leapfrog (i.e. Verlet) algorithm is maintained in the modified VS scheme. Simulations for a LJ fluid with the WC thermostat were carried out and the error of a conserved quantity was estimated in both the modified and original VS scheme. The results confirm that the Verlet's accuracy (of $O(\Delta t^3)$) is realized in the modified VS, while the accuracy in the original VS is of $O(\Delta t^2)$.

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APPENDIX: THE MVS ALGORITHM FOR THE NPT MD

Melchionna *et al.* [7] introduced a modified version of Hoover's constant temperature and pressure method [12,14]. Their modification realizes the exact NPT ensemble [14]. In this appendix, an algorithm with the MVS to integrate the EOM for this NPT MD is presented.

The EOM for the exact NPT MD by Melchionna *et al.* are the following:

$$\dot{q}_i = \frac{p_i}{m_i} + \eta(q_i - R_0), \tag{A1}$$

$$\dot{p}_i = -\frac{\partial \Phi}{\partial q_i} - (\xi + \eta)p_i, \tag{A2}$$

$$\dot{\xi} = (2K - 3NkT_{\mathrm{ex}})/Q, \tag{A3}$$

$$\dot{\eta} = 3V(P_{\mathrm{in}} - P_{\mathrm{ex}})/W, \tag{A4}$$

$$\eta = \frac{1}{3}\frac{\mathrm{d}}{\mathrm{d}t}(\ln V), \tag{A5}$$

where $R_0 = \sum_i m_i q_i / \sum_j m_j$, T_{ex} and P_{ex} are pre-set temperature and pressure, respectively, and P_{in} is the instantaneous internal pressure described in Eq. (36). ξ and η are dynamical variables to control temperature and pressure and corresponding fictitious masses are Q and W, respectively. It should be noted that R_0 is invariant with respect to time evolution unless the Car–Parrinello type MD is employed [15,16]. This is easily checked by considering the total sum of Eqs. (A1) and (A2) and assuming the initial total momentum is zero [16].

To integrate these equations by the MVS, we employ the following relations just as the Andersen's constant pressure method (Section 4.3),

$$q_i = V^{1/3} s_i, \tag{A6}$$

$$p_i = m_i V^{1/3} \dot{s}_i. \tag{A7}$$

By these relations, Eq. (A2) can be reexpressed as

$$m_i\ddot{s}_i = -V^{-1/3}\frac{\partial \Phi}{\partial q_i} - (\xi + 2\eta)m_i\dot{s}_i. \tag{A8}$$

Equations (A6)–(A8) correspond to Eq. (A1) without the third term in the right-hand side and Eq. (A2).

For the exact NPT dynamics, an algorithm for integrations of the EOM can be constructed as the following:

$$\dot{s}_i(t + \Delta t/2) = \dot{s}_i(t - \Delta t/2) + \frac{\Delta t F_i(t)}{m_i V^{1/3}(t)}, \tag{A9}$$

$$\dot{s}_i^*(t) = \dot{s}_i(t - \Delta t/2) + \frac{\Delta t}{2m_i}\left[\frac{F_i(t)}{V^{1/3}(t)} - \zeta_{\mathrm{NPT}}(t - \Delta t/2)m_i\dot{s}_i(t - \Delta t/2)\right], \tag{A10}$$

$$\xi(t + \Delta t/2) = \xi(t - \Delta/2) + \frac{\Delta t}{Q}\left[\sum m_i V^{2/3}(t)\dot{s}_i^{*2}(t) - 3NkT_{\mathrm{ex}}\right], \tag{A11}$$

$$\eta(t + \Delta t/2) = \eta(t - \Delta t/2) + \Delta t\frac{3V(t)}{W}\left[\left(\sum m_i V^{2/3}(t)\dot{s}_i^{*2}(t) + \sum F_i(t)q_i(t)\right]/3V(t) - P_{\mathrm{ex}}\right), \tag{A12}$$

$$\xi(t) = [\xi(t + \Delta t/2) + \xi(t - \Delta t/2)]/2, \tag{A13}$$

$$\eta(t) = [\eta(t + \Delta t/2) + \eta(t - \Delta t/2)]/2, \tag{A14}$$

where $F_i = -\partial\Phi/\partial q_i$ and $\zeta_{\mathrm{NPT}}(t) = \xi(t) + 2\eta(t)$. Equation (A10) corresponds to Eq. (27)

Here, we can obtain the MVS scaling factor S_{NPT} as

$$S_{\mathrm{NPT}} = 1 - \zeta_{\mathrm{NPT}}(t)\Delta t + \left[\frac{\zeta_{\mathrm{NPT}}(t)^2}{2} + \frac{\zeta_{\mathrm{NPT}}(t)F_i(t)}{2m_i V^{1/3}(t)\dot{s}_i(t)}\right]\Delta t^2. \tag{A15}$$

By this scaling factor, we can proceed the rest of the integration,

$$\dot{s}_i^*(t + \Delta t/2) = S_{\mathrm{NPT}}\dot{s}_i(t + \Delta t/2), \tag{A16}$$

$$\ln V(t + \Delta t) = \ln V(t) + 3\eta(t + \Delta t/2)\Delta t, \tag{A17}$$

$$q_i(t + \Delta t) = V^{1/3}(t + \Delta t)[s_i(t) + \Delta t\dot{s}_i^*(t + \Delta t/2)] - \eta(t + \Delta t/2)R_0\Delta t, \tag{A18}$$

$$s_i(t + \Delta t) = q_i(t + \Delta t)/V^{1/3}(t + \Delta t). \tag{A19}$$

The difference between the set of Eqs. (A1) and (A2) and that of Eqs. (A6)–(A8) is corrected in Eq. (A18). R_0 is determined by an initial configuration.

In the above procedure, $s_i(t)$, $\dot{s}_i(t - \Delta t/2)$, $V(t)$, $\xi(t - \Delta t/2)$, and $\eta(t - \Delta t/2)$ are given at the beginning. After one iteration, these variables at the next time step can be obtained with the MVS scheme. This algorithm is consistent with the leapfrog algorithm and is more easily performed than that described in the original paper by Melchinna *et al.* [7].